

Electrochemical Synthesis and Characterisation of Multimetallic Nanostructured Electrocatalysts

by

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degree of

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DECLARATION

I declare that this thesis, which I hereby submit for the degree of Doctor of Philosophy in Chemistry at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

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Signature:

Date:

SUMMARY

Title of Thesis: *Electrochemical Synthesis and Characterisation of Multimetallic Nanostructured Electrocatalysts*

Degree: *PhD (Chemistry)*

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This thesis concerns investigations on novel multistage electrochemical deposition of nanostructured systems composed of noble metals platinum, ruthenium, and gold. Various electrochemical synthetic pathways were systematically explored producing multilayered nanoscale electrode systems composed of Pt, Ru, or Au on glassy carbon or crystalline gold used as substrates. Electrochemical pathways involved sequential surface-limited redox-replacement (SLRR) reactions of underpotentially-deposited or overpotentially-deposited copper, potentiostatic dealloying, direct spontaneous deposition of noble metals (without intermediary steps involving redox-replacement templating reactions) as well as sequential codeposition of noble metals (with or without SLRR templating reactions).

Fundamental studies were conducted using thermodynamic and kinetic models, *in situ* electrochemical techniques and *ex situ* microscopic, spectroscopic, or spectrophotometric techniques employed for probing factors controlling electrode dynamics, electrocatalysis, morphology, bulk and surface compositional properties of the noble metal-based electrode systems.

Unique multilayered multimetallic nanoclusters synthesized (with binary active sites of Pt with Ru or Au) exhibited superior electrocatalytic activity towards methanol or formic acid oxidation reactions when benchmarked to equivalent

monometallic multilayered Pt. Hydrodynamic electrokinetic studies of the oxygen reduction reaction (ORR) on the multilayered monometallic Pt and bimetallic Ru-containing nanoclusters revealed that the monometallic nanoclusters exhibited direct four-electron ORR whereas electrocatalysis on the bimetallic ones could be tuned to proceed via a two-electron reaction pathway. Electrocatalytic bifunctional reaction mechanisms were especially enhanced by the nanostructured systems investigated.

Characterisation of multilayered nanoclusters' surface and near-surface metal contents revealed interactions between metal centers, carbon and oxygen containing surface functional groups on the glassy carbon, which appeared to have played a significant role in the overall stabilization and catalytic activity of the electrochemically immobilized nanoclusters.

Physico-chemical models and characteristics of intermediary Cu adlayers in the electrosynthetic pathways revealed role of Cu surface coverage (within the framework of electrochemical isotherms with kinetic and thermodynamic parameters) and heterogeneity effects, adatom-substrate interactions as well as adatom-adatom lateral interactions within individual adlayers during multilayer Pt growth on crystalline Au. New relationships for computing trends in the apparent Gibbs free energy of the SLRR reaction provided insights on reaction energetics of the interfacial Pt layered growth.

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LIST OF PUBLICATIONS

The original contributions to the scientific knowledge-base presented in this thesis have been primarily published as research articles with bibliographic details:

- I. T. S. Mkwizu, M. K. Mathe, and I. Cukrowski,
Automated electrodeposition of bimetallic noble-metal nanoclusters via redox-replacement reactions for electrocatalysis,
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- II. T. S. Mkwizu, M. K. Mathe, and I. Cukrowski,
Electrodeposition of multilayered bimetallic nanoclusters of ruthenium and platinum via surface-limited redox-replacement reactions for electrocatalytic applications,
Langmuir, Vol. **26**, Issue 1, p. 570-580 (2010).

- III. T. S. Mkwizu, M. K. Mathe, and I. Cukrowski,
Multilayered nanoclusters of platinum and gold: Insights on electrodeposition pathways, electrocatalysis, surface and bulk compositional properties,
Journal of the Electrochemical Society, Vol. **160**, Issue 9, p. H529-H546 (2013).

- IV. T. S. Mkwizu and I. Cukrowski,
Physico-chemical modelling of adlayer phase formation via surface-limited reactions of copper in relation to sequential electrodeposition of multilayered platinum on crystalline gold,
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SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

$a.c$	Alternating current
a.u	Arbitrary units
A	Area(of a solid electrode)
A_{EAS}	Inner-sphere electrochemically-active surface area
A_{ES}	Outer-sphere electrochemically-active surface area
AFM	Atomic Force Microscopy
A_G	Electrode's geometric area
ALD	Atomic Layer Deposition
ALE	Atomic Layer Epitaxy
a_M	Activity of metal M
$a_{M,UPD}$	Activity of UPD metal M
$a_{M^{z+}}$	Activity of ions of metal M with charge $z+$
ASV	Anodic Stripping Voltammetry
Au_{film}	Gold film deposited on glass slide substrate
BE	Background (Blank) electrolyte solution
C	Capacitance
CA	Chronoamperometry
$C_{At\%x}$	Atomic concentration of elemental component x
C_{dl}	Capacitance of an electrode's double-layer interface
ccp	Cubic close-packed
$C_{N^{P+}}^{\infty}$	Concentration of metal ions N^{P+} in the bulk solution
CE	Counter electrode
$C_{N^{P+}}^s$	Surface concentration of metal ions N^{P+}
$C_{M,UPD}$	Surface concentration of UPD metal M (e.g. when $M = Cu$, then $C_{Cu,UPD}$)
CPE_{dl}	Double-layer constant-phase element
Cu_{UPD}/Au_{film}	Underpotentially deposited adlayer of copper on the substrate Au_{film}

CV	Cyclic Voltammetry
CVs	Cyclic voltammograms
CVD	Chemical Vapour Deposition
D	Diffusion coefficient
$D_{N^{p+}}$	Diffusion coefficient of metal ions N^{p+}
2-D	Two-Dimensional
3-D	Three-Dimensional
DAFC	Direct Alcohol Fuel Cell
$d.c$	Direct current
DEFC	Direct Ethanol Fuel Cell
DFAFC	Direct Formic Acid Fuel Cell
DLFC	Direct Liquid Fuel Cell
DMFC	Direct Methanol Fuel Cell
E	Electrode potential
E_{appl}	Applied potential
E_B	Binding energy (in relation to electrons)
EC-ALD	Electrochemical Atomic Layer Deposition
E_{dep}	Deposition potential
EDX / EDS	Energy Dispersive X-Ray Spectroscopy
E_{eq}	Electrode potential at equilibrium
EIS	Electrochemical Impedance Spectroscopy
E_{OC}	Open-circuit potential
E_p	Peak potential
$E_{p,ox}$	Oxidation peak potential
$E_{p,red}$	Reduction peak potential
$E-pH$	Potential-pH
E_{SLRR}	Electrode potential arising from a surface-limited redox-replacement reaction
$E-t$	Potential-time

E_{UPD}	Electrode potential corresponding to a underpotential deposition
$E^{\theta=0.5}$	Electrode potential at coverage of 0.5 during a surface-limited reaction
$E^{\theta \rightarrow 0}$	Electrode potential in the limit of zero-coverage during a surface-limited redox replacement reaction
f	Temkin-type isotherm adatom-substrate interaction parameter
F	Faraday constant
FAOR	Formic acid oxidation reaction
FC	Fuel Cell
FEG-SEM	Field Emission Gun Scanning Electron Microscopy
FWHM	Full-width-at-half-maximum value (of a spectral peak)
g	Frumkin-type isotherm adatom-adatom interaction parameter
GC	Glassy Carbon
GDL	Gas Diffusion Layer
h	Half-of-the-height of a dimensional flow-cell channel
hcp	hexagonal close-packed
HLSV	Hydrodynamic linear sweep voltammetry
HOR	Hydrogen oxidation reaction
i	Current
i	Electrode current
$i-E-t$	Current-potential-time
i_p	Peak current
$i_{p,\text{ox}}$	Oxidation peak current
$i_{p,\text{red}}$	Reduction peak current
j	Current density (= current / electrode area)
J_{or}	Order of a surface-limited redox reaction with respect to the concentration of involved noble metal ions
k	Fundamental reaction rate constant
k'	Reaction rate constant related to a surface-limited redox-replacement reaction in terms of surface concentration of noble metal ions and an order of reaction with respect to the noble metal ions, J_{or}

k_0	Rate constant for zero-order reaction with respect to adlayer coverage generated by underpotential deposition related to a surface-limited redox-replacement reaction
k_r	An overall reaction rate constant related to a surface-limited redox-replacement reaction in terms of a surface concentration of underpotentially-deposited adatoms and order of reaction with respect to the adatoms as non-zero and greater than one.
k_{r1}	Reaction rate constant related to a surface-limited redox-replacement reaction in terms of surface concentration of underpotentially-deposited adatoms with unity order of reaction.
MBE	Molecular Beam Epitaxy
MEA	Membrane Electrode Assembly
ML	Monolayer-equivalent coverage
MOR	Methanol oxidation reaction
M_{UPD}	Underpotentially deposited adlayer of metal M
NP	Nanoparticle
NM	Noble metal
η	Overpotential ($E_{appl} - E_{eq}$)
N_{or}	Order of a surface-limited redox-replacement reaction with respect to surface concentration/coverage of underpotentially-deposited metal
$n(Au)_{Cu}/GC$	Glassy carbon supported n -layered monometallic Au nanostructure obtained through n cycles of sequential open circuit surface-limited redox replacement of a sacrificial Cu adlayers by metallic Pt from its precursor salt
$n(Au Pt)_{Cu}/GC$	Glassy carbon supported n -layered nanostructure obtained through n cycles of (i) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Pt from a Pt salt solution, followed by (ii) sequential open circuit surface-limited redox replacement of sacrificial Cu adlayers by Au from a Au salt solution. The first and last deposition for this nanostructure involve Pt and Au, respectively
$n(Au Ru Pt)_{Cu}/GC$	Glassy carbon supported n -layered nanostructure obtained through n cycles of (i) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Pt from a Pt salt solution, followed by (ii) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Ru from a Ru salt solution, followed by (iii) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Au from a Au salt solution. The first and last deposition for this nanostructure involve Pt and Au, respectively

$n(\text{Pt})$	n -layered monometallic Pt nanostructure obtained through n cycles of sequential deposition of Pt from its precursor salt
$n(\text{Pt})_{\text{Cu}}/\text{Au}_{\text{film}}$	n -layered monometallic Pt film using Au thin-film as deposition substrate obtained through n cycles of sequential open circuit surface-limited redox replacement of sacrificial Cu adlayers by metallic Pt from its precursor salt.
$n(\text{Pt})_{\text{Cu}}/\text{GC}$	Glassy carbon supported n -layered monometallic Pt nanostructure obtained through n cycles of sequential open circuit surface-limited redox replacement of a sacrificial Cu adlayers by metallic Pt from its precursor salt
$n(\text{Pt} \text{Au})_{\text{Cu}}/\text{GC}$	Glassy carbon supported n -layered nanostructure obtained through n cycles of (i) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Au from a Au salt solution, followed by (ii) sequential open circuit surface-limited redox replacement of sacrificial Cu adlayers by Pt from a Pt salt solution. The first and last deposition for this nanostructure involve Au and Pt, respectively
$n(\text{Pt-Ru})$	n -layered nanostructure of an alloy-type bimetallic nanoparticles obtained through n cycles of sequential codeposition from a mixed precursor solution of Pt and Ru salts
$n(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$	Glassy carbon supported n -layered nanostructure obtained through n cycles of (i) sequential open circuit surface-limited redox replacement of a sacrificial Cu by Pt and Ru from a mixed precursor solution of Pt and Ru salts
$n(\text{Ru} \text{Pt})$	n -layered nanostructure of bimetallic nanoparticles obtained through n cycles of sequential deposition of individual elements from separate solutions
$n(\text{Ru} \text{Pt})/\text{GC}$	Glassy carbon supported n -layered nanostructure obtained through n cycles of (i) an open circuit spontaneous deposition of metallic Pt from a Pt salt solution, followed by (ii) an open circuit spontaneous deposition of Ru from its salt solution. The first and last deposition for this nanostructure involve Pt and Ru, respectively
$n(\text{Ru} \text{Pt})_{\text{Cu}}/\text{GC}$	Glassy carbon supported n -layered nanostructure obtained through n cycles of (i) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Pt from a Pt salt solution, followed by (ii) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Ru from a Ru salt solution. The first and last deposition for this nanostructure involve Pt and Ru, respectively

$n(\text{Ru} \text{Au} \text{Pt})_{\text{Cu}}/\text{GC}$	Glassy carbon supported n -layered nanostructure obtained through n cycles of (i) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Pt from a Pt salt solution, followed by (ii) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Ru from a Ru salt solution, followed by (iii) sequential open circuit surface limited redox replacement of sacrificial Cu adlayers by Au from a Au salt solution. The first and last deposition for this nanostructure involve Pt and Ru, respectively
PEMFC	Polymer Electrolyte Membrane Fuel Cell
ppm	Parts-per-million
PGM	Platinum Group Metals
Φ	Phase angle (in relation to electrochemical impedance)
Q	Charge
$Q_{\text{Cu,max}}$	Maximum total charge of electrochemical stripping of copper from an electrode substrate
$Q_{\text{Cu,str}}$	Charge from electrochemical stripping of copper at a given time
$Q_{\text{M,UPD}}$	Charge arising from underpotential deposition of a metal M
Q_{UPD}	Charge arising from underpotential deposition
R	Universal gas constant
R_{ct}	Charge-transfer resistance
Ref.	Reference
RE	Reference electrode
R_s	Electrolyte solution resistance
r_{SLRR}	Rate of a surface-limited redox-replacement reaction
$\text{Ru} \text{Pt}$	Bimetallic nanoparticulate system consisting of Pt and Ru adlayers sequentially deposited from separate precursor solutions
SEM	Scanning Electron Microscopy
SLRR	Surface-Limited Redox Replacement
SLRR_{Pt}	Surface limited redox replacement of a sacrificial metal by more noble metal Pt from its precursor solution.
STM	Scanning Tunnelling Microscopy
t	Time
T	Temperature
t_{dep}	Deposition time

TEM	Transmission Electron Microscopy
UHV	Ultra-High Vacuum
UPD	Underpotential deposition
v_f	Flow rate
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
$\Gamma_{i,UPD}$	Initial surface concentration of metal adatoms generated by underpotential deposition
δ	Thickness of a diffusion layer
ΔG°_{UPD}	Standard Gibbs free energy of underpotentially-deposited metal adlayer
ΔG_{SLRR}	Phenomenological Gibbs free energy of a surface-limited redox-replacement reaction at given time and coverage of underlying adlayer
ΔG_{UPD}	Gibbs free energy of underpotentially-deposited metal adlayer at particular coverage
$\Delta G^{\theta \rightarrow 0}$	Gibbs free energy of adlayer adsorption/desorption in the limit of zero-coverage
θ_{diff}	Diffraction angle (in X-ray diffraction measurements)
θ_{UPD}	Surface coverage of underpotentially-deposited adlayer at a given time of deposition
ν	Voltammetric scan rate (dE/dt)
ν	Frequency (in Hertz)
ω	Radial frequency (in radians/second)
WE	Working electrode
z	Elementary number of electrons in a reduction/oxidation reaction
Z	Impedance
Z'	Real part of impedance in complex notation
Z''	Imaginary part of impedance in complex notation

CHAPTER I

General Introduction

1.1. Nanoscale materials

The physical and chemical properties of nanoscale materials (usually defined in the 1 – 100 nanometre range) are of enormous interest and ever-increasing significance for current and future scientific and technological applications. Materials reduced to the nanoscale can remarkably show very different properties compared to what they exhibit on a macroscale or bulk matter, enabling unique applications. Properties such as magnetism, optics, melting point temperature, latent heat of fusion, and surface reactivity can be remarkably affected by the nature of the nanoscale substances [1-4]. Research efforts continue to find applications of nanoscale materials (nanomaterials), with potential impact to shape the modern society, in areas such as energy production and storage [5], healthcare [6], water purification and pollution control [7]. Indeed, versatile chemical and electrical energy conversion, facilitated at atomic and molecular levels with cost-effective materials, is of fundamental and technological importance in our modern world constrained by requirements for adjustment in sustainable utilisation of fossil minerals and fuels.

Nanoscale objects have always existed in nature, both in the living and non-living systems (Most biological processes occur at these minute scales). Most sophisticated biological processes, such as protein assembly and photosynthesis, involve nanostructured units. Solids such as clays and minerals formed geologically in the natural world also occur as nanoscale entities [8]. The correlation between properties and particle size has been known since the nineteenth century, when Michael Faraday demonstrated that the colour of colloidal gold particles can be modified via changes in the size of the constituent particles, albeit, with no in-depth knowledge of the actual dimensions of the particles he synthesized, which are now known to have been in the range of 12 – 60 nm as a result of advances in microscopic techniques in the twentieth century [9].

Despite the occurrence in nature and a few historical products, the size-related aspects of nanoscale materials had not been focused on explicitly by the scientific community until evolution of new tools capable of monitoring and manipulating materials at the nanoscale became available in recent times [8]. The quest to construct tiny objects, atom-by-atom or molecule-by-molecule, is in the realm of the

exciting prospects of the emerging fields of ‘Nanoscience’ and ‘Nanotechnology’. Nanoscience involves the study of materials on the nanoscale level between approximately 1 and 100 nm [10] as well as the study of how to control the formation of two- and three-dimensional assemblies of molecular scale building blocks into well-defined nanostructures or nanomaterials [11]. Nanotechnology relates to such activities undertaken to build functional devices based on the controlled assembly of nanoscale objects, for specific technological applications [8].

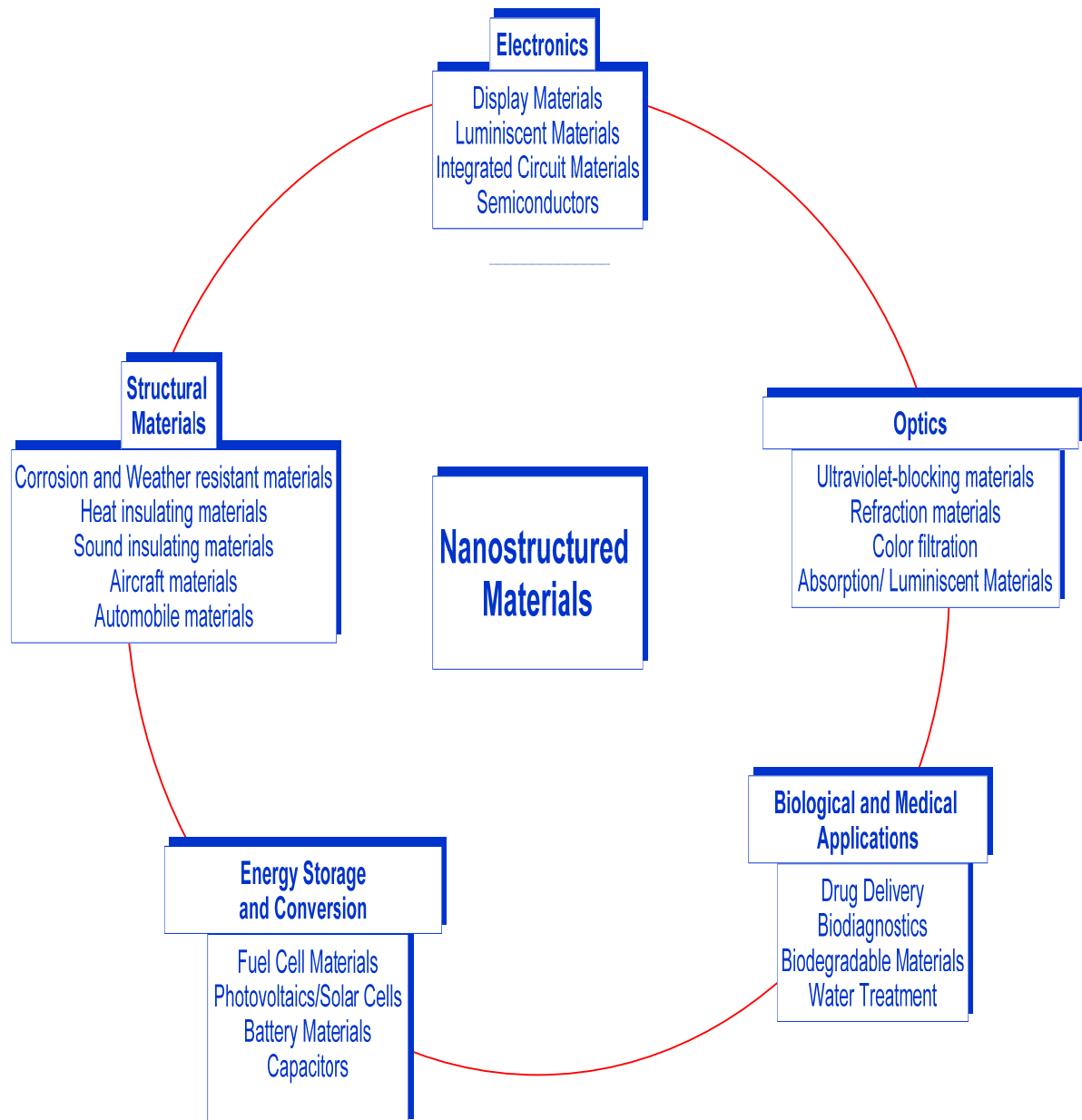


Figure 1.1: Applications of nanostructured materials (Adapted from Ref. [12]).

Generally, nanomaterials can be categorized into carbon-based materials such as fullerenes and carbon nanotubes and inorganic nanomaterials formed from metals

and metal oxides. In solid-state, these materials can further be classified as (i) nanomaterials with property changes related directly to size (that is, changes occur as the size of a solid material is reduced to nanoscale); and (ii) nanostructured solids that can be uniquely assembled atom-by-atom to create a completely different materials, not just a smaller fragment of a larger solid [8]. Nanoscience is highly cross-disciplinary research area combining elements from modern physics and chemistry, materials science and molecular biology. Nanotechnology includes the integration of these nanoscale objects into larger functional material components and systems, with at least one characteristic dimension measured in the nanometre range [13]. Various applications of nanostructured materials are schematically shown in Figure 1.1.

The past few decades have seen a significant increase in studies of nanoscale systems with a huge emphasis on controlled synthesis of new nanoparticles with different sizes and shapes and in-depth understanding of their chemical and physical properties [14]. There is a wide range of techniques explored for producing different kinds of nanoparticles. Generally, two strategies are used in synthesis of nanoparticulate systems, referred to as “top-down” and “bottom-up” approaches or strategies. In the top-down approach large particles are used as starting materials and using appropriate techniques they are broken down into smaller particles of nanoscale dimensions. In the bottom-up approach, smaller particles, typically ions or molecules are used as precursors to grow larger particles, restricted to nanoscale dimensions [2,5]. Broadly these approaches essentially utilize three processes: (i) condensation from vapour, (ii) chemical reactions, and (iii) solid-state processing such as milling [15].

The nanoparticulate preparation methods could be classified into two categories; physical and chemical methods. In the physical methods, evaporation or laser abrasion from bulk samples, such as solid metal blocks, is typically utilized to generate nanoparticles. These methods include annealing techniques and vacuum and gas-phase techniques such as atomic layer deposition (ALD), chemical vapour deposition (CVD), and molecular beam epitaxy (MBE) [16-21]. ALD is a well-established crystallization technique for growing thin-films. It is based on chemical

reactions at a heated surface of a solid substrate, to which the constituent elements of the compound to be grown, or the gaseous reactants containing these elements, are transported sequentially as pulses of neutral molecules or atoms, either as beams in high-vacuum, or as alternating streams of vapour in near-atmospheric pressure reactors. ALD is more a substrate-controlled growth process than a reactant source-controlled process [22].

In a typical CVD process, a substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. Molecular Beam Epitaxy (MBE) is an Ultra-High-Vacuum (UHV)-based technique for producing epitaxial structures with monolayer (ML) control. The principle underlying MBE growth is relatively simple: it consists essentially of atoms or clusters of atoms, which are produced by heating up a solid source. They then migrate in an UHV environment and impinge on a hot substrate surface, where they can diffuse and eventually incorporate into the growing film. Despite the conceptual simplicity, a great technological effort is required to produce systems that yield the desired quality in terms of material purity, uniformity and interface control. The choice of MBE and other growth techniques depends on the desired structure and needs.

Some of the disadvantages of the gas-phase methods such as physical ALD, CVD and MBE include their inherent requirement for expensive equipment, the use of costly and ultra-pure precursors, and production of large volumes of mostly toxic gaseous wastes. Even if a high quality structure is produced at elevated temperatures, cooling to ambient conditions inevitably could lead to stresses, cracking, and substrate failure as constituents cool at varying rates [19,23].

On the other hand, chemical methods to synthesize metal particles generally involve use of chemical reactions to convert ions to neutral atoms or oxides, usually achieved by precipitation followed by particle growth from aqueous or non-aqueous solutions. The precipitation process typically involves chemical reduction of a metal cation or complex precursor in an electroless process using reducing agents such as gaseous hydrogen and alkali metals such as ABH_4 (A = alkali metal;

for example, Na or Li), or via electrochemical means utilizing an external power supply as indicated in Reactions 1.1 – 1.2 [24,25].



(RA = Reducing Agent)



(e^{-} = electrons)

Chemical methods are typically bottom-up approaches, and relatively low-cost in nature, where precursors used are in ionic or molecular forms (in gas or liquid phases), and these are converted through a series of chemical reactions into solid nanoparticles (in free-standing particulate forms) or nanostructured films as desired products (immobilized on some suitable substrate).

Metallic nanoparticles of low-size (monodispersed or shape-controlled) are also generally synthesized by chemical reduction of metal salts, dissolved in applicable solvents, in the presence of surface-stabilizing agents which could be surfactants (such as inverse micelles), dendrimeric or polymeric encapsulating materials. The stabilizing agents are generally referred as *capping agents* (which arrest the growth of particles when they reach a certain critical size and effectively stabilize kinetically stable nanoparticles which should be stabilized against aggregation into larger particles) [2,26]. Stabilization can be regarded to be accomplished either through electrostatic or steric mechanisms. Electrostatic stabilization occurs by adsorption of appropriate ions to the often electrophilic metal surface (such adsorptive processes create an electrical multilayer which results in Coulombic repulsion between individual particles) [26]. Steric stabilization is derived from layers of bulky molecules (such as dendrimers or surfactants) that surround the metal center [26].

Control of average particle size and size distribution in chemical methods of nanoparticulate synthesis are generally achieved by tuning the preparation conditions, for example, optimization of solvents, surfactants, and reducing agents employed, as well as variation in the molecular nature of stabilizing agents [2,26]. However, for the metallic nanoparticles to be effective in surface-sensitive

applications (for example, metal-based catalysis - described in detail later) intense purification steps are required to completely remove the stabilizing agents from the surface of the nanoparticulate catalysts. In fact, if interaction between the stabilizing agent and the metal surface is too strong, the catalytic activity can be severely modified [27].

1.2. Overview of catalysis and electrocatalysis involving nanoscale materials of noble metals

1.2.1. Noble metals

The noble metals (or precious metals) consist of gold, silver, and the Platinum Group Metals (PGMs) – platinum, palladium, iridium, rhodium, osmium, and ruthenium. Noble metals or precious metals are referred as such because of their characteristic chemical stability; they have very high positive standard reduction potentials, and many of them are highly resistant to oxidation (or corrosion), even at high temperatures [28,29]. Economically, the noble metals command premium prices generally attributable to their low abundance on the Earth's crust. The noble metals are transition metals and belong to Groups 8 – 11 in the periodic table. Typical physico-chemical properties of the noble elements are shown in Table 1.1.

Given the high enthalpies of sublimation (high boiling and melting points), as summarised in Table 1.1, any synthetic technique for generation of nanoparticulate forms of the noble metals requiring transformation of bulk forms to nanoscale ones (Top-bottom approach) will be inherently costly due to the high-energy requirements. On the other hand, 'bottom-up' synthetic strategies are attractive since the noble metals have interesting ionic chemistry that is almost exclusively that of complex compounds.

In particular, aquo ions of Ag^+ , Ag^{2+} , Ru^{2+} , Ru^{3+} , Rh^{3+} , Ir^{3+} , and Pt^{2+} exist, but complex ions are formed in the presence of anions other than ClO_4^- and BF_4^- [30].

Table 1.1: Some physico-chemical properties of noble metals

Element	Atomic Number	Melting Point (°C)	Boiling Point (°C)	Enthalpy Of Sublimation (kJ mol ⁻¹) at 298 K	First Ionization Energy (eV)	Metallic State Crystal Structure*	Atomic Radius (Å)
Ruthenium	44	2282	4050	642.7	7.35	hcp	1.350
Rhodium	45	1960	3760	556.9	7.46	ccp	1.345
Palladium	46	1552	2940	378.2	8.34	ccp	1.375
Silver	47	961	2155	284.9	5.17	ccp	1.445
Osmium	76	3045	5025	791.0	8.7	hcp	1.365
Iridium	77	2443	4550	665.3	9.1	ccp	1.355
Platinum	78	1769	4170	565.3	9.0	ccp	1.385
Gold	79	1064	2807	366.1	9.23	ccp	1.440

*ccp = cubic close-packed; hcp = hexagonal close-packed; Data from Ref. [31,32]

Noble metals have a wide range of applications because of their catalytic, chemical, optical, magnetic, mechanical, and electrical properties. The catalytic activity of noble metals is exploited in production or disposal of different chemical compounds, for instance, hydrocarbon conversion reactions and nitrogen-related chemistries [33-35].

1.2.2. Catalysis: General concepts

Many chemical reactions, although thermodynamically very favourable, do not by themselves occur at an appreciable rate. For such reactions to be useful, it is often necessary to invoke *catalysis*, a coupling chemical phenomenon that changes the rate of a chemical reaction, usually by several orders of magnitude [36]. Classical definition of a catalyst “is a substance one adds to a chemical reaction to speed up the reaction without the catalyst undergoing a chemical change itself” [37]. In effect catalysts do undergo chemical changes during the course of the reaction, albeit, the changes are reversible. Catalysis is a crucial part of the technology that spins industrially developed societies. Various chemical reactions of technological importance are facilitated by catalysts. In such reactions chemical bonds are broken and new chemical bonds are formed during the catalytic process. These molecular events occur repeatedly, usually without a significant change of the catalyst. In case

of omission of catalyst, the chemical transformations would either not occur, or proceed at very slow rates or lower efficiencies [37,38]. Production of transportation fuels, pollution control in modern automobile exhausts (which utilize platinum-based catalysts to convert harmful carbon monoxide and nitrogen oxide to nitrogen gas and carbon dioxide), and conversions of natural gas to hydrocarbon liquids, are just some of the areas in which catalysis shows a remarkable impact [39]. In most of these applications, metals, metal oxides, and metal-ligand systems are the key components of the catalyst formulations.

Generally there are two kinds of catalysts: homogeneous catalysts and heterogeneous catalysts. In homogeneous catalysis substances that are dissolved in a liquid or a gas promote a reaction in a uniform liquid or gas mixture. Homogeneous catalysts include acids, bases, enzymes, transition metal ions and metal complexes. In heterogeneous catalysis the catalyst is in a different phase from the reacting species, typically the catalyst is a solid and the reactants are gases or liquids, and so the rate-limiting step occurs at the solid surface. Thus heterogeneous catalysis is also referred to as *surface catalysis*. Although catalysts are not consumed by the reaction itself they may be inhibited, deactivated, or destroyed by secondary processes, typically intermediate products that form during the course of the reaction being catalyzed.

Among challenges in synthesizing highly-active catalysts is improvement of properties that minimize deactivation and inhibition processes [38], issues that are being pursued vigorously addressed by research and development in use of nanomaterials for catalytic processes [40].

A typical cycle for a heterogeneous catalytic reaction begins with the adsorption of the reacting gases or liquids on the surfaces of the catalyst's *active sites*, where intramolecular bonds are broken or weakened. Next, the adsorbed species react on the surface, often in several consecutive steps. Finally, the products desorb from the surface into the surrounding gas or liquid phase, consequently regenerating the active sites on the surface, ready for the next catalytic cycle. It is well established that the efficiency of a catalyst is directly proportional to its surface area [37,38,41]. For this reason, many of the heterogeneous catalysts, used in industry today, consist

of one or several catalytically active component(s), typically in the form of very small particles in the size range of 1-100 nm, that are deposited on the surface of appropriate high-surface area supports, such as carbon-based materials [42,43]. The use of nanoparticles results in a large contact area between the active material of the catalyst and surrounding gas or liquid phase reactants. This ensures that the catalytic material is used efficiently. The small size of the particles maximizes effective surface area exposed to the reactant, allowing more molecular reactions to occur.

As a result of reduction of particle size the relative proportion of active sites per unit area of the particles increases, so that much higher catalytic activity and/or highly selective reactions may be expected on the relevant particles. Moreover, the physical-chemical properties of the constituent particles of also change as a result of reduction in particle size. For example, if a metal particle, initially having bulk properties, is reduced in size down to a few hundreds or dozens of atoms, the density of states in the valence and conduction bands decreases and the electronic properties change significantly. The quasi-continuous density of states of a bulk metal is replaced by quantized levels with a size-dependent spacing; these changes are generally referred to as quantum size effects [1]. As far as catalysis is concerned, quantum size effects can lead to new properties. Therefore, tuning particle sizes provides the possibility to manipulate catalytic activity [43]. In this respect, a typical example is represented by gold. Au was for a long time in history considered catalytically inert, but in 1987 Haruta and co-workers [44] demonstrated that nanosized Au particles can be very effective catalysts, using oxidation of carbon monoxide at sub-zero temperatures as a case study. Subsequently, vigorous research on catalytic properties of Au persist [45].

1.2.3. Multimetallic catalysts

Multimetallic catalysts can lead to enhancement of molecular-level properties not obtainable with monometallic catalysts [46]. For example, various molecular level effects on platinum-based bimetallic systems in electrocatalysis have largely been interpreted using three models, namely; (i) ensemble effects; (ii) bifunctional mechanisms, and (iii) electronic effects [47,48]. *Ensemble effects* involve the role of

metal adatoms in blocking surface sites for side reactions that generate poisoning species, or blocking adsorption of inhibiting species that require more than one surface site for their adsorption [49,50]. In a *bifunctional mechanism*, the surface of the electrocatalyst is considered to have two types of sites that play distinct roles in the electrocatalytic reaction [51]; in bimetallic platinum-based catalytic systems, for example, platinum sites are understood to play the role of breaking bonds such as H-C of organic molecules upon adsorption, while the second metal or adatom, can adsorb oxygenated species, such as O-H groups, and assist in subsequent oxidation of strongly-adsorbing intermediates such as adsorbed CO (CO_{ads}) [52].

Electronic effects are thought to come to play when there is some modification of the electronic properties of accessible surface sites of one metal and adjacent sites of a second metal, such that reactions on the surface sites proceed differently compared to the situation with an absence of the second metal [47,53,54]. Theoretically, the preceding electronic effects in metal-based catalysts can be explained using the infamous *d*-band model pioneered by Hammer and Norskov [55]. The Hammer-Norskov model prescribes that the variation in adsorption energy (and hence the catalytic activity) from one metal to the next is determined by the electronic structure of the surface whereby for the transition metals the coupling between the adsorbate valence states and the metal *d*-states principally establish such variations; the tenet of the *d*-band model is that the higher in energy the *d*-states are relative to the highest occupied state – the Fermi energy – of the metal, the stronger the interaction with adsorbate states. The reason is that when the *d*-states are close to the Fermi energy, antibonding states can be shifted well above it and become empty (or bonding states can be shifted below it and become occupied), effectively increasing the bond strength. With respect to multimetallic Pt-based surface, the underlying electronic structure, and in turn its overall reactivity, can be tuned by inserting another metal in its lattice and this can directly influence the oxygen and hydrogen adsorption energies due to an up-shift of the platinum surface *d*-states [56].

1.2.4. Electrocatalysis

When reactions being catalysed take place at electrodic surfaces (that is, electrolyte/electrode interfaces), the process is referred to as *electrocatalysis* [57]. Figure 1.2 illustrates an electrocatalytic reaction in which three fundamental steps occur: (I) transport and adsorption of reactants (dissociative) at the electrolyte-electrode interface, (II) electron transfer between a reactant and the electrode, and (III) desorption of the formed products from the electrode surface. Similar to conventional catalysis, in the absence of a catalyst, many electrode reactions occur, if at all, with poor kinetics. The objective of subjecting an electrochemical reaction to a catalytic interface is simply to either seek an alternative reaction pathway or diminishment of the activation energy of a rate-limiting step [58]; schematically, the fundamental catalytic process is illustrated in Figure 1.3. Typically, in an electrocatalytic process there is either enhancement of the rate or current density of an electrode reaction, at a given overpotential, or reduction in the overpotential for a given rate of reaction (essentially, the electrocatalytic substance is not consumed in the process or its changes happen in a reversible fashion). As in conventional chemical catalysis, electrocatalysis can involve either homogeneous or heterogeneous processes. In *homogeneous electrocatalysis*, both the catalyst and the reactants are in the same phase, commonly dissolved in the bulk phase, and the processes at the interface do not influence the chemical steps that involve it. In *heterogeneous electrocatalysis*, the catalyst is immobilized on the electrode's surface or the electrode itself performs the catalytic role [59].

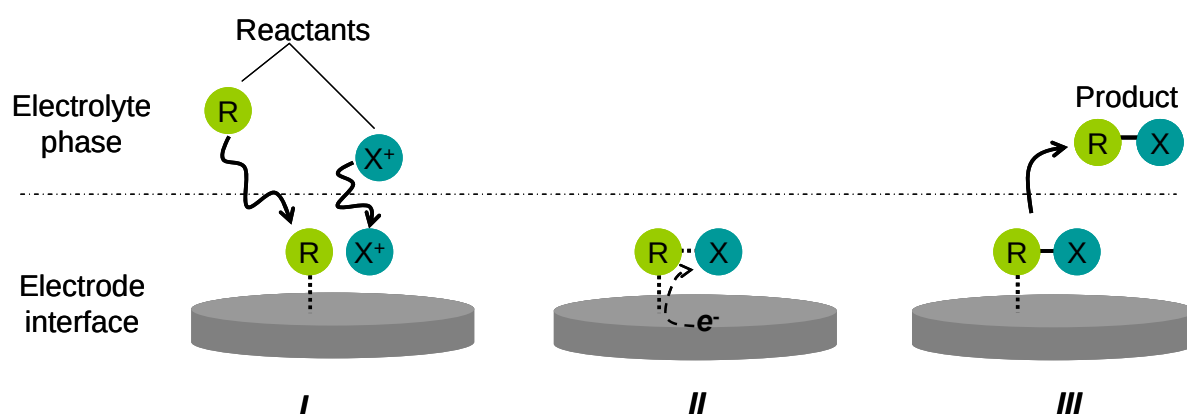


Figure 1.2: Main steps (I – III) of an electrocatalytic reaction with electron transfer from the electrode to an adsorbed species on its surface (a reduction reaction).

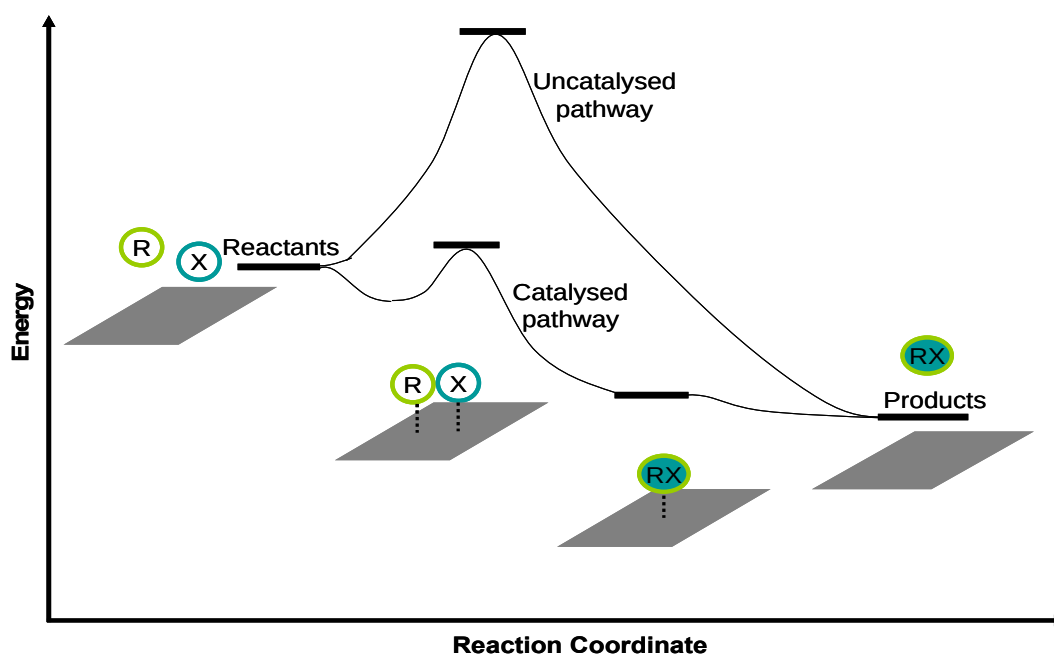


Figure 1.3: Schematic representation of catalysed and uncatalysed reaction pathways.

The rate of the reaction is primarily governed by the highest activation along the reaction coordinate – the lower the activation barrier, the higher the rate of the reaction. If there is reaction of an adsorbed species on the catalyst's surface, the reaction mechanism is termed a *Langmuir-Hinshelwood*. On the other hand, if one of the reactants is sourced directly from the gas or liquid phase, the mechanism is known as *Eley-Rideal* [60]. The rate of the overall reaction is limited by the rate-limiting step and a good catalyst must have a balance between binding energies of reactants, intermediate complexes and products with activation barriers as low as possible [60].

Figure 1.4 depicts various applications of heterogeneous electrocatalysts and related research and development basis. Advantages of the use of an electrocatalyst include more efficient utilization of energy (in an electrolysis cell) or more efficient conversion of chemical to electrical energy (in a fuel cell), a more selective route for reaction (that is, greater yield of a desired product), longer electrode service life, and reduced electrode material cost [61].

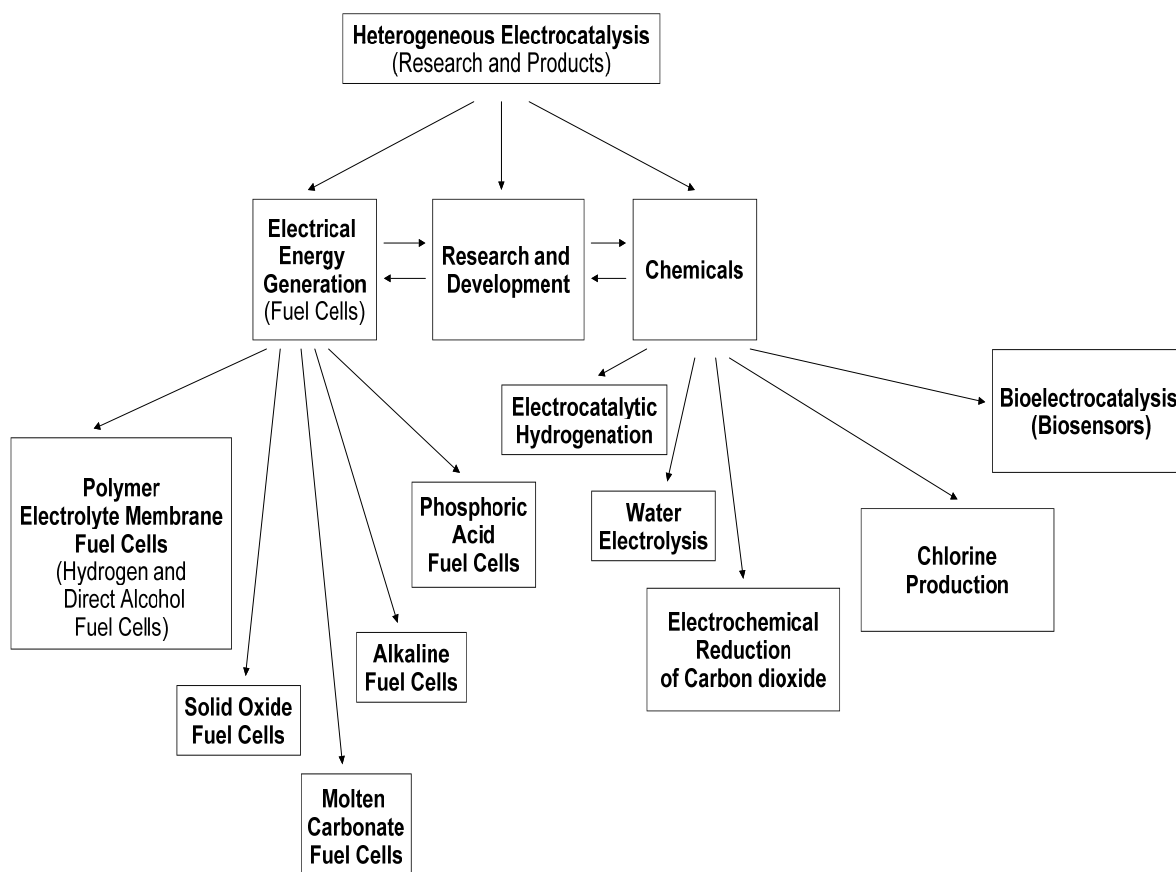


Figure 1.4: Various applications, research and development areas of heterogeneous electrocatalysis {Adapted from Ref. [62]}.

1.2.5. Electrocatalysts in fuel cells

Electrochemistry is increasingly playing a significant role in the domain of materials science, particularly in advancement of nanoscience and nanotechnology [63,64]. A great deal of focus on the use of nanostructured materials is currently being placed on production and consumption of energy. It is widely accepted that the reliance on the combustion of fossil fuels might have a severe future impact on world economics and ecology if alternative sources of energy that are environmentally friendly and affordable are not commercialized fast enough. Fuel cells are now extensively recognized as very attractive devices to obtain directly electric energy from a continuous supply of a chemical product, such as hydrogen, natural gas, or methanol, and an oxidant such as air or oxygen [65]. In addition to high efficiency and low emissions, fuel cells are attractive for their modular and distributed nature, and zero noise pollution. They are also envisaged to play a role in any future

hydrogen economy, whereby hydrogen used to power fuel cells could be generated from renewable resources such as wind or solar energy [66-69].

A schematic diagram showing the main components of a fuel cell is given in Figure 1.5. In a typical fuel cell, a stream of chemical liquid or gas (the fuel) such as methanol or hydrogen is fed to a catalyzed anode that converts the fuel molecules into protons (H^+) in the case of a hydrogen fuel cell or H^+ and carbon dioxide for methanol fuel cells. The protons produced at the anode pass through a Polymer Electrolyte Membrane (PEM), also known as Proton Exchange Membrane (PEM), to the cathode side of the cell. By connecting a conductive wire from the anode to the cathode side, the electrons stripped from the fuel (for example, hydrogen or methanol) on the anode side, can travel to the cathode side and combine with oxygen (usually carried in an air feed stream) to form oxygen ions that combine with the protons to form water, and the overall processes lead to production of electricity that can be harnessed to do useful work [66,67,70-72].

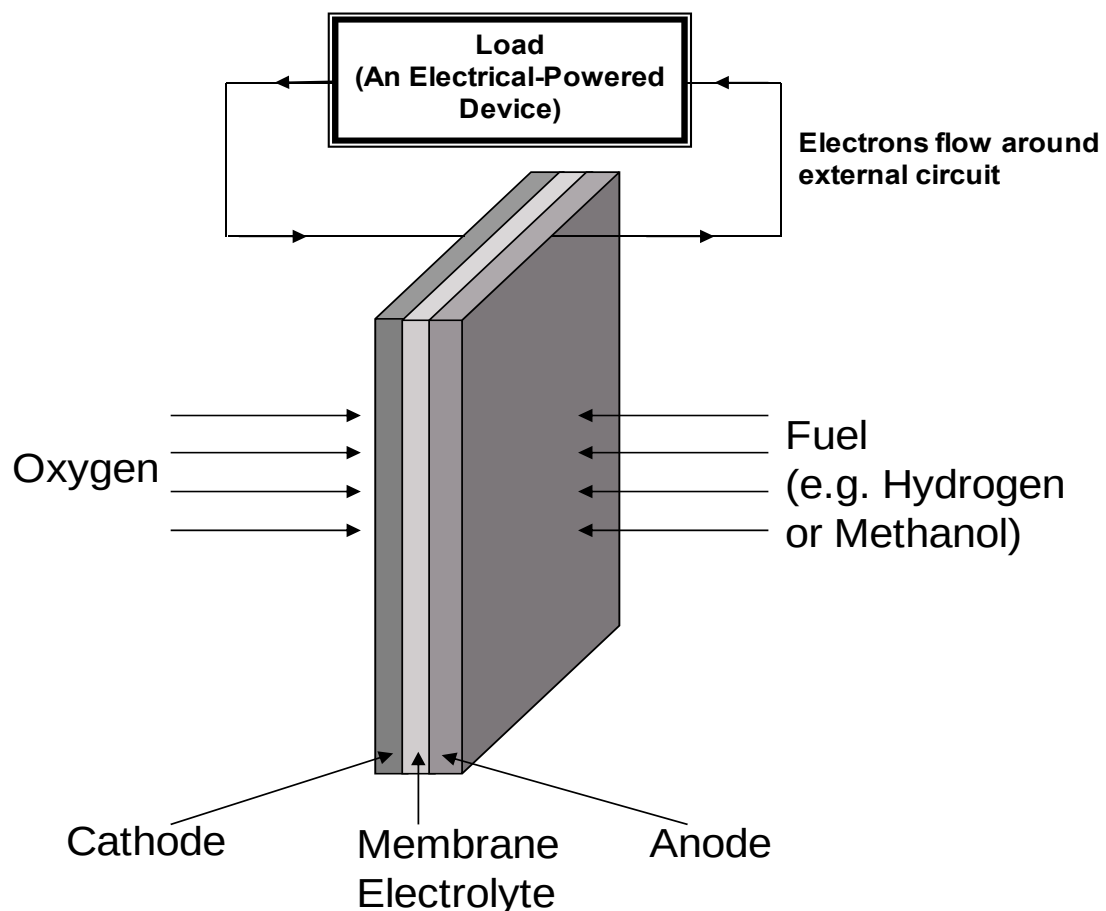
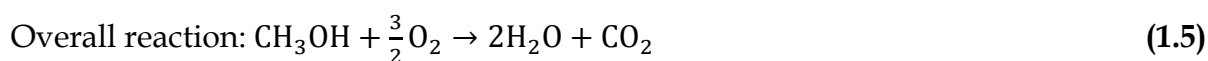
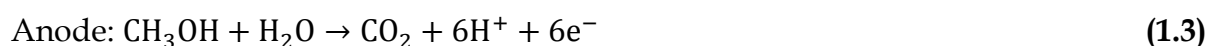


Figure 1.5: A schematic diagram of a fuel cell.

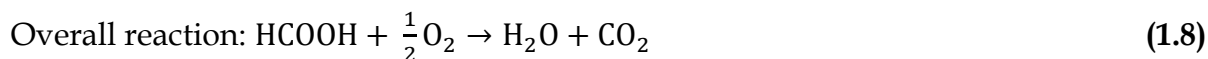
There are several types of fuel cells, including those having electrolytes of: phosphoric acid, molten carbonate, solid oxide, potassium hydroxide, and polymer electrolyte membrane. The most promising fuel cells that operate at relatively low temperatures (70 – 110°C) are ones based on the polymer electrolyte membrane (PEM), such as the one shown in Figure 1.5.

Different kinds of liquid organic compounds, such as methanol, formic acid, and ethanol have also been investigated as alternative fuels, primarily, in connection to their higher volumetric energy densities [73]. Direct oxidation of these liquid fuels is the keystone of Direct liquid Fuel Cells (DLFCs). For example, liquid methanol and formic acid have been explored in PEM fuel cells, termed Direct Methanol Fuel Cell (DMFC) and Direct Formic Acid Fuel Cell (DFAFC), respectively, where the following electrochemical reactions take place [74]:

DMFC



DFAFC



The DMFC and DFAFC are deemed as a promising candidates for several FC applications, including powering of electric vehicles and stationary uninterrupted power backup systems [74]. The liquid fuels have inherent advantages of easy storage, handling, and large-scale chemical production from oil, natural gas, coal or biomass. Thus, the oxygenated hydrocarbons can be widely available and relatively inexpensive. Moreover, the DLFCs can run at low temperatures (around 100 °C) and do not require fuel processing [75,76].

According to literature [69,77], it is clear that high power densities (and high efficiencies) of fuel cells are expected to result:

- (i) when gas diffusion and electron transport through the electrolytes (for example, polymer electrolyte membranes) are slow,
- (ii) electrocatalysis at the electrodes is efficient,
- (iii) the conductivity of each of the components, in particular, the electrolyte, is high, and
- (iv) mass diffusion of fuel molecules through the porous electrodes is facile.

Thus, the ideal fuel cell membrane electrolyte is not only highly ionically conducting but also impermeable to gases, electronically resistive and chemically stable under a wide range of conditions. Moreover, the electrolyte must exhibit sufficient mechanical and chemical integrity so as not to develop cracks, or pores either during manufacture or in the course of long-term operation [77]. The ideal electrode in a fuel cell must transport gaseous (or liquid) species, ions and electrons; and at the points where all three meet, the so-called triple-point boundaries, the electrocatalysts must rapidly catalyze electro-oxidation (anode) or electro-reduction (cathode). Thus, the electrodes must be porous, electronically and ionically conducting, and electrochemically active with high surface areas. It is rare for a single material to fulfill all these properties, especially at low temperatures, and consequently a composite electrode, of which the electrocatalyst is a key component, is often utilized.

PEM-based FCs

The underlying principle in fuel cells is the direct electrochemical conversion of chemical energy into electricity. The performance of a fuel cell is mainly determined by the kinetics of the reactions occurring at the anodes and cathodes, and by the transport processes through the solution onto the electrodes. The ideal or maximum efficiency of an electrochemical energy converter depends upon electrochemical thermodynamics, while the real efficiency is dependent on electrode kinetics. Since power output in fuel cell applications is the rate of producing energy, the kinetics of

the electricity producing interfacial charge transfer reactions, that is, electrode kinetics, becomes important [74].

The most widely implemented membrane electrolyte in PEM fuel cells is NafionTM manufactured by DuPont. Nafion and related polymers are comprised of perfluorinated back-bones, which provide chemical stability of sulfonated side-groups, which aggregate and facilitate hydration. It is these hydrated, acidic regions of the membrane electrolyte which allow relatively facile transport of protons, but also restrict PEMFCs to low temperatures of operation. As a consequence, precious metals are required for electrocatalysis [77].

For the oxidation and reduction reactions in a fuel cell to proceed at useful rates, especially at low operating temperatures below 300 °C, electrocatalytic materials are typically provided at the electrodes. The electrocatalysts are precious metals such as Pt, Pd, Rh, Os, Ag, or Au because they are able to withstand the corrosive environment - Pt being the most efficient and stable single-metal electrocatalyst for fuel cells operating below 300 °C. However, the uses of precious metal electrocatalysts play a significant role in the cost of producing fuel cells in a large scale [72,78].

For PEMFCs, electrocatalysis of hydrogen on metals such as Pt and Ni is relatively facile, and anode overpotentials are a small contribution to the overall drop in fuel cell voltage. The rate limiting step is the adsorption of hydrogen onto the metal surface, as opposed to the subsequent reaction of that hydrogen to produce protons and electrons. Obstacles in PEMFCs electrocatalysis arise when the hydrogen fuel contains residual carbon monoxide, or when liquid fuels (in the case of DLFCs), are to be directly electro-oxidized. CO is produced as an intermediate in the oxidation pathway during oxidation of liquid fuels such as alcohols and formic acid. Pure Pt electrocatalysts are not resistant to CO poisoning (which is typically present in H₂ obtained from hydrocarbon sources). CO is strongly adsorbed on platinum and other metals of the platinum group. For example, the presence of as low as 150 ppm CO almost destroys the catalytic activity of platinum for anodic hydrogen oxidation due to adsorptive poisoning effect of CO. The CO blocking of the catalyst surface

causes a significant anodic overpotential and therefore, a lower cell output voltage and smaller power densities of the fuel cells [69,72].

A simple alternative to decrease the CO poisoning effect on monometallic Pt is the addition of secondary elements. For example, several Pt alloys, such as Pt-Ru [79-82], Pt-Sn [83-86], Pt-W [87], Pt-Rh [88,89], and Pt-Mo [90-92], have been pursued for electro-oxidation of alcohols or hydrogen with the aim of alleviating the CO poisoning problem while maintaining good catalytic activity. The non-platinum metals are by themselves not necessarily H₂-oxidizing or alcohol-oxidizing catalysts, but have catalytic activity for CO oxidation. The enhancement in activity has been attributed to the bi-functional nature of the alloy surface and electronic effects resulting from electron transfer from the promoter elements to the d-band of Pt. The Pt-Ru binary metallic catalyst is widely accepted as the most promising electrocatalyst for DLFCs [72].

Research and development on more complicated systems, such as ternary and quaternary alloys, has also been forthcoming. For example, ternary and quaternary alloys such as PtRuOs [93], PtRuNi [94], and PtRuRhNi [95] have been investigated as potential highly active catalysts for methanol oxidation. Despite these extensive efforts, factors such as structure-property relations are still not completely understood and research efforts in determining optimal compositions of the alloy catalysts are on-going [96].

Another interesting noble metal is gold. Gold clusters have also been realized to have catalytic activity for CO oxidation and, when incorporated as adatoms to Pt, they have also been demonstrated to have a stabilizing effect on underlying Pt metal surfaces, effectively suppressing Pt dissolution under highly oxidizing conditions [97].

Particle size effects

For structure-sensitive reactions, the formation of smaller particles of supported electrocatalysts is of considerable importance in order to enlarge the catalytic area and, accordingly, enhance the catalytic activity [98]. As a consequence, the development of catalyst preparation methods for loading small and uniform metal

particles has become necessary. However, methods of controlling the metal particle size of supported catalysts, regardless of metal content are still not adequately available to date [99,100].

The search for abundant, inexpensive, and efficient electrocatalytic materials as substitutes for Pt-based oxygen cathodes in PEMFCs is currently an active area of research. Efforts are also under way to increase the heterogeneous electron-transfer kinetics and the utilization of Pt, for example, by modification of carbon supports [101,102] and novel platinum deposition techniques [103,104] to increase the effective catalytic area (thereby decreasing the loading of precious metal). Novel approaches toward improving cathodic electrocatalysis in PEMFCs have also included partial replacement of platinum with an alternative, less expensive metal (e.g., Co, Cr, Ni) [105-108]. While this approach has yielded some materials that have improved electrocatalytic activities and are less expensive than pure Pt catalysts, the costs associated with these materials are still rather prohibitive for full exploitation of fuel cell technology. Probably the most ambitious approach to this problem and with the greatest potential is to completely remove Pt from these systems and replace it with less expensive materials, while retaining catalytic activity at least equal to that of Pt. Some advances using this approach have been made in recent years. For example, electroreduction of oxygen at non-platinum metallic combinations [109]; inorganic and organometallic complexes [110,111], transition metal oxides [112,113], chalcogenides [114] and enzyme electrodes [115,116] have been studied.

The use of high level of Pt loading in PEMFCs can result in increase in their performance and longer lifespan. However, the limited supply and high cost of the Pt used in PEMFC electrocatalysts necessitate a reduction in the Pt amount used while maintaining high performance.

Since electrocatalytic reactions are structure-sensitive as determined by the composition and solid-state structure of the electrocatalyst employed, generally, synthetic challenges of multimetallic electrocatalysts include; (i) generation of well-dispersed particles and control of their sizes, (ii) efficient utilization of the catalytic material by way of increasing surface-activity of constituent metals, (iii)

maximization of synergistic effects at primary active sites, especially on bimetallic systems, and (iv) overall low fabrication costs [117,118]. Thus, the development of electrocatalysts with low-Pt-loadings and high-Pt-utilization is critical. Such development strongly depends on the electrode fabrication method and the nature of the substrate [119].

Electrocatalytic reaction mechanisms: Oxygen reduction, Methanol oxidation, and formic acid oxidation

The complete Oxygen Reduction Reaction (ORR) - Reaction 1.9 in acidic medium - is a four-electron reaction (for each O₂ molecule reduced), in addition to the transfer of four proton, the cleavage of the O-O bond and formation of two water molecules.



The general consensus on the reaction mechanism for ORR on Pt (in monometallic state) involve a 'dissociative' or an 'associative' adsorption pathways of O₂ [120-122]. The *dissociative pathway* involves initial adsorption of O₂ molecule on neighbouring Pt atoms, of course, in a dissociative manner



On the other hand, the *associative pathway* involves several intermediary steps



The final steps (given in Reactions 1.14 - 1.15) are common for the ORR mechanisms.



Particularly, the associative pathway of ORR also yields (through Reactions 1.11 - 1.13) H₂O₂. Clearly, ORR catalysis on metallic surfaces is a complex reaction. Recent

theoretical works, for instance, using Density Functional Theory (DFT), suggest that the binding energies of O and OH species to the catalytic metal are a determining factor for the overall ORR [123,124]. It has also been determined that no one-component material has higher activity for the ORR than Pt; however, possibilities exist to raise the catalytic activity by modifying the electronic properties of Pt, for example, by alloying to the extent that the electronic structure of Pt *d*-electrons is modified [123,124]. Periodic DFT studies of ORR on pseudomorphic Pt-on-Ru overlayers showed that there is a strong interaction between Pt and Ru layers, resulting in hexagonal-closed pack (*hcp*) stacking for the first Pt layer on Ru and subsequent cubic close-packed (*ccp*) stacking of Pt-on-Pt overlayers. In essence, the Pt atop layers on Ru reduce the atomic and molecular oxygen adsorption energies compared to pure Pt and Ru surfaces [125].

The thermodynamic potential for Methanol Oxidation Reaction (MOR) to CO₂ (Reaction 1.16, $E^0 = 0.02$ V (vs Standard Hydrogen Electrode (SHE))) in acidic medium lies very close to the equilibrium potential of hydrogen oxidation reaction (HOR) given in Reaction 1.17 ($E^0 = 0$ V (vs SHE)):



In comparison to the HOR, the MOR is several orders of magnitude slower [48,126]. The complete oxidation of CH₃OH molecule on a monometallic Pt surface proceeds with complex parallel reaction pathways depicted in Figure 1.6. The MOR pathways require a catalyst which should be able to (i) dissociate the C-H bond and (ii) aid the reactions of formed intermediates with some oxygen-containing species to form CO₂ (or HCOOH). Pure Pt is known as the best catalyst for breaking the C-H bond and the MOR takes place via two processes requiring different activation energies [48,126]:

- Adsorption of CH₃OH that requires several neighbouring active sites at the Pt surface (that is, sufficient number of Pt surface-active sites free from adsorbed hydrogen (H_{ads}), and

- Dissociation of water (the oxygen donor of the reaction). On pure monometallic Pt the strong interaction of water with Pt is generally only possible at potentials greater than 0.4 V (vs SHE).

The above processes occur in different potential regions in electrochemical environments. Therefore, on a pure Pt catalyst MOR cannot begin below say 0.45 V [126]. Incorporation of a secondary metal Pt (alloys, bimetallic catalysts and so forth) is the drive to tweak the pathways of MOR and other (electro)catalytic oxidation reactions of oxygenated hydrocarbon substances [42,127].

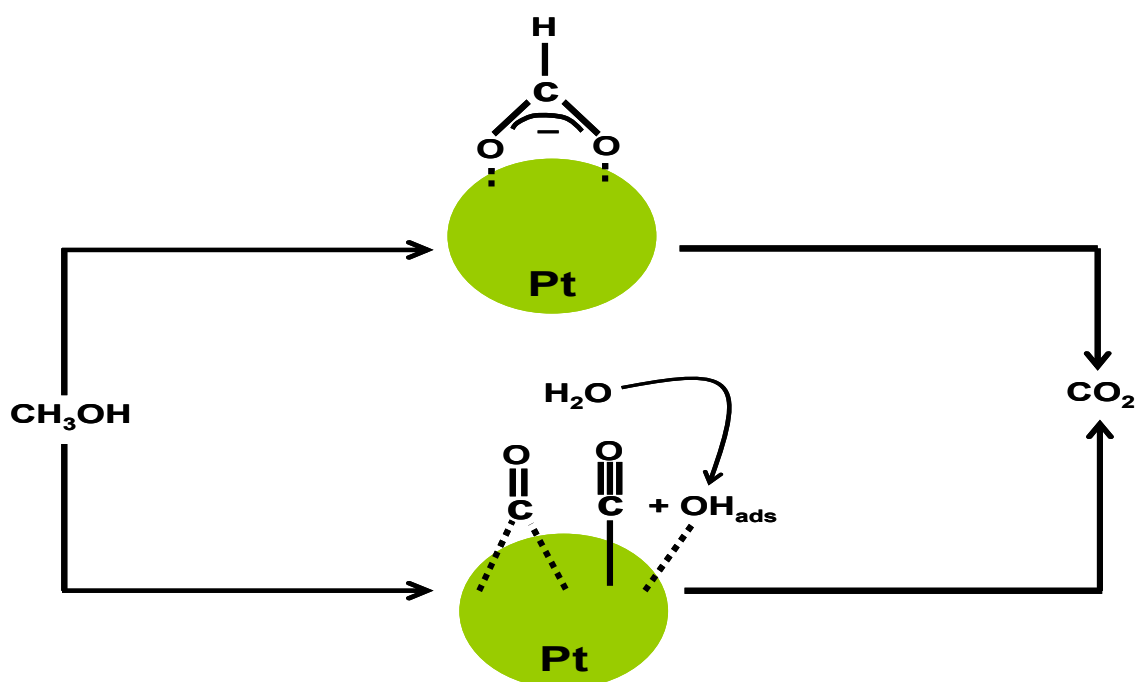


Figure 1.6: Main reaction pathways involved in methanol oxidation on pure Pt electrocatalyst. (Adapted from Ref. [128]).

The electrocatalysis of formic acid oxidation reaction (FAOR) on PGMs has attracted significant interest over the past decades due to its relevance as a fundamental electrochemical oxidation reaction as well as its attractiveness in low-temperature direct liquid fuel cells [48,129]. It is generally accepted that the electrocatalytic oxidation of HCOOH to CO_2 on a metal surface proceeds via a 'dual path' mechanism [48,129]; the direct oxidation of a reactive weakly-adsorbed intermediates to form CO_2 in parallel with an indirect oxidation pathway involving HCOOH dehydration and further electro-oxidation of resulting strongly adsorbing

CO_{ads} to CO₂. Developing highly active catalysts for FAOR is necessary in order to improve catalytic performance and resistance to poisoning [129].

1.2.5. Electrocatalysts in electroanalysis

Another highly promising area of electrochemical application of noble metal-based nanoscale materials is in *electroanalysis*, by definition, a means of determination of species in gas or liquid phase, both quantitatively and qualitatively, by application of electrochemical signals to initiate some electrochemical reaction of the species or retrieval of electrochemical signal resulting from electroactive species [130]. Characteristics of metallic nanoparticulate electrodes may include convergent rather than linear mass transport (diffusion) at the nanoparticles, high active surface area, improved selectivity, catalytic activity, higher signal-to-noise ratio, and unique optical properties. Typical noble metals explored for nanoscale electroanalytical applications include Au, Ag, Pd, Rh and Pt [130,131].

One major area of research interest of noble metal-based electrocatalytic sensors is oxidation of glucose. Fast and reliable monitoring of blood sugar for the treatment and control of diabetes has seen development of electrocatalytic (amperometric) glucose sensors where most studies have involved the use of the enzyme glucose oxidase which catalyzes the oxidation of glucose to gluconolactone [131,132]. The principal disadvantage is the requirement for an enzyme, which is the least durable part of the sensor. Unfortunately, eliminating the enzyme places severe constraints on the electrocatalyst, which must perform multielectron oxidation reaction in the presence of easily oxidized interfering agents. Hence, the electro-oxidation of glucose on noble-metals, such as Pt and Au, has been explored towards development of enzyme-free sensors [131,133-135]. In glucose solutions, pure (or monometallic) Pt electrodes lose their activity rather quickly through accumulation of chemisorbed intermediates, which poison the electrocatalyst surface. Moreover, pure noble metal electrodes lack the inherent selectivity of glucose oxidase, and various organic substances can be oxidized on these electrode surfaces. A potential solution to such problems has been explored through the use of alloy electrocatalysts, which combine the electrochemical properties of their constituent metallic components [131].

Another important analyte is hydrogen peroxide (H_2O_2), a strong oxidant which is widespread in industrial applications such food processing, pharmaceutical research, medical diagnostics, minerals processing. It is also involved in several biological events and intracellular biochemical pathways and is a by-product of oxidases, such as glucose oxidase. Due to their unique characteristics such as good biocompatibility noble metals such as Au, Ag, Pt, Pd, especially in their nanoscale forms, are also being exploited in electrochemical sensing of H_2O_2 in various electrocatalytic sensors involving heme protein-based biosensors and nonenzymatic sensors that either utilize electron transfer mediators or induce direct electron transfer on the metal-based nanoparticulate electrodes for reduction of H_2O_2 to water [130,136].

Indeed, various synthetic methods are utilized in preparation and fabrication of nanoparticulate electrochemical sensors ranging from colloidal precipitation of nanoparticles in suspensions to direct immobilization using electrochemical deposition. The ability to control the size and morphology of nanoparticles in a synthetic procedure is vitally important as these factors can greatly influence the electrochemical behaviour of NPs [130].

1.3. Advances in electrochemical synthetic methods of nanoparticulate noble metals

Given that electrocatalytic reactions are structure-sensitive, as determined by the composition and solid-state structure of the electrocatalyst employed, generally, synthetic challenges of multimetallic electrocatalysts include; (i) generation of well-dispersed particles and control of their sizes, (ii) efficient utilization of the catalytic material by way of increasing surface-activity of constituent metals, (iii) maximization of synergistic effects at primary active sites, especially on bimetallic systems, and (iv) overall low fabrication costs [117,118]. Most conventional synthetic approaches of noble metal nanoparticulate electrocatalysts utilise reduction of metal salts in chemical baths and multiple additional purification steps and fabrication of the prepared particles to an electrode arrangement required in subsequent electrocatalytic applications [69,137]. These methods generally involve substantial challenges in controlling locations and compositions of electrocatalytically-active

nanoparticles. Electrochemical methods inherently involve growth of nanoparticles at interfaces of conductive surfaces and the electrolyte used, and the requirement for electronic conduction is essentially maintained during subsequent electrocatalytic reactions at the active sites of the support. The same sites where electrodeposition takes place will, in principle, be active during subsequent electrocatalysis. In addition, electrochemical methods are relatively low-cost techniques [138].

Electrochemistry provides versatile means for synthesis of nanostructures and thin-films directly and selectively onto conductive substrates [64]. Electrochemical deposition or electrodeposition is a versatile technique by which a thin desired metallic coating can be obtained on the surface of another metal (or substrate) by electrolysis of a solution containing the desired metal ion or its complex. Electrodeposition is basically an electrochemical liquid phase thin film or powder preparation method where the reactions, either reduction or oxidation, are accomplished using an external current source. The deposition is carried out in an electrochemical cell consisting of a reaction vessel and two or three electrodes. In the two electrode cell the reactions are controlled by the current applied between a working electrode (substrate) and a counter electrode. In the three electrode cell a reference electrode is used to control or measure the potential of the working electrode, and depositions are carried out by controlling either current or potential and the corresponding potential or current respectively, may be measured that may be useful for mechanistic studies of the deposition process [139].

Electrodeposition is a technique that is conceptually well-suited to the preparation and fabrication of nanostructured materials. It is usually a low-temperature technique which gives it advantages on growth of small grain size particles as deposited. Another essential property of electrodeposition is the precise nature in control of the amount of material deposited through Faraday's law, which relates the amount of material deposited to the amount of charge passed. Thus, a known amount of charge will result in a defined amount of material deposited, of course, this aspect assumed 100% current efficiency, absence of side reactions and insignificant double-layer charging effects [140].

Electrochemical codeposition is the most prevalent traditional method in use for direct growth of multimetallic thin-films or alloys; generally, the electrosynthetic technique involves the use of soluble oxidized precursors of all the elements making up the film or alloy of interest in a single bath [23]. For example, a number of platinum-based alloys and thin-films have been electrochemically codeposited by several workers endeavouring to generate micro- and nano-structural deposits of importance to electronic industry, corrosion-resistant materials, sensors, magnetic devices and electrocatalysts, amongst others [25,130,141-153]. The stoichiometry of the deposited is maintained by selecting potentials in such a way that the less noble species (more reactive), or the first to be deposited, will not deposit on itself, but only on the second element in the scheme, or the more noble (less reactive) of the two. The concentration of the more noble element is set at very low amounts (ratios of 10 : 1 are typical) relative to the less noble element. In this way, the second element quickly reacts to form the compound as the higher concentration first element arrives at the surface, and 3-D growth is avoided [23].

The main challenge with multimetallic electrodeposition by single-bath codeposition is that the only control points are the deposition potential, or current density, in most cases. Also, codeposition has frequently resulted in deposits with poor crystallinity and side-products [23].

Multilayered metallic structures were first produced by electrodeposition by William Blum in 1921 using a 'dual bath' method that proceeded by alternating the deposition of Cu and Ni layers. The layers generated were fairly thick ($> 24 \mu\text{m}$), and the films were explored for their higher tensile strengths than the corresponding pure metal or alloys [154]. Typically, multilayered materials are composed of alternating layers of material A and B, with bilayer thickness called the modulation wavelength. Superlattices are a particular type of crystalline multilayer structure in which there is a coherent stacking of atomic planes, and periodic modulation of the structure or composition or both [155]. Multilayers and superlattices are both modulated materials, but superlattices have the additional constraint that they are crystallographically coherent. Because of this constraint, superlattices are produced with alternating layers of materials with very low lattice

mismatch, while multilayers can be produced using even amorphous materials [154].

Generally electrochemical deposition or electrocrystallisation involves a number of distinct steps that include [156]:

- Diffusion of ions in solution to the electrode surface;
- Electron transfer;
- Partial or complete loss of the solvation sheath, resulting in the formation of adatoms;
- Surface diffusion of adatoms;
- Clustering of ad-atoms to form critical nuclei on a perfectly smooth surface or on a foreign substrate;
- Incorporation of adatoms at lattice sites; and
- Development of crystallographic and morphological characteristics of the deposit.

Electrochemical deposition is a relatively low-cost fabrication method [25,157,158]. For a case of electrochemical deposition of a metal M from its metal ions M^{z+} , the reaction can be represented as:



Electrochemical deposition can be categorized into: (i) an *electrodeposition* process in which z electrons are generated by an external power supply either potentiostatically (with forced potential) or galvanostatically (with forced current); and (ii) an *electroless deposition* process whereby a reducing agent in the solution (or attached to a substrate) is the source of the z electrons (no external current is used to achieve reduction of metal ions M^{z+}) [139]. In the general case of metal M being in equilibrium with its ions in solution (Reaction 1.18), the equilibrium potential of the M^{z+}/M couple, E_{eq} , as a function of activity of the products and reactants in the equilibrium reaction, is given by Equation 1.19:

$$E_{eq} = E^{\circ}_{M^{z+}/M} + \frac{RT}{zF} \ln \frac{a_{M^{z+}} a_e^z}{a_M} \quad (1.19)$$

where a_i , in general, is the activity of species i inside the brackets (when the concentration of metal z are the number of electrons involved in the reaction, $E_{M^{z+}/M}^0$ is the standard reduction potential of the M^{z+}/M couple. Conventionally, the activities of metal (a_M) and electrons (a_e) in the metal lattice are equal to one.

When a metallic deposit M is part of an electrochemical cell through which current is flowing, its potential will differ from the equilibrium potential. The magnitude of the deviation of the electrode potential from the equilibrium value is termed the overpotential (η); that is, $\eta = E_{M^{z+}/M} - E_{eq}$. Overpotential deposition (OPD) utilizes such potentials $E_{M^{z+}/M}$ where current from an external source is forced through the substrate to drive reduction reactions, nucleation and growth of the solid metal phase from its corresponding metal ions, in effect with $E_{M^{z+}/M}$ more negative than E_{eq} . On the other hand, underpotential deposition (UPD) refers to deposition of atoms (so-called adatoms) of a metal on a foreign metal substrate at potentials that are more positive than E_{eq} of the metal ion deposition on its own metal surface, as predicted by the Nernst equation (Equation 1.19), typically producing sub-monolayer to monolayer phase of the metal [159]. In UPD, the metal M being an atomic layer on the foreign substrate with a different electronic structure than its bulk structure, activity of adatoms of M is consequently less than one, resulting in the shift in equilibrium potential [160].

Moreover, spontaneous deposition of noble metals such as Ru or Pt may proceed on appropriate electrodic substrates without any utilization of an external current to achieve reduction of metal ions (This method forms part of deposition techniques generally referred as Electroless Deposition in which case the reducing equivalents required are characteristically inherent on the surfaces of the substrates used) [161-163].

Typical electrochemical methods being exploited in synthesis and fabrication of Pt-based nanostructured systems include direct potentiostatic electrodeposition [164] and pulsed electrodeposition [162,165], where the nanostructure is tuned by the applied deposition potential or current density. Alloying of noble metals such as Pt or Au through underpotential codeposition of typical base metals Co, Fe, Ni and Cu have also been explored as compositionally modulated alloyed films [166-169].

Furthermore, careful manipulation of UPD can be exploited to synthesize various monolayer-restricted nanofilms and nanostructured Pt-based systems. Adzic and coworkers pioneered “the concept of noble metal monolayer electrocatalysts” using Cu sub-monolayers (generated at UPD) on suitable non-platinum metal nanoparticles or single-crystal substrates as sacrificial layers in surface-limited redox-replacement (SLRR) reaction (or galvanic displacement) of Cu by Pt (Figure 1.7), resulting in Pt monolayer decorated crystalline facets [97,170]. Recently, formation of mixed and alloy-type Pt-M nanoclusters (M = Au, Pd, Ir, Rh, Re, Ru, or Os) on Pd (111) single-crystal and carbon-supported Pd nanoparticles has been explored for a potential use in oxygen reduction [171]. Typically, this involved the generation of a Cu sub-monolayer templates by UPD followed by codeposition of two noble metals (as Pt-M mixture) from a common solution containing their chloride salts by the SLRR reaction [171].

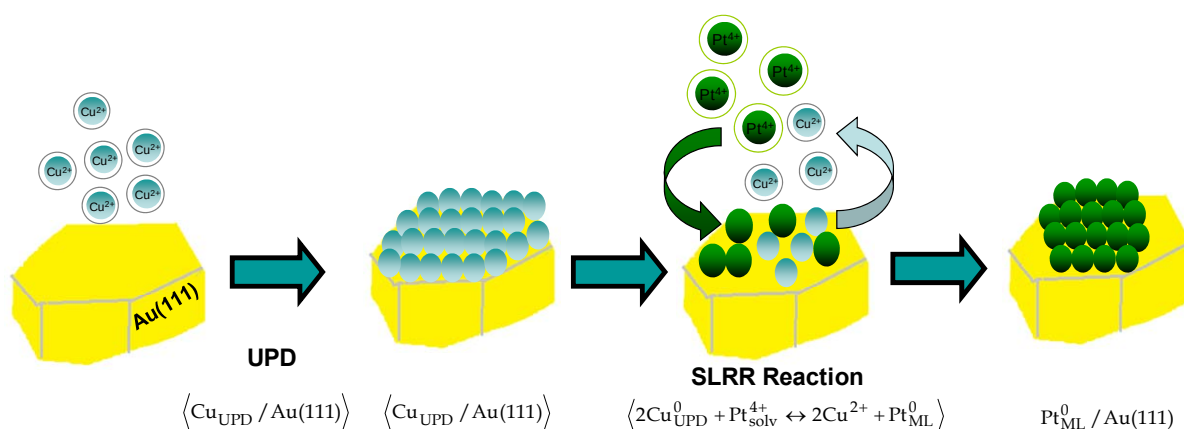


Figure 1.7: Scheme for formation of templating Cu adatoms via UPD (Cu_{UPD}) followed by SLRR reaction to deposit a Pt monolayer (Pt_{ML}) on Au(111) substrate. (Adapted from Ref. [170]).

Coating monolayers (‘shells’) of noble metals on ‘core-shell’ type of nanoparticulate catalysts, through utilisation of the UPD coupled to templating SLRR reactions, has been demonstrated on metallic ‘cores’ composed of chemically synthesized colloidal gold nanoparticles (Figure 1.8) [172] as well as carbon-supported non-noble metal nanoparticles (Figures 1.9) [173,174].

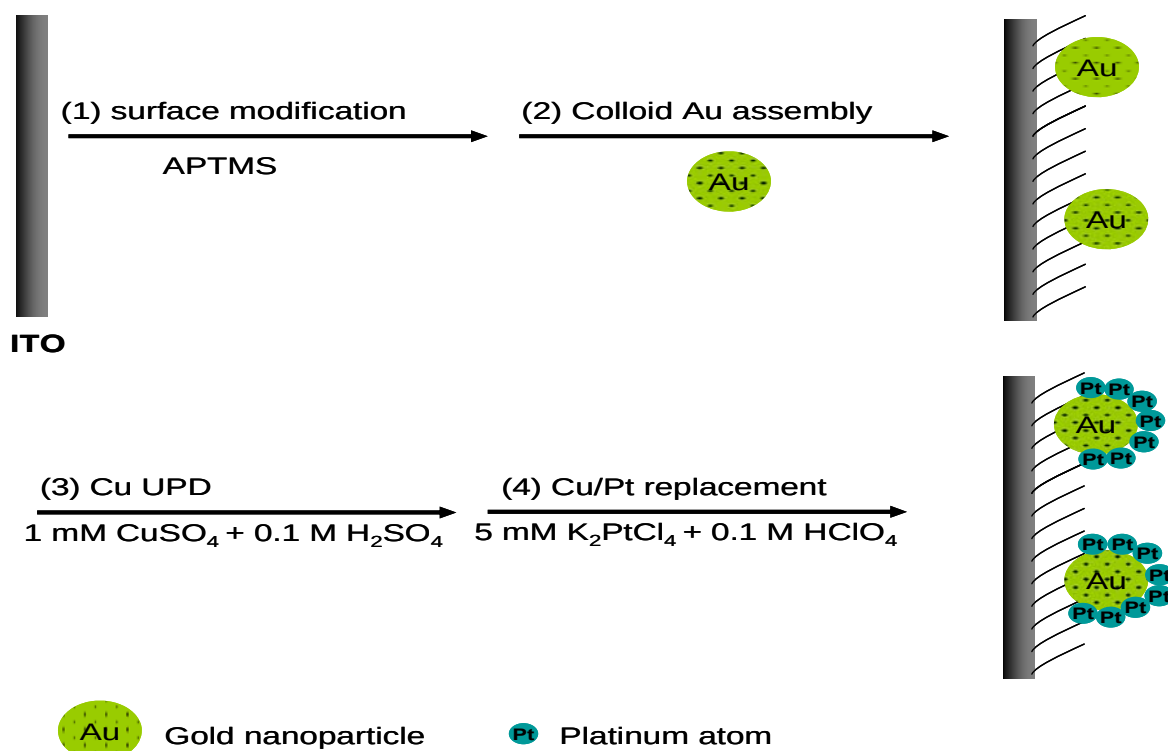


Figure 1.8: Illustrative scheme of preparation procedures (Steps 1 - 4) of ultrathin (nominally monolayer-level) platinum-coated colloidal gold nanoparticles chemically attached on amine-terminated surface functionalities produced on indium-tin-oxide (ITO) substrate through surface reactions with of 3-aminopropyltrimethoxysilane (APTMS), UPD of Cu and redox-replacement by Pt. (Adapted from Ref. [172]).

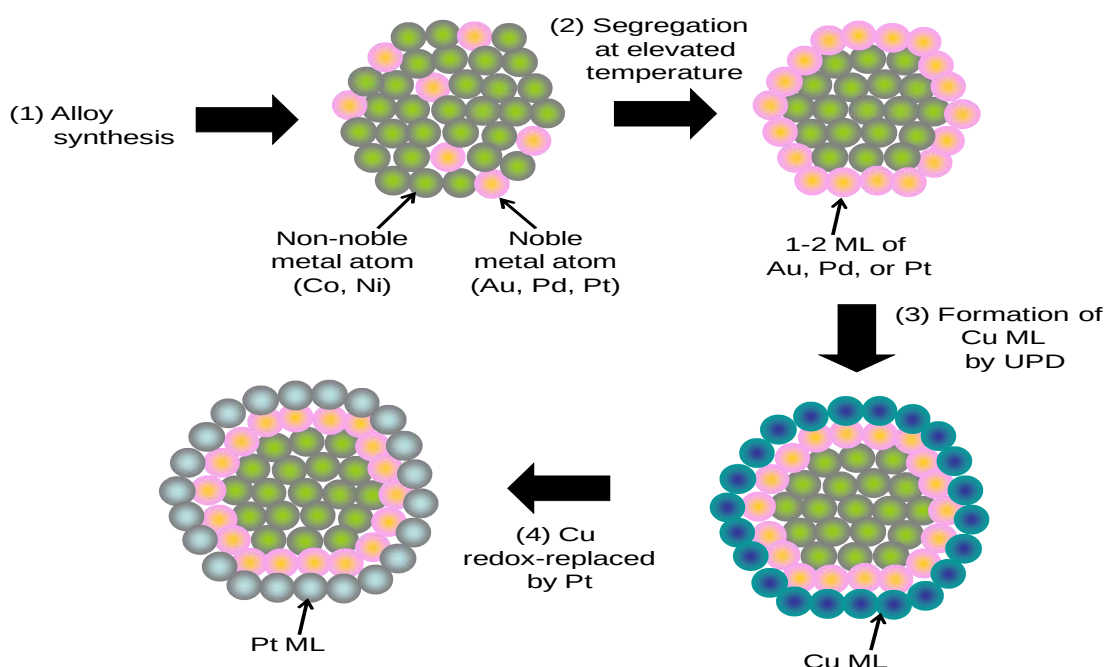


Figure 1.9: Scheme for synthesis of Pt monolayer catalysts on carbon-supported non-noble metal-noble metal (core-shell) nanoparticles. (Adapted from Ref. [173]).

Obradovic and co-workers explored electrochemical studies on synergistic effects of Pt adlayers on bulk Au polycrystalline electrodes and Au adlayers on bulk polycrystalline Pt electrodes via SLRR steps involving UPD Cu [175]; it was also observed that electronic modification of Pt by Au is insignificant on Au-modified Pt electrodes and considerable on Pt-modified Au electrodes as probed using formic acid electrocatalysis.

Essentially, the electrochemical deposition methodology pertaining SLRR reaction involve coupling of direct or fixed-potential electrodeposition and electroless deposition whereby adatoms of a non-noble metal or sacrificial metal M , generated at a controlled potential (Reaction 1.20), are used as templates for driving electroless deposition of noble metal N through redox-replacement under no external current. SLRR reactions take advantage of differences in electrochemical equilibrium potentials of the sacrificial metal M relative to the noble metal as the driving force for the overall redox-replacement reaction (Reaction 1.21).



Monometallic thin-films of PGMs such as Pt and Ru on crystalline gold as substrate have also been pursued via repeated SLRR cycles involving the noble metal precursors with either Cu or Pb (generated by UPD); essentially, these studies involved the layer-by-layer deposition mechanisms of Electrochemical Atomic Layer Deposition [176-179] whose primary aim is to controllably deposit conformal thin-films or superlattices. Overpotentially-deposited Ni templating bilayers, from a modified Watts electrolyte, have also recently been implemented for SLRR reactions involving Pt on polycrystalline Au and demonstrated to be just as effective as Cu UPD based SLRR in synthesizing Pt monolayer level films [180].

Strasser and coworkers have recently explored an electrosynthetic methodology to generate core-shell type of nanomaterials (dealloyed electrocatalysts – Figure 1.10) [181,182]. Principally, the dealloying process involves formation of a bimetallic alloy precursor consisting of a more noble and a less noble component, with larger ratio

of the less noble component (for example, Pt₂₅Cu₇₅ alloy synthesized by impregnation methods [2]), undergoes an electrochemical treatment which selectively removes the less noble metal from the surface of the nanoalloy. Consequently, a nanoparticulate 'shell' of Pt (or another noble metal) is formed about the surface region of the resulting bimetallic core-shell nanoparticle, whose thickness can be controlled by choice of dealloying conditions [181].

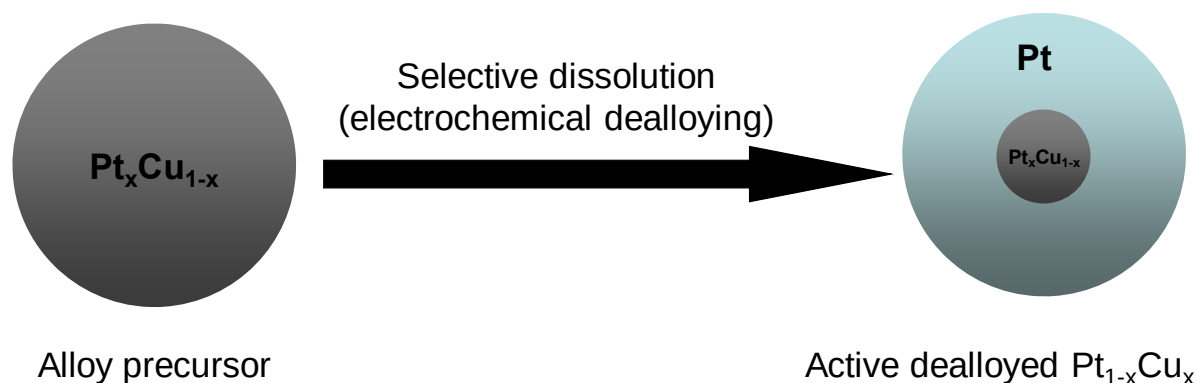


Figure 1.10: Representation of the principle of selective surface dissolution of Cu via electrochemical dealloying of a Cu-rich stoichiometric Pt_xCu_{1-x} alloy precursor producing core-shell nanoparticulate structure with Pt-rich shell. (Adapted from Refs. [181,182]).

General galvanic replacement involving prefabricated nanostructure base metals or alloyed systems, such as Ni/Al, Cu_xAl_{100-x} , and Au_xCu_{100-x} , has also been demonstrated in fabrication of nanoporous core-shell structured systems which use *in situ* the more noble metal components as both reducing agents and three-dimensional substrates [183-185].

The main synthetic challenge for mono- or multi-metallic electrocatalysts is to have good dispersion and control of the particle sizes as well as maximizing proximity of the primary metallic particles to active areas of electrode surfaces to increase their effective utilization in subsequent electrocatalytic applications [51].

1.4. Thesis context and theme

Electrochemical deposition of transition metals, with atomic control using single-step or multi-step surface-limited redox-replacement (SLRR) reactions of UPD adlayers, is of fundamental and potential technological importance in fabrication of

monolayer-decorated nanoparticles, monolayer-coated surfaces, epitaxial ultra-thin films, as well as multilayered nanoclusters [47,170,176,178,179,186-194].

The existing body of research work (with respect to SLRR reactions and related deposition mechanisms) has largely been empirical in optimization of the deposition conditions to grow the various layered thin-films on crystalline metallic substrates such as Au(111). Underlying physico-chemical factors (both from thermodynamic and kinetic standpoints) still remain weakly understood. Growth modes of sequentially deposited multimetallic noble metal-based systems on carbonaceous substrates have not been systematically studied. Incorporation of potentiostatic dealloying of templating or sacrificial metals such as Cu, en par with sequential deposition of substrate-immobilized 'core-shell' type of nanostructured bimetallic noble metal-based systems, seems to be unexplored. Thus, this thesis has endeavoured to pursue both fundamental and practical questions with respect to sequential deposition methodologies (incorporating SLRR reaction of Cu and its controlled effects upon its elimination from the synthetic pathways) to generate multilayered nanostructured systems containing noble metals Pt, Ru, or Au. Insights on the underlying deposition pathways have been pursued within frameworks of thermodynamics and kinetics. The resultant electrocatalytic properties of the various nanostructured systems are also systematically investigated in tandem with characteristic structural properties.

In particular, UPD has been modelled through formalisms based on the so-called 'pseudo-Nernstian' relationships between the electrode potential and surface activity of formed adlayer where the standard state can be phenomenologically chosen to correspond to the bulk metal or an appropriate submonolayer state [195-200]. To this effect, the surface coverage phenomena resulting from UPD process are describable through electrochemical adsorption isotherms. Modelling of the UPD processes based on Langmuir-type isotherm presumes adlayer formation on a homogeneous surface and neglects any interactions between the adatoms within the adlayer. More involved models, such as those derived from Temkin and Frumkin isotherms, take into account surface heterogeneity, adatom-substrate interactions, adatom-adatom interactions as well as induced surface effects upon adlayer

adsorption/desorption [195,196,201-203]. Moreover, the relationship between surface coverage of adlayers generated by UPD (θ_{UPD}) and the activity of the depositing species in the coverage range $0 \leq \theta_{\text{UPD}} \leq 1$, may be approximated in terms of a thermodynamic formalism based on the concept of “submonolayer equilibrium potential” [196], formulated within the framework of equal electrochemical potentials of the parent species in solution and in the corresponding substrate phases.

Since phase formation by SLRR reaction is intimately linked to UPD (both processes being surface-limited in their overall outcome), formalisms thus far explored are derived from well-established physico-chemical models of UPD; a phenomenon that has been extensively explored in electrochemical literature prior to exploration of the SLRR deposition methodology [193,204]. The realization that thermodynamically the chemical potential of a metal in a monolayer could be lower than its chemical potential in the bulk metal, hence, its activity in a monolayer can be less than unity, have led to various UPD models based on phase transitions or specific adsorption formalisms aimed at describing the potential-dependence or charge-dependence of surface coverage of UPD adlayers [160,197,199,200,205-207].

Kinetics of redox exchange in a single-step UPD/SLRR process have only recently been explored based on adsorption kinetics and potential-dependency of surface coverage; the models were tested for UPD of Pb or Cu on single-crystalline substrates Cu(111) and Ag(111) with Langmuir- and Frumkin-type adsorption considerations [204] and more rigorously, based on kinetics of UPD and surface coverage as well as charge-transfer mechanisms with adatom-adatom interactions of Temkin- and Frumkin-type adsorption models on Au(111) [193]. The development of formalisms to understand thermodynamic and kinetic factors governing such SLRR reactions can be regarded as being at their infancy.

As highlighted earlier, platinum-based nanostructured materials find widespread applications in catalysis and electrocatalysis [137]. The arrangement of the exposed atoms, or active sites for catalysis, determines the performance of the catalytic material used [208]. Indeed, surface-catalyzed reactions involving metallic catalysts are extremely sensitive to the atomic-level details of the catalytic surface. In

particular, bimetallic catalysts are known to enhance alcohol oxidation at fuel cell anodes as well as hydrogen oxidation through improved tolerance with respect to traces of CO in reformat-air fuel cells [52,209,210] and some bimetallic catalysts have superior activity compared to pure platinum for oxygen reduction at the cathode [51,211]. Enhancement of catalytic activity of multimetallic surfaces is now attributed to ligand (or electronic) and bifunctional effects [212].

It has been noted that the ratio of Pt to Ru in electrocatalysts prepared by various physical methods, such as vacuum deposition and chemical reduction or electrochemical codeposition, has significant effects on the performance of the Pt–Ru alloy-type catalysts for methanol oxidation [53,213,214]. Au clusters have been realized to have catalytic activity for CO oxidation and, when incorporated as adatoms to Pt, they have also been demonstrated to also have a stabilizing effect on underlying Pt metal surfaces, effectively suppressing Pt dissolution under highly oxidizing conditions [97]. Moreover, recent theoretical studies of clusters of the type Pt_mAu_n ($m + n = 4$), performed within the framework of Density Functional Theory (DFT), indicate that there are some underlying electronic effects that change the interaction of CO with Pt in the bimetallic systems [215,216].

Thus, there is a strong interest in fabrication of well-defined bimetallic (multi-element) catalytic systems involving Pt with Ru or Au, offering highly dispersed and maximized atomic contacts of constituent elements, with consequences in catalytically and electrochemically active surface areas that promote both bifunctional and electronic effects. In pursuit of controlled synthesis of robust electrocatalyst this thesis endeavored to investigate sequential electrochemical deposition strategies that could generate multimetallic nanoparticulate electrode systems possessing tunable electrocatalytic properties with tunable morphology and composition.

As noted earlier, electrodeposition of alloys by conventional methods is typically performed with either a preformed layer containing one metal, or codeposition of metals of interest from a common electrolytic bath. The deposition potential or current density, deposition time, and precursor concentrations have to be optimized simultaneously (and often compromised) to deposit the desired bimetallic alloy.

Regarding direct deposition of noble-metals, such as Pt (from their dissolved ionic forms), spontaneous (or electroless) deposition may occur at open-circuit conditions when a thermodynamically-favorable potential is established and availability of organic (or inorganic) surface functionalities that may act as electron sinks (a typical scenario for graphitic substrates) [162,217,218]. Much more refined control of deposits can, in principle, be achieved by sequential deposition of nanostructured and multi-element catalysts, with maximized atomic-level contacts, leading to enhanced catalytic utilization of the constituent particles. However, this synthetic avenue still has knowledge gaps in terms of in-depth understanding of thermodynamic and kinetic factors of underlying deposition processes and formed noble metal-based species.

In this work, glassy carbon (GC) was chosen as a widely applied electrode material that presents very low oxidation rates, high chemical inertness and very small pore sizes with low gas and liquid permeability [219]. GC is a reasonable model carbonaceous substrate for electrocatalytic reactions of importance to electrochemical sensors and electrochemical energy conversion devices alike. The microstructure of GC adapts an intertwined ribbon-like morphology composed of small microcrystalline graphitic domains [220] and recent high-resolution transmission electron microscopic studies [221] revealed compact fullerene-type domains dominate its microstructure. Gold thin-films as substrate materials have the following properties (proper for fundamental electrodeposition studies): extreme smoothness, inherent crystallinity; and electrochemical stability [222]. Crystalline Au films were applied in fundamental studies involving stepwise formation of multilayered Pt and the underlying kinetics, submonolayer thermodynamics and heterogeneity effects.

As highlighted above, the smallest changes in the metallic nanoparticle structure and composition might have a decisive effect on the particle's catalytic properties. From that one would conclude that noble metal-based bimetallic systems, denoted here as $n(M|N)$ to indicate n monometallic M and N adlayers plated over each other (instead of equivalent mixed, an alloy-type M_x-N_y deposits where M, N = Pt, Ru, or Au), might be desirable materials with unique properties. Interestingly, to the

best of our knowledge, the formation of the multilayered M|N nanostructures obtained by repeated sequential deposition from separate precursor solutions via the SLRR reaction has not so far been thoroughly investigated on carbonaceous substrates. In comparison to codeposition, a wider degree of freedom to fine tune the morphology and hence properties of the desired multilayered, multimetallic nanoparticles using sequential electrodeposition coupled to SLRR should be obtained and several advantages could be realized. For example, the surface composition of the resulting electrodeposited multimetallic structures may be adjusted by (i) the inherent rates of mass transport to the sites of cluster growth, (ii) the concentration of precursors used, (iii) nature of electrolyte used, (iv) the rates of reduction of the templating metal on the more noble metals, (v) thermodynamic properties of the metals of interest, and (vi) the nature of interactions between the metals of interest with their support.

Because electrochemical synthetic methodologies which integrate procedures for generation of core-shell type noble metal-based nanostructures, electrochemical dealloying, and surface-limited reactions, to generate multilayered electrocatalysts, are generally lacking in fundamental mechanisms and practical aspects of controlling nanoparticulate phase formation, this study chiefly pursued the following general aims:

- Development of various electrochemical synthetic methodologies for multimetallic electrocatalysts;
- Systematic physico-chemical modelling and characteristic investigations of the electrosynthetic pathways, surface and compositional properties of the multimetallic electrodic systems; and
- Characterization of the variety of multilayered electrocatalysts in oxidative and reductive reactions of importance in electrochemical technologies.

Specific research objectives were:

- To develop an automated instrumental setup capable of sequential electrodeposition from multiple elements sourced from independent electrolytic precursors using substrates of various geometries;
- To explore sequential deposition modes (with or without SLRR reactions involving Cu) to electrodeposit Pt, Ru, and Au multilayered systems on suitable gold and carbon-based substrate glassy carbon;
- To investigate the growth processes and associated mechanisms (pursued within thermodynamic and kinetic frameworks) of the Pt, Ru and Au using sequential electrodeposition modes involving SLRR reactions of Cu;
- To characterize the generated electrodeposits as electrocatalysts for reactions of interest for electrochemical technologies; and
- To comprehend underlying electrodeposition factors in relation to the nanoparticulate surface and bulk properties of multilayered systems of Pt, Ru, and Au on glassy carbon or gold as deposition substrates.

Research questions that have been posed include:

- What happens when repeated SLRR reactions are implemented (in a sequential fashion) to grow nanoparticulate deposits of two different noble-metals on carbonaceous and crystalline Au as deposition substrates?
- How different are deposits obtained by sequential spontaneous deposition (without using any SLRR steps)?
- What kind of deposits are obtained when sequential *codeposition* of noble-metals is implemented using simultaneous SLRR steps?
- What is the role of Cu in SLRR steps and its intermediary potentiostatic dealloying in sequential deposition of Pt-based multimetallic systems?
- What kinds of interfacial or electrocatalytic properties do the various deposits generate?

1.4.1. Thesis outline

In general, the thesis presents novel nanoscale electrode materials of precious metals platinum, ruthenium and gold as electrodic systems. The systems have been systematically explored beginning with their stepwise electrochemical deposition on model carbonaceous and gold substrates (in aqueous media and cost-effective ambient conditions) and ending with their characteristic nanostructured properties as well as tunable catalytic features for reactions of interest in electrochemical energy conversion and renewable processes. Fundamental insights are reported on physico-chemical characteristics of the multilayered electrode-immobilized nanostructured films, generated *in situ* via sequentially-implemented surface-limited redox-replacement reactions involving intermediary electrodeposited copper adlayers and gradual electrochemical dealloying of such adlayers. Thermodynamic and kinetic factors as well as overall reaction mechanisms of the electrochemical processes controlling composition, morphology, and electrocatalysis of the multilayered systems have been methodically studied. In particular, electrocatalysis on the nanostructured systems for oxygen reduction reaction, methanol and formic acid oxidation reactions were probed.

This thesis is presented in six chapters. In the *General Introduction (Chapter 1)*, literature overviews were presented for nanoscale materials and their current impetus in systematic research, both at fundamental and applied levels. In particular, key aspects on nanoscale catalysis and electrocatalysis as well as highlights on electrochemical technologies have been presented with emphasis on nanoparticulate systems of noble metals, in line with the theme of this thesis.

Chapter 2 details fundamental and practical characterisation techniques and methods of interest in the thesis. In particular, the chapter reviews electrochemical methods and techniques applicable for *in situ* studies of nanoscale electrodes as well as *ex situ* microscopic and spectroscopic characterisation.

The main thesis anecdotes (experimental methodologies, models, obtained results and discussions) are systematically presented in *Chapters 3 to 5*, the content of which has been published in relevant scientific journals (see List of Publications).

Table 1.2 summarises the set of metal-based systems, substrates and electrocatalytic reactions systematically studied in this work.

This work systematically investigated the ORR, MOR, and FAOR on uniquely synthesized Pt-based multilayered systems, and explored characteristic physico-chemical linkages between the underlying structural, compositional, and electrochemical activity controlling factors and the overall electrocatalysis of these reactions of interest in various electrochemical technologies.

Table 1.2: Multimetallic electrode systems, substrates, and electrocatalytic reactions investigated in this thesis

Multimetallic Systems	Substrates*	Electrocatalytic Reactions
M; M-X; and M-X-Y where, M, X, or Y could be: Pt, Ru, Au	- Vitreous Carbon (Glassy Carbon) - Gold thin-films	- Methanol Oxidation - Formic Acid Oxidation - Oxygen Reduction

* The *substrate* is the platform upon which the modifying layers are assembled [222] - in this work such assembly was pursued directly by electrochemical synthetic means in a 'bottom-up' approach.

Finally, *Chapter 6* provides key conclusions of the thesis as well as fundamental and applied perspectives on plausible derivations of the findings from the research work. In particular, perspectives on multilayered trimetallic systems of the type $n(M|N|Pt)$ (where M, N interchangeably as Ru or Au) are highlighted. Recommendations for advanced studies on characterization and potential electrocatalytic properties of the nanosystems developed and the associated synthetic pathways are expoused.

The complete list of references cited in all chapters is given separately at the end of the thesis. Supplementary information and data have also been appended.

CHAPTER II

Characterisation of Electrodes and Electrochemical Processes: An Overview of Concepts, Techniques and Practical Aspects

2.1. Introduction

Properties of deposited materials on various substrates, and mechanistic aspects of their nucleation and growth habits, can best be understood if the unmodified and modified substrates are characterized during synthesis (using *in situ* techniques) and immediately after the deposition process has ended (using *ex situ* techniques) [1,64,130,223]. This chapter aims to present an overview of the subset of such experimental methods and characterisation techniques (applicable in this research work). The overall methodology pursued in this work is presented in flow-chart format shown in Figure 2.1.

Fundamental quantities controlled or measured in electrochemical-based techniques are potential, current, and charge. This chapter provides general principles of electroanalytical techniques employing time-dependent controlled application and measurements of these fundamental quantities from electrochemical cells. To this effect, potentiometry, voltammetry, amperometry, coulometry and impedance spectroscopy are typical electrochemical techniques employed; this chapter gives a survey of principles and applications of some of these electrochemical techniques as applicable to the experimental research work of this thesis. In fact, the essence of this thesis is aqueous solution-solid phase electrochemical deposition, where variations in potential, current and charge are intricate quantities. Therefore, an overview of physico-chemical insights emanating from measurable electrochemical quantities in deposition processes is also highlighted. The chapter also provides a theoretical background on physico-chemical modelling involving thermodynamic, kinetic, and mass-transport effects in electrochemical studies.

Finally, a survey of microscopic and spectroscopic characterisation techniques used in this research to provide *ex situ* insights on elemental identities, surface and near-surface composition, bulk composition, and solid-state structural configurations of materials is provided. Techniques described include electron microscopy, atomic force microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction.

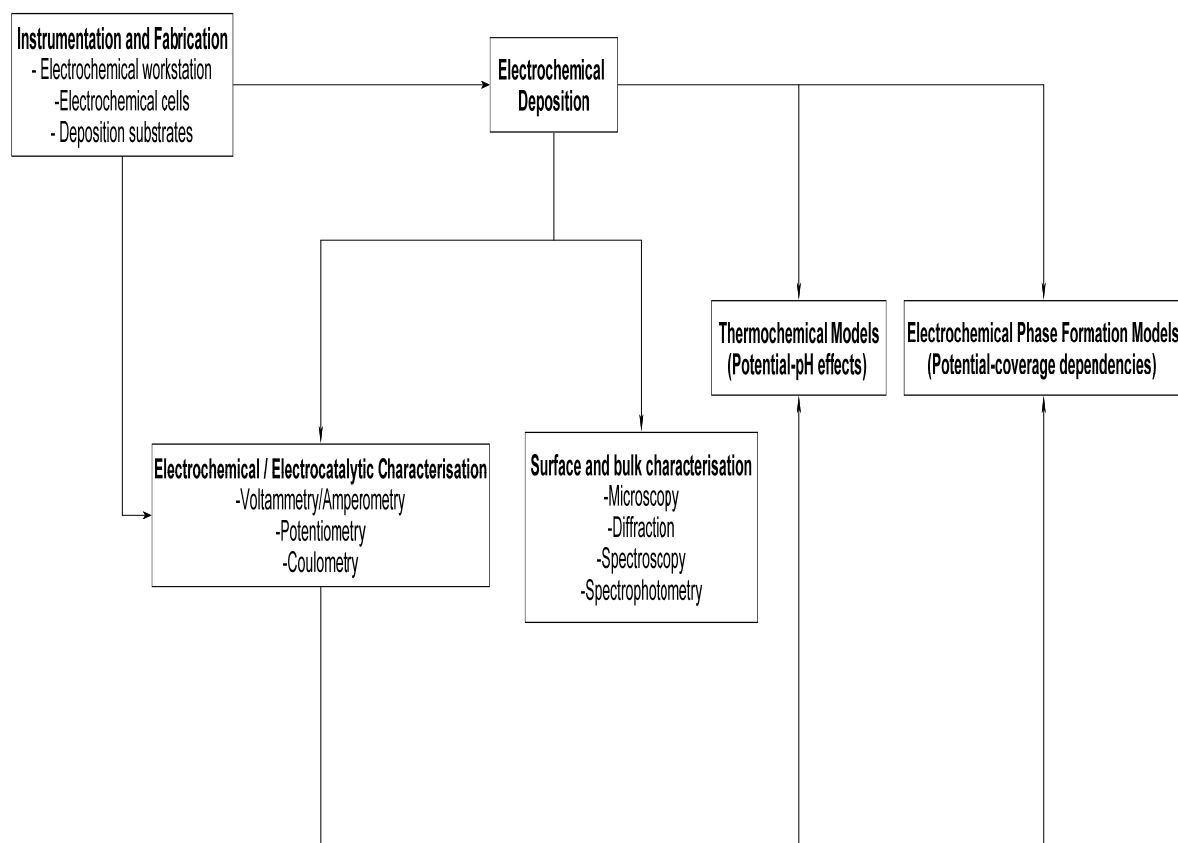


Figure 2.1: Flow-chart showing inter-relations between electrochemical experimental methods, physico-chemical modelling and characterisation techniques employed in this research.

2.2. Electrochemical methods

Electrochemical methods involve the use of electrodes to study changes on the electrodes themselves or follow transformation of dissolved species in solution through ionic or electronic transfer between the electrode-solution interfaces. In general, electrochemically-induced properties involve changes in potential (E), generation of current (i), or accumulation of charge (Q) over time (t).

2.2.1. Electrochemical cells

In electrochemical systems, it is generally of interest to investigate the processes and factors that affect the transfer of charge across an interface between chemical phases and accompanying transformations of involved chemical species; typically, the interface is between an electronic conductor (an *electrode*) and an ionic conductor (an *electrolyte*). In dedicated chapters presented hereafter, this thesis will be concerned with the studies of *nanostructured electrode/electrolyte interface* and the events that

occur there, from the electrochemical synthetic standpoint during generation of such interfaces to effects when electrocatalytic reactions are undertaken on them. Two types of processes normally occur at electrodes. One set of processes consists of reactions in which charged entities (e.g. electrons) are transferred across the electrode-solution interface.

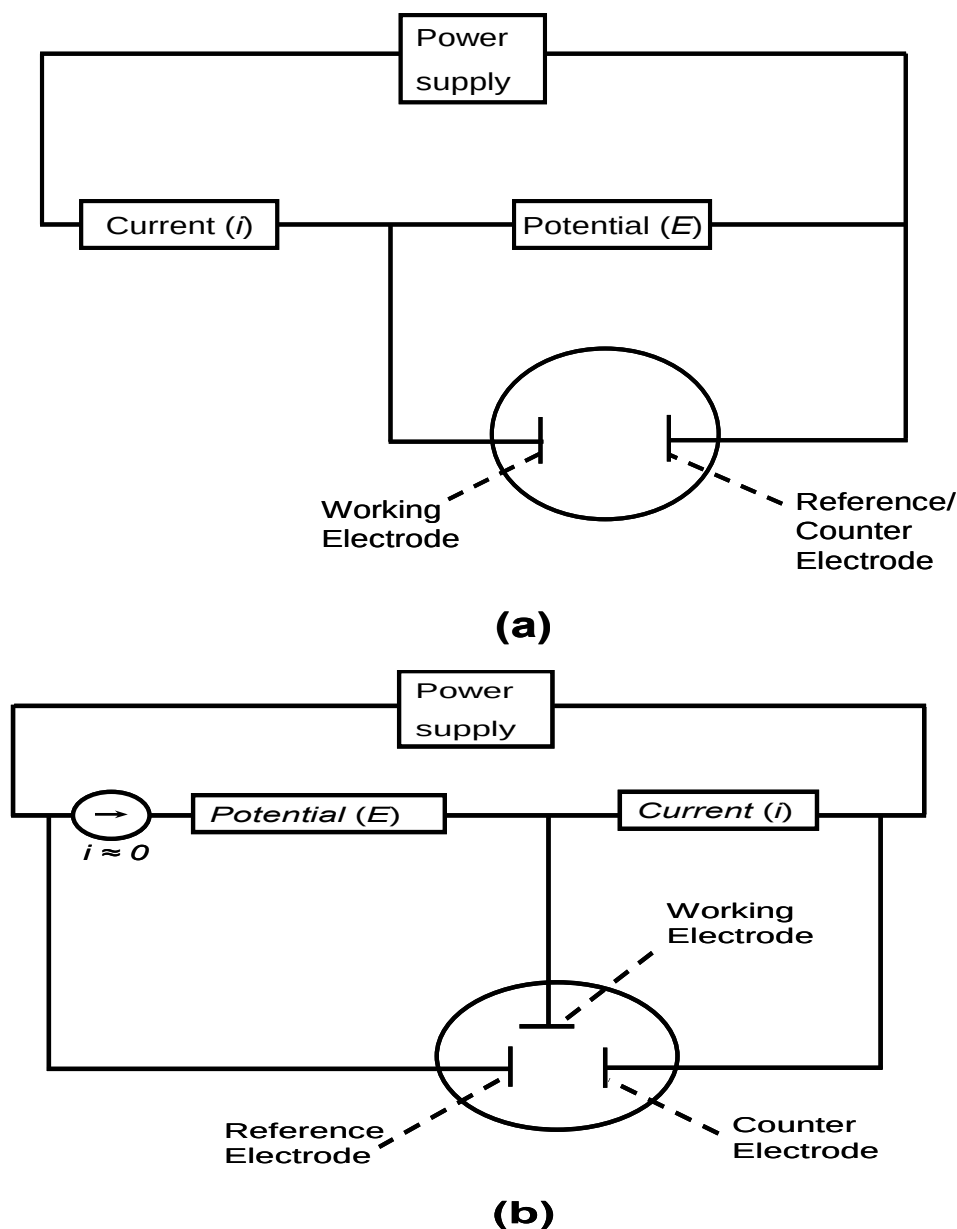


Figure 2.2: Electrode arrangements for electrochemical experiments showing (a) a two-electrode system and (b) a three-electrode system.

In particular, electron transfer may cause oxidation (the electrode concerned is referred to as an *anode*) or reduction (the electrode involved being the *cathode*) to occur. The charge-transfer electrochemical reactions are governed by Faraday's law

(that is, the extent of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), and simply referred to as *Faradaic processes*. When charged-entities do not cross the electrode-solution interface (the structure of the interface can be influenced with changing potential or solution composition and external currents can flow upon such changes), the electrode processes involved are referred to as *non-faradaic*. The faradaic processes are usually of primary interest in the investigation of an electrode reaction, the effects of non-faradaic processes have to be considered in order to obtain information about the charge-transfer and associated reactions. Since an individual interface is not feasible to be studied experimentally on a single electrode interface, typical experimental setups investigate *electrochemical cells* that involve several types of coupled interfaces. Electrochemical cells where an imposed passage of an electrical current invokes transformation of a chemical substance are termed *electrolytic cells* and the underlying process, *electrolysis*, effectively, involves conversion of electrical energy to chemical energy. Electrochemical cells in which the electrode reactions take place spontaneously (that is, without imposition of an external current), giving rise to an electrical current, are referred as *galvanic cells* and typically involve direct conversion of chemical to electrical energy [224,225].

In most electrochemical studies, one is interested in reactions that occur at only one electrode. In a simplest situation, an electrochemical cell involving two electrodes may suffice as schematically presented in Figure 2.2a. Such a cell is composed of the electrode system of interest, called the *working electrode (WE)*, coupled with a second electrode of fixed potential, and which is ideally non-polarisable, called the *reference electrode (RE)*. In a typical experiment where the potential difference between the electrodes immersed in an electrolyte solution is varied by means of an external power supply, a current may flow in the external circuit as electrons are transferred across the electrode/solution interfaces due to occurring reactions. The number of electrons can be measured in terms of charge, Q , passed in the circuit in accordance with Faraday's law which relates the Q and the amount of product electrochemically formed in time, t . Equation 2.1 is the expression of Faraday's law relating the charge required to convert λ moles of reactant to product in time t in an electrode reaction involving transfer of z electrons.

$$Q = \int_0^t i dt = \lambda zF \quad (2.1)$$

where, the current i can be viewed as the rate of flow of coulombs (or electrons); a current of 1 ampere (A) is equivalent to 1 C/s and 1 coulomb (C) is equivalent to 6.24×10^{18} electrons; F is the Faraday's constant (96485 C/mol) - in effect passage of 96,485 C causes 1 equivalent of reaction or consumption of 1 mole of reactant [224].

In general, a difference in electric potential can be measured between the electrodes (e.g. with a high-impedance voltmeter); this *cell potential*, measured in volts (V), where $1 \text{ V} = 1 \text{ joule/coulomb (J/C)}$, is a measure of the energy available to drive charge externally between the electrodes. The potential measured with no appreciable current during the measurement is the *open-circuit potential* of the cell, also known as *zero-current potential* or the *rest potential*.

2.2.1.1. Equilibrium Electrochemistry

Thermodynamic factors governing potential difference resulting in electrochemical cells can be appreciated if we illustratively consider a two-electrode cell interconnected with an external circuit (with no imposition of external current from a power supply) where the general redox reaction (Reaction 2.2) occurs at the *WE* and the cell measurements are done with respect to a *RE* at which a species REF_r is reversibly oxidised to REF_o (Reaction 2.3). For such a galvanic cell, thermodynamics impose that for transformation of λ moles of reactants to products, through exchange of z elementary electrons, the amount of electrical work equal to $zF(\Delta E)$ will be performed in the external circuit where ΔE is the potential difference between the electrodes. The maximum electrical work obtainable will correspond to the maximum cell potential for the given net reaction (Reaction 2.4) which in the context of chemical thermodynamics is the equilibrium potential (E_{eq}) of the overall redox couple. Furthermore, the maximum useful work obtainable from such a chemical reaction is the molar Gibbs free energy of the reaction (ΔG_r) given by Equation 2.5. As a function of activities of reactants and products for the given redox couple, ΔG_r is given by Equation 2.6. It follows from Equations 2.5 and 2.6 that a direct relationship between the equilibrium potential of the redox couple and

activities (or concentrations in ideal phases) of reactants and products is tacitly described by the Nernst equation (Equation 2.7) [222,224,226,227].



$$\Delta G_r = -zFE_{eq} \quad (2.5)$$

$$\Delta G_r = \Delta G_r^0 + RT \ln \left\{ \frac{a_R^{\lambda_R} a_{REF,r}^{\lambda_{REF,r}}}{a_O^{\lambda_o} a_{REF,o}^{\lambda_{REF,o}}} \right\} \quad (2.6)$$

$$E_{eq} = E^0 + \frac{RT}{zF} \ln \left\{ \frac{a_O^{\lambda_o} a_{REF,o}^{\lambda_{REF,o}}}{a_R^{\lambda_R} a_{REF,r}^{\lambda_{REF,r}}} \right\} \quad (2.7)$$

In Equations 2.5 - 2.7, a_i is the activity of reactant or product species i in a reaction phase ($a_i = \gamma_i[i]$, for concentration of dissolved i , $[i]$, and its activity coefficient γ_i , which in case of an ideal phase it is simply 1); λ_i represents the stoichiometric coefficient of reactant or product i ; R is the gas constant ($8.3145 \text{ J.K}^{-1}.\text{mol}^{-1}$); T stands for temperature; z stands for number of electrons exchanged in a single act of a reaction; F is the Faraday constant; the free energy at standard state involving unit activities of all reactants and products is ΔG_r^0 ($\Delta G_r^0 = -zFE^0$, where E^0 is the standard state potential).

Potential differences measured experimentally are effectively quoted with *reference* to the *standard hydrogen electrode* (SHE) conventionally chosen with an absolute potential arbitrarily set equal to *zero*. The SHE (as reference electrode) consists of a platinised platinum sheet immersed in an aqueous solution of unit activity of H^+ ions in contact with hydrogen gas at a pressure of 1 atm where the potential-determining reaction is



Essentially the standard electrode potentials, E^0 's, of all other electrode systems are tabulated against the SHE as a primary reference electrode system, with all the ions present at unit activity and gas pressure of 1 atm for any other gaseous substance involved in the electrode reaction of interest. However, secondary reference electrodes are more practical than the SHE. The most important types are metal-ion electrodes, where the activity of the potential-determining metal, $a_{M^{z+}}$, in the dissolved phase is effectively controlled by ensuring that the solution is in contact with a second solid phase composed of a sparingly soluble salt of M^{z+} and that $a_{M^{z+}}$ is determinable from the solubility product of the salt [227]. The silver-silver chloride (Ag/AgCl/Cl⁻) reference electrode is a common one (and employed in the electrochemical cells studied in this research work); the sparingly soluble salt AgCl at equilibrium according to Reaction 2.9:



from which the solubility product, K_s , is

$$K_s = a_{\text{Ag}^+} a_{\text{Cl}^-} \quad (2.10)$$

From thermodynamic conventions, an electrochemical cell reaction will only occur *spontaneously* if ΔG is negative; effectively, the process must have a *positive* electrode potential. Indeed, if current flows as a result of a spontaneous chemical process in a discharging electrochemical cell (such as a fuel cell), then the cell potential observed during discharge process, $E_{c,galv} < E^0$, and it follows that [227] the inequality

$$\Delta G_r^0 + zFE_{c,galv} < 0 \quad (2.11)$$

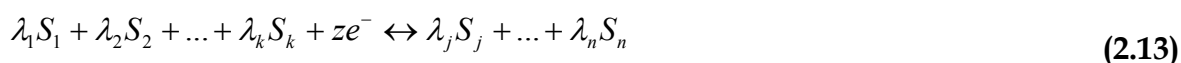
must hold. Similarly, if current is to flow in an electrolytic cell which transforms chemical species at electrodes, then the potential required to drive the electrolytic reactions $E_{c,elec} > E^0$ and

$$\Delta G_r^0 + zFE_{c,elec} > 0 \quad (2.12)$$

If a system follows the Nernst equation or an equation derived from it, the electrode reaction is generally referred as thermodynamically or electrochemically reversible (or *nernstian*). Potentiometry involves direct measurements of cell potentials that develop between electrodes in response to changes in activity (or concentration) of some analyte in a solution phase. When such measurements are performed at equilibrium with no current flow, the Nernst equation is useful in directly linking the measured potential and the analyte concentration. In other modes of electrochemical measurements, such as voltammetry, where a voltage perturbation to the system under study is applied, the system may still behave 'nernstian' depending on the time domain of the measurements, the rate of change of the force driving the observed process, and the speed with which the system can re-establish equilibrium. Hence, if the perturbation imposed on the system is small enough, or the system can attain equilibrium rapidly enough compared to the measuring time, thermodynamic relations will apply and may accordingly be used to approximate the observed potentials in relation to changes in activities (or concentrations) of electro-active species in an electrolytic cell [222].

Given the standard potential, E^0 , for a particular electrode reaction, it is possible to calculate ΔG_r^0 , for any set of concentrations (or activities) of involved reactants and products. The converse is also true; knowledge of ΔG_r^0 from available thermodynamic data for the overall cell reaction allows computation of E^0 and corresponding equilibrium potential, E_{eq} , for the reaction [222].

For a generic Reaction 2.13 involving arbitrary ionic activities and gas pressures of reactants and products [222]:



for which E^0 is given by

$$E^0 = \frac{\Delta G_r^0}{zF} \quad (2.14)$$

and

E_{eq} is given by

$$E_{\text{eq}} = \frac{\Delta G_r}{zF} \quad (2.15)$$

where

$$\Delta G_r = \Delta G_r^0 + \sum_i \lambda_i RT \ln a_i \quad (2.16)$$

from which it follows that

$$E_{\text{eq}} = E^0 - \left(\frac{RT}{zF} \right) \sum_i \lambda_i \ln a_i \quad (2.17)$$

where, conventionally, λ_i is positive for products and negative for reactants and if a substance i in the reaction is a dissolved gas in the electrolyte solution, in equilibrium with the corresponding gas in the vapour phase, then a_i is strictly (p_i/p^0) , for partial pressure p_i of the species i with p^0 its standard state pressure.

The thermodynamic relationship (Equation 2.18) between ΔG_r^0 , standard change in enthalpy (ΔH_r^0) and the standard change in entropy (ΔS_r^0), for a set of reactants and products, is useful in computation of ΔG_r^0 from known values of standard enthalpy of formation (ΔH_f^0) and standard entropy of formation (S^0) of substances involved as implemented through Equations 2.19 – 2.20.

$$\Delta G_r^0 = \Delta H_r^0 - T\Delta S_r^0 \quad (2.18)$$

$$\Delta H_r^0 = \sum_{R,P} (\lambda_P \Delta H_{f,P}^0 - \lambda_R \Delta H_{f,R}^0) \quad (2.19)$$

$$\Delta S_r^0 = \sum_{R,P} (\lambda_P S_P^0 - \lambda_R S_R^0) \quad (2.20)$$

where the subscript P refers to products and R to reactants.

Such thermodynamic relationships described above are the basis of modelling works performed in this thesis involving computation of potential-pH equilibrium diagrams generated for a mixture of metal ions-metallic solid phases.

2.2.1.2. Dynamic Electrochemistry

The two-electrode setup is relatively accurate when measurements involving low currents (< 100 nA) are performed where the ohmic drop is negligible and minimal changes to the composition of the *RE* can occur; changes in composition of *RE* result in unstable reference electrode potential. For large current situations, for example, when large electrodes are used, a three-electrode arrangement (Figure 2.2b) where in addition to the *WE* and *RE*, a *counter electrode* (*CE*) is normally employed. The control potential is applied between the working and reference electrodes, but no current flows through the *RE*, rather this role is played by the *CE*, which provides the current required by the working electrode without limiting the response. The corresponding process at the *CE* is normally electrolysis of the supporting electrolyte or solvent such that current flows without the need for a large overpotential. In regards to instrumentation and electronics, control of the applied potential to the working electrode (versus the reference electrode) is achieved with a *potentiostat* and measurements of associated current-potential (*i-E*) signals emanating from the electrochemical cell are undertaken with feedback circuits based on operational amplifiers referred as voltage follower and current follower circuits (Figure A.1, **Appendix A**). With a potentiostat, the feedback circuit drives the current between the working and counter electrodes while ensuring that none passes through the reference electrode circuit. Typically, electrochemical workstations also incorporate an additional circuit, a *galvanostat*, that allows controlled imposition of a fixed current through the cell whilst measuring the potential of the *WE* with respect to the *RE* [222,224,226].

The electrochemical measurements performed for purposes of this thesis were solely based on the potentiostatic mode; therefore, further descriptions of electrochemical methods will be exclusively based on the potentiostatic configuration.

To investigate chemical processes proceeding on solid-liquid interphases, it is important to take into consideration both the thermodynamics and kinetics of the

electron transfer reactions between electrodes and reactants (usually ions or molecules in a solution phase) as well as mass transport of species to and from the reaction sites. Many parameters can influence the dynamics of an electrode reaction. Generally [222,228], the rate of charge transfer can be controlled by:

- The electrode potential;
- Transport of material between the electrode and bulk solution (mass transport);
- The reactivity (ease of oxidation or reduction) of the solution species;
- The nature of the electrode surface; and
- The structure of the interfacial region over which the electron transfer occurs.

Figure 2.3 presents a summary of some processes involved for a general redox reaction (Reaction 2.21) at a working electrode. As highlighted in the foregoing concepts on ‘equilibrium electrochemistry’, the cell potential is monitored under no current flow through the cell with eventual establishment of a steady-state value indicative of the cell reaction in equilibrium. For Reaction 2.21, the equilibrium potential of the WE, E_{WE} (vs. SHE), can be described by the Nernst equation (Equation 2.22).



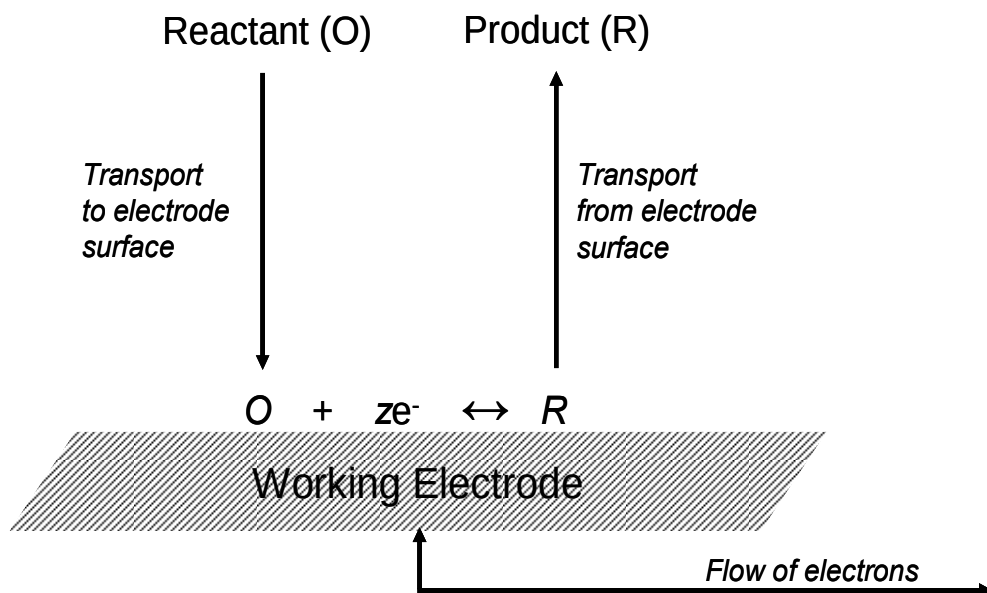


Figure 2.3: Schematic of processes influencing the rate of an electrode reaction (Adapted from Ref. [228]).

$$E_{\text{eq}} = E^0 + \frac{RT}{zF} \ln \left\{ \frac{C_{\text{O}}^{\text{s}}}{C_{\text{R}}^{\text{s}}} \right\} \quad (2.22)$$

where C_{O}^{s} and C_{R}^{s} are surface concentrations of O and R (assuming that their activity coefficients are unity so that concentrations rather than activities may be used).

If no current has passed through the cell, hence, no chemical change could have occurred, the surface concentrations of O and R would essentially be the same as their corresponding bulk concentrations, C_{O}^{∞} and C_{R}^{∞} during the particular experiment. Therefore, Equation 2.22 may be written in terms of bulk concentrations as shown in Equation 2.23 (with SHE as reference electrode):

$$E_{\text{eq}} = E^0 + \frac{RT}{zF} \ln \left\{ \frac{C_{\text{O}}^{\infty}}{C_{\text{R}}^{\infty}} \right\} \quad (2.23)$$

In a cell under conditions of zero net current, i , a *dynamic equilibrium* at the surface of the WE must be established, in which case the reduction of O (generating reduction current, i_{red}) and oxidation of R (generating oxidation current, i_{ox}) are both proceeding, but the processes are of equal rate (Equation 2.24).

$$i = i_{\text{red}} + i_{\text{ox}} = 0 \quad (2.24)$$

For electrolysis to occur (to reduce O to R), thermodynamically, the applied electrode potential (E_{appl}) different to E_{eq} for the reaction of interest must be applied to the WE; this deviation of E_{appl} from the equilibrium potential is defined as the *overpotential* (η):

$$\eta = E_{\text{appl}} - E_{\text{eq}} \quad (2.25)$$

If E_{appl} is made more negative than E_{eq} determined by the bulk concentrations of O and R for Reaction 2.21, equilibrium can only be re-established when the surface concentrations of O and R change in synchronization demanded by the Nernst equation at the given E_{appl} . To this effect, current may flow through the electrode/solution interface and a decrease of the ratio $C_{\text{O}}^{\text{s}}/C_{\text{R}}^{\text{s}}$ is necessitated. Such concentration decrease can only be brought about by conversion of O to R by passage of a reductive (cathodic) current. Conversely, when E_{appl} is made more positive than E_{eq} , an oxidative (anodic) current may be observed. Overall, current flow is governed by the kinetics of the electron transfer reaction and any other rate-determining step associated with the electrode/solution interface process [222,226,228]. Since electrode reactions are heterogeneous reactions occurring only at the electrode-electrolyte interface, the reaction rate of a general electrode reaction, v_{r} , is usually described as flux of electrons across a unit electrode area, A (Equation 2.26).

$$v_{\text{r}} = \frac{i}{zFA} = \frac{j}{zF} \quad (2.26)$$

where j is the *current density* (current per unit area, i/A).

For Reaction 2.21, the forward (reductive) reaction proceeds at a rate v_{red} that must be proportional to the surface concentration of reactant O (C_{O}^{s}); the constant of proportionality linking the reduction reaction is the rate constant for reduction, k_{red} , according to Equation 2.27. Likewise, the rate of the oxidation reaction, v_{ox} , is given by Equation 2.29 [222].

$$v_{\text{red}} = k_{\text{red}} C_{\text{O}}^{\text{s}} = \frac{i_{\text{red}}}{zFA} \quad (2.27)$$

$$v_{\text{ox}} = k_{\text{ox}} C_{\text{R}}^{\text{s}} = \frac{i_{\text{ox}}}{zFA} \quad (2.28)$$

At any applied potential, the net reaction rate, and corresponding net current i , is given by Equation 2.29

$$v_{\text{r}} = v_{\text{red}} - v_{\text{ox}} = k_{\text{red}} C_{\text{O}}^{\text{s}} - k_{\text{ox}} C_{\text{R}}^{\text{s}} = \frac{i}{zFA} \quad (2.29a)$$

and the net current i is simply

$$i = i_{\text{red}} - i_{\text{ox}} = zFA \{ k_{\text{red}} C_{\text{O}}^{\text{s}} - k_{\text{ox}} C_{\text{R}}^{\text{s}} \} \quad (2.29b)$$

In terms of the *standard heterogeneous rate constant*, k^0 (the potential-independent rate constant corresponding to the equilibrium formal potential of the redox couple, $E^{0'}$, where equal surface concentrations of the electroactive species prevail), the heterogeneous rate constants at any given applied potential can be expressed for the case of Reaction 2.21 by Equations 2.30 – 2.31 [222,226,228].

$$k_{\text{red}} = k^0 \exp\left(\frac{-azF(E_{\text{appl}} - E^{0'})}{RT}\right) \quad (2.30)$$

$$k_{\text{ox}} = k^0 \exp\left(\frac{(1-a)zF(E_{\text{appl}} - E^{0'})}{RT}\right) \quad (2.31)$$

where α is known as the transfer coefficient of the electrode reaction ($0 < \alpha < 1$).

Insertion of Equations 2.30 - 2.31 into Equation 2.29b yields the fundamental i - E relationship (Equation 2.32), commonly known as the *Butler-Volmer* formulation of electrode kinetics:

$$i = FAk^0 \left[C_{\text{O}}^{\text{s}} \exp\left(\frac{-azF(E_{\text{appl}} - E^{0'})}{RT}\right) - C_{\text{R}}^{\text{s}} \exp\left(\frac{(1-a)zF(E_{\text{appl}} - E^{0'})}{RT}\right) \right] \quad (2.32)$$

k^0 can be viewed as a measure of kinetic facility of a redox couple whereby a system with large k^0 will achieve equilibrium on a short time scale and one with small k^0 will be sluggish [222,226,229].

Establishment of opposing oxidative and reductive reactions in a state of *dynamic* equilibrium, where the net current i is zero and surface concentrations of O and R being the same as their bulk concentrations, the ‘thermodynamic’ Nernst equation (Equation 2.23) is also recoverable directly from the ‘kinetic’ Butler-Volmer equation. Even though the net current is zero at equilibrium, a balanced faradaic activity is envisioned that is expressible in terms of the *exchange current*, i_0 , which is effectively equal in magnitude to the opposing reduction and oxidative currents (Equation 2.33). i_0 is proportional to k^0 and can be substituted for k^0 as an effective kinetic parameter for current-potential characteristics of electrode reactions in terms of deviations from the equilibrium potential, E_{eq} , as given by the re-arranged Butler-Volmer equation (Equation 2.34) [222,226,229]. If i_0 is normalized to unit area it is known as *exchange current density*, $j_0 = i_0/A$.

$$i_0 = -i_{red} = i_{ox} = F A k^0 (C_O^\infty)^{(1-\alpha)} (C_R^\infty)^\alpha \quad (2.33)$$

$$i = i_0 \left[\frac{C_O^s}{C_O^\infty} \exp\left(\frac{-azF\eta}{RT}\right) - \frac{C_R^s}{C_R^\infty} \exp\left(\frac{(1-a)zF\eta}{RT}\right) \right] \quad (2.34)$$

where the overpotential, $\eta = E_{appl} - E_{eq}$.

For well-mixed electrolyte solutions and situations of low currents and negligible mass transfer effects, such that the surface concentrations do not differ appreciably from the bulk values, then Equation 2.34 is simplified as

$$i = i_0 \left[\exp\left(\frac{-azF\eta}{RT}\right) - \exp\left(\frac{(1-a)zF\eta}{RT}\right) \right] \quad (2.35)$$

Under conditions of negligible mass-transport effects of reactants and products to and from the electrode surface, the overpotential associated with any given current serves solely to supply the activation energy required to drive the heterogeneous process at the rate reflected by the current. When i_0 is large, small overpotentials are

required to drive the reaction and current flows readily in both anodic and cathodic directions, depending on the direction of the applied potential (see Figure 2.4). The lower the exchange current, the more sluggish the kinetics; hence, the larger the activation energy (activation overpotential) required for any appreciable net current (see Figure 2.4).

Indeed, many electrode-based reactions, although fairly favourable (thermodynamically), do not by themselves proceed at a significant rate (except at very high overpotentials) because of poor kinetics (with characteristic low values of i_0). One of the objectives of electrocatalytic research is to seek electrode materials that will provide alternative, lower energy of activation pathways (with characteristic high i_0) and consequently permit electrode reactions of interest to occur at high current density close to the equilibrium potential [36].

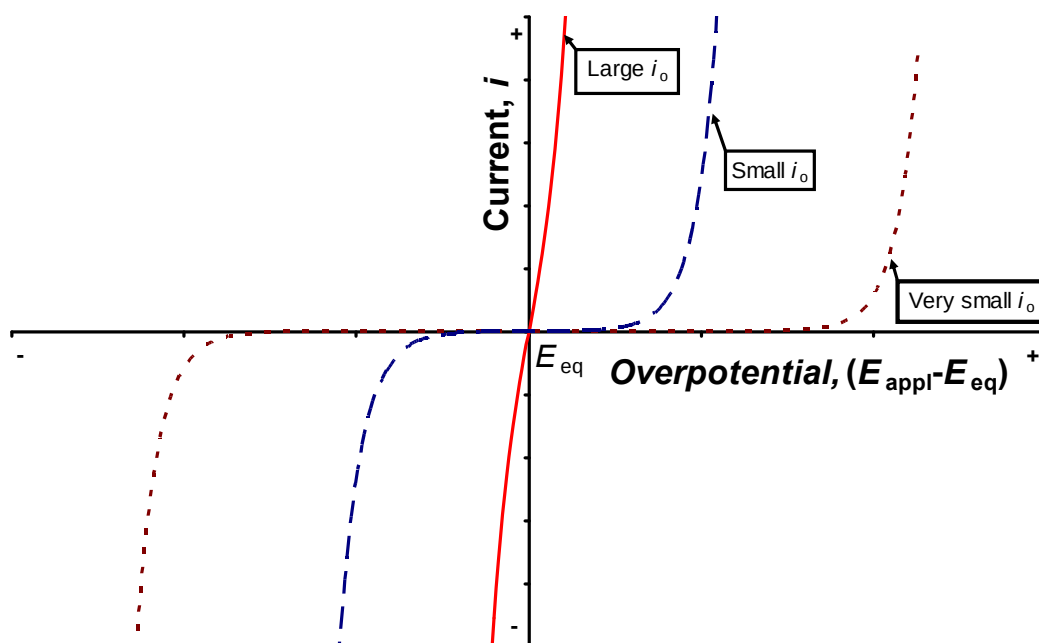


Figure 2.4: Influence of exchange current, i_0 , on overpotentials required to drive an electrolytic reaction and generation of net current.

2.2.1.3. Charge transfer resistance

It follows from the Butler-Volmer model, for a general multi-electron electrode reaction, that at low overpotentials ($\eta \ll RT/zF$) the net current is linearly related to η (Equation 2.36) in a potential range near the E_{eq} where the ratio η/i is similar to

Ohm's law and is defined as the charge-transfer resistance, R_{ct} according to Equation 2.37 [59,63,222].

$$i = i_0 \frac{zF}{RT} \eta \quad (2.36)$$

$$R_{ct} = \frac{RT}{zFi_0} \quad (2.37)$$

It follows from Equation 2.37 that the higher is i_0 , the smaller is R_{ct} , hence, R_{ct} is also a robust parameter that is associated directly with the kinetics of the electrode reaction of interest. R_{ct} can also be calculated at different potentials away from the equilibrium value, as usually done in *electrochemical impedance spectroscopy* (described in Section 2.2.4), where a small perturbation potential signal is imposed to ensure a linear response.

2.2.1.4. Mass transport effects

The foregoing background on fundamental principles of electrode reactions underpinned the influence of electrode potential on the thermodynamics and the kinetics of such interfacial electron-transfer reactions per se. However, the overall kinetics are governed by the slowest step in the overall process, where there is an interplay of dynamics of electron-transfer reaction at the electrode/solution interface (as induced by application of activation overpotential) and the rate of mass transport of electroactive species to the electrode surface from the bulk solution or vice versa (see Figure 2.3). Generally, in electrochemical systems it is essential to consider significant transport processes that may arise under experimental conditions or can be kept under systematic control. Three modes of mass transport mainly found are: diffusion, migration, and convection. Diffusion is the transfer of a substance down a concentration gradient. Migration involves movement of charged species due to a potential gradient. Convection is a form of mass transfer involving movement of species due to mechanical forces [222,225,226,228-230].

Migration is the mechanism by which charge passes through an electrolyte solution; the current of electrons through the external circuit must be balanced by the passage of ions through the solution between the electrodes. However, in most

electrochemical cells dissolved electroactive ionic species are in a large excess of a chemically and electrochemically inert (or background) electrolyte of ionic constituents, which ensures that the ionic strength of the solution is high and the electric fields remain homogenous and do not build up in the solution as electrolysis proceeds. In this way, migration is effectively suppressed as a form of mass transport of the ionic electroactive species undergoing electrolysis [226,228]. Electroanalytical techniques employed in such experimental arrangements, under suitable time scales where convection can be neglected quantitative current-potential regimes may be approximated to a diffusion-only problem greatly facilitating interpretation of data [231].

During electrochemical conversion of a reactant to product ($O \rightarrow R$), a boundary layer (commonly known as the *diffusion layer*) develops in which the concentrations of O and R are a function of distance from the electrode surface. The concentration of O is lower at the surface than in the bulk, whereas the converse is the case for the product R. To this effect, during electrolysis, O will diffuse towards the surface of the electrode and R away from it [226,228]. *Fick's first law of diffusion* [222,225,226,228-230] mathematically describes the rate of linear diffusion of a species i (in one dimension) to a planar surface at a perpendicular incremental distance x to the bulk liquid (Equation 2.37)

$$J_i = -D_i \frac{\partial C_i}{\partial x} \quad (2.37)$$

where J_i is the diffusional flux of species i , that is, the amount of materials diffusing through a unit plane per given time; C_i is the concentration of i ; D_i is a constant known as the diffusion coefficient that is characteristic of the diffusing species i .

Fick's second law of diffusion describes the change of concentration of a species with time due to diffusion across a dimensional zone bounded by two planes separated by an incremental distance x , y , or z as given by Equation 2.38 for linear diffusion in one-dimension and Equation 2.39 as a general form extended to describe diffusional transport in three-dimensions with Cartesian directions x , y , z [222,225,226,228-230].

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} \quad (2.38)$$

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + D_i \frac{\partial^2 C_i}{\partial y^2} + D_i \frac{\partial^2 C_i}{\partial z^2} \quad (2.39)$$

For electrolysis of O to R (Reaction 2.21), the concentration of O, C_O , will only change from its bulk concentration value, C_O^∞ , at points very close to the electrode surface, giving steep concentration profiles. With increasing reaction time, natural convection in the bulk and diffusion to the electrode surface will cause the concentration profiles to relax to a steady value extending into solution and becoming less steep producing a constant diffusion layer thickness (known as the Nernst diffusion layer thickness, δ) (see Figure 2.5a).

At the electrode surface ($x = 0$), balance of diffusional flux of O, J_O (according to Fick's first law, and flux of electrons from reduction of O to R leads to an approximation of the current limited by linear diffusion at a planar electrode of area A given by Equation 2.40 (see also Figure 2.5b) [226,228].

$$\frac{i}{zFA} = J_O = D_O \frac{C_O^\infty - C_O^s}{\delta} \quad (2.40)$$

Since electroactive species must be transported to the electrode surface for electrolysis to occur, it follows that the maximum obtainable current is limited by the rate at which reactant molecules or ions reach the electrode/solution interface. Equation 2.40 reveals that if the electrode potential is gradually changed so that the surface concentration eventually becomes zero, a limiting current, i_L , will be reached as approximated by Equation 2.41. Under such conditions of sufficiently large overpotentials, all electroactive material transported to the electrode is instantly converted to products [228].

$$i_L = \frac{zFAD_O C_O^\infty}{\delta} \quad (2.41)$$

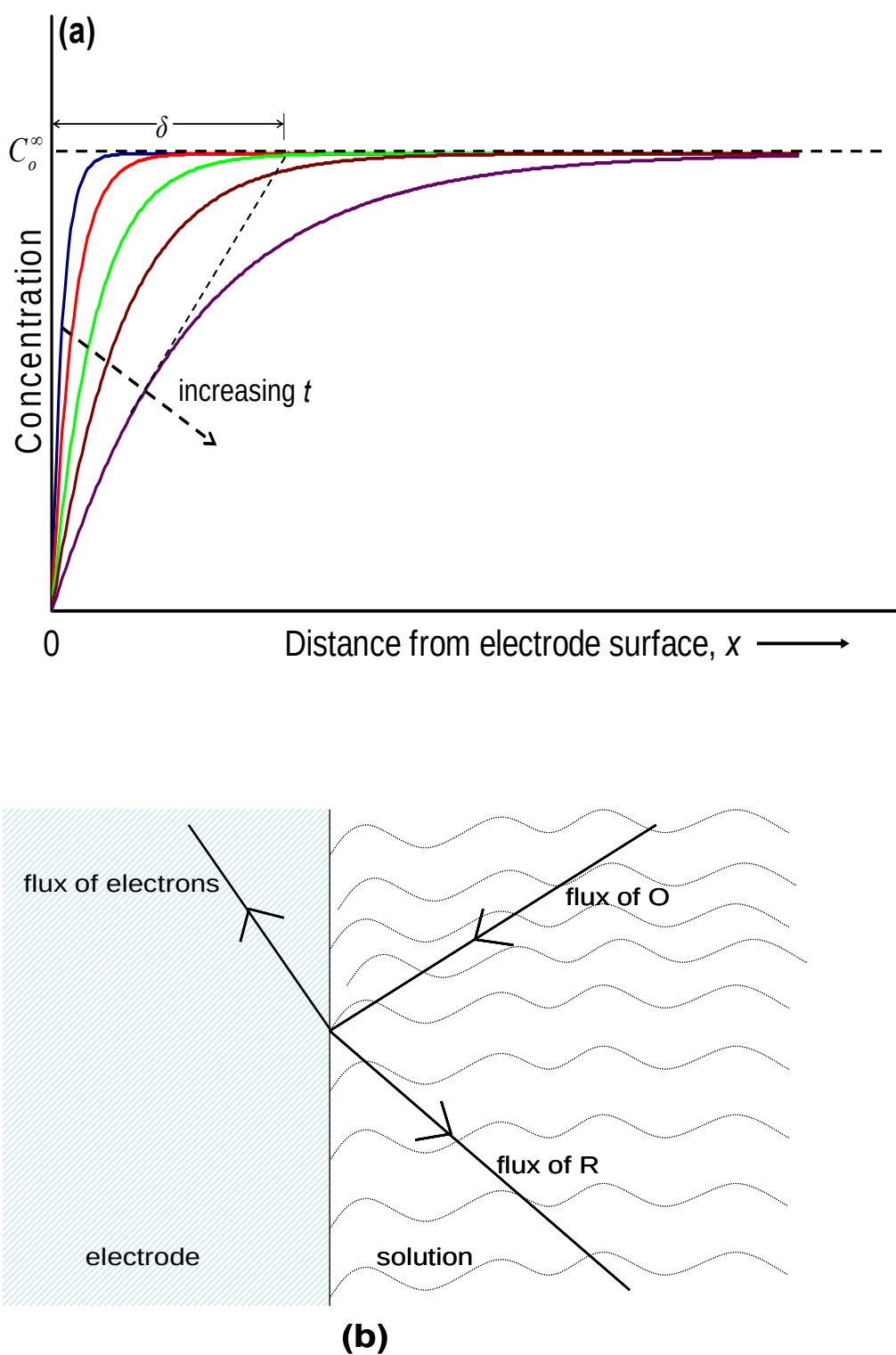


Figure 2.5: (a) Concentration profiles of electrolytically-reacting species O and growth of diffusion layer thickness, δ , as function of electrolysis time t . (b) A schematic representation of the balance of fluxes at the electrode surface for the reaction $O + ze^- \rightarrow R$ (Adapted from Ref. [226]).

2.2.2. Electric double layer, inner-sphere and outer-sphere electrode reactions

Any electrode reaction is an interfacial (that is, heterogeneous) reaction that necessarily involves a charge transfer step and a series of re-arrangement of reactive species from the bulk electrolyte and eventual discharge at the electrode surface. For charged solid surface, such as a metallic electrode under potential immersed in a liquid electrolyte (a solid-liquid interface), there must be a balancing counter charge which will occur in the vicinity of the liquid phase. Thus there is a small but finite volume of the liquid phase which is different from the extended (bulk) liquid phase.

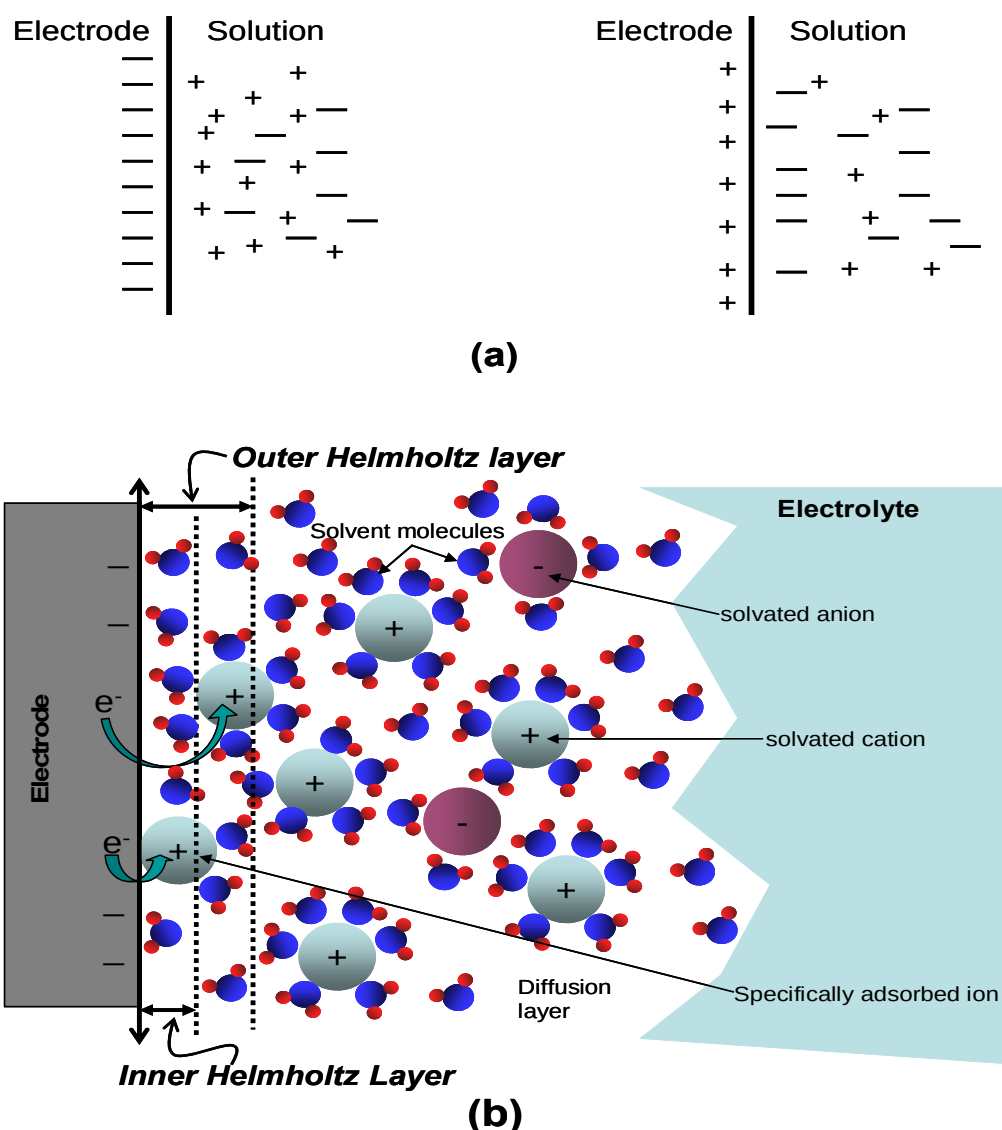


Figure 2.6: (a) A schematic representation of the electrode-solution interface as a capacitor. (b) A schematic model of the double-layer region around an electrode-electrolyte solution interface.

The electrode-solution interface has been shown to behave like a typical electrical capacitor, and models of the interfacial region resembling capacitors can be derived. Indeed, at a given potential, there will exist a cumulative charge on the electrode, Q_{Elec} , and a cumulative charge in the solution, Q_s – whether the charge on the electrode is negative or positive with respect to the solution depends on the potential across the interface and the composition of the solution (Figure 2.6a). At all times, however, $Q_{\text{Elec}} = -Q_s$. The charge on the electrode represents an excess or deficiency of electrons and resides in a very thin layer (< 0.01 nm) on the electrode surface, whereas the charge in solution is made up of an excess of either cations or anions in the vicinity of the electrode surface. The array of charged species and oriented dipoles existing at the electrode-solution interface is generally known as the *electrical double layer* that is characterized by a double-layer capacitance, C_{dl} , which is often a function of potential. A charging current or capacitive current will generally flow upon change of potential difference at the electrode's double-layer; the associated capacitive charge is the *double-layer charge*, Q_{dl} [222].

The electrolyte solution side around the electrical double-layer can be thought of being composed of several distinct layers (Figure 2.6b). The closest to the electrode is the *inner layer* (also referred as the *inner Helmholtz layer*) which contains solvent molecules and under certain circumstances other species (ionic or molecular) that are said to be *specifically-adsorbed*. Adjacent to the inner layer is the *outer Helmholtz layer* comprising solvated ions (*non-specifically adsorbed*) that can be regarded to approach the charged electrode with their solvation spheres intact such that the interaction of the solvated ions with the electrode involves only long-range electrostatic forces. The diffusion layer extends between the zone of non-specifically adsorbed solvated ions interacting with the charged electrode and the bulk of the electrolyte solution (Figure 2.6b) [222]. The charge transfer always results in chemical changes in that the oxidation state of the reacting species changes. However, in electrolyte which has excess of solvent (for example, in dilute aqueous electrolyte solutions), electron transfer may or may not involve the reorganization of the bonds of the solvated electro-active ionic complexes or molecules. When only the rearrangement of the solvation sphere or ligands occurs during electron transfer, the reaction is generally termed an *outer-sphere electrode reaction*. On the other hand,

an electron transfer process accompanied by bond cleavage or strong interaction between the electro-active reactants, intermediates or products and a charged electrode surface is referred as *inner-sphere electrode reaction* [222,232]. Various aspects of heterogeneous electrode reactions involving inner-sphere and outer-sphere mechanisms will be dealt with in later chapters involving electron-transfer, electrocatalysis and manipulation of electrochemically-active area involving nanostructured electrode surfaces.

Systematic studies of the electrode-solution interfaces are amenable by various electrochemical instrumental techniques surveyed hereafter.

2.2.3. Potential step and sweep techniques

2.2.3.1. Chronoamperometry

Chronoamperometry is a technique where the current from an electrochemical process is measured strictly as function of time [222,230]. As noted in preceding sections, there generally exist potential regions where faradaic processes do not occur. The current response as a function of time of a redox system is typically determined when the electrode potential is varied by a potential step - from an initial potential E_1 , where only one redox species is stable in solution (either as the oxidised form or reduced form) to a potential E_2 where facile oxidation or reduction occurs (Figure A.2, **Appendix A**).

If the electrode reaction (Reaction 2.21) converting O to R (or vice versa) is fast and reversible, and after application of the potential step is (i) limited by the rate of diffusion of the electroactive ions or molecules to a planar electrode of unit area A , and (ii) the concentration gradient of the reacting species decreases according to Fick's laws, then the diffusion-controlled current (i_d) response as a function of time can be described by the *Cottrell equation* (Equation 2.41 for reduction and Equation 2.42 for oxidation). Immediately following the potential step, a large current is controlled by the rate of diffusion to the electrode. The concentration gradients shortly after the step are extremely large because there is little time for any depletion of the electroactive material. Gradually as electrolysis proceeds, the

diffusion layer thickness increases and the current decreases in the limit of zero [222,228,230].

$$i_d = \frac{zFAD_o^{1/2}C_o^\infty}{\pi^{1/2}t^{1/2}} \quad (2.41)$$

$$-i_d = \frac{zFAD_R^{1/2}C_R^\infty}{\pi^{1/2}t^{1/2}} \quad (2.42)$$

where z , F , D_x and C_x^∞ ($x = O$ or R) have their usual meaning and the convention for reduction current as negative, whilst oxidation current is positive is used.

The Cottrell equation is of practical use in determination of electrochemical surface area of an electrode. To this end, available data on number of elementary electrons in the electrode reaction of interest, appropriate diffusion coefficient value and experimentally-fixed bulk concentration of the electroactive species can be used to deduce the electrode area A . Following a chronoamperometric experiment performed at an applied potential, where the rate of the electrode reaction is diffusion-limited, the slope of a plot of i_d versus $t^{1/2}$ avails the required value of A . Likewise, any other unknown parameter in the Cottrell equation (such as the diffusion coefficient) can be deduced if the chronoamperometric experiment is setup such that the electrode area is accurately known, along with other relevant equation parameters.

2.2.3.2. Chronocoulometry

Chronocoulometry involves measurement of charge (Q) as a function of time, t , resulting from an electrochemical process at an electrode by integration of current, i , measured with respect to t . This can be achieved through instrumental electronics during actual electrochemical measurements or by mathematical manipulation of recorded i - t response; cumulative charge from current response between two time intervals t_1 and t_2 is simply the integral

$$Q = \int_{t_1}^{t_2} i dt \quad (2.42)$$

Chronocoulometry practically gives similar information that is provided by chronoamperometry, because it is just based on the integration of the i - t response. Nevertheless, the former offers some experimental advantages: (i) the measured signal usually increases with time, (ii) it offers better signal-to-noise ratio, and (iii) contributions to measured Q from the electrochemical double layer charge (Q_{dl}) and any capacitive features, for example, due to adsorbed species, can be distinguished from those due to diffusing electro-active reactants either discharging through the inner-sphere or outer-sphere mechanisms [222].

2.2.3.3. Voltammetry

Voltammetry (*volt-amperometry*) comprises a special group of chronoamperometric electrochemical methods in which information about an electrochemically-active species is derived from the measurement of current through a working electrode as a function of time, while the applied potential to the electrode is controlled as a linear function of time [233]. The use of the three electrodes (working, counter, and reference), along with the potentiostat instrument, allows accurate application of a perturbation potential waveform and the measurement of the resultant signal from the electrochemical cell. Typically, a *current-potential* (i - E) plot (commonly referred to as a *voltammogram*) is obtained by measuring the current at the working electrode during the potential sweep. The primary event is the oxidation or reduction of a chemical species at a working electrode and the i - E response measured can be considered as an 'electrochemical spectrum' specifically indicating the potentials at which various redox processes occur with information on coupled homogeneous reactions and other complications such as adsorption often recognisable [222,228,234].

The various voltammetric techniques that are used are distinguished from each other primarily by the potential function that is applied to the *WE* to drive the reactions of interest, and by the material used. The technique can provide thermodynamic information as well as kinetic parameters related to electron transfer reactions at an electrode-solution interface. In addition, voltammetry can provide information related to the kinetics and mechanisms of chemical reactions subsequent to an electron transfer step. Some of the main advantages of sweep

voltammetry are based on the fact that a wide potential range can be scanned rapidly for reducible and oxidisable species. These experiments can also be performed with variable time scales by applying different potential scan rates [222,228,234].

2.2.3.3.1. Linear sweep voltammetry

In *linear sweep voltammetry* (LSV), a potentiostat is employed to sweep the potential of the working electrode with a constant scan rate ν (that is, $\Delta E/\Delta t$; for sufficiently small increments dE/dt) from potential E_i to potential E_f prior to halting the scan (Figure A.3a, **Appendix A**). The applied potential E at any given time is a function of the scan rate (ν) and the time of the sweep (t) as implied by Equation 2.43.

$$E(t) = E_i - \frac{dE}{dt} t = E_i - \nu t \quad (2.43)$$

Typical i - E responses in LSV, exemplified for a diffusion-controlled, outer-sphere oxidation reaction (R/O couple), are shown in Figure A.3 (**Appendix A**). If the scan is initiated at E_i (well negative of E_{eq}) only nonfaradaic (or background) currents flow for a while, since the applied potentials are not sufficient enough (both thermodynamically and kinetically) to induce electron transfer at the working electrode. When the potential is swept in the positive direction to the vicinity of E_{eq} , oxidation begins and current starts to flow. As the potential is swept more positive (increase in overpotential), the oxidation becomes more facile, effectively, the heterogeneous rate constant k_{ox} becomes greater (Equation 2.31) and current rises exponentially as described by Butler-Volmer model (Equation 2.34), the steepness of which depends on the underlying electrode kinetics. For reversible electron-transfer process (Figure A.3b, curve I, **Appendix A**) appreciable currents flow when the electrode attains a potential close to E_{eq} ; as soon as oxidation is thermodynamically viable, it takes place due to rapid electrode kinetics implicit of a reversible couple with large i_0 . In case the electron transfer reaction is irreversible (Figure A.3b, curve II, **Appendix A**), no appreciable faradaic currents flow until the overpotential is considerably increased, that is, potentials well positive of the thermodynamic E_{eq} must be imposed in order to drive the oxidation of R to O; such irreversible processes are characteristic of small i_0 values as was discussed previously for Figure

2.4. As the potential continues to become even more positive past the E_{eq} , although kinetics of electron-transfer increase, the surface concentration of R steadily decreases as electrolysis at the electrode surface consumes R, which is only partially replenished by diffusion of fresh R from the bulk solution. The rate of mass-transport reaches its maximum and declines as depletion effects at the electrode surface persist at high rates. The net observation is therefore a peaked current-potential curve with maximum peak current i_p and peak potential E_p , where the maximum reflects a balance between an increasing heterogeneous rate and a decrease in surface concentration [59,222,228,233,235].

As electrolysis proceeds at sufficiently high rates beyond E_p , the diffusion zone around the electrode in which R is depleted thickens, thus R has to diffuse further to the electrode, the concentration gradient at the electrode-solution interface continues to decrease resulting in a reduced rate of mass transport (according to Fick's laws). Consequently, there is an establishment of an unchanging concentration profile and net current decay to a steady-state (Figure A.3c, **Appendix A**).

2.2.3.3.2. Cyclic voltammetry

Linear sweep voltammetry can be extended so that when the potential is swept from E_i and reaches a switching potential E_λ where the direction of sweep is reversed and the electrode potential is scanned back towards the initial value E_i ; the technique is termed *cyclic voltammetry* (CV) as exemplified in Figure A.4 (**Appendix A**) for a diffusion-controlled reversible outer-sphere R/O redox couple. The reverse scan in CV depends on the exact position of E_λ the potential at which the electrochemical generation of the oxidised species that accumulated in the diffusion layer during the forward scan begins to be transformed back to the reduced species. During the forward scan, the oxidation maximum peak potential, $E_{p,ox}$ with maximum oxidation peak current i_p is observed and upon reversal of the scan the reduction maximum peak potential, $E_{p,red}$ is obtained due to the interplay of mass-transport and electron-transfer kinetics. In either LSV or CV, quantitatively, the peak current, i_p , for a reversible oxidation or reduction process, with diffusion-limitations, is given by the Randles-Sevcik equation (Equation 2.44) [59,222,228,233,235].

$$i_p = 0.4463zFAD_i^{1/2}C_i^\infty\nu^{1/2} \quad (2.44)$$

where z , F , A , and ν have their usual meaning, D_i is the diffusion coefficient of the electroactive reactant species during the appropriated voltammetric scan, and C_i^∞ is the concentration of the reactant species in the bulk electrolyte.

In voltammetric scans, the scan rate ν employed determines the timescale of the experiment. For short timescales (high ν), the diffusion-controlled current is over that for longer timescales (smaller ν). This is due to the fact that the concentration gradient and the flux of reactants to the electrode surface increase with increasing ν . Notably for reversible electron-transfer processes, i_p is proportional to $\nu^{1/2}$ and plots of this relationship from experimental voltammetric data are useful in diagnosing diffusion-control of the current as opposed to currents due to surface-bound or adsorbed redox species. Moreover, E_p is independent of scan rate and in CV reversible redox reactions result in a characteristic peak separation between $E_{p,ox}$ and $E_{p,red}$ (Equations 2.45 – 2.46). Also, a unity ratio of the respective peak currents is expected for reversible cases (Equation 2.47) [59,222,228,233,235].

$$\Delta E_p = E_{p,ox} - E_{p,red} \approx \frac{0.059}{z} \quad (V) \text{ at } 298 \text{ K} \quad (2.45)$$

$$\left| E_p - \frac{E_p}{2} \right| \approx \frac{0.059}{z} \quad (V) \text{ at } 298 \text{ K} \quad (2.46)$$

$$\frac{i_{p,ox}}{i_{p,red}} \approx 1 \quad (2.47)$$

Diagnostic relationships involving i_p , scan rate and E_p from voltammetry of diffusion-controlled, *non-reversible* electron-transfer processes are also available and useful in interpretation of voltammetric data [222,228,235,236].

2.2.3.4. Hydrodynamic voltammetry

In systems where there is convection in addition to diffusion, greater amounts of the electro-active materials are brought to the electrode surface with consequences on the electrochemical responses generated. Typically, for potentiostatic electrode

reactions, larger currents are observed upon electrolysis with forced convection than those observed when diffusion alone operates. The use of deliberate introduction of convection as a dominant mode of transport of electro-active materials to electrode surfaces involves *hydrodynamic electrodes*. The related current-potential measurements on a hydrodynamic working electrode are referred as *hydrodynamic voltammetry* (HV) [222,228,237,238]. Convection within the electrochemical cell may be invoked in several practical ways: (i) the electrode itself may be set in motion inducing convection in the liquid electrolyte solution, or (ii) the electrode material may be stationary and an electrolyte solution forced to flow past its surface. In the former case, examples include rotating disc, rotating wire, streaming, and vibrating electrodes; the latter case include wall-jet, tubular, channel, and packed-bed electrodes in fluid streams [222,237].

The rotating disc electrode (RDE) and the channel electrode (CE) are typical examples of practical hydrodynamic electrodes amenable to rigorous theoretical description as employed in voltammetric experiments (see Figure 2.7). For simplification of the associated theoretical description, experiments and the positioning of electrodes are designed so that laminar flow (Figures 2.11b and 2.11d) as opposed to turbulent flow is obtained. For RDE, the imposed rotation (of constant radial speed or frequency) spins the solution out from the cylinder surface in a radial direction and this movement in turn, draws fresh reactants up towards the exposed disc electrode. To this effect, the hydrodynamics sustain a steady supply of electroactive species to the electrode. Viewed along the axis normal to the disc electrode (the z -axis, Figure 2.7a), there is a diffusion layer across which the reactant species diffuse to the electrode. The diffusion layer thickness, δ_d , is dependent on the rotation frequency, ω , diffusion coefficient of the electroactive substance, D , and the kinematic viscosity, ν_s , of the solvent (cm^2s^{-1}) as given by Equation 2.48.

$$\delta_d = 1.61D^{1/3}\omega^{-1/2}\nu_s^{1/6} \quad (2.48)$$

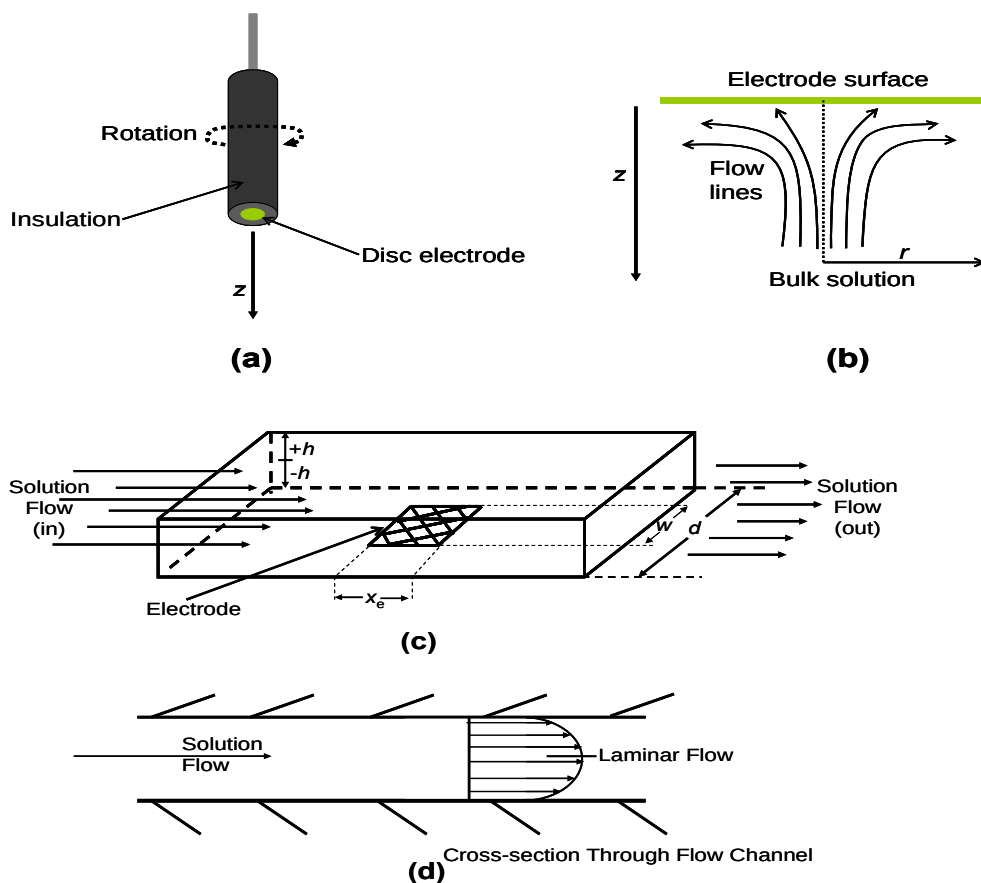


Figure 2.7: Hydrodynamic electrodes. (a) Rotating-disk electrode. (b) Laminar flow pattern at a rotating disc. (c) Flow-channel electrode; h is the cell half-height, d is the width of the flow-channel, w is the width of the embedded electrode, and x_1 is the length of the embedded electrode. (d) Laminar flow profile in the channel electrode in typical flow-cell. (Adapted from Refs. [228,238]).

In rigorous description of the flux of electroactive species to the hydrodynamic electrode, both diffusion and convection are considered and solutions of boundary value problems under steady-state mass transport conditions and electron-transfer flux at the electrode surface leads to equations describing the mass-transport limiting current, i_L , for electrolysis at the hydrodynamic electrodes [222,228,237,238].

For an RDE with electrode area A and concentration of the electroactive species in the bulk solution C^∞ , with elementary number of electrons transferred in the electrode reaction z , the diffusion-limited current (i_L) is given by the Levich equation (Equation 2.49) - the general convention of positive current for oxidation and negative current for reduction reactions is implied by the $\pm$ sign.

$$i_L = \pm 0.62 z F A D^{2/3} \omega^{1/2} \nu_s^{-1/6} C^\infty \quad (2.49)$$

Generally, the current in the absence of diffusion control, that is, in case of electron transfer control with rate constant k_e as a function of the electrode potential E is given by

$$i_K = \pm F A k_e(E) C^\infty \quad (2.50)$$

The general current relationship at an RDE, taking into account both mass transport and electron transfer kinetics, is given by the Equation 2.51 (the Koutecky-Levich equation) [222,228,237,238].

$$\frac{1}{i} = \frac{1}{i_K} \pm \frac{1}{i_L} = \frac{1}{i_K} \pm \frac{1}{0.62 z F A D^{2/3} \omega^{1/2} \nu_s^{-1/6} C^\infty} \quad (2.51)$$

In flow-channel electrodes the electrolyte solution is mechanically pumped into a thin duct containing a fixed working electrode of particular dimensions (Figure 2.7c). Solutions of convective-diffusion boundary-value problems for mass-transport at a flow-channel electrode, can provide theoretical descriptions of mass-transport limited current as a function of the solution volume flow rate (v_f) in an analogous fashion to the RDE [228,237,238]. Figure 2.8 provides representative hydrodynamic linear sweep voltammetric curves for the one-electron transfer outer-sphere oxidation reaction in a flow-channel electrochemical cell.

The Levich equation for mass-transport limited current i_L for a channel electrode (channel dimensions as exemplified in Figure 2.7c) where an electroactive species with bulk concentration C^∞ and constant solution volume flow-rate v_f , is given by

$$i_L = \pm 0.925 z F D^{2/3} C^\infty \left(\frac{v_f}{h^2 d} \right)^{1/3} w x_1^{2/3} \quad (2.52)$$

where i_K is given by Equation 2.50.

Equation 2.52 holds when the flow rate is sufficiently fast that diffusion layer thickness is much smaller than the height of the flow channel and i_L in this case varies with the cube root of the volume flow rate.

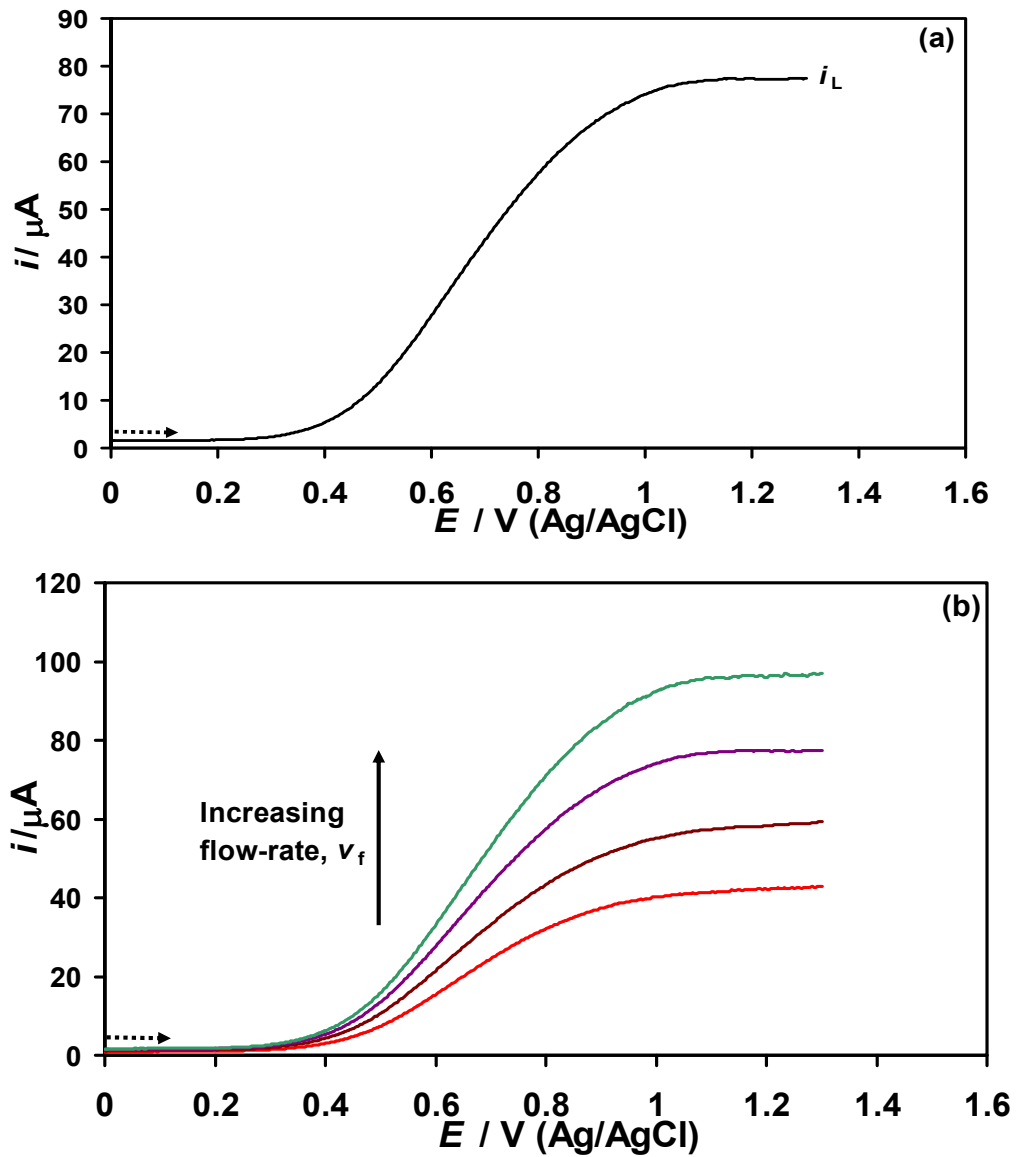


Figure 2.8: Current - potential responses during hydrodynamic linear sweep voltammetry involving outer-sphere oxidation of $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$ at a planar glassy carbon working electrode in an electrochemical flow-cell. Electrolyte solution: Nitrogen-saturated 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in 0.1 M KCl; voltammetric scan rate = 50mV/s; (a) solution flow-rate, $v_f = 0.1 \text{ cm}^3/\text{s}$; (b) v_f : 0.02, 0.05, 0.1, 0.17 cm^3/s .

The Koutecky-Levich relationship for a channel electrode is given by Equation 2.53

$$\frac{1}{i} = \frac{1}{i_K} \pm \frac{1}{i_L} = \frac{1}{i_K} \pm \frac{1}{0.925zFD^{2/3}C^\infty \left(\frac{v_f}{h^2d} \right)^{1/3} wx_1^{2/3}} \quad (2.53)$$

Determination of i_K at different values of E from plots of $1/I$ vs $\omega^{-1/2}$ or $1/I$ vs $v_f^{1/3}$ for appropriate hydrodynamic working electrode allows for evaluation of electrokinetic parameters for an electrode reaction of interest.

This thesis will exclusively explore electrochemical measurements and electrosynthetic procedures utilizing flow-channel electrochemical cells, with the advantage to automation of electrolyte solution exchange (performed *in situ* for sequential electrodeposition of multimetallic systems as systematically-modified working electrode materials) allowing for in-depth understanding of their surface electrochemical and electrocatalytic properties under static and hydrodynamic conditions. The various features of such flow-cell based studies are presented in Chapters 3 - 5.

2.2.3.5. Voltammetry of inner-sphere electrode reactions

In addition to the redox processes thus far reviewed in this chapter, in which electron transfer takes place between the electrode surface and species restricted in the outer Helmholtz plane (see Figure 2.6), there is a wide range of electrochemical processes that incorporation of reactants and or products on the electrode surface itself, that is, involvement of the inner Helmholtz layer. Such electrochemical surface phenomena include metal adlayer formation (for example, through surface-limited reactions introduced in Chapter 2), surface oxide formation and adsorption processes (physisorption or chemisorption) of reactants and/or products on the electrode surface itself. This is particularly true for all electrocatalytic processes, for which adsorption is a requisite feature. From microscopic perspective, electrode surfaces are rarely homogeneous and surface processes, such as adsorption, involves interaction with *active sites* on the surface (for example, isolated atomic clusters on otherwise flat planes). Such surface sites play a crucial role in the overall electrochemistry of nanostructured electrodes and their systematic formation and characterisation is a key aspect of this thesis (explored in depth within the context of Chapters 4 – 6).

In this section we present an overview of basic principles and characteristic electrochemical features involving inner-sphere electrode reactions as exemplified by voltammetry on bulk Pt and Au electrodes.

2.2.3.5.1. Surface electrochemistry

Voltammetry is tremendously useful technique for probing multiple electrode processes in wide-potential range. In particular, for noble metallic electrodes in aqueous media, surface electrochemistry is characteristic of a particular noble metal. Figure 2.9 provides examples of CVs of polycrystalline bulk Pt and Au electrodes in aqueous acidic medium. Formation of adsorbed hydrogen and its oxidative desorption is characteristic of Pt surface in the potential range +0.05 to -0.2 V (vs Ag/AgCl/3M KCl) as shown in Figure 2.9a.

The inner-sphere reduction reaction of H^+ and concomitant chemisorption of H_{ads} on the *active site* (a surface Pt atom, as schematically depicted in Figure 2.9b) can be viewed to proceed as Reaction 2.54. This process continues as electrode potentials become more and more negative, until the formation of a H_{ads} monolayer is achieved. With further negative potential scanning, adsorbed atoms join to form hydrogen molecules as gas bubbles that detach from the Pt surface (H_2 evolution stage – Figure 2.9b, Reactions 2.55 – 2.56)



In essence, the hydrogen adsorption is a UPD process [239] as the reduction of H^+ occurs at more positive potentials with respect to the E_r for H_2 evolution reaction (0 V vs SHE or -0.205 V vs Ag/AgCl/3M KCl). The double-layer potential region, where only non-faradaic capacitive double-layer charging (Section 2.2.2, Figure 2.6a) proceeds, is also clearly discernible on voltammetric signals of Pt electrodes in acidic aqueous medium (0.05 to 0.3 V in Figures 2.13a and 2.13c).

Another feature of the surface electrochemistry of Pt discernible from voltammetry is the surface oxide formation and reduction.

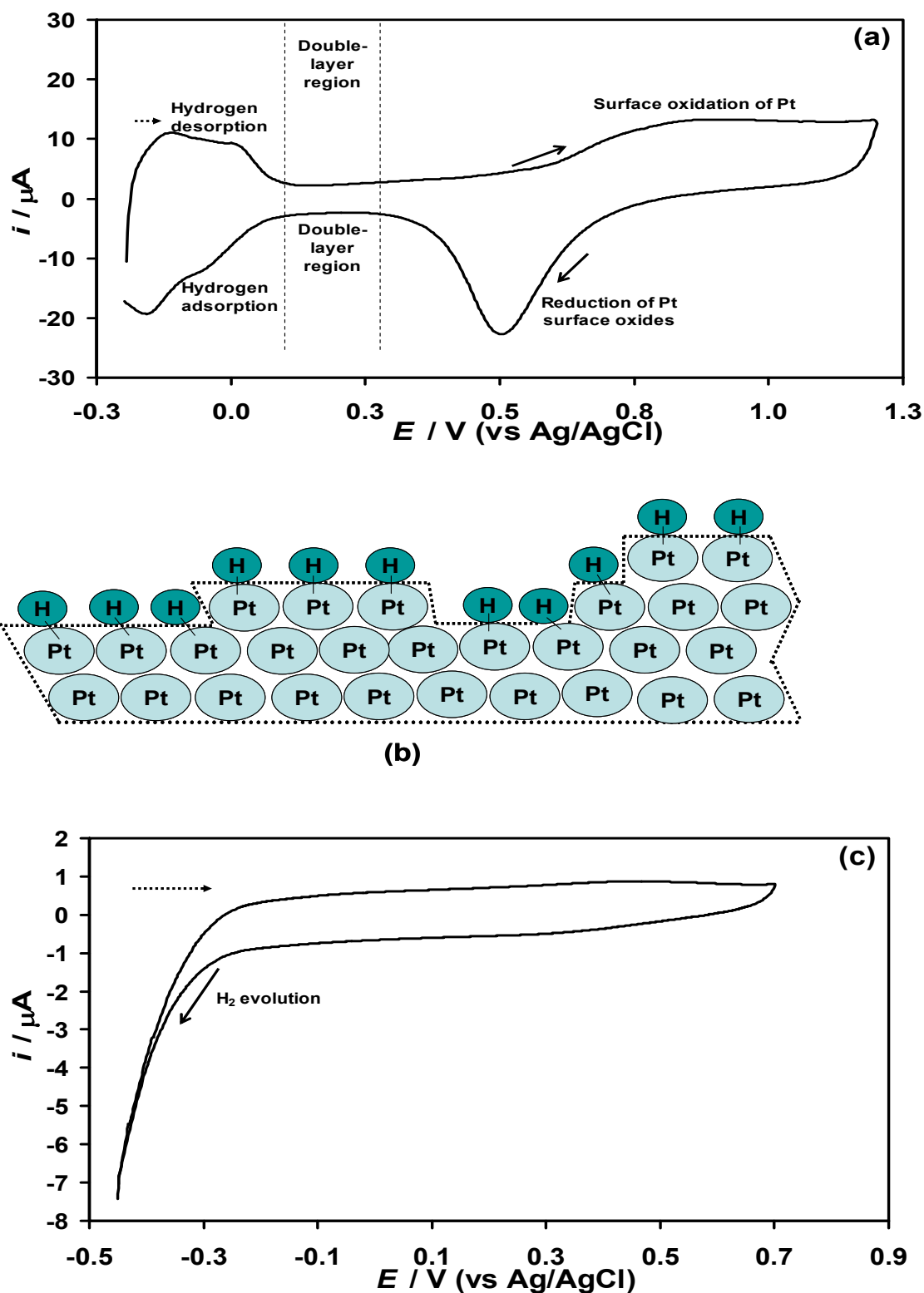


Figure 2.9: (a) Cyclic voltammogram of polycrystalline Pt recorded in nitrogen-saturated 10 mL of 0.5 M H₂SO₄ at 25 °C. (b) Schematic representation of hydrogen adsorption on Pt surface. (c) CV of polycrystalline Pt as in (a) but with adjusted potential boundaries. WE: Pt disc (2 mm disc diameter); CE: Pt rod. Broken arrows indicate the starting potential of scans; solid arrows show scan directions. Scan rate: (a) 50 mV/s, (c) 10mV/s.

Mechanistically, the characteristic surface oxide growth at Pt electrodes - from the double-layer potential region to a maximum anodic potential of 1.4 V (vs SHE) - is deemed to proceed to formation of a quasi-dimensional PtO surface lattice comprising of Pt^{2+} and O^{2-} moieties (Reactions 2.57-2.59, Figure 2.10) [240]:

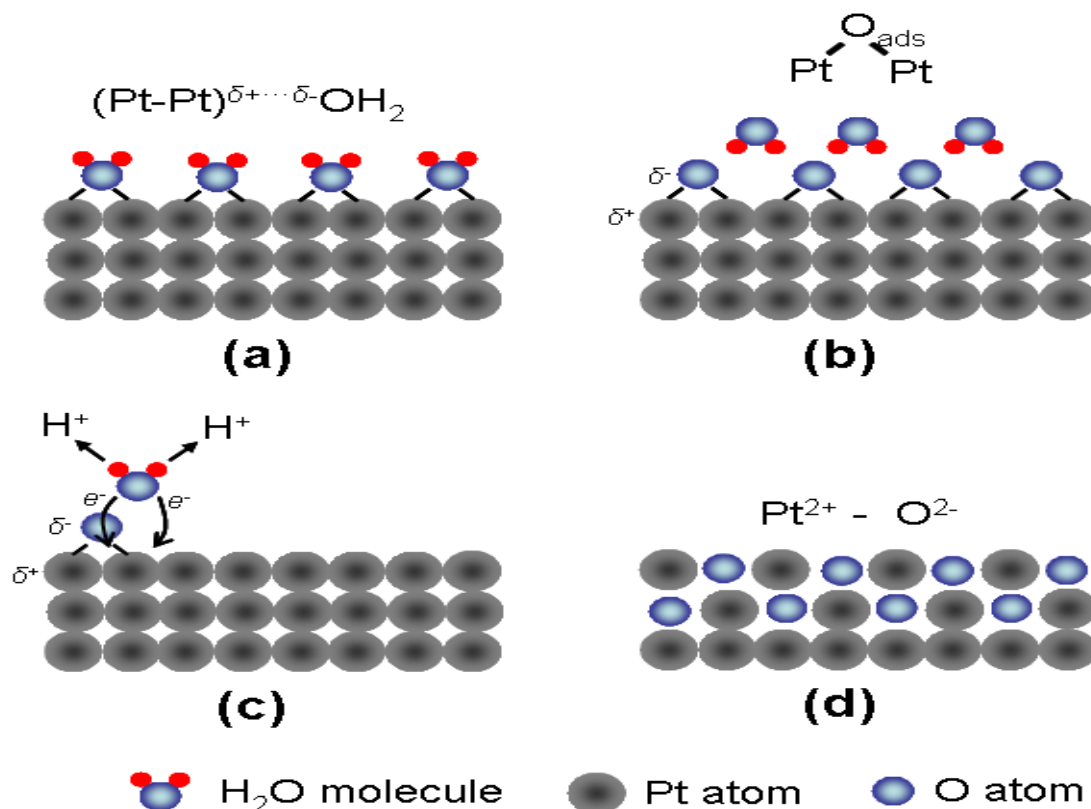
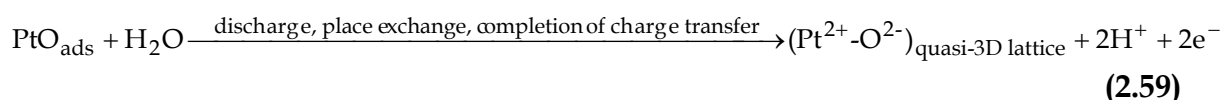
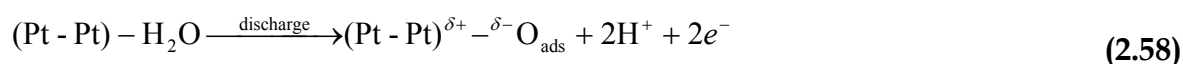
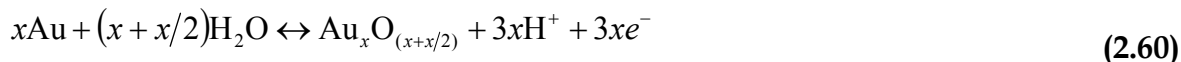


Figure 2.10: Scheme of electrochemical surface oxide growth on Pt electrode in aqueous acidic medium: (a) interaction of H_2O molecules with the Pt surface; (b) discharge of a sub-monolayer of H_2O molecules and formation of chemisorbed oxygen (O_{ads}); (c) discharge of sub-monolayer of H_2O molecules accompanied by dipole-dipole interactions between surface species; and (d) stabilized quasi-3D surface PtO lattice comprising Pt^{2+} and O^{2-} moieties (Adapted from Ref. [240]).

In regards to surface electrochemistry of Au electrodes in acidic aqueous medium, surface oxidation begins at potentials > 1.2 V and subsequent reduction in the cathodic scan direction between 1 and 0.8 V (see Figure 2.11) according to the global reaction mechanism - Reaction 2.60 [241,242].



Characteristic electrolysis of the solvent itself, that is H_2O to evolve O_2 (Reaction 2.61, $E^0 = 1.22$ V vs SHE) occurs at potentials > 1.5 V as revealed by large currents beyond the decomposition potential in Figure 2.11.

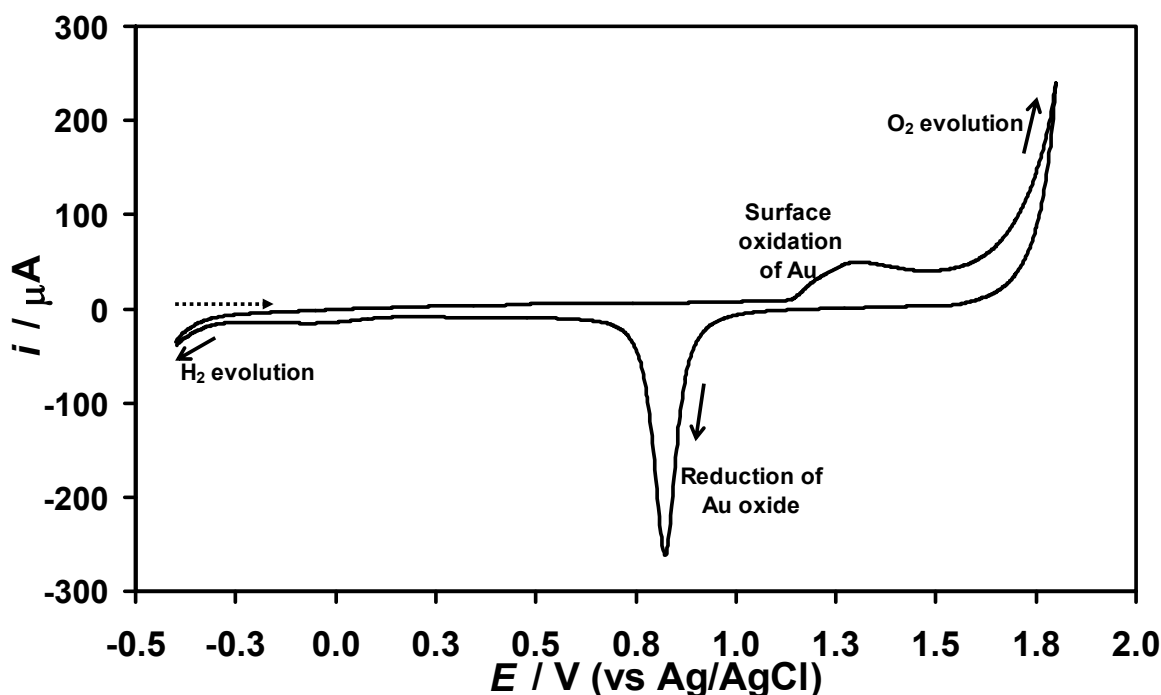


Figure 2.11: Cyclic voltammogram of polycrystalline gold recorded in nitrogen-saturated 10 mL of 0.5 M H_2SO_4 at 25 °C. WE: Au disc (2 mm disc diameter); CE: Pt rod. Broken arrows indicate the starting potential of scans; solid arrows show scan directions. Scan rate: 200 mV/s.

From cyclic voltammograms (CVs) of Pt and Au electrodes it is clear that, in comparison to Pt, a wider potential range where the Au surface is stable and un-oxidised is inherent on the Au surface, which is nobler than Pt. Moreover, the monometallic Au surface does not undergo voltammetrically expressible hydrogen

adsorption as its counterpart Pt [243,244]. The above-mentioned surface features position gold as a robust substrate for studying deposition processes of other metals; this thesis exploits some of these characteristics in later chapters where properties of uniquely electrodeposited nanostructured Pt-based films are investigated.

2.2.3.5.2. Surface area

The voltammetric effect of monolayer-restricted adsorption/desorption of H_{ads} and surface oxide layer inner-sphere electrode processes on noble metal surfaces is useful in deduction of the real surface area of electrode surfaces [241,245-249]. Following surface science conventions, evaluation of the real surface area (or herewith referred as the electrochemically-active surface area, A_{EAS}) requires the determination of the adsorbed amount and the surface density of atoms (d_m) of the hypothetically flat metal (that is, the number of surface atoms forming a monolayer per unit area) as described by Equation 2.62.

$$A_{EAS} = \frac{n_a N_A}{d_m} \quad (2.62)$$

where n_a is the amount (in moles) of adsorbed atoms, N_A is the Avogadro's number ($6.02214 \times 10^{23} \text{ mol}^{-1}$) and d_m is the surface metal atom density.

The value of d_m is readily approximated using the Anderson Criterion [250], which stipulates that for polycrystalline surfaces, the lower Miller index planes (100), (110), and (111) predominate in a proportion of 33 % for each plane. To this effect, polycrystalline Pt has a d_m value of $1.3 \times 10^{15} \text{ atoms/cm}^2$ [246-248]. From electrochemical hydrogen adsorption or desorption coulometry, essentially, within the premises of Faraday's law and surface density approximations, it follows from Equation 2.62 that A_{EAS} can be evaluated as

$$A_{EAS} = \frac{Q_H N_A}{F d_m} = \frac{Q_H}{Q_H^s} \quad (2.63)$$

where F is the Faraday's constant; N_A is the Avogadro's number; d_m surface density of metal atoms; Q_H is the charge corresponding to hydrogen adsorption/ desorption

on/off the electrode surface of interest; $Q_H^s = Fd_m/N_A$ is the charge associated with a one-to-one adsorption/desorption process on a unit surface area of a hypothetical monoatomic flat surface (for polycrystalline Pt the value is $210 \mu\text{C}/\text{cm}^2$) [248].

A_{EAS} can readily be obtained from appropriate integration of voltammetric curves in the hydrogen adsorption potential region (Figure 2.9) – the potentials where the cathodic current deviates from the double-layer current and the onset of hydrogen evolution. Taking into account the double-layer charge Q_{dl} in the same potential range and the facts $i = dQ/dt$ and scan rate $\nu = dE/dt$, it follows from Equation 2.58 that A_{EAS} can be deduced as

$$A_{\text{EAS}} = \frac{\int_{t_i}^{t_f} i dt - Q_{\text{dl}}}{Q_H^s} = \frac{1/\nu \int_{(E_0-E_i)/\nu}^{(E_0-E_f)/\nu} i dE - Q_{\text{dl}}}{Q_H^s} \quad (2.59)$$

where t_i is the time when the hydrogen adsorption starts at potential E_i and t_f is the moment when the process is completed at potential E_f (taking into account that in sweep voltammetry the applied potential E is a function of time t and varies from the starting potential of the scan, E_0 , as $E = E_0 - \nu t$); Q_{dl} is the constant charge associated with the double-layer capacitive processes on the electrode of interest in the potential range under consideration [249].

Tuning the maximum anodic potential prior to O_2 evolution, such that oxygen is electrochemically adsorbed on a monoatomic layer (with a facile one-to-one correspondence with surface metal atoms), A_{EAS} can be deduced from the total charge across the interface during surface oxide formation or its reduction (Q_o). In an analogous formalism of real surface area determination from hydrogen adsorption/desorption, given the stoichiometric number of exchanged electrons in the surface oxide reaction, z , the density of surface atoms per unit surface area, d_m , and taking into account the background double-layer charge Q_{dl} , A_{EAS} can be obtained from integration of appropriate voltammetric iE section; typically, from integration of the surface oxide reduction peak (see Figures 2.13a and 2.15):

$$A_{\text{EAS}} = \frac{Q_{\text{O}} N_{\text{A}}}{z F d_{\text{m}} Q_{\text{O}}^{\text{s}}} = \frac{\int_{E_i}^{E_f} i dt - Q_{\text{dl}}}{Q_{\text{O}}^{\text{s}}} = \frac{1/\nu \int_{(E_0-E_i)/\nu}^{(E_0-E_f)/\nu} i dE - Q_{\text{dl}}}{Q_{\text{O}}^{\text{s}}} \quad (2.60)$$

where $Q_{\text{O}}^{\text{s}} = z F d_{\text{m}} / N_{\text{A}}$ is the charge associated with a one-to-one process involving surface oxide reduction/desorption per unit surface area of monolayer breadth of a hypothetical flat surface (with $z = 2$, for polycrystalline Pt surface the typical Q_{O}^{s} value is $420 \mu\text{C}/\text{cm}^2$ (for polycrystalline Au surface the averaged value is about $400 \mu\text{C}/\text{cm}^2$) [242,246,248].

2.2.3.5.3. Voltammetry and electrocatalysis

Cyclic voltammograms of a much more complex forms are usually found for more involved electrochemical processes, for example, electro-oxidation of small organic substances.

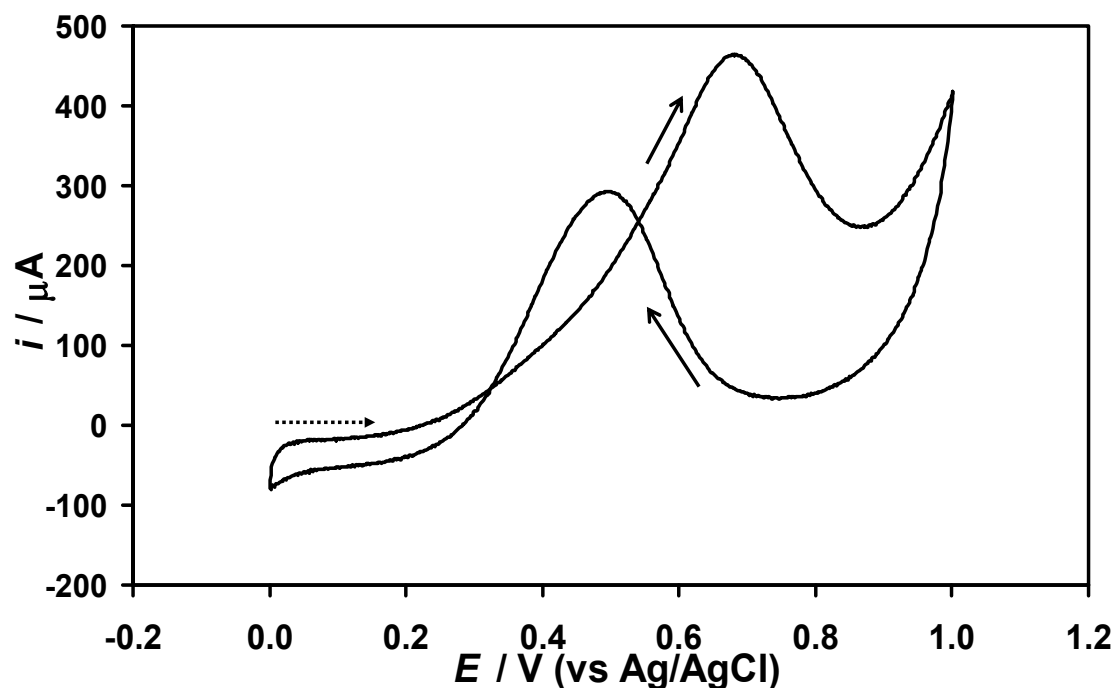


Figure 2.12: Cyclic voltammetry of CH_3OH in acidic medium on polycrystalline Pt disc electrode. Electrolyte solution: 10 mL 0.5 M CH_3OH + 0.5 M H_2SO_4 (nitrogen-saturated). WE: Pt disc (2mm disc diameter) CE: Pt rod. Broken arrow indicates the starting potential and initial scan direction; solid arrows show forward and reverse sweep directions. Scan rate: 50 mV/s.

The CV for electro-oxidation of methanol on bulk polycrystalline Pt (Figure 2.12) characteristically has several features: (i) the suppression of hydrogen adsorption/desorption peaks (see Figure 2.9a), essentially, due to chemisorption of methanol molecules; (ii) a relatively low methanol oxidation current at potentials in the double-layer region; (iii) a peak in the oxidation current (net positive current) near 0.7 V on the forward sweep, followed by a decline in the current as the surface is blocked by formation of surface oxides of Pt (further increase in overpotential drives the oxidation of methanol on the oxide surface ($E > 1.0$ V)); and (iv) reversal of the sweep ('cathodic scan'), reductive stripping of the oxide layer reveals fresh bare Pt surface giving rise to auto-catalytic oxidation current as the methanol (in excess in the electrolyte solution) is spontaneously oxidised on the bare Pt surface [234].

Net positive peaks in both the forward and the reverse scans of CVs in the presence of organic substances are typical signatures of electrocatalytic reactions, even though the reverse scan is 'cathodic' [225,234]. Various aspects of electrocatalysis of small organic molecules, methanol and formic acid, and characteristic voltammetric behaviour on nanostructured multilayered Pt-based systems are presented in this thesis within Chapters 4-5.

2.2.3.6. Anodic stripping voltammetry

Anodic stripping voltammetry (ASV) [59,222] refers to a family of techniques involving a pre-concentration step by electrochemical reduction/adsorption of an electroactive species from solution phase onto (or into) the working electrode prior to its direct or indirect oxidation by a sweep voltammetric scan (Figure A.5, **Appendix A**). Normally, the deposition step involves either an application of a fixed potential such that there is inner-sphere electron-transfer to transform the species of interest (for example, electrochemical deposition of metal M from its parent ions in solution, M^{z+}) or the potential of the WE leads to a non-faradaic surface adsorption (for instance, of gas molecules from their dissolved state). To this effect, the deposition potential (E_{dep}) is chosen to maximize such inner-sphere electrode processes for a set deposition time, t_{dep} (Figure A.5a, **Appendix A**). Thereafter, a usual linear sweep voltammetric scan is employed to oxidatively strip the pre-accumulated material (Figure A.5b, **Appendix A**). The amount deposited is directly

determinable from the charge obtained through integration of the voltammetric curve in the potential window where the stripping process proceeds (E_{s1} to E_{s2} in Figure A.5b, **Appendix A**).

2.2.3.6.1. Electrochemically-active surface area

Due to feasibility of selective deposition at suitable potentials in ASV, the technique is particularly useful in determination of active surface and monolayer coverage of metals or electrochemically adsorbed gas molecules.

ASV is appropriate for a wide range of metal surfaces where the previous methods of hydrogen or oxygen chemisorption do not readily proceed, for instance with Ru. Correction for background current is aptly achieved by running the deposition and stripping steps in the absence of the electroactive material; normally, in the background electrolyte solution prior to introduction of the species of interest in the solution. The charge associated with underpotential deposition (UPD) of a suitable metal Q_{UPD} (effectively obtainable from anodic stripping voltammetry of UPD-derived deposit) can be directly linked to the electrochemically-active surface area A_{EAS} of the substrate. This is achieved on a basis of a chosen model charge of a reference monolayer surface per unit area Q_M^s [248,251].

$$A_{EAS} = \frac{Q_{UPD}}{Q_M^s} \quad (2.61)$$

2.2.4. Electrochemical impedance spectroscopy

The classical electrical resistance R for an ideal resistor obeying Ohm's Law ($R = E/i$ at potential E and current i) has simplistic properties. Amongst others, the value of R is independent of frequency of current /voltage signals, which are also restricted to be in-phase with each other at all frequencies. Impedance, Z is a more general circuit circuit parameter on alternating current (*ac*) signal perturbation on circuit elements corresponding to frequency-dependent potential ($E(t)$) and current ($i(t)$) signals (Equation 2.62).

$$Z = \frac{E(t)}{i(t)} \quad (2.62)$$

The fundamental approach of impedance methods is application of a small amplitude sinusoidal excitation signal (voltage or current) to the system under investigation and the response (current or voltage) is measured. When measurements are carried out at different frequencies, plausibly, the technique is referred as impedance spectroscopy. Electrochemical impedance spectroscopy (EIS) generally involves application of a sinusoidal potential signal of variable frequencies to an electrochemical cell and measurements of the resultant alternating current (*ac*) signal through the cell. Analysis of the system response may contain information about the interface, its structure and reactions taking place there [252,253].

Since the polarization of electrochemical systems can exhibit highly nonlinear behavior, impedance measurements are normally conducted using small amplitude perturbation signals. This approach allows confinement to an approximately linear segment of the polarization *i*-*E* curve. In this pseudo-linear system, the current response will oscillate at the same frequency as the input potential, but will be phase-shifted (see Figure 2.13). Analysis of the input and output signals leads to determination of the total cell impedance, Z_T at any given frequency [254]. Z_T is a vector quantity and can be mathematically presented in complex notation as

$$Z_T = Z_0(\cos\phi + i \sin\phi) = Z' + iZ'' \quad (2.63)$$

where $i = \sqrt{-1}$, Z' is the real part and Z'' the imaginary part of the impedance.

Impedance test equipment typically incorporates electronics for *a.c.* waveform generation and measurement unit coupled to a potentiostat or galvanostat. Generally, the *a.c.* measurements can be categorized into two main groups; *single-sine* and *multiple-sine* techniques. In single-sine technique, a small-amplitude sinusoidal signal with a prescribed frequency is applied to the test electrochemical cell. The response signal is then analysed to extract the two components of the impedance (real and imaginary parts or magnitude and phase). Such an experiment is then repeated at a series of different test frequencies; ideally, starting at the highest frequency and stopping at the lowest in order to minimize the test electrode's perturbation. In the case of multi-sine techniques, a typical EIS measurement is carried out at several frequencies simultaneously.

Data presentation of EIS is normally provided in two types of impedance plots; (i) Z' versus Z'' at different frequencies plotted in a complex plane (that is, *Nyquist plot*); and (ii) impedance magnitude (Z_0) or phase angle (Φ) versus frequency (ν) called *Bode plots* [253,254].

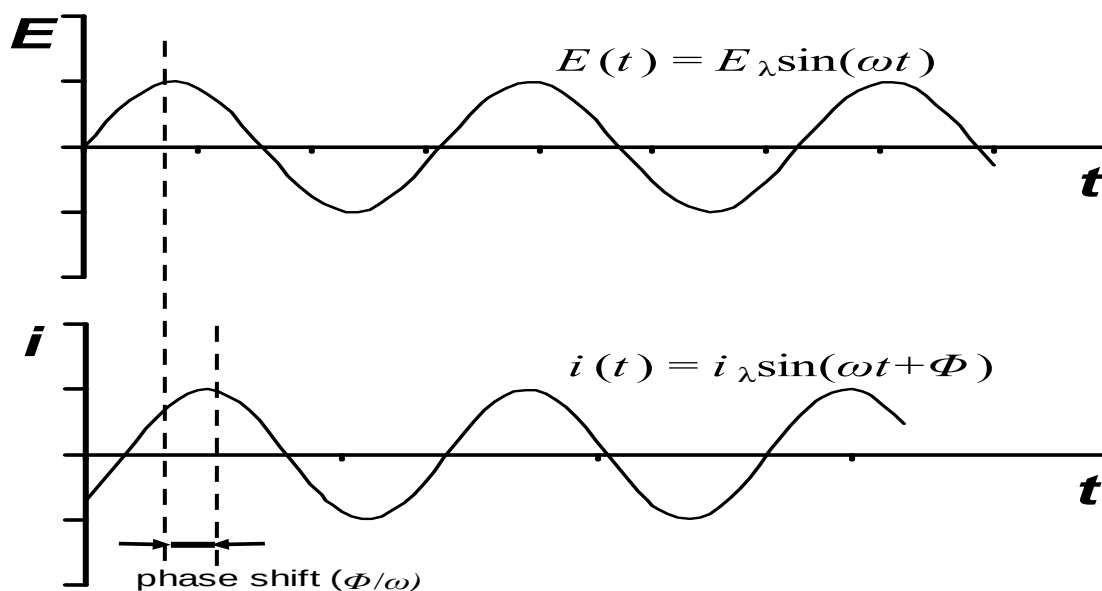


Figure 2.13: Sinusoidal potential signal with potential amplitude E_λ and corresponding current response signal with current amplitude i_λ and radial frequency ω (radians/second) and phase angle Φ (The relationship between the radial frequency and the frequency ν (in Hz) is $\omega = 2\pi\nu$) (Adapted from Ref. [254]).

For EIS on electrochemical systems, usually, a potentiostat (Section 2.2.1.2) of appropriate bandwidth is integrated into the impedance measurement setup. The potentiostat is not only responsible for maintaining a fixed direct-current (*d.c.*) potential, but also maintaining a correct *a.c.* voltage to the working electrode (WE). The electronic circuit assembly called the Frequency Response Analyzer (FRA) is the most widely used measurement technique in modern EIS instruments (Figure A.6, **Appendix A**). FRA is a versatile electronic signal processing system for extracting a small signal from a very high background of noise with inherent rejection of *d.c.* and harmonic responses. Typically, in FRA-based EIS setups the polarization *d.c.* potential and the *a.c.* input perturbation are simultaneously applied to the electrochemical cell at the counter electrode (CE terminal, Figure A.6a, **Appendix A**). The potential difference between two reference electrodes' terminals (RE_1 and RE_2 , Figure A.6a, **Appendix A**) is measured and fed back to the control loop, which

corrects the voltage applied to the counter electrode until the required potential difference between RE_1 and RE_2 (ΔRE) is established.

The potential difference and the current measured at the *WE* are amplified by the potentiostat and fed into the FRA as voltage signals, digitized and integrated over several cycles in order to reject noise, provide *d.c* signal rejection and harmonics as well as compensation for undesirable solution resistance (*iR* compensation) [253,254].

Typically, a two- or three-electrode cell is characterized by the EIS measurements. In a *two-electrode cell* (Figure A.6b, **Appendix A**), terminal RE_1 is coupled to the CE and terminal RE_2 is linked to the *WE*. The impedance is always measured between RE_1 and RE_2 , in this way, the impedance measured includes that of the counter electrode, the electrolyte solution, and the working electrode. For characterisation of properties of a single electrode (the working electrode), the three-electrode cell (Figure A.6c, **Appendix A**) is more fitting. In such an electrode arrangement, terminal RE_1 is connected to a reference electrode is positioned close to the *WE*, which itself is linked to terminal RE_2 . In this manner, the impedance measured will only be influenced by the properties of the working electrode and the contributions of the electrolyte solution between the *WE* and the reference electrode; effectively, the influence of the counter electrode on the impedance spectrum is eliminated and that of the resistance of the electrolyte solution is minimized [253,254].

2.2.4.1. Equivalent circuits and electrochemical cells

In general, an electrochemical cell can be considered simply an impedance to a sinusoidal perturbation. The total impedance consists of contributions of the electrolyte, the electrode-solution interface and the electrochemical reactions proceeding on the working electrode. Consequently, the electrochemical cell and processes occurring on it can be modelled by networks of electrical circuit elements (referred as *equivalent circuits*) where such circuit elements (for example, resistors, capacitors, and inductors) pass current with the same amplitude and phase angle that a real cell does under a given sinusoidal perturbation [222,254].

In order to represent a straightforward three-electrode electrochemical cell, within the framework of equivalent circuits (Figure A.6d, **Appendix A**), at least three processes and related electrical quantities need to be considered:

- the resistance of the electrolyte solution (R_s),
- the electrochemical double-layer, expressible as double-layer capacitance (C_{dl}); and
- the impedance of the faradaic charge-transfer process, Z_f .

All current (between the *WE* and *CE*) pass through the electrolyte solution, hence, R_s is inserted as a series element in the circuit. The parallel circuit elements are introduced given that the total current through the working electrode interface is the sum of separate contributions from the faradaic processes, generating current i_f , and double-layer charging current i_c . The faradaic impedance is expressed as a general impedance Z_f its property being dependent on frequency. However, in the absence of electroactive species, Z_f , becomes infinitely large and the equivalent circuit can be simplified to a serial combination of R_s and C_{dl} . In the presence of electroactive species, Z_f can be simplified to a simple resistor R_{ct} , the charge-transfer resistance, or a series combination of R_{ct} with other impedances representing mass-transfer limitations or surface inhibitions coupled to the overall charge-transfer process [222,254].

Figure 2.14a shows an impedance spectrum corresponding to an equivalent circuit of an electrochemical cell with a faradaic reaction proceeding on an ideally-polarizable WE without mass-transfer limitations. Strictly, the total impedance, Z_T of the circuit of Figure 2.14a is given as

$$Z_T = Z_s + \frac{Z_{ct}Z_{dl}}{Z_{dl} + Z_{ct}} \quad (2.64)$$

where Z_s is the impedance of the electrolyte solution, Z_{ct} is the impedance due to activation-controlled charge-transfer and Z_{dl} is the impedance due to the double-layer.

For the equivalent circuit of Figure 2.14a, in general, Z_s is simply the Ohmic resistance of the electrolyte solution given as

$$Z_s = R_s \quad (2.65)$$

Z_{dl} is the impedance of an ideal pure capacitor with the double-layer capacitance, C_{dl} according to the relationship

$$Z_{dl} = \frac{1}{i\omega C_{dl}} \quad (2.66)$$

Z_{ct} is also taken as impedance of a pure resistor, R_{ct} according to

$$Z_{ct} = R_{ct} \quad (2.67)$$

Therefore, in complex notation, Z_T for the circuit in Figure 2.14a can be derived as

$$Z_T = R_{ct} + \frac{1}{i\omega C_{dl} + 1/R_{ct}} \quad (2.68)$$

with deducible real and imaginary components of the radial frequency ω , in accordance with Equation 2.63.

Diffusion of the electroactive species can create an impedance (generally called a Warburg impedance, Z_w) [222,254]. Figure 2.14b exhibits an impedance response from a general electrochemical reaction ($O + ze^- \leftrightarrow R$) where both the oxidised and reducible species are soluble in the electrolyte solution with linear diffusional flux. Z_w depends on the frequency of the potential perturbation according to

$$Z_W = \sigma(\omega^{-1/2})(1-i) \quad (2.69)$$

where σ is the Warburg coefficient defined as

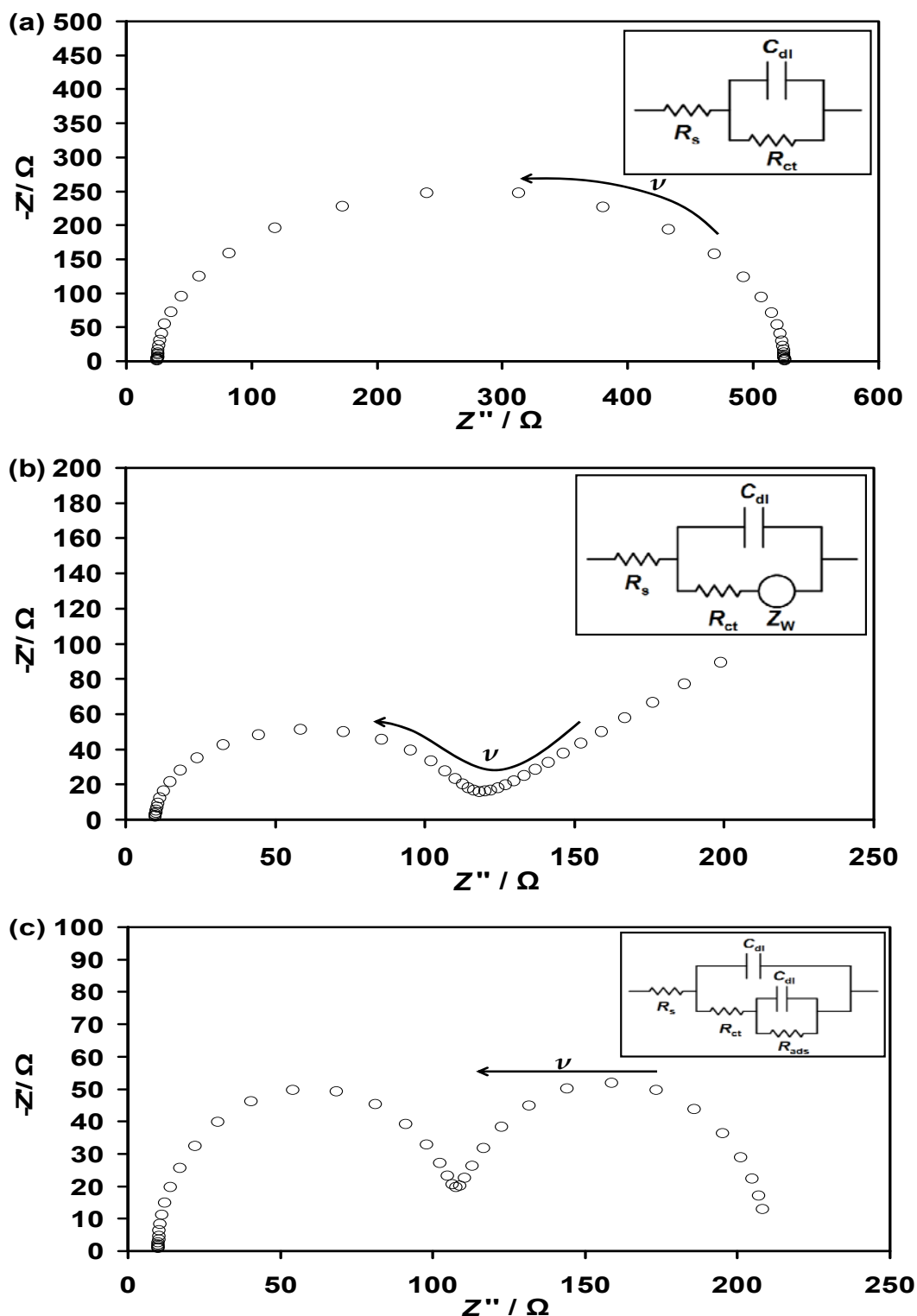


Figure 2.14: Electrochemical impedance responses (as Nyquist plots) corresponding to equivalent circuits (Insets) of an electrochemical cell involving (a) faradaic electron-transfer without mass-transfer limitations with $R_s = 10 \Omega$, $R_{ct} = 100 \Omega$; and $C_{dl} = 1 \times 10^{-5} \text{ F}$; (b) an electron-transfer with diffusion-limitations of the electroactive species - $R_s = 10 \Omega$, $R_{ct} = 100 \Omega$; $C_{dl} = 10 \mu\text{F}$, $\sigma = 10 \Omega \cdot \text{s}^{-1/2}$; (c) electron-transfer without diffusion-limitations and adsorption of reacting species - $R_s = 10 \Omega$, $R_{ct} = 100 \Omega$; $C_{dl} = 10 \mu\text{F}$, $R_{ads} = 100 \Omega$, $C_{ads} = 2 \text{ mF}$. The arrow points in the direction of increasing perturbation frequency, ν (in the range 0.1 – 10000 Hz, where the radial frequency, $\omega = 2\pi\nu$).

$$\sigma = \frac{RT}{z^2 F^2 A \sqrt{2}} \left(\frac{1}{C_O^\infty \sqrt{D_O}} + \frac{1}{C_R^\infty \sqrt{D_R}} \right) \quad (2.70)$$

in which R , T , z , F , and A have their usual meaning, D_O the diffusion coefficient of species x in electrolyte solution, and C_x^∞ the concentration of x in the electrolyte solution.

To suppress diffusional effects in studying other impedances due to surface phenomena such as adsorption, large concentrations of the electroactive species are generally used [253-255]. More complex circuits and underlying impedances due to faradaic and adsorption of reacting species are exemplified in Figure 2.14c where circuit elements R_{ads} , resistance due to adsorbing species, and C_{ads} , capacitance due to adsorption are included in the equivalent circuit with R_{ct} and R_s as for simpler faradaic charge-transfer cases.

The objective of the analysis of the EIS data is to elucidate the electrode process and derive its characteristic physico-chemical parameters. Measurement modelling explains the experimental impedances in terms of the mathematical functions in order to obtain good fit between the calculated and experimental impedances. Process modelling links measured impedances with physico-chemical parameters of the electrochemical process of interest [253,255]. Generally, an equivalent circuit is chosen and the fit to the experimental data is performed using the *complex non-linear least-squares* (CNLS) technique that fits the real and imaginary parts to a given model.

In general, the sum of squares, S , minimized during CNLS computations is given by

$$S = \sum_{x=1}^N \left\{ w'_x [z'_x - z'_{x,calc}]^2 + w''_x [z''_x - z''_{x,calc}]^2 \right\} \quad (2.71)$$

where z'_x and z''_x are the real and imaginary components of the experimental impedances at the various frequencies; $z'_{x,calc}$ and $z''_{x,calc}$ are the values calculated from a given model, w'_x and w''_x are the statistical weights of the data. In CNLS, the

summation and minimization is carried out over all N experimentally used frequencies according to a dedicated iterative algorithm [253,255].

2.3. Techniques for compositional, structural and morphological characterisation

The main characterisation of electrochemical systems is, of course, the electrochemically-based evaluation from the various techniques. However, it is also important to characterise the electrode's structure and composition and overall bulk properties as such exhibits supplement our understanding of electrochemical behaviour. A large number of surface science tools and techniques are available and continue to be explored to probe nanomaterials and, in particular, nanostructured electrodes. Almost all physico-chemical techniques known to material scientists can be adopted for studies of electrodes. Techniques generally employed for compositional, surface and bulk structural features use X-rays, ultra-violet radiation, ion or electron beams as primary probes [12,42,137,223]. In this work some microscopic analytical techniques and spectroscopic methods have been utilized as *ex situ* techniques where the unmodified electrodes and were removed from the electrochemical cell and analysed in ambient air or high-vacuum environments. An overview of the appropriate methods is given in this section.

2.3.1. Electron microscopy

Electron microscopy in materials characterisation is mainly used to determine the size (distribution), shape, and surface morphology. One distinguishes between Transmission and Scanning Microscopy. In both modes, accelerated electrons are applied to generate the images. Electron microscopy is usually performed in a high vacuum chamber to ensure a sufficient large free electron pathway. A primary electron beam is usually produced via cathode lamps. Similar to optical lenses in an optical microscope, electromagnetic condenser lenses are applied to generate a parallel electron beam [256].

In the transmission mode an electron beam of 100 - 400 kV passes through the sample. The transmitted electrons form a two dimensional projection of the sample which is further magnified by an electromagnetic lens system. The resulting image is a so-called bright-field image. In addition, diffraction of the electron beam while

passing through the sample is observed. By analysis of these electrons a diffraction image, a so-called dark field image is obtained, which can be used for collecting crystallographic information. Electron transmission is dependent on the density and thickness of the material. As the penetration depth of electrons is usually low, thin sample layers have to be prepared [3].

In the scanning mode the electron beam is focused on a small spot of the sample (roughly 10 nm). Detected are either the electrons or the X-rays or gamma rays, which escape from the sample (either forward or backward emission). Imaging is obtained by scanning the electron beam line by line over the sample surface and detecting the number of emitted secondary electrons or the beam intensity. As the detection probability of secondary electrons is high, a weak primary electron beam can be used, which prevents destruction of the sample. As the secondary electron yield depends on the sample material, different phases (e.g. of alloys) or crystallographic orientations can be distinguished. The probability of the emission of secondary electrons on edges is higher than the emission from planes thus causing a stereoscopic effect of the images. Conducting samples do not need any pre-preparation, whereas non-conducting samples have to be covered with a conducting film, e.g. a carbon film or a metal film [256].

In the SEM mode an electron beam is focused into a fine probe and subsequently raster scanned over a small rectangular area. As the beam interacts with the sample it creates various signals (secondary electrons, internal currents, photon emission, etc.), all of which can be appropriately detected. These signals are highly localized to the area directly under the beam. By using these signals to modulate the brightness of a cathode-ray tube, which is raster scanned in synchronism with the electron beam, an image is formed on the screen. This image is highly magnified in the typical operating range (10x – 300000x); consequently, SEM is a very useful *ex situ* imaging technique of metal-based nanostructured systems [137,257]. Often additional analytical tools are offered together with the electron microscope like backscattering of the primary beam, induced emission of photoelectrons, Auger electrons, or X-ray fluorescence. The induced X-rays are often analyzed to determine

the composition of a part of the surface, so-called energy dispersive X-ray spectroscopy, EDX (see Section 2.3.3).

2.3.2. Scanning Probe Microscopy

In Scanning Probe Microscopy (SPM), a solid specimen in air, liquid, or vacuum is scanned by a sharp probe tip located within a few angstroms of the surface. The major sub-categories in SPM are; (i) Scanning Tunnelling Microscopy (STM), where a quantum-mechanical tunnelling current flows between atoms on the surface and those on the probe tip, and (ii) Atomic Force Microscopy (AFM) in which case interatomic forces between the atoms on the surface and those on the tip cause a feedback-controlled deflection of a microfabricated cantilever. The magnitude of the tunnelling current or cantilever deflection depends strongly on the separation between the surface and tip atoms, SPM can uniquely be used to map out surface topography, with atomic resolution, in all three dimensions. STM is strictly applicable for conductive specimens, whereas AFM is uniquely adoptable for both conductive and insulating samples [258-260].

Particularly in AFM, the interactions between the surface and the probe tip may be van der Waals type or of a chemical, magnetic or electrostatic nature. Figure 2.15 displays typical arrangement and operation of an atomic force microscope. The probe tip is attached to a flexible cantilever and the force experienced by the tip causes the cantilever to deflect. The measurement of such subtle movements is normally carried out by detecting the position of a laser beam reflected off the cantilever. AFM can image conducting as well as insulating specimens. The sample is held on *piezoelectric*¹ micropositioner, which moves it vertically (in the z -direction toward and away from the probe tip) as well as laterally (in the x - and y -directions). The laser beam is typically reflected to photodiode detectors by a special metal coating on the top surface of the cantilever. Motions of the cantilever as it interacts with the specimen's surface causes changes in the amount of light on each photodiode detector, generating a distinct electrical signal which is captured by raster-type electronics and further processed by the controlling computer [258,260].

¹ Piezoelectric effect is the ability of certain crystals to generate a voltage in response to deformation or other mechanical stress [59].

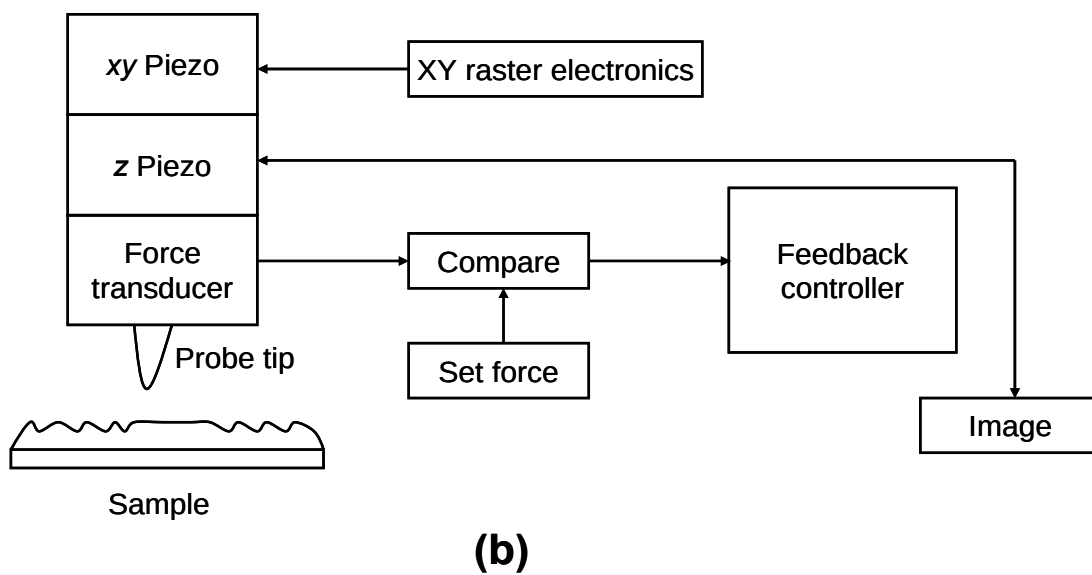
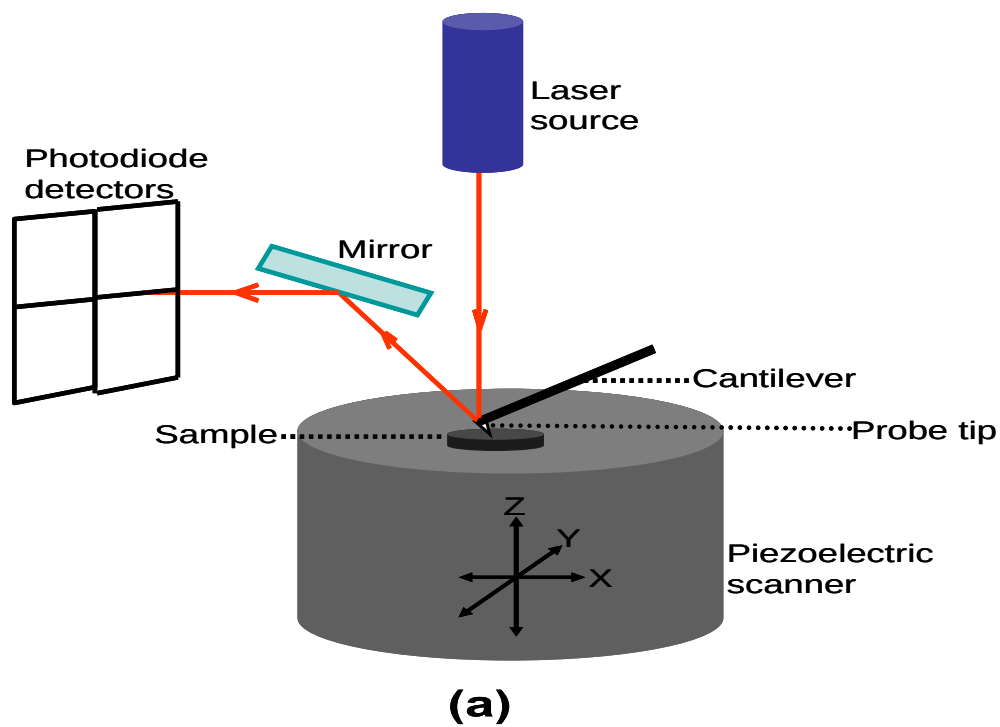


Figure 2.15: (a) A schematic representation of principal components of an atomic force microscope. (b) A block diagram of instrumentation for atomic force microscopy (Adapted from Ref. [258]).

The AFM cantilevers are very small, generally between 50 and 300 μm long, 20 – 60 μm wide, and 1 μm thick. As the AFM cantilever is moved by the action of piezoelectric drive, the motion of the probe tip attached to the cantilever exactly reproduces the movement of the piezoelectric element attached to it [258]. In general, as the AFM probe tip approaches a surface it experiences any one of a number of forces. The action of a force on the tip leads to displacement of the probe tip in addition to the movement of the piezoelectric drive, Δz . If the force constant, k_N of the is known, then the displacement can be translated into a force according to

$$F_N = k_N \Delta z \quad (2.72)$$

In this way the cantilever and associated probe tip act as force transducer in overall operation of an atomic force microscope. An important feature of AMF operation is a feedback control mechanism used to maintain a set force between the probe and the sample. Normally, the control electronics take the signal from the force transducers and use it to drive the piezoelectrics so as to maintain the probe-sample distance, and thus the interaction force at a set level. The xy piezoelectric elements (piezos) are used to scan the probe across the surface in a raster-like pattern. The displacement the z-piezo experiences vertically (up and down) to maintain tip-sample distance fixed is taken to be equal to the specimen's topography. In this way monitoring the voltage applied to the z-piezo, a map of the surface shape (a height 3-D image) is aptly measured as schematically shown in Figure 2.15b [258].

There are several modes in which AFM images can be acquired. The modes can be categorized into those that measure the static deflections of the AFM cantilever, and those that measure the dynamic oscillation of the cantilever [258]. In *contact mode*, the AFM probe tip is controlled to move toward the surface until physical contact is made. Furthermore, the feedback controller (Figure 2.15) is set to maintain a constant imaging parameter which is often taken to be the force (from Equation 2.72) by deflection of the laser beam off the cantilever. For such contact imaging mode, the cantilever is scanned in 2-D and the feedback is concomitantly acquired to produce a topographic image of the surface [258,260]. In *tapping mode*, the piezoelectric scanning is employed to manoeuvre the cantilever at a frequency resonant with one of its characteristic oscillations. With this mode, the probe tip is

brought close enough to the surface such that it touches at the bottom of each oscillation. In tapping mode, changes in the oscillation amplitude or phase can be measured as the tip is scanned across the surface to produce a topographic image [258,260].

Overall, the basis of AFM as robust microscopic technique is that it measures the topography of the sample. The datasets generated in this way are not conventional images, as generated by normal optical microscopy, but rather a map of height measurements which are systematically transformed into a more naturalistic image (surface plot) with light shading, perspective and so forth, in the quest to help in the overall visualisation of the shape of the material of interest [258].

2.3.3. Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) is a technique that is based on the collection and energy dispersion of characteristic X-rays. When atoms in a material are ionized by a high-energy radiation they emit characteristic X-rays. In a typical EDS system there is a source of high-energy radiation, usually an electron beam, a solid state detector and signal processing electronics, as well as the sample. X-rays that enter the detector are converted into signals which can be processed by the electronics into an X-ray energy spectrum. This spectrum consists of a series of peaks representative of the type and relative amount of each element in the sample. The number of counts in each peak may be further converted into elemental weight concentration either by comparison with standards or by standardless calculations. Accuracy is nominally in the range of 4-5 % and detection limits are 100-200 ppm for isolated elements with atomic number greater than 11, 1-2% wt. for low atomic number elements and overlapped peaks [257].

2.3.4. X-ray photoelectron spectroscopy

The wavelength of X-rays (with typical energy in the range 12 – 15 keV) is about 1 Å, a value comparable to atomic spacings in chemical substances; therefore, the interaction of X-ray radiation with matter can provide high-resolution structural and compositional information on the atomic scale [260,261]. In X-ray photoelectron spectroscopy (XPS), a surface of a sample material is irradiated in vacuum with soft

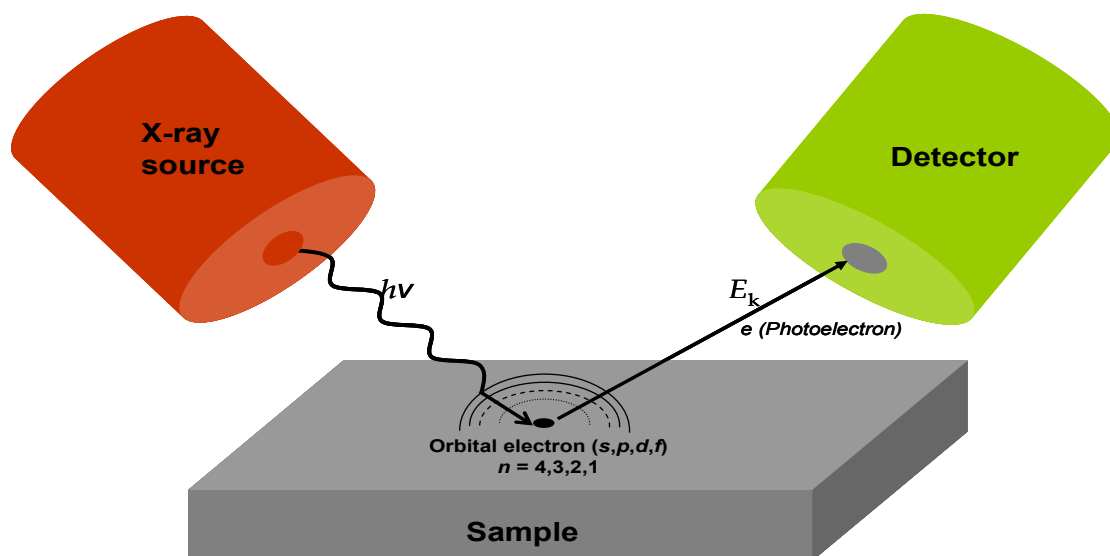
monochromatic X-ray, generally Al (K_{α}) at 1486.6 eV or Mg (K_{α}) at 1253.6 eV, where core-level or valence electrons (orbital electrons) will be ejected from the atoms of the sample into the surrounding vacuum (Figure 2.16a) [260,262]. An X-ray with energy $h\nu$ incident on a solid surface (h is the Planck's constant and ν is the frequency of the radiation) is related to the electron binding energy (E_B) in the atomic orbital from which the electron originates and the kinetic energy (E_K) of the emitted electrons (photoelectrons) by Einstein equation

$$E_B = h\nu - E_K - \phi_s \quad (2.73)$$

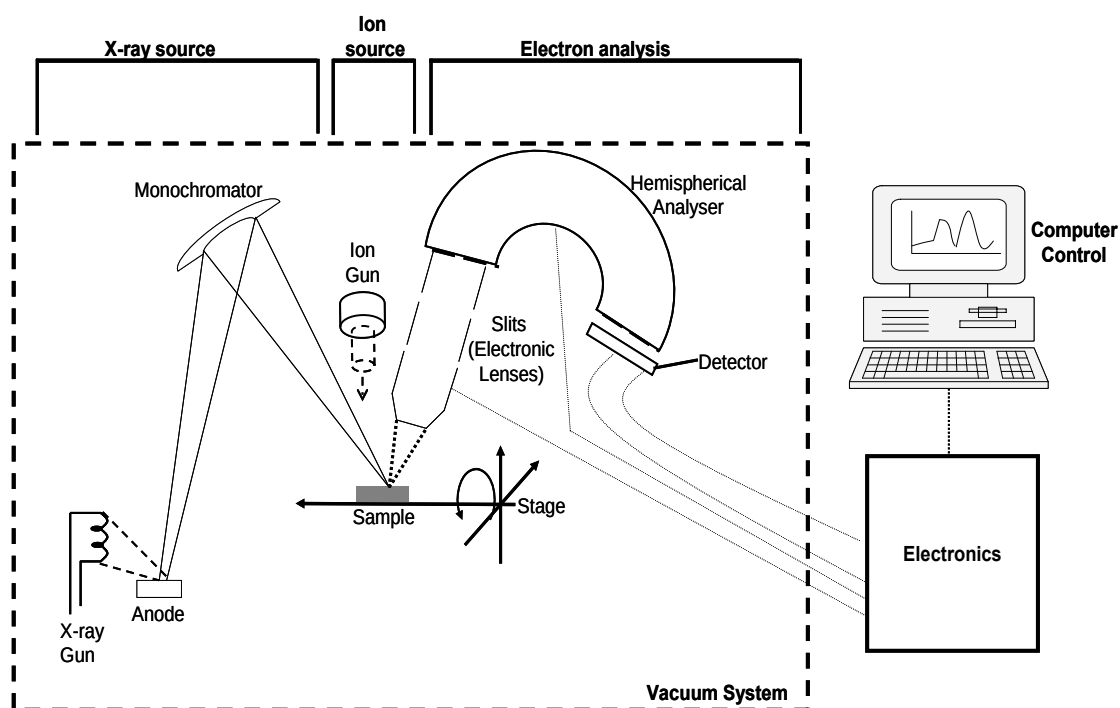
where ϕ_s is the spectrometer's workfunction [262].

Effectively, XPS employs the photoelectric effect (Figure 2.19a) where the spectrum of the ejected photoelectron displays characteristic peaks at respective kinetic energies (E_K values) from which the binding energies (E_B values) can be deduced from Equation 2.73. Since the core binding energies are signatures of the elements present on the specimen, the photoelectron spectra can be used for elemental analysis of solid electrodes. Not only can XPS identify the composition of a sample but it can also be used to determine quantitatively such composition [222,261].

Typical XPS setup is schematically shown in Figure 2.16b. By and large, XPS can detect elements with atomic numbers greater than 3 with a sensitivity of about 1% of a monolayer. The monochromatic X-rays have limited penetrating power in a solid (on the order of 1 – 10 μm) with consequences on the inelastic mean free path of the ejected electrons and the detection volume. Therefore, XPS only probes the first few layers of a surface (approximately, 0.3 – 2nm) because of the limited escape depth of the photoelectrons. Typically, depth profiling of the sample can be achieved by *in situ* removal of the successive top few monolayers using ion-sputtering of the sample) and probing the new surface that is freshly generated.



(a)



(b)

Figure 2.16: Schematic representation of (a) the photoelectron emission process by an incident X-ray photon on a solid surface in vacuum; (b) principle components of an X-ray photoelectron spectroscopy instrument. (Adapted from Ref [222]).

Moreover, the actual value of the binding energy of core electrons is affected by the electron density in the valence band (the chemical shift effect). For instance, the chemical shift depends on the oxidation state of the atom. Generally, as the oxidation state increases the binding energies increase. The greater the electron withdrawing power of the substituents bound to an atom, the higher the binding energy. Consequently, small shifts in the observed E_B of the core-level electrons can be used to distinguish the same element in different chemical environments [260,262].

2.3.5. X-ray diffraction

X-ray sources typically used in laboratory diffraction experiments (ranging from 0.5 to 2.5 Å) are of the same order than the shortest interatomic distances. X-ray diffraction (XRD) techniques involve measurement of reflectivity or diffraction pattern of a specimen resulting from scattering of a monochromatic X-ray beam directed onto the sample. If the material is crystalline, the beam will be diffracted by the crystalline phases in the specimen according to Bragg's law (Equation 2.74):

$$\gamma = 2d \sin \theta_{\text{diff}} \quad (2.74)$$

where d is the spacing between atomic planes in the crystalline phase, γ is the wavelength of the incident X-ray beam, and θ_{diff} is the diffraction angle of the beam from the specimen [257,260,263,264].

XRD is a useful method in the determination of the bulk crystallographic structure of materials; it is also commonly used for the characterisation of metallic and alloyed materials and suitable for characterization of solid electrodes [257,260]. Typically, the intensity of the diffracted X-rays is measured as a function of the diffraction angle (typically as $2\theta_{\text{diff}}$) and the specimen's orientation. The diffraction pattern can be used to identify the specimen's crystalline phases and measure its structural properties, which may include average crystallite size [257,260,263,264].

The positions (angles) and intensities of the reflections in the diffraction patterns are characteristic for each compound or metallic substance and can be transformed into the underlying atomic arrangement and overall determination of crystalline phases in the material of interest. The X-ray diffraction patterns are widely used to identify

the type of material in any mixture by comparing them with the standard patterns of the International Powder Diffraction File (PDF) database [265]. The crystalline phase identification is particularly important for solid electrodes which widely consist of small domains with different crystal facets (Figure 2.17) which are conventionally indicated by their *Miller indices*² [257,260].

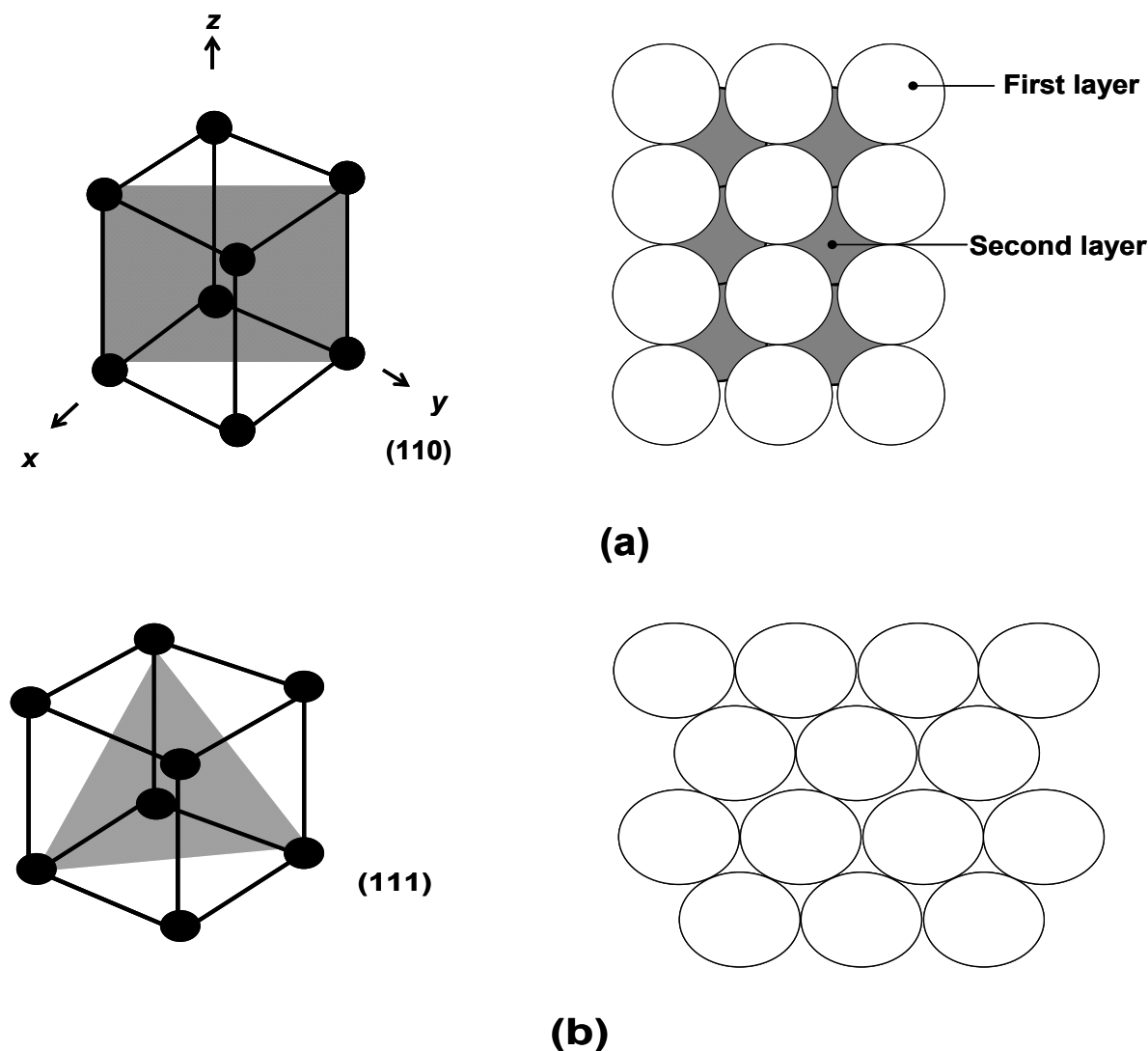


Figure 2.17: The atomic representations of typical low-Miller-index planes of a face-centered cubic (fcc) crystal structure. (a) fcc (110) and (b) fcc (111) facet obtained by cutting through the greyed planes on the corresponding unit cells.

² Miller indices (hkl) are related to the positions of the atoms in a crystalline lattice; they are the smallest integers h , k , and l such that $h:k:l = (1/p) : (1/q) : (1/r)$, where p , q , and r are the coordinates of the intersections with the x , y , and z axes with the plane of interest in a unit cell of the respective crystal structure. For example, if a plane intersects the unit cell axes at $x = 2$, $y = 2$, $z = 2$, then $h:k:l = (1/2) : (1/2) : (1/2)$; therefore, the plane is identified as (111) plane [222,260]

Different crystal planes and sites are sensitive to overall electrochemical behaviour on the crystalline electrodes. The low index planes can be regarded as the basic building blocks of surface structures of crystalline metals as they represent the simplest and flattest of the fundamental planes [222,260]. Many noble metals used as electrodes, such as Pt and Au, form *fcc* crystal structures (See Table 1.1).

2.4. Summary

The properties of electrodes and electrochemically synthesized surfaces and bulk materials as well as related mechanistic aspects can best be understood if the electrodes are characterised *in situ* or within reasonable time after the synthetic processes have ended. In line with the theme of this thesis, this chapter has reviewed the relevant electrochemical characterization techniques monitoring inner- and outer-sphere redox processes and electrodic surface activities. Electrochemical techniques reviewed included amperometry, coulometry, voltammetry (linear and cyclic modes, anodic stripping, and hydrodynamic voltammetric methods) and electrochemical impedance spectroscopy. Moreover, applicable *ex situ* non-electrochemical techniques used in this thesis for physico-chemical characterization, surface, bulk, compositional and morphological properties of electrodes (before and after electrochemical modification) were also surveyed. To this end, electron and scanning probe microscopic methods, X-ray photoelectron and energy-dispersive spectroscopic techniques as well as X-ray diffraction were reviewed insofar as basic and general principles for characterization of solid materials were concerned.

CHAPTER III

Automated Sequential Electrodeposition, Surface-Limited Redox-Replacement Reactions and Electrocatalysis: Nanostructured Electrodes of Platinum and Ruthenium on Glassy Carbon

Content of this chapter has been published in journal articles:

- (I) T. S. Mkwizu, M. K. Mathe, and I. Cukrowski, *ECS Transactions*, Vol. 19 (24), 97-113 (2009); and
- (II) T. S. Mkwizu, M.K. Mathe, and I. Cukrowski, *Langmuir*, Vol. 26 (1), 570-580 (2010).

3.1. Introduction

In tandem with the aims and objectives of this thesis, the research experimentation, results and discussions embodied hereafter involve:

- development of dedicated automated systems for implementation of sequential electrodeposition methodologies, with capabilities for *in situ* electrochemical characterisation;
- examination of the efficiency of the sequentially-implemented open-circuit surface-limited redox-replacement reactions for deposition of bimetallic nanostructured multilayers, including controlled investigations on the role of sacrificial Cu adlayers in the overall scheme in relation to thermodynamic factors;
- physico-chemical characterization of the nanostructured systems, sequentially-deposited from separate precursors and those synthesized via equivalent codeposition from mixed precursors; and
- investigations of surface and other electrochemical/electrocatalytic features of the various types of model platinum- and ruthenium-based nanostructured electrodes.

In this chapter an in-depth study of the sequential electrodeposition of $n(\text{Pt} | \text{Ru})$ nanoclusters on glassy carbon (through extensions of the SLRR reaction methodology involving Cu templating adlayers in deposition of each noble metal component) is explored. The inherent advantages of the sequential deposition methodology have been systematically implemented (here in fully automated mode to achieve the best reproducibility). Because the role of sacrificial Cu in generating several noble-metal layers was not studied before, we have examined the efficiency of incorporating SLRR reactions in the electrodeposition pathways for growth of multilayered structures on a carbonaceous electrode. The role of the sacrificial Cu is systematically probed by running several control experiments that eliminate its use; effectively, the studies bring to light sequential spontaneous deposition of the noble metals. Furthermore, it was of utmost importance to investigate the surface

electrochemistry, outer-sphere, and inner-sphere electrochemical activity as well as electrocatalytic properties of generated structures and compare them with data obtained on the nanoclusters obtained via *sequential codeposition*, $n(\text{Pt-Ru})$, (in which case simultaneous SLRR reactions from Pt and Ru precursor mixture are uniquely reported). To this effect, bimetallic systems generated were probed *as prepared* for electrocatalytic methanol oxidation as well as oxygen reduction reactions, both in acidic medium. Results obtained are also compared to the electrochemical and catalytic properties of Pt monometallic nanoclusters, $n(\text{Pt})$, generated under the same experimental conditions and with the use of the same electrochemical cells and automated equipment.

3.2. Experimental details

3.2.1. Instrumentation and apparatus

Dedicated instrumentation and apparatus for automated electrodeposition and electrochemical characterization experiments were custom-assembled for this research and its potential applications; essentially, in line with various existing designs in related sequentially-implemented automated electrochemical deposition systems [266-268]. The distinguishing requirements in this study were the need for an automated deposition system coupled to electrochemical characterisation techniques (including hydrodynamic voltammetry and electrochemical impedance), utilization of pumps with variable flow-rates, employment of substrates of varying dimensions (including carbonaceous substrate such as glassy carbon), and solution reservoirs with minimal utilization of precursor electrolyte solutions. The dedicated electrochemical workstation developed hereby consisted of:

- a three-electrode electrochemical flow-cell;
- piston pumps (Model 765 Dosimat, Metrohm, Switzerland) configured for delivery of appropriate electrolyte solutions to the flow-cell;
- rotatable multi-valve (models R36781 and 36760 valve heads and model R77810 valve drive, Hamilton, Switzerland);
- gas distribution assembly with vacuum system;

- an electrochemical workstation capable of potentiostatic measurements (model PGSTAT 30(2), EcoChemie, Autolab, The Netherlands); and
- a personal computer equipped with appropriate data acquisition systems and software development packages. To this end, computer-control and data acquisition from the various hardware components was achieved through custom-developed software modules (virtual instruments) using the graphical programming package LabVIEW (National Instruments, Texas, USA). LabVIEW is an acronym for Laboratory Virtual Instrument Engineering Workbench and is an object-oriented, general-purpose programming language designed as a complete set of applications for instrument and process control, data acquisition and scientific computing, including simulation and data analysis [269].

The piston pumps, multi-valve system, and the electrochemical workstation were all computer-controlled via standard serial data acquisition interfaces RS-232 and Universal Serial Bus (USB). Up to six different solutions could be independently delivered to the flow-cell with the use of an appropriate multi-valve positioner and piston pumps. Detailed descriptions of the various LabVIEW software modules and associated instrumental configurations are provided in **Appendix A**. Gas distribution was preset as required.

3.2.1.1. Electrochemical flow-cells

The central ‘mini-reactors’ of the electrochemical workstation were exchangeable dedicated electrochemical flow-cells (Figure 3.1). They were designed and constructed with the following general considerations:

- Separable solid components that were mechanically sound and robust for flow-cell based electrochemistry and sufficient chemical inertness for a range of aqueous electrolytic systems at ambient conditions were sought. Accordingly, solid blocks were made from poly(methyl methacrylate), a thermoplastic with trademarks Plexiglas or Perspex. The thermoplastic blocks were transparent solid pieces that could withstand extreme pressures

for holding solid electrodes and allowed for visual observations of sample solutions upon assembly of a complete flow-cell.

- Flow-cell components which were quick to dismantle for cleaning purposes and replacement of electrodes as well as *ex-situ* analysis of the electrochemically modified electrodes were to be utilized. To this end, for each flow-cell design, two separable Plexiglas blocks were intended to be clamped together with the use of simple nuts and bolts at moderate torques. The reference and counter electrodes were designed such that they could be directly inserted and removed to and from the body of the appropriate Perspex block. Special holders were made for the electrodes under study, either with screwing or sliding mechanisms, into the relevant Perspex piece. Proper sealing embodiments were made of inert silicone O-rings and polytetrafluoroethylene (PTFE) fittings.
- Variable flow-cell volume, by use of replaceable gaskets of various thicknesses and with a centrally-positioned opening, was inherent in the design.
- Hydrodynamic laminar flow profile in the flow-cells (see Section 2.2.3.4, Chapter 2) was achieved in the design of the internal flow-channels which were machined to be angled and flared at their inlet and outlet positions. The flow-cells were robust for *in situ* electrochemical characterization of the substrates and electrochemically formed deposits [270].

The flow-channels were defined by appropriate openings on a 1 mm- or 2 mm-thick, chemically inert, silicone rubber gaskets (Medical Extrusions (Pty) Ltd, Johannesburg, South Africa). In the flow-cells designed and constructed (Figure 3.1a), two Perspex solid blocks (Maizey's (Pty) Ltd, Pretoria, South Africa) were used for holding: (i) the working electrode, WE (in electrodeposition terminology the substrate under study) in the first block, and (ii) reference electrode (RE) together with a counter electrode (CE) in the second block.

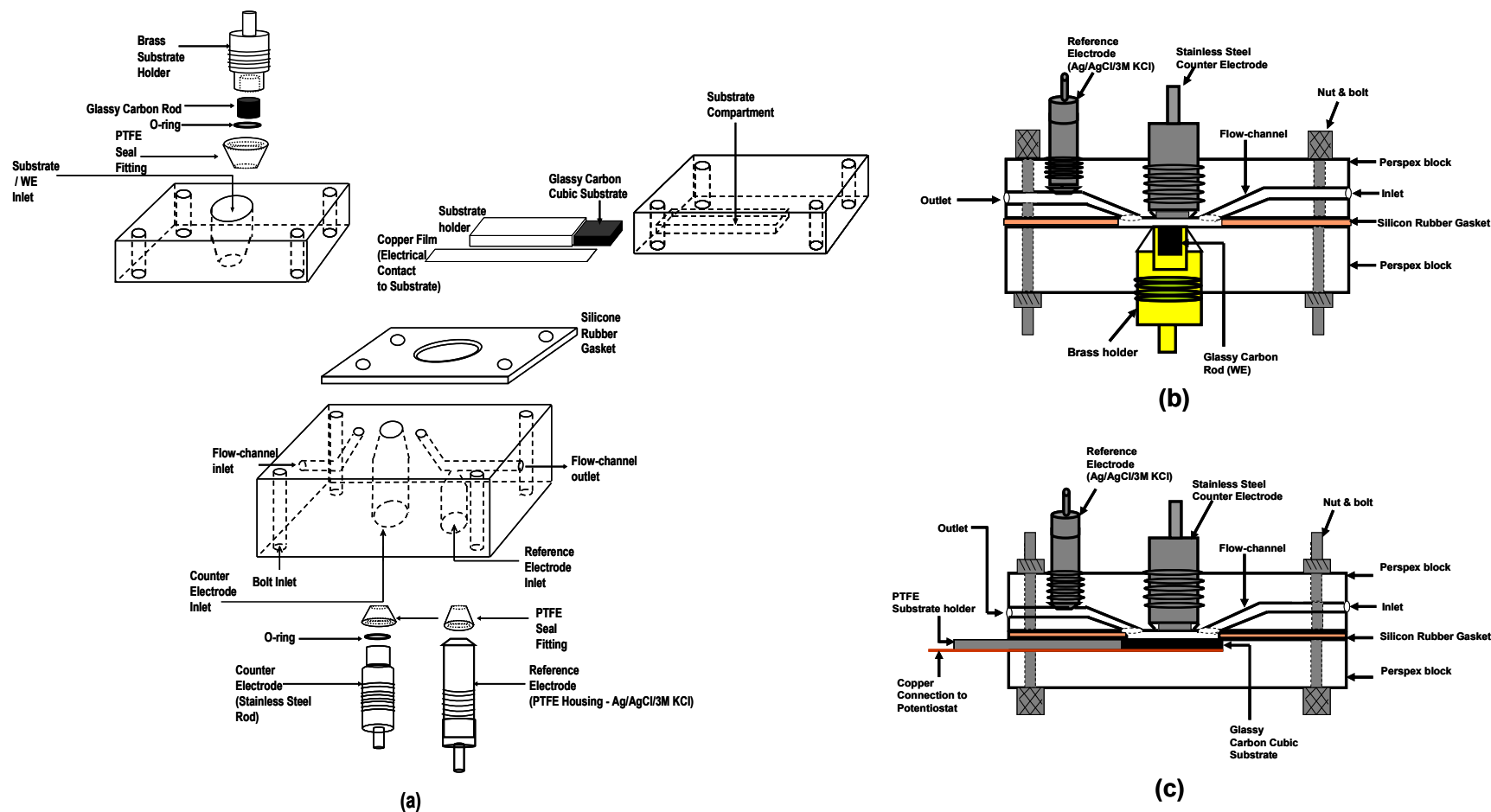


Figure 3.1: Schematics showing (a) typical components of electrochemical flow-cells designed in this work for use in sequential electrodeposition as well as characterization experiments; (b) side-view of flow-cell assembly using cylindrical glassy carbon rod as working electrode/substrate; and (c) side-view of the flow-cell assembly using cubic glassy carbon as working electrode/substrate.

In all cases, the RE was a PTFE embodied Ag/AgCl/3M KCl (model 6.0727.000, Metrohm, Switzerland) that was placed at the outlet stream of the flow-cell. In flow-cell of configuration shown in Figure 3.1b, the glassy carbon (GC) cylindrical rod (grade V-25, 5 mm diameter, SPI Supplies, USA), as a WE or substrate, was embedded in an electrically-conductive brass alloy holder that was secured via fine threading into the Perspex block with appropriate silicone o-rings and hollow PTFE fittings for sealing purposes. To this effect, the exposed geometric area of GC rod electrode in the flow-channel was about 0.2 cm².

In flow-cell of configuration shown in Figure 3.2c, a GC piece (10 mm x 10 mm x 2 mm cubic block, grade V-25, SPI Supplies, USA) was secured into an engraved compartment of the Perspex block via a cubic PTFE holder. Thin copper tape (3M, USA) was attached underneath the cubic GC substrate for electrical contact to the electrochemical measurement workstation.

In all cases, the CE was a machined stainless steel cylindrical rod directly screwed into the Perspex block using silicone o-rings for sealing purposes; upon assembly, the CE disc was at least 5 mm in diameter at level with the base of the appropriate flow-channels (Figure 3.1b-c).

3.2.2. Electrochemical deposition: Modelling and experimental procedures

3.2.2.1. Electrochemical potential and pH: Thermodynamic modelling

Potential-pH (E -pH) dependent speciation for Pt-Cu-H₂O and Ru-Cu-H₂O systems were generated using the thermochemical modelling software package FactSageTM version 5.5 or 6.0 [271]. Theoretical backgrounds on this aspect of thermodynamic modelling (with corresponding thermochemical data of the systems considered) are detailed in **Appendix B**.

3.3.2.2. Materials and electrolyte solutions

Aqueous solutions were prepared with high-purity water obtained with Milli-Q water purifier system (Millipore Inc. USA) with resistivity of 18 MΩ·cm. Precursor electrolyte solutions of Cu²⁺, Pb²⁺, Pt⁴⁺, Au³⁺ and Ru³⁺ (each 1 mM, pH = 1 ± 0.05) were prepared from CuSO₄·6H₂O (Merck), H₂PtCl₆·6H₂O, and RuCl₃·3H₂O (SA Precious Metals Ltd, South Africa) in 0.1 M HClO₄ (Merck). CH₃OH (Merck), 0.5 M

solution, was also prepared in 0.1 M HClO_4 . All chemicals were of analytical grade of minimum 99% purity. High purity compressed nitrogen and oxygen gases were supplied by Afrox (South Africa) and used in gas saturation of electrolyte solutions using the appropriate gas line. A vacuum pump was used to degas sample solutions prior to gas saturation.

3.3.2.3. Pre-treatment of working electrode and deposition substrate: glassy carbon

Prior to assembling of the flow-cell, the appropriate GC working electrode/substrate was polished with a sand paper (grit 1200), followed by alumina slurries on a polishing cloth, then washed in 0.5 M nitric acid, rinsed in ultrasonic bath in a 1:1 water-acetone mixture, and finally thoroughly rinsed in ultra-sonicated de-ionized water before use. Electrochemical pre-treatment of the electrodes was done in nitrogen-saturated 0.1 M HClO_4 by cyclic voltammetry (see Section 2.2.3.3, Chapter 2) between -0.1 and $+1.2$ V at 200 mV/s until stable cycles were obtained.

3.3.2.4. Pre-treatment of reference and counter electrodes

Prior to any given flow-cell experiment, the RE and CE employed were activated. In this regard, the RE ($\text{Ag}/\text{AgCl}/3$ M KCl) was treated by replenishing the required 3 M KCl filling solution in the relevant electrolyte compartment of the electrode assembly. The CE metallic disc surface was polished in similar fashion to GC electrodes (see Section 3.3.2.3) and soaked in 0.5 M HNO_3 for about 120 s, followed by ultra-sonification in 1:1 water-acetone mixture and finally thorough rinsing in de-ionized water and dried in gently stream of N_2 gas around the electrode assembly.

3.3.2.5. Electrosynthesis of monometallic multilayered platinum on glassy carbon

Deposition of n -layered Pt nanoclusters immobilized on GC via sequentially-implemented surface-limited redox-replacement (SLRR) reactions involving Cu (denoted as $n(\text{Pt})_{\text{Cu}}/\text{GC}$) were carried out with instrumental setup shown in Figure 3.2a; computer-control was achieved with the LabVIEW virtual instrument *Autolab-SeqDep-3Pumps-Autorefill.vi* (**Appendix A**). The specific deposition scheme for generation of $n(\text{Pt})_{\text{Cu}}/\text{GC}$ is shown in Figure 3.2b where a typical single deposition cycle involved: (1) rinsing the cell with the BE, followed by filling the cell with Cu^{2+}

solution at selected applied potential E_{appl} , (2) Cu deposition at E_{dep} , followed by rinsing the cell with the BE at E_{dep} , (3) filling the cell with the Pt^{4+} solution at open circuit (OC), followed by the OC SLRR reaction of Cu adlayers by Pt adlayers (reaction denoted as OC SLRR_{Pt}) at quiescent conditions. During all these steps, actual current and potential readings that resulted from the deposition processes were sampled as a function of time to generate online current-potential-time (i - E - t) transients. N_2 atmosphere was maintained throughout the experiment.

3.3.2.6. Electrosynthesis of bimetallic multilayered systems of platinum and ruthenium on glassy carbon

3.3.2.6.1. Sequential surface-limited redox-replacement reactions involving copper

The dedicated LabVIEW virtual instrument, *Autolab-SeqDep-4Pumps-Autorefill.vi* (see **Appendix A**) was used to synthesize the Ru | Pt nanoclusters, supported on the GC substrate, using SLRR reactions involving sacrificial Cu adlayers (denoted as $n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$). Repeatable steps (n deposition cycles) directed either a precursor solution (CuSO_4 , H_2PtCl_6 , or RuCl_3) or the BE solution (0.1 M HClO_4) to the relevant flow-cell (Figure 3.1) at a preset nominal flow-rate of 5 mL/min and appropriate deposition time, t_{dep} , for each deposition stage (four pumps and the appropriate multi-valve were used as schematically represented in Figure 3.3a). The potential of the substrate/WE and time of each operation was pre-programmed for each step.

The deposition scheme (Figure 3.3b) involved: (1) rinsing the cell with the BE, followed by filling the cell with Cu^{2+} solution at selected applied potential E_{appl} , (2) Cu deposition at E_{dep} , followed by rinsing the cell with the BE at E_{dep} , (3) filling the cell with the Pt^{4+} solution at open circuit (OC), followed by the OC SLRR reaction of Cu adlayers by Pt adlayers (reaction denoted as OC SLRR_{Pt}) at quiescent conditions, (4) rinsing with BE and filling the cell with the Cu^{2+} solution at E_{appl} , (5) Cu deposition at E_{dep} , followed by rinsing the cell with the BE at E_{dep} , and (6) rinsing with the Ru^{3+} solution at OC followed by the OC SLRR reaction of Cu adlayers by Ru (OC SLRR_{Ru}) at quiescent conditions; i - E - t datasets were sampled *in situ*. N_2 saturation of electrolyte solutions was maintained throughout the experiment.

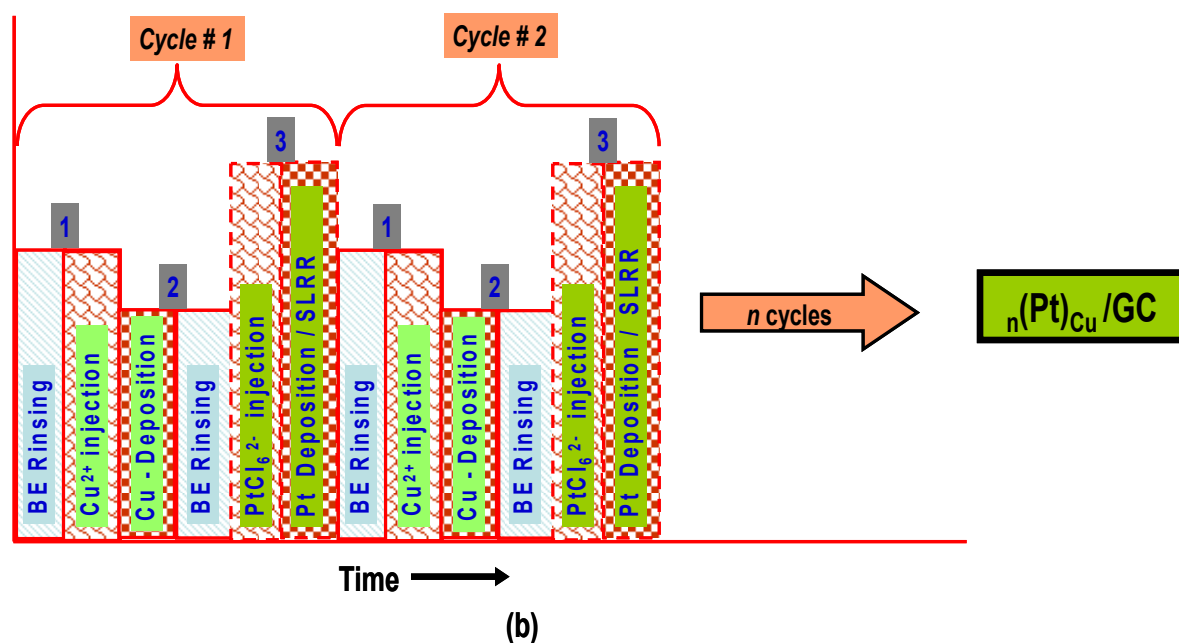
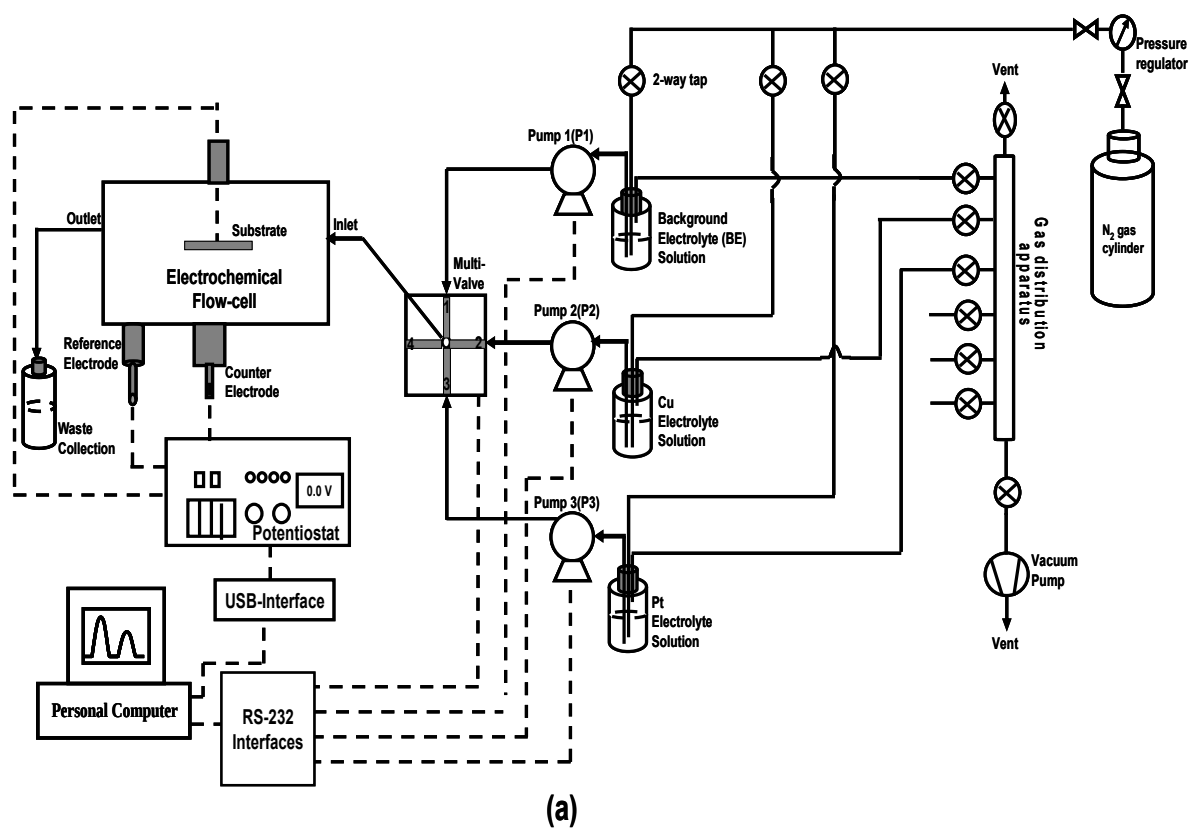


Figure 3.2: (a) Instrumental configuration for electrochemical deposition of multilayered monometallic system $n(\text{Pt})_{\text{Cu}}/\text{GC}$ via SLRR reaction involving Cu using the sequential scheme depicted in (b).

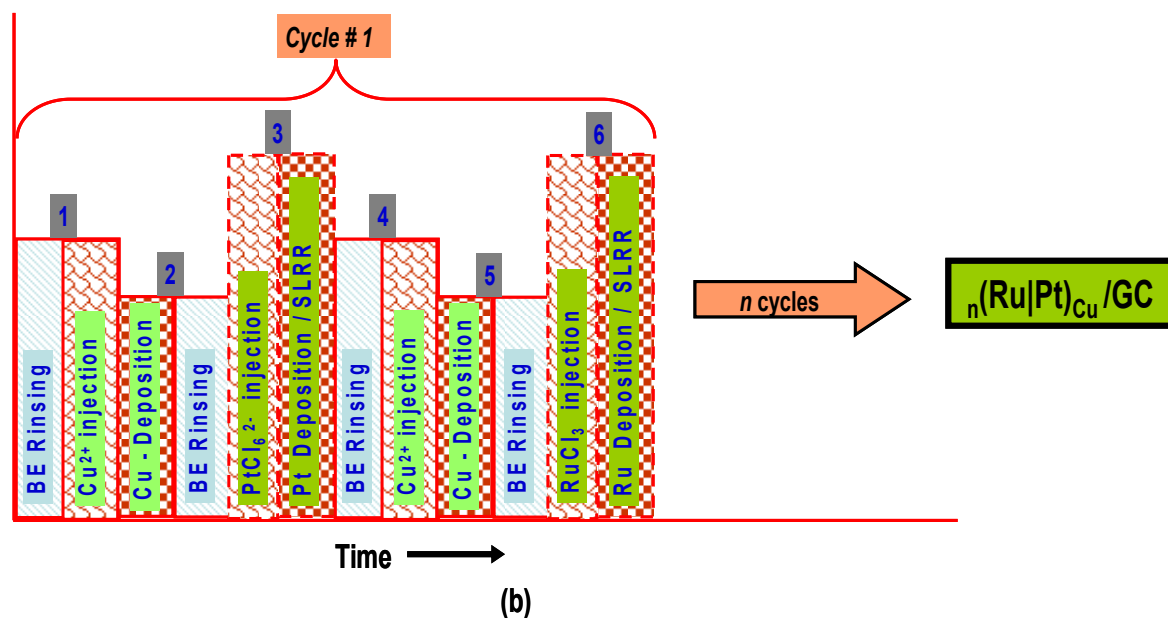
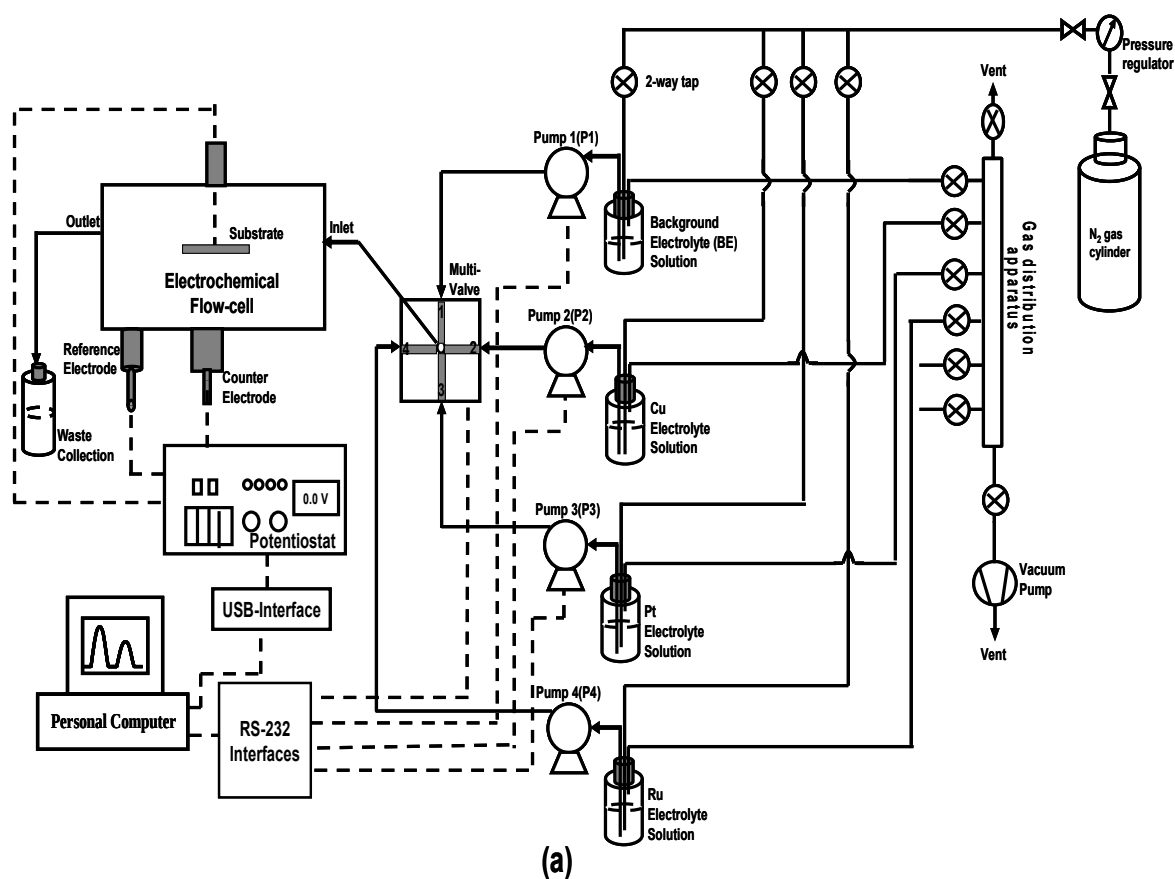


Figure 3.3: (a) Instrumental configuration in electrochemical deposition of the multilayered bimetallic system $n(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ via SLRR reaction involving Cu using the sequential scheme shown in (b).

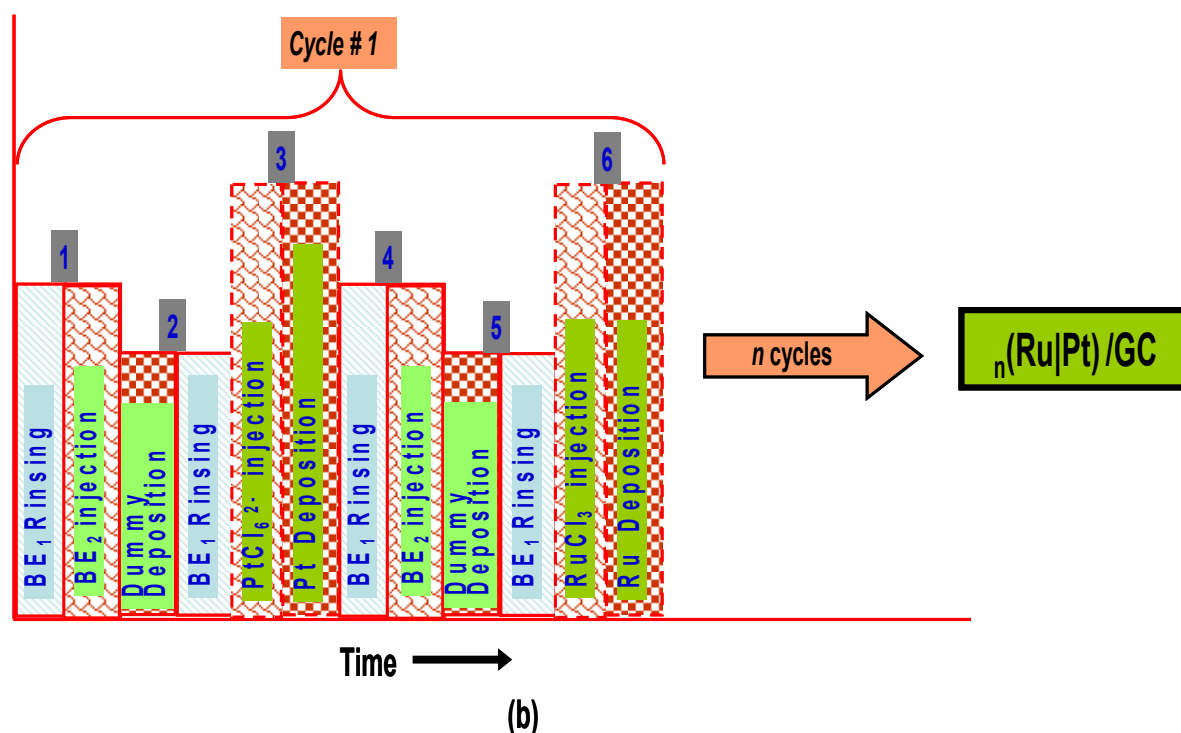
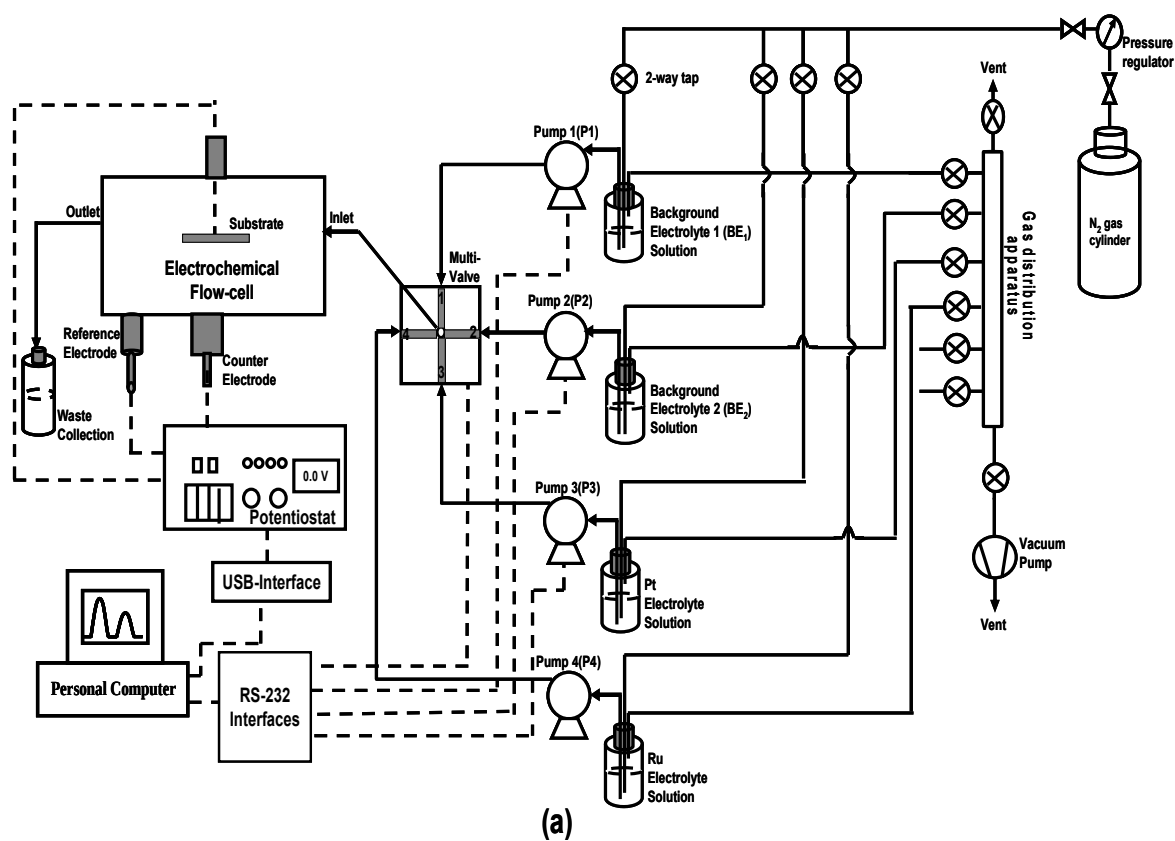


Figure 3.4: (a) Instrumental configuration in electrochemical deposition of the bimetallic system $n(\text{Ru}|\text{Pt})/\text{GC}$ by sequential open-circuit spontaneous deposition of Pt and Ru through deposition scheme shown in (b).

3.3.2.6.2. Sequential spontaneous deposition

To study the effect of Cu sacrificial adlayers, control experiments were performed to electrodeposit Pt and Ru bimetallic multilayers without the involvement of Cu. In this regard direct spontaneous deposition of Pt and Ru adlayers at OC (without involvement of sacrificial Cu adlayers) was performed. The general procedure - as described above for generation of $n(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ - was followed, but with the Cu^{2+} solution replaced with a second background electrolyte solution. Effectively, two background electrolyte solutions (BE_1 and BE_2) were used as shown in Figure 3.4a-b; effectively, both BE_1 and BE_2 solutions were 0.1 M HClO_4 . The *Autolab-SeqDep-4Pumps-Autorefill.vi* (**Appendix A**) was used for the automated deposition process. The generated electrode is hereafter denoted $n(\text{Ru}|\text{Pt})/\text{GC}$. N_2 saturation of the electrolyte solutions was maintained throughout the experiment.

3.3.2.6.3. Sequential codeposition

Another bimetallic electrode was obtained with the use of sacrificial Cu by SLRR reactions involving codeposition of Pt and Ru ($\text{OC SLRR}_{\text{Pt-Ru}}$) from a mixed precursor electrolyte solution (1 mM H_2PtCl_6 and 1 mM RuCl_3 in 0.1 M HClO_4). The instrumental setup and deposition steps employed are shown in Figure 3.5; the *Autolab-SeqDep-3Pumps-Autorefill.vi* (**Appendix A**) was employed for the sequential codeposition process. The resultant electrode generated by the sequential codeposition electrosynthetic pathway is denoted hereafter as $n(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$.

Sequential spontaneous codeposition of Pt and Ru on GC substrate was carried out similar to foregoing process described in Section 3.3.2.6.2 in the absence of sacrificial Cu adlayers but utilizing the mixed precursor electrolyte solution; the resultant electrode is denoted as $n(\text{Pt-Ru})/\text{GC}$ with instrumental configuration shown in Figure 3.6.

In all electrochemical deposition experiments described above, upon completion of the n deposition cycles, the BE solution was injected into the flow-cell at OC (a stand-by stage of the electrochemical systems and processes under study).

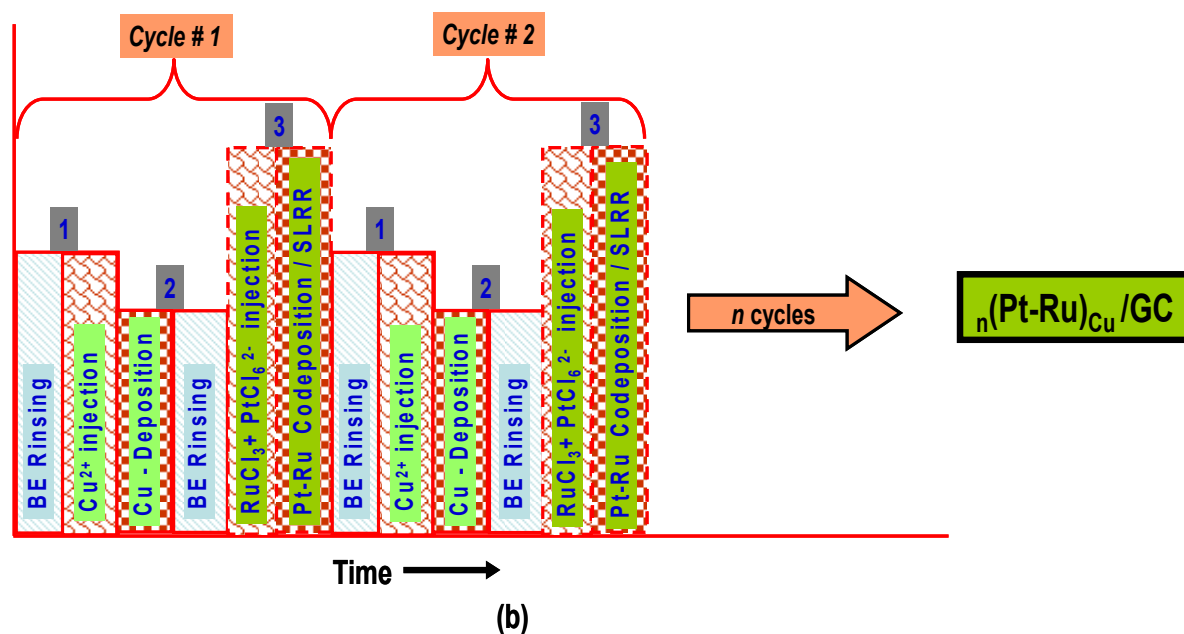
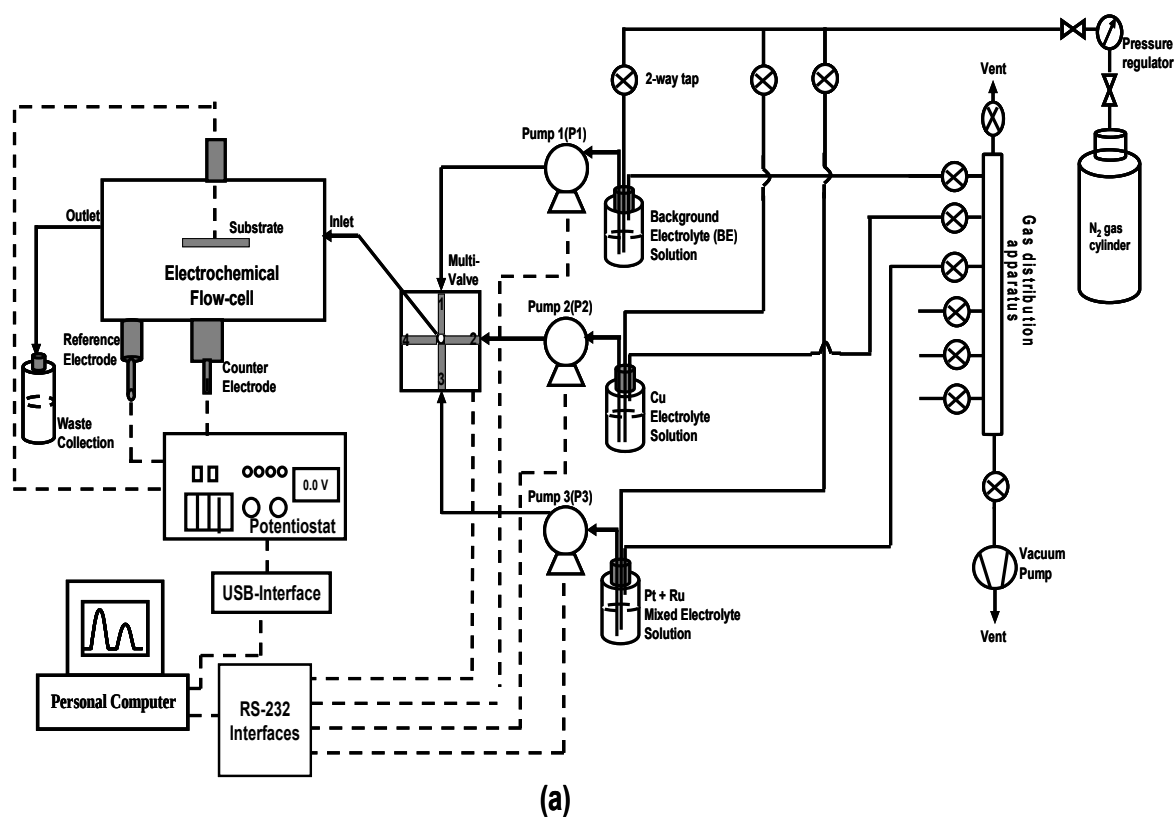


Figure 3.5: (a) Instrumental configuration in electrochemical deposition of the bimetallic system $n(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ by sequential codeposition of Pt and Ru via parallel SLRR reactions involving Cu.

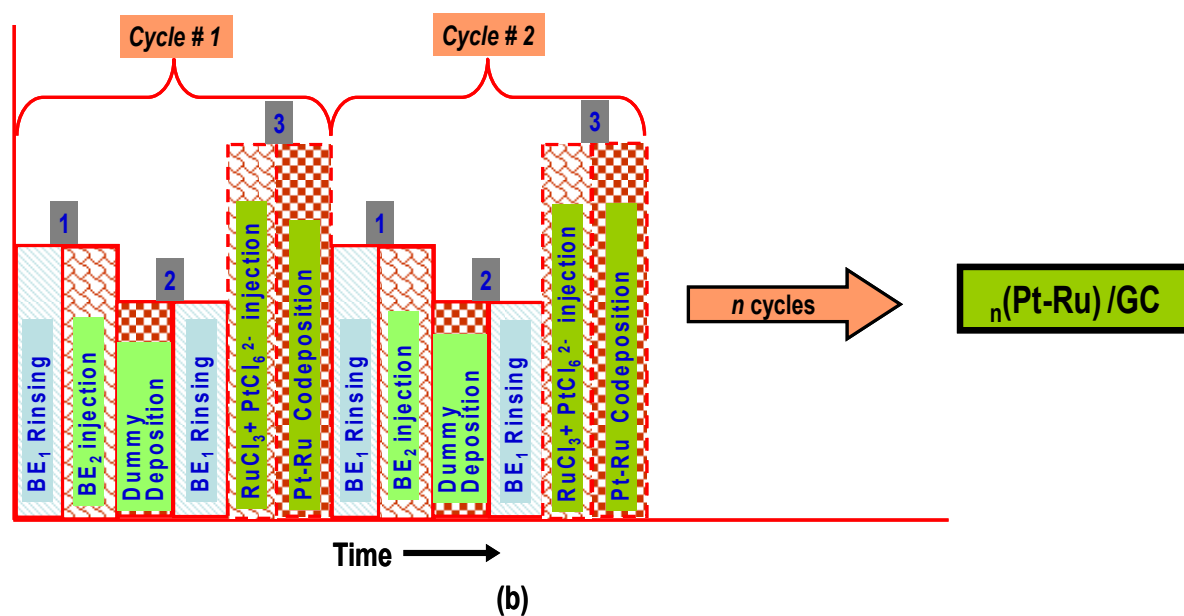
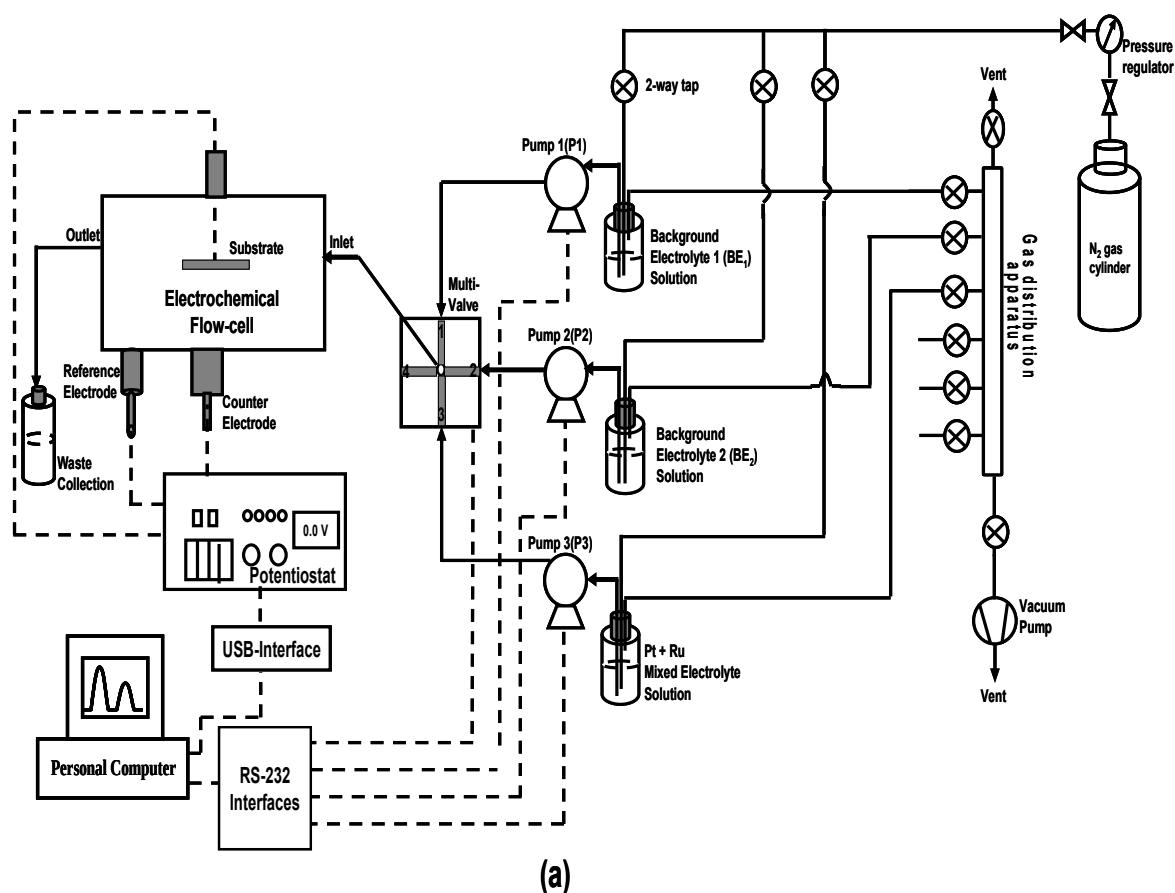


Figure 3.6: (a) Instrumental configuration in electrochemical deposition of the bimetallic system $n(\text{Ru-Pt})/\text{GC}$ by sequential open-circuit spontaneous codeposition of Pt and Ru as per scheme depicted in (b).

3.3.3. Physico-chemical and analytical characterization experiments

3.3.3.1. Microscopic and spectroscopic analyses

Ex situ microscopic investigations were carried out within 24 hours of preparation of various electrodeposits. A JEOL model JSM-5800LV scanning electron microscope - operated at 10 kV for Scanning Electron Microscopy (SEM) imaging and 20 kV for Energy Dispersive X-ray Spectroscopy (EDX) - was employed to study the morphology and acquisition of elemental EDX signatures of various electrodeposits. Atomic Force Microscopy (AFM) studies were carried out using model DI Nanoscope IVa (Digital Instruments, Inc., USA) microscope (operated in tapping mode) in ambient environment. The tip used was a model RTESPW (Veeco Manufacturing, USA).

3.3.3.2. Analytical electrochemistry

Studies involving electrochemical properties were performed with freshly prepared samples, as benchmark for further stability studies that were out of the scope of this research.

Surface electrochemical behavior of as-prepared Pt-based electrode systems was probed in quiescent N₂-saturated 0.1 M HClO₄ by CV between -0.2 V and 1.2 V at 50 mV s⁻¹ between -0.2 V and +1.4 V for up to five cycles. Outer-sphere electron transfer (see Section 2.2, Chapter 2) involving the redox couple Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ was investigated with CV within the potential range 0.15 V - 0.65 V on the pristine GC as well as on the various Pt-based electrode systems using N₂-saturated 1 mM K₄Fe(CN)₆ (in 0.1 M HClO₄) electrolyte solution. Electrochemical surface area involving outer-sphere electron transfer (*A*_{ES}) of the electrode systems was estimated using the Fe²⁺/Fe³⁺ couple using chronoamperometry (CA) of the redox couple, under the diffusion-controlled current regime. The Cottrell equation [222] (Equation 2.42 - Chapter 2) was employed to determine the outer-sphere *A*_{ES} values from the chronoamperometric data (corrected for background current obtained from measurements performed in neat 0.1 M HClO₄). Inner-sphere heterogeneous electrode properties (see Section 2.2, Chapter 2) were probed using 1 mM CuSO₄ (in 0.1 M HClO₄) electrolyte solution (nitrogen-purged). To this end, linear sweep ASV involving UPD of Cu and its oxidative stripping from +0.05 V to +0.8 V and CV

scans in the range -0.2 V to 1.0 V were carried out. From ASV of UPD of Cu, the inner-sphere electrochemically-active surface area (A_{EAS}) was aptly deduced from appropriate anodic stripping charge of the underpotentially-deposited Cu (Equation 2.61, Section 2.2.3.6, Chapter 2) using the reference charge of $420 \mu\text{C}/\text{cm}^2$ for a hypothetical flat surface of Cu monolayer, a common value for crystalline Pt and Ru surfaces, following the method described elsewhere [251].

The instrumental setup for electrochemical characterization of the various electrodes is shown in Figure 3.7. The electrolyte containing the precursor reactant of the test reaction was placed in an appropriate storage bottle connected to the required gas supply; a designated pump and multi-valve ensured direct injection to the electrochemical flow-cell containing freshly synthesized deposits. Experimental steps were carried with the aid of the custom-developed computer program *AutolabPumpsMainControl.vi* (**Appendix A**) that automated injection steps of the test and BE solutions to the flow-cell prior to execution of The General Purpose Electrochemical System (GPES) 4.9 and Frequency Response Analyzer (FRA) 4.9 software modules (EcoChemie, Autolab, The Netherlands) that were employed in running the applicable electrochemical techniques - Linear Sweep Voltammetry (LSV), Anodic Stripping Voltammetry (ASV), Cyclic Voltammetry (CV), Chronoamperometry (CA), and Electrochemical Impedance Spectroscopy (EIS).

3.3.4. Electrocatalysis: characterization experiments

3.3.4.1. Methanol oxidation reaction

Methanol electro-oxidation studies were carried out in quiescent 0.5 M CH_3OH in 0.1 M HClO_4 solutions using as-prepared electrodes, which were conditioned initially in 0.1 M HClO_4 by scanning the potential at 50 mV s^{-1} from -0.2 to 1.2 V for 5 cycles. The CH_3OH concentration regime was in line with its polar nature and electrical neutrality in the aqueous medium of 0.1 M HClO_4 allowing electrocatalytic and related adsorption phenomena of the MOR on various as prepared surfaces, as per well-established literature procedures [126,272,273], to be studied. CVs for methanol tests were ran at 50 mV s^{-1} for 5 cycles in the potential range from 0 to 1.0 V, followed by EIS measurements in freshly-injected CH_3OH solution, at bias potential of 0.4 V, using sine-wave signal of 10 mV amplitude in the

frequency range of 0.5 Hz to 100 kHz. CA measurements were performed at applied potential of 0.4 V for 300 s. Between electrochemical measurements the flow-cell was rinsed at OC with the blank electrolyte (0.1 M HClO₄).

3.3.4.2. Oxygen reduction reaction

Oxygen reduction reaction (ORR) was studied in ultra-high purity O₂-saturated 0.1 M HClO₄ solution (pre-saturated for 2 hours and thereafter continuously saturated with the O₂ gas in a dedicated stock bottle). The ORR on as-prepared nanoclusters was studied at hydrodynamic conditions at various flow-rates (2 – 20 mL/min) of the 0.1 M HClO₄ solution by recording cathodic linear sweep voltammograms at 50 mV s⁻¹ in the potential range 0.8 – 0.1 V. A dedicated pump line of the instrumental setup and appropriate flow-cell (Figure 3.7) were used to probe the ORR activity on the as-prepared electrodes.

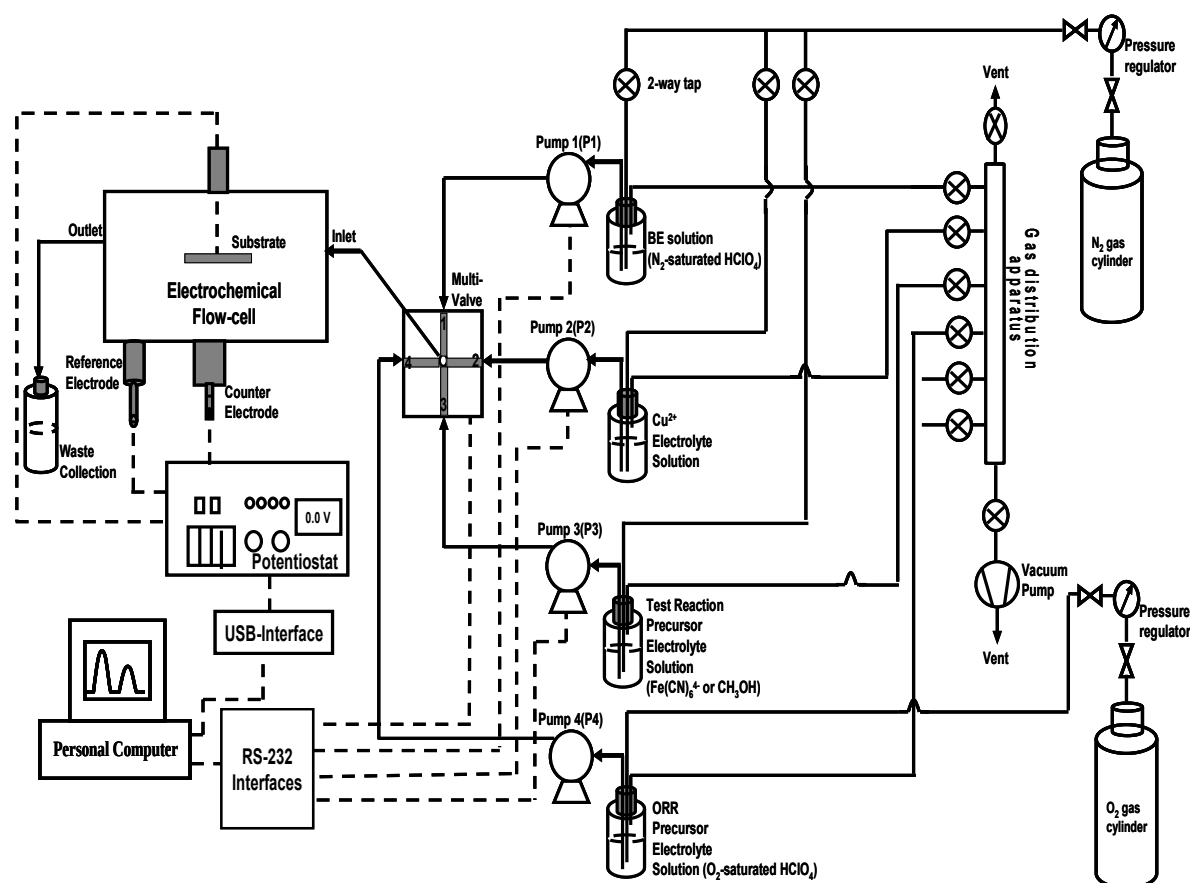


Figure 3.7: Instrumental configuration for electrochemical and electrocatalytic characterization experiments.

3.4. Results and discussion

3.4.1. Effects of electrochemical deposition potential and pH on Pt-Cu-H₂O and Ru-Cu-H₂O systems: Thermodynamic considerations

Insight onto the effect of pH and potentials on the formation of various Pt, Ru, and Cu species, our main aim being deposition of metallic states, was gained from thermodynamic potential-pH (E -pH) models (theoretical background on this type of thermochemical modelling is given in **Appendix B**). Typical potential-pH (E -pH) stability models for the Pt-Cu-H₂O and Ru-Cu-H₂O systems at 25 °C are shown in Figure 3.8; relevant thermochemical data of the modelling input species are provided in Tables B.1 and B.2 in **Appendix B**. The models showed that (i) metallic Pt exists at $E < 0.89$ V and pH between 0 and 3.5, (ii) metallic Pt and Ru coexist below pH of 1.2 when $E < 0.55$ V, and (iii) metallic Cu exists in the same pH-range but only at $E < 0.25$ V (potentials are with respect to Standard Hydrogen Electrode (SHE)). Based on this information, all deposition experiments were performed at pH of 1 ± 0.05 .

3.4.2. Electrodeposition of templating Cu on glassy carbon

Typical stages in the reductive formation of a metal layer from precursor ions predominantly involve nucleation and subsequent growth of metal nuclei on the surface. The reduction process can either be kinetic- or diffusion-controlled [274]. Further insights on Cu electrodeposition mechanism on the GC substrate were obtained from CV performed on 0.1 M HClO₄ solution, as shown in Figure 3.9a, where no distinct peaks for Cu UPD peaks were recorded. There was some insignificant shoulder observed at potentials between 0 and 0.1 V. This potential range overlaps with the bulk (3D) Cu deposition that theoretically starts at $E < 0.05$ V (The Nernst formal potential for the Cu²⁺/Cu(s) couple is 0.046 V (vs. Ag/AgCl/3M KCl) for 1 mM Cu²⁺). The shoulder observed in Figure 3.9a could be indicative of a nucleation step as was demonstrated elsewhere by in situ Cu nucleation mechanistic studies by Electrochemical AFM [275]. Several attempts to plate Cu at $E_{\text{dep}} = 0.05$ V resulted in no significant deposits at reasonable and acceptable time intervals. Because of that we have opted for the use of relatively small overpotentials in relation to $E_{\text{Cu}^{2+}/\text{Cu}}$ where deposition of Cu(s) occurs most likely through kinetically-controlled 3D nucleation and progressive growth of nanoclusters.

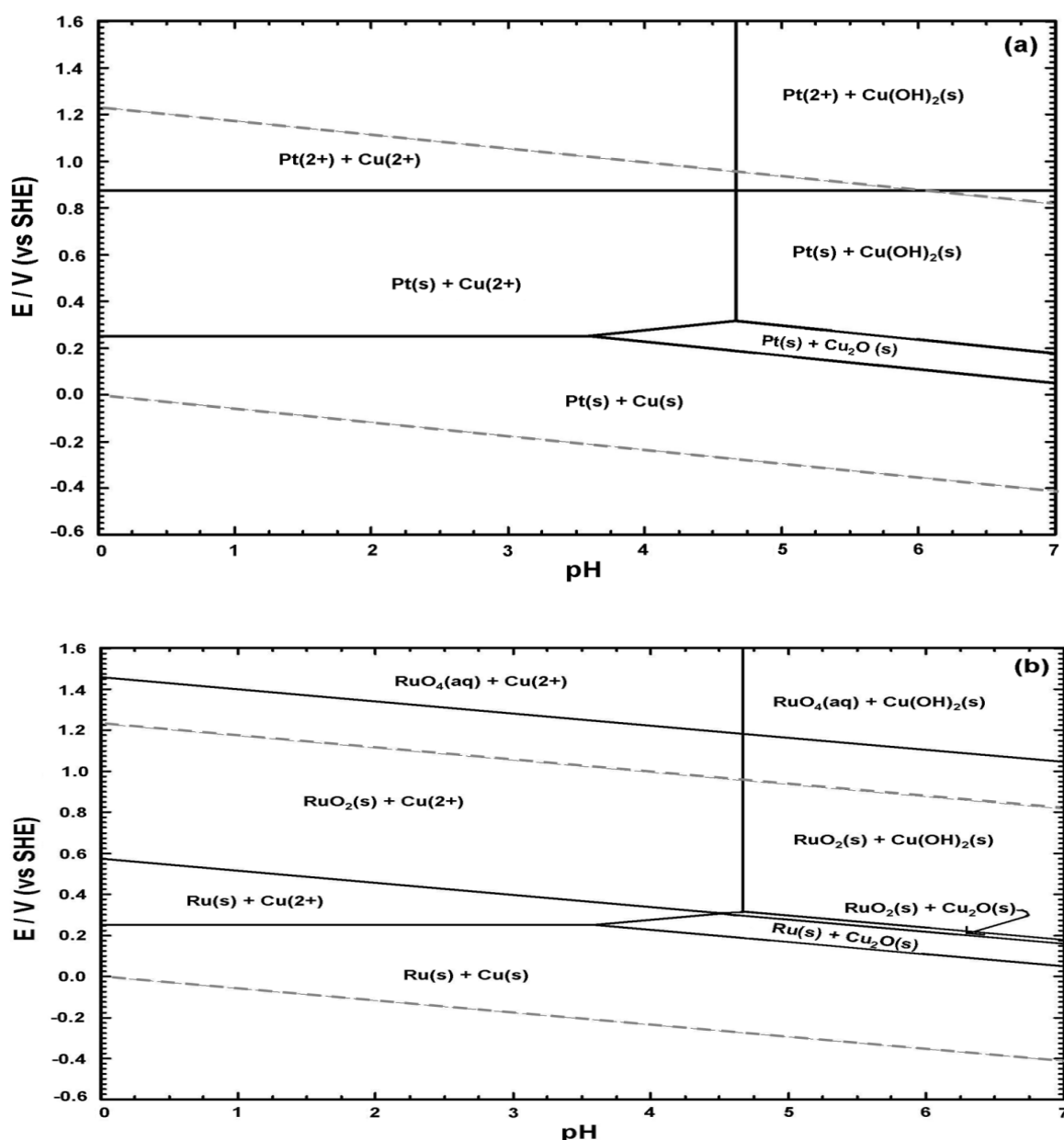


Figure 3.8: Potential-pH (E - pH) models of (a) Pt-Cu-H₂O, (b) Ru-Cu-H₂O systems. Conditions: 0.001 mol/Kg set for all aqueous forms of Pt, Ru, and Cu and models generated at temperature of 298.15 K.

Effect of deposition time was probed by ASV at $E_{\text{dep}} = -0.05$ V for t_{dep} ranging from 5 to 150 s. Analysis of variation in total charge density (derived from the integrated ASV curves – Figure 3.9b) led to the deduction that about 1 monolayer-equivalent of Cu nanoclusters was obtained for t_{dep} of about 90 s (the term *monolayer-equivalent* is used here to indicate formation of Cu nanoclusters on the GC substrate's geometric area equivalent to deposition of a hypothetical monolayer of Cu calculated from a theoretical charge density required for such monolayer deposition [276]).

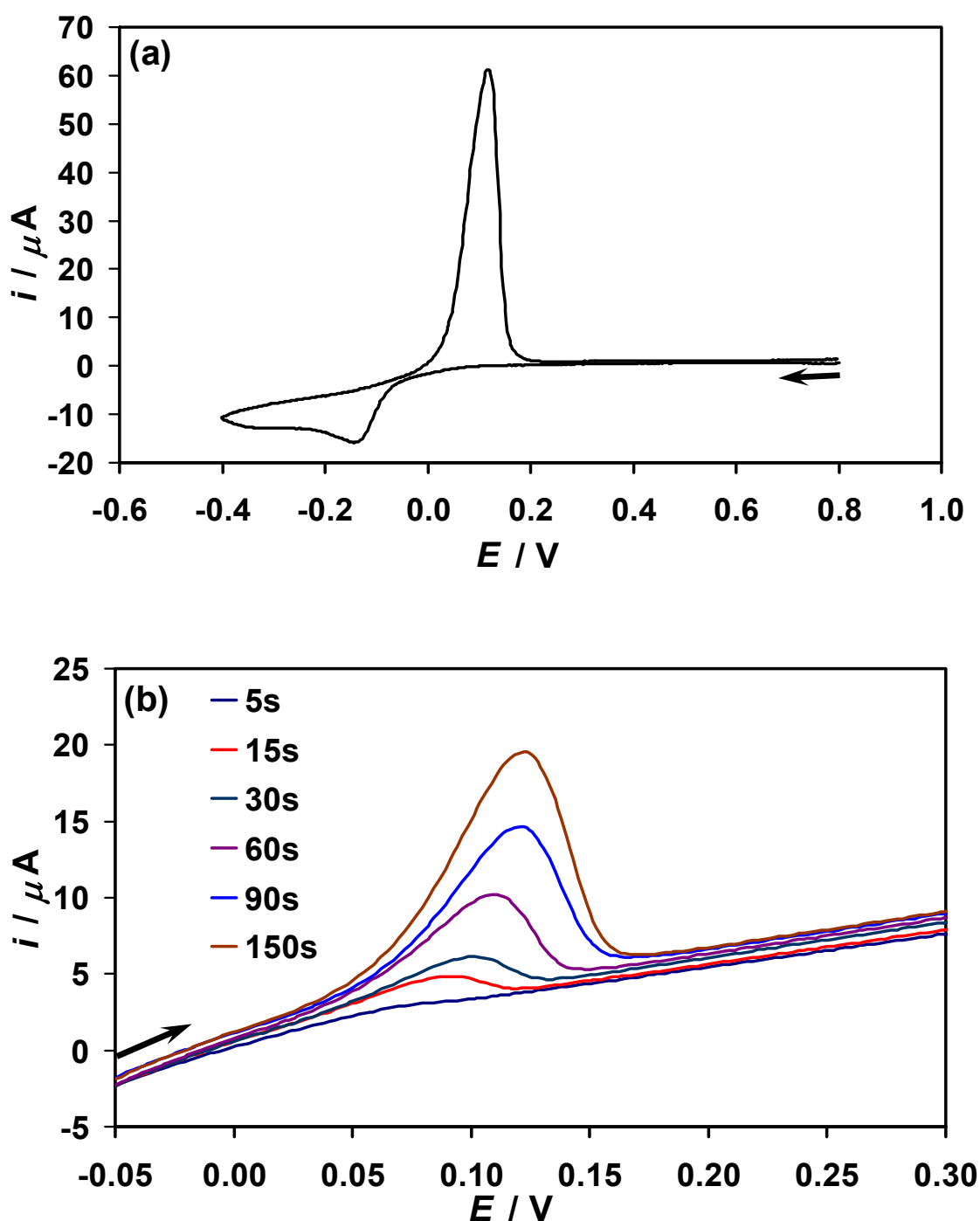


Figure 3.9: (a) CV recorded from 1 mM CuSO_4 + 0.1 M HClO_4 with bare GC electrode; (b) ASV curves recorded after deposition of Cu (from 1 mM CuSO_4 + 0.1 M HClO_4) at E_{dep} of -0.05 V for indicated deposition time.

Studies performed on Cu electrodeposition on GC substrate [277] indicate that indeed fast electrocrystallization of well-dispersed Cu nanoclusters occurs at kinetically-controlled deposition overpotentials in Figure 3.9b.

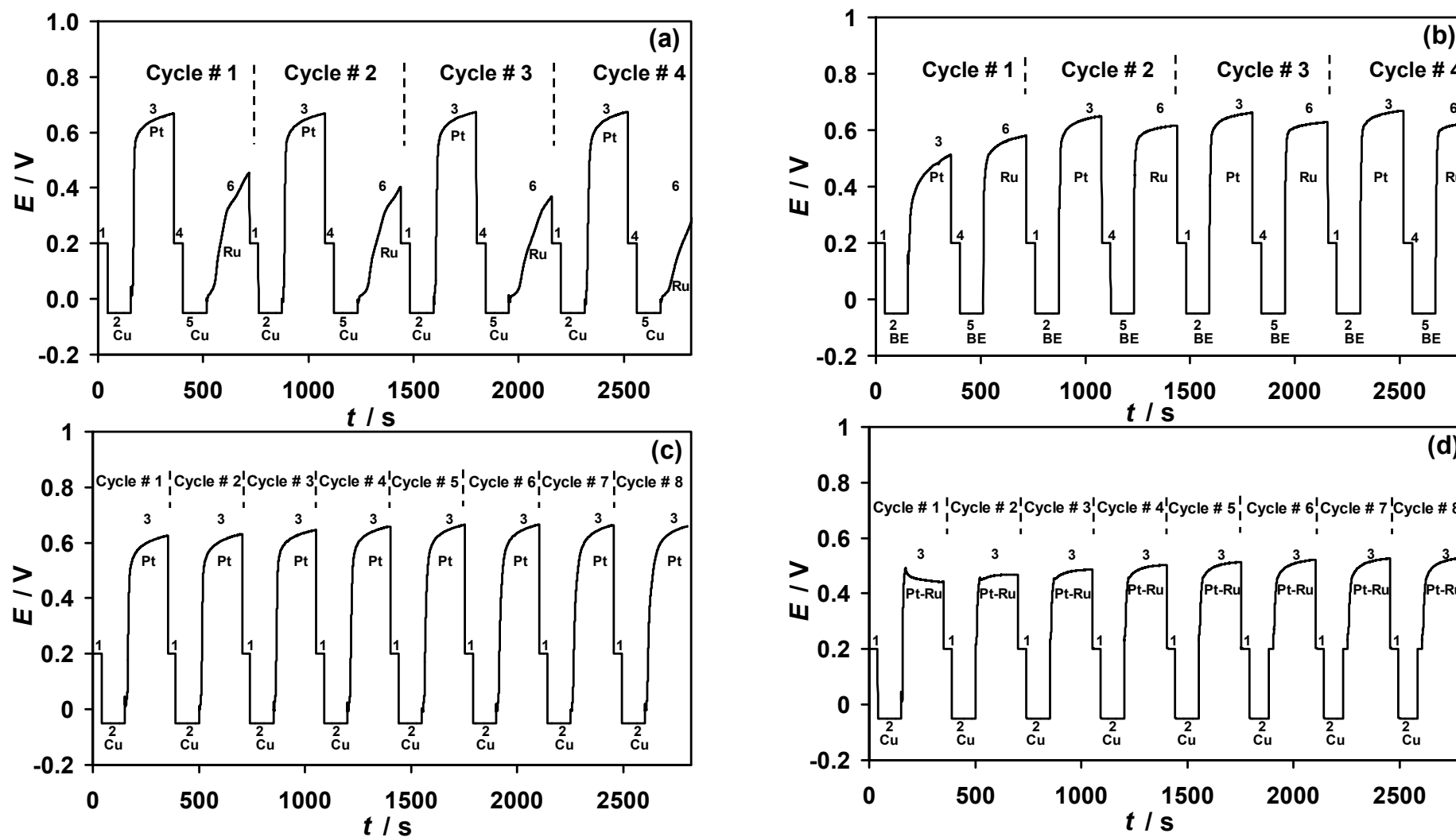


Figure 3.10: E - t transients recorded during typical sequential electrodeposition of (a) $n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$, (b) $n(\text{Ru} | \text{Pt})/\text{GC}$, (c) $n(\text{Pt})_{\text{Cu}}/\text{GC}$, and (d) $n(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$. See text for parameters used at numbered steps.

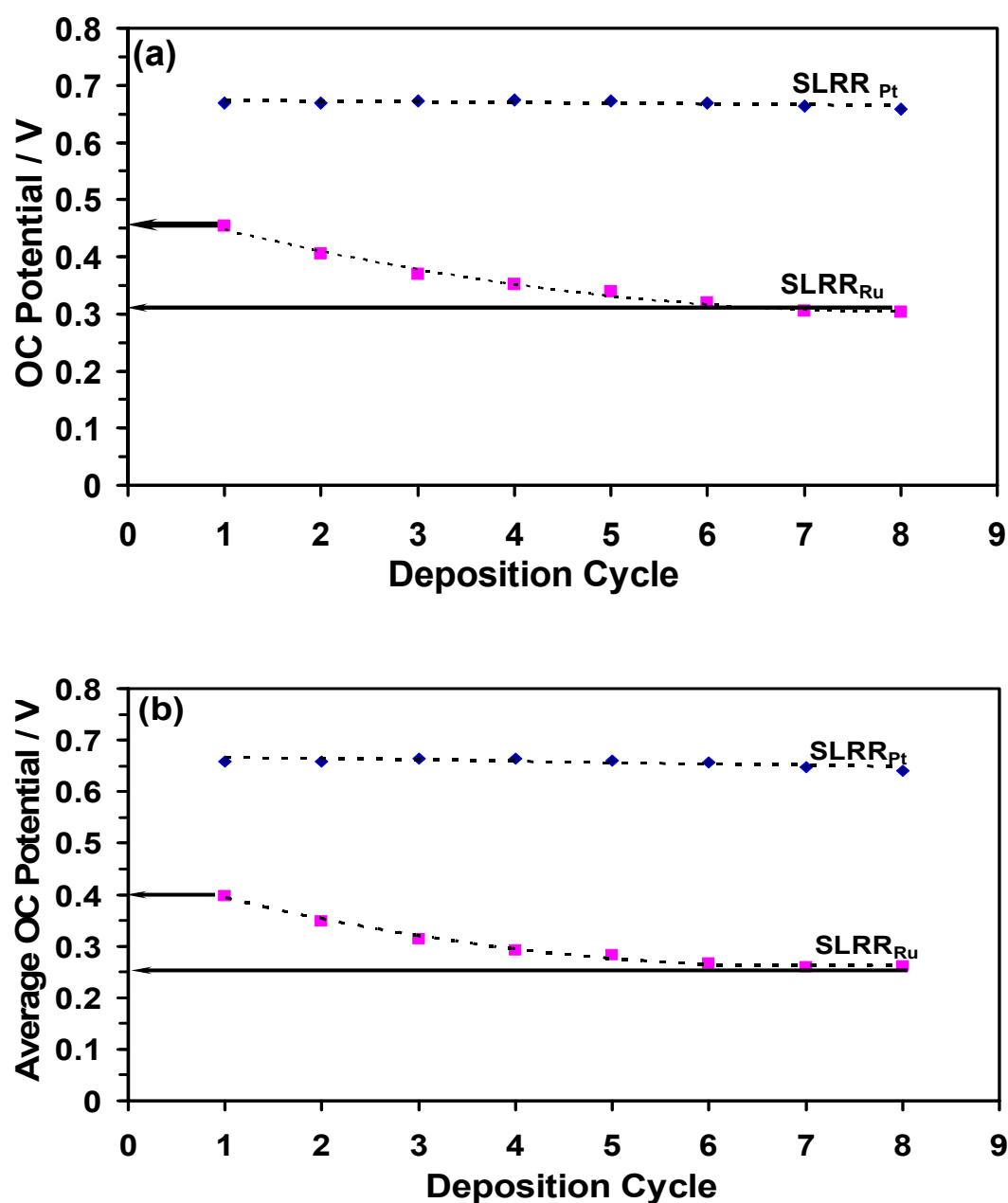
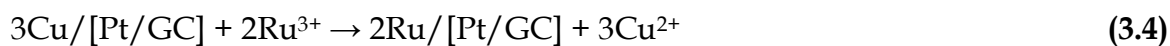


Figure 3.11: Variation in (a) maximum open-circuit (OC) potential attained during Pt and Ru surface-limited redox-replacement reaction stages, SLRR_{Pt} and SLRR_{Ru} , respectively during deposition of the bimetallic nanoclusters ${}_8(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$. (b) Average OC potential (last 90s of SLRR stage) during deposition of ${}_8(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$.

Assuming the preferential redox-reaction pathways, leading to zero-valent metallic states, as described by electrode-based Reactions 3.1 – 3.4,





the following electrochemical parameters were selected for each stage employed to generate $n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$ (see Figure 3.10a): (1) rinsing the cell with BE at $E_{\text{appl}} = 0.2$ V for 20 s, followed by rinsing with the Cu^{2+} solution at E_{appl} for 20 s; (2) Cu deposition at $E_{\text{dep}} = -0.05$ V for 90 s, followed by rinsing with BE at E_{dep} for 20 s; (3) rinsing with the Pt^{4+} solution at OC for 20 s, followed by the OC SLRR_{Pt} for 180 s; (4) rinsing, initially with BE, followed by the Cu solution at E_{appl} for 20 s (for both solutions); (5) Cu deposition at E_{dep} for 90 s, followed by rinsing with BE at E_{appl} for 20 s; and (6) rinsing with the Ru^{3+} precursor solution at OC for 20 s, followed by the OC SLRR_{Ru} 180s. This protocol was repeated for $1 \leq n \leq 8$ cycles in order to systematically generate larger bimetallic nanoclusters. In the comparative studies, to probe the influence of Cu templating adlayers, to generate: (i) ${}_8(\text{Ru} | \text{Pt})/\text{GC}$, the same sequence of stages was followed, but the Cu solution was replaced by BE, as depicted by $E-t$ transients shown in Figure 3.10b, (ii) $E-t$ transients for ${}_8(\text{Pt})_{\text{Cu}}/\text{GC}$ and ${}_8(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ are shown in Figure 3.10c-d, where Stages 1 and 2 are exactly the same as employed for the generation of ${}_8(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$. For clarity, only four initial cycles are shown in Figure 3.10a-b and eight cycles are shown in Figure 3.10c-d.

3.4.3. Sequential electrodeposition: characteristics of surface-limited redox-replacement of copper by platinum and ruthenium

Variations in open-circuit potential (E_{OC}) during Pt and Ru redox-exchange reactions with Cu (Stages 3 and 6 in Figure 3.10a) to form $n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$ clearly indicate that there are two distinctive processes taking place that might be used as signatures for the OC SLRR_{Pt} and SLRR_{Ru} reactions, involving replacement of Cu adlayers by Pt and Ru, respectively. It was observed that E_{OC} during OC SLRR_{Pt} reaches a maximum and constant value of about 0.66 V; the variation in E_{OC} (as a maximum value attained) for all 8 cycles during the deposition of Pt as well as Ru is shown in Figure 3.11a-b. It is clear that, when $E-t$ transients of Stage 3 (Figure 3.10a) and the maximum E_{OC} values attained (Figure 11a-b) are compared with computed equilibrium potentials at pH 1 (Figure 3.8), metallic Pt(s) is indeed deposited; for

most of the deposition period, E_{OC} is within the potential range where Pt(s) and Cu^{2+} are thermodynamically predicted to coexist and only when E_{OC} reaches its maximum value in Stage 3 a possibility of coexistence of Pt(s), Pt^{2+} and Cu^{2+} might be considered. In case of Ru deposition, E_{OC} approaches a value of about 0.45 V in the first cycle and gradually decreases reaching a constant maximum value of about 0.32 V (see Figure 3.11). The variation in the maximum value of E_{OC} suggests that, initially, besides Ru(s), $RuO_2(s)$ might also be formed, but after the fifth cycle the only thermodynamically predicted equilibrium (Figure 3.8) involves Ru(s) and Cu^{2+} . Overall, the experimentally obtained OC potentials strongly suggest deposition of metallic Pt(s) and Ru(s).

Representative $i-t$ data sets at Stages 2 and 4 (during Cu deposition at various cycles of generation of $n(Ru|Pt)_{Cu}/GC$ nanoclusters) are shown in Figure C.1 (Appendix C). Corresponding variation in total charges (determined from integration of $i-t$ data) are supplied in Figure C.2 (Appendix C). There is a clear difference for the first cycle, during which Cu deposits on pristine GC substrate as compared to subsequent cycles for which Cu deposits on formed Pt or Ru nuclei. We observe a gradual increase of the total Cu charge with increasing number of cycles, with a tendency to a steady value after the third cycle, probably indicating more uniform Cu deposition on the well-developed noble metal clusters.

3.4.4. Effects of templating copper adlayers: spontaneous deposition of platinum and ruthenium

A very different reaction mechanism appears to take place when the $n(Ru|Pt)/GC$ electrode was generated (without involvement of Cu templating adlayers) – see Figure 3.10b. From the second cycle onwards there is not a large difference in E_{OC} at Stages 3 and 6 where maximum E_{OC} approached 0.65 V and 0.60 V during OC $SLRR_{Pt}$ and OC $SLRR_{Ru}$, respectively, but an obvious pattern emerges. This strongly suggests that during Stage 3 metallic Pt is formed, but at Stage 6 most likely RuO_2 is somewhat formed as predicted from thermodynamic E -pH modeling (Figure 3.8b), where the calculated equilibrium potential for coexistence of $RuO_2(s)$ and Cu^{2+} matches well the experimentally observed E_{OC} . These observations indicate that during direct spontaneous deposition of Pt and Ru, without involvement of

sacrificial Cu, preferentially $\text{RuO}_2(\text{s})$ rather than $\text{Ru}(\text{s})$ adlayers are generated on metallic Pt.

From Figure 3.10c it follows that the sequential deposition of metallic Pt took place (to form the $\text{s}(\text{Pt})_{\text{Cu}}/\text{GC}$ electrode) via the same mechanism as discussed above for plating of Pt on the Ru-layer of the $\text{s}(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ electrode. Maximum E_{OC} of about 0.48 V, observed at Stage 3 in Figure 3.10d, is well within the potential windows where Pt(s) and $\text{RuO}_2(\text{s})$ are predicted to coexist with Cu^{2+} .

3.4.5. Sequential codeposition of platinum and ruthenium

Interesting and somewhat unexpected result was obtained in the case of a sequential OC SLRR co-deposition of Pt and Ru involving sacrificial copper. The OC deposition potential of about 0.48 V observed in Stage 3 in Figure 3.10d is well within the potential windows where Pt(s) and $\text{RuO}_2(\text{s})$ are predicted to co-exist with Cu^{2+} as shown in Figure 3.8. If this is indeed the case then $\text{n}(\text{RuO}_2\text{-Pt})_{\text{Cu}}/\text{GC}$ rather than $\text{n}(\text{Ru-Pt})_{\text{Cu}}/\text{GC}$ electrode was generated. An E -pH diagram, computed for the mixture of Pt and Ru (Figure 3.12), predicts that at pH = 1 metallic forms of these two noble metals exist only at $E < 0.55$ V vs. SHE, (0.33 V vs. Ag/AgCl); the observed E_{OC} of 0.48 V in Figure 3.10d is significantly more positive.

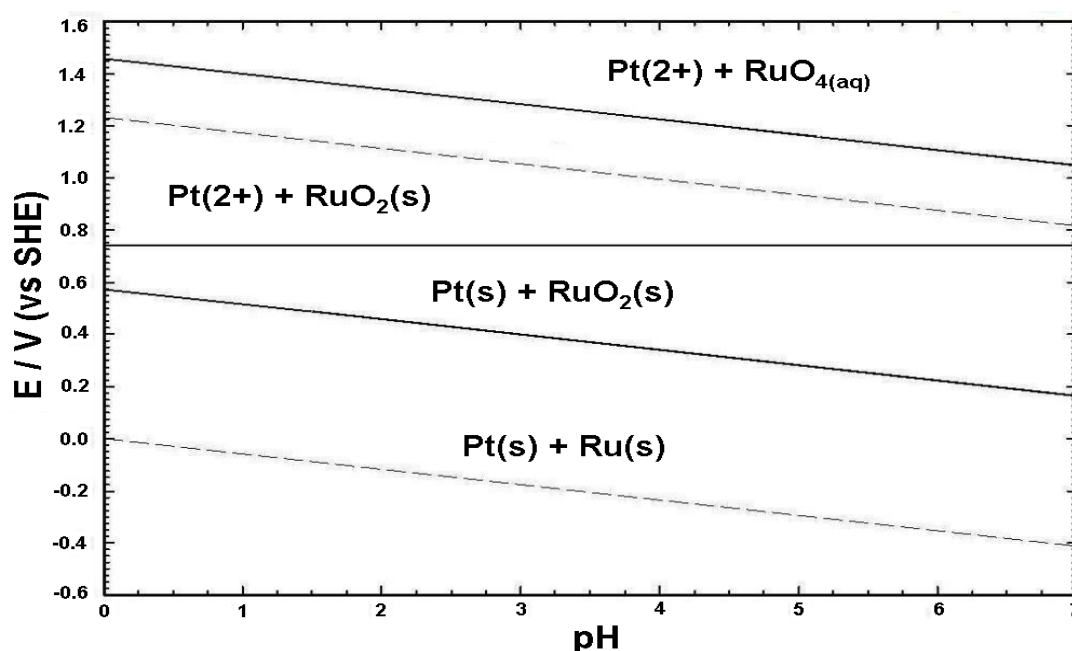
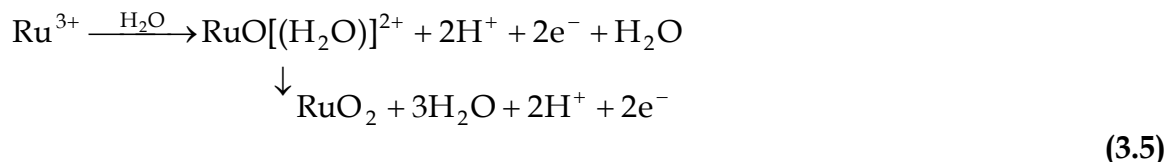


Figure 3.12: Potential-pH (E -pH) models of Pt-Ru- H_2O system. Conditions: 0.001 mol/Kg set for all aqueous forms of Pt and Ru; temperature = 298.15 K.

Interpretation of Ru oxide adlayer formation (from inferences of Figure 3.10) correlates well with data reported by Wieckowski et al [161] for the spontaneous Ru deposition on Pt (single-crystal to polycrystalline) electrodes if hydrolysis of Ru^{3+} (Reaction 3.5) is feasible in a given electrolyte solution:



Furthermore, the sequence of deposition may involve reductive steps to $\text{Ru}(0)$, spontaneous re-oxidation to RuO and RuO_2 adventitiously taking proceeding according to Reactions 3.6 and 3.7:



In our studies, it appears that only in case of the sequential OC SLRR reactions involving sacrificial Cu, and separate solutions of Pt and Ru, these two elements are preferentially deposited in their metallic forms when Ru^{3+} ions are in contact with metallic Cu. In case of the common mixture of Pt with the less noble Ru ions, Pt deposits preferentially and the spontaneous deposition of Ru must result in formation of $\text{RuO}_2(\text{s})$ on $\text{Pt}(\text{s})$. However, separating their deposition leads to some kind of leverage in favor of both noble metals (in this regard the nobility of Pt and Ru being referenced to Cu, the sacrificial element).

Within the framework of the preceding analysis, it is possible that Ru oxides formed during OC deposition stages, as noted above, have been reduced at stage 2 (upon application of E_{dep} to deposit Cu at second and subsequent cycles), but this does not apply to the last deposition cycle where the final Ru layer is formed. Results discussed further strongly indicate that the final layer deposited during the OC SLRR reaction has a decisive impact on electrochemical and electrokinetic activities of generated nanostructures.

3.4.6. Microscopy and energy-dispersive X-ray spectroscopy

Figure 3.13 depicts SEM images and corresponding EDX spectra for ${}_8(\text{Pt})_{\text{Cu}}/\text{GC}$, ${}_8(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$, and ${}_8(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$. Reasonably uniform coverage was obtained after 8 deposition cycles with the GC surface providing electrochemically active sites for preferential growth of the nanoclusters. Somewhat different in size nanostructures were attained for the ${}_8(\text{Pt})_{\text{Cu}}/\text{GC}$ and ${}_8(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ electrodes (Figure 3.13, parts a and b), with the latter one showing smaller number and larger in size particles.

Since the only difference in generating the two electrodes was the use of one or two precursor solutions of the same analytical concentrations and they all were used in eight deposition operation of 180 s, the deposited stack of (Ru | Pt) layers (the overall deposition time was $8 \times 2 \times 180$ s) resulted in larger particles when compared with the stack of Pt layers generated in half of that time, 8×180 s. It is also possible that with the prolonged deposition time the adjacent small particles had undergone conglomeration, hence, the smaller number of nanoclusters is observed in case of the ${}_8(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ electrode.

The most striking difference in morphology, however, is observed between the deposits seen in Figure 3.13a-b and those in Figure 3.13c. The observed difference correlates well with the fact that metallic Pt(s) and (Ru | Pt)(s) deposits were formed when single metal ion solutions were used, but a mixture of $\text{RuO}_2(\text{s})$ and Pt(s) was generated in case of the codeposition process. It appears that the formation of $\text{RuO}_2(\text{s})$ during the SLRR codeposition process has a profound influence on the deposit morphology – large nanostructures are not present but rather highly dispersed and uniformly distributed layers of $\text{RuO}_2(\text{s})$ and Pt(s) were obtained as seen in Figure 3.13c. Interestingly, similar morphology was obtained when a spontaneous codeposition without the use of a sacrificial Cu (to obtain the ${}_n(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ electrode) took place (Figure 3.13d); the analysis of corresponding E_{OC} (not shown) also indicated thermodynamic favorability of spontaneous formation of RuO_2 .

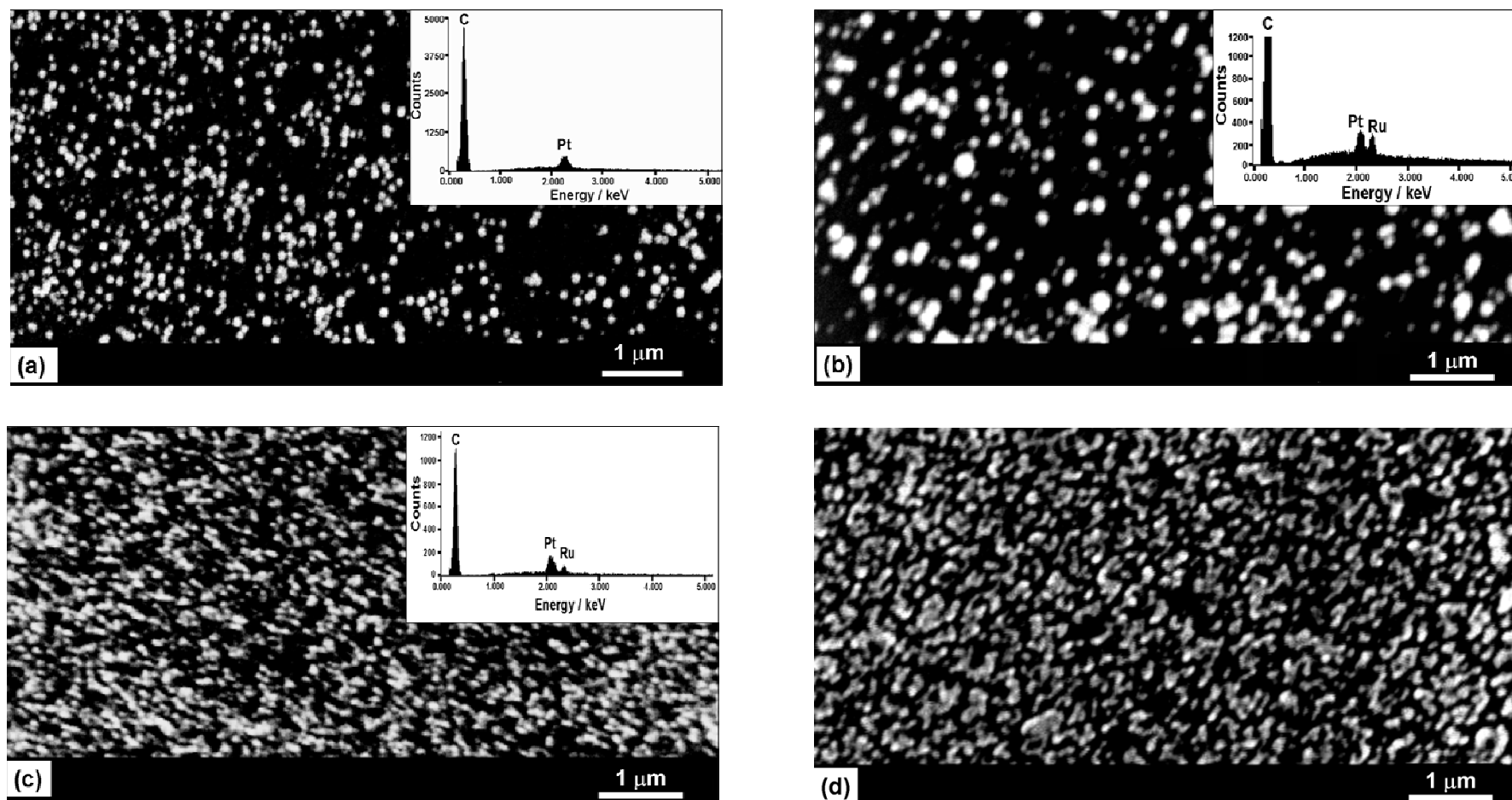


Figure 3.13: SEM micrographs and corresponding EDX spectra (insets) of: (a) monometallic nanoclusters $n(\text{Pt})_{\text{Cu}}/\text{GC}$; (b) bimetallic nanoclusters $n(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$; (c) sequentially codeposited bimetallic clusters $n(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$; (d) bimetallic nanostructures $n(\text{Ru}|\text{Pt})/\text{GC}$ deposited by direct spontaneous deposition without SLRR reactions involving Cu. All deposits shown were obtained after eight deposition cycles ($n = 8$).

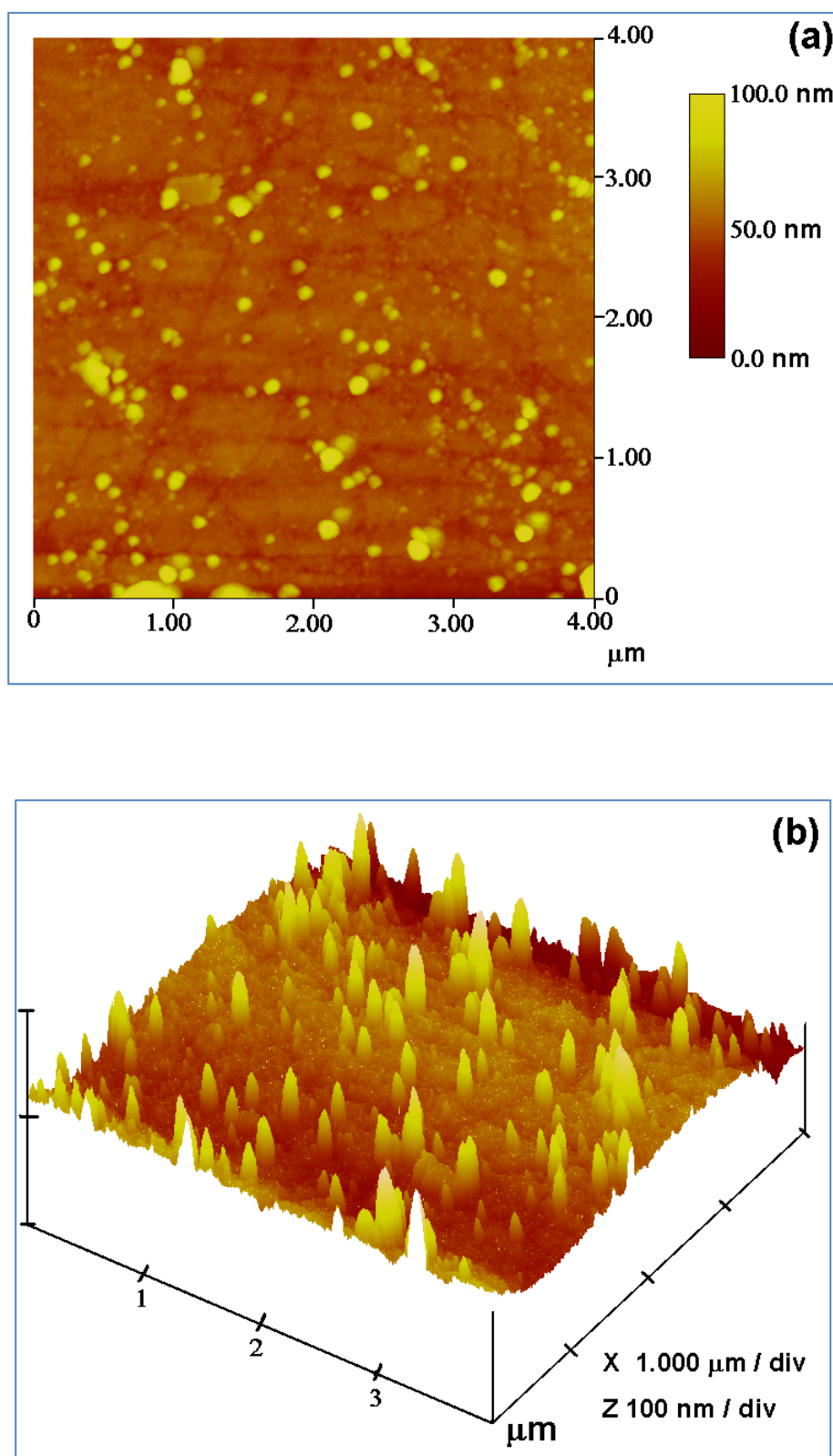


Figure 3.14: AFM images obtained in tapping mode for the bimetallic Ru|Pt nanoclusters obtained after 8 deposition cycles with SLRR reactions involving Cu. (a) Flattened image showing the morphology of the Ru|Pt nanoclusters on the GC substrate. (b) 3D surface image of the same area in (a) showing topographic features of the Ru|Pt nanoclusters.

The relevant EDX spectra (see insets of Figure 3.13a–c) of the $s(\text{Pt})_{\text{Cu}}/\text{GC}$, $s(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$, and $s(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ electrode surfaces qualitatively confirmed (i) the presence of Pt and Ru (where expected) and (ii) quantitative (or close to) replacement of Cu by Pt as well as Ru during the OC SLRR reactions, as EDX showed no detectable traces of Cu. Relevant literature suggests difficulty of quantitative deductions of nanoscale Pt and Ru deposits on carbonic substrates from EDX examination [142,278].

Additional and important information on morphology and topography was obtained from the AFM images (Figure 3.14) obtained for the $s(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ electrode system (this was of main interest in this work). The AFM topographic image shows individual as well as densely packed nanostructures (small needle-like immobilized islands) and this most likely can be attributed to the random distribution of electroactive centers on the GC substrate on which the growth of the nanoparticles preferentially occurred. Cross-sectional analysis of the AFM images showed that many of the nanoparticles attained the height of about 10 – 50 nm, a strong suggestion of a preferential 2D vertical, layer-by-layer growth that produced many free-standing immobilized nanoclusters; minimally, overall 3D growth might have proceeded from one deposition cycle to another.

3.4.7. Electrochemistry of platinum and ruthenium nanostructured multilayered electrode systems on glassy carbon

3.4.7.1. Surface electrochemistry

The influence of increasing deposition cycles on electrochemical activity is demonstrated in a set of CVs (Figure 3.15a), involving the $n(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ electrode and recorded in N_2 -saturated 0.1 M HClO_4 solution after $n = 2, 4, 6$, and 8 cycles. The constancy in the reduction peak potential at about 0.45 V (reduction of surface oxides formed during anodic scans between 0.2 and 1.2 V), abrupt increase in oxidation current at about 1.2 V, and adsorption/desorption peaks of hydrogen (between 0 and -0.2 V) suggest that the morphology of deposits does not change significantly from cycle to cycle but the surface area of the nanostructures increases because recorded currents were progressively larger. Hence, for further comparison, results obtained on electrodes generated after 8 cycles were used.

CVs obtained on the $s(\text{Pt})_{\text{Cu}}/\text{GC}$ and $s(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ electrodes (Figure 3.15b) confirm that: (i) Pt nanostructures were generated in case of $s(\text{Pt})_{\text{Cu}}/\text{GC}$ (well-known electrochemical signature of Pt-electrode [222,248] in acidic medium is observed), (ii) Ru was deposited in the case of $s(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$; a rapid rise in oxidation current between 1 and 1.2 V is observed that is consistent with electrochemical formation of surface RuO_2 , considered a reversible oxide at $E < 1.3$ V (vs Ag/AgCl) as noted elsewhere [279] and (iii) electrochemical and catalytic properties of Pt adlayers have not been influenced by deposited Ru adlayers as indicated by almost identical hydrogen adsorption/desorption peaks observed for the two CVs. The influence of Cu sacrificial adlayers is clearly shown in Figure 3.15c, obtained with electrodes generated from OC SLRR and direct spontaneous sequential deposition of Pt and Ru without sacrificial Cu. Even though both CVs show similarities (confirming presence of Pt and Ru), the electrochemical activity of Pt facets when Cu was not involved appears to be significantly decreased.

The foregoing surface electrochemical characteristic (of spontaneously deposited $(\text{Ru}|\text{Pt})/\text{GC}$) might be attributed to (and correlates very well with) unique morphologies of the electrodeposits obtained (as predicted in Section 3.4.3 and 3.4.4). The deposition cycles used to generate the various electrodeposits explicitly resulted in Pt and Ru existing in metallic (reduced) forms in the $n(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ and metallic Pt with oxides of Ru conceivably generated when cycles with non-involvement of redox-replacement reactions of templating Cu adlayers were undertaken.

A similar decrease in the activity of Pt is also observed in the case of codeposited noble metals (Figure 3.15d), where the formation of metallic Pt and $\text{RuO}_2(\text{s})$ was also predicted from analysis of potential transients (see Figures 3.8, 3.10d and 3.12). In addition, voltammetric features of Figure 3.15 revealed large anodic currents starting at about 1.2 V (in contrast to surface electrochemistry of monometallic Pt at such anodic potentials), strongly, confirming the presence and influence of Ru on the bimetallic electrodes. Overall, these observations support conclusions made with respect to the relevant open-circuit potential transients and thermodynamic stability diagrams.

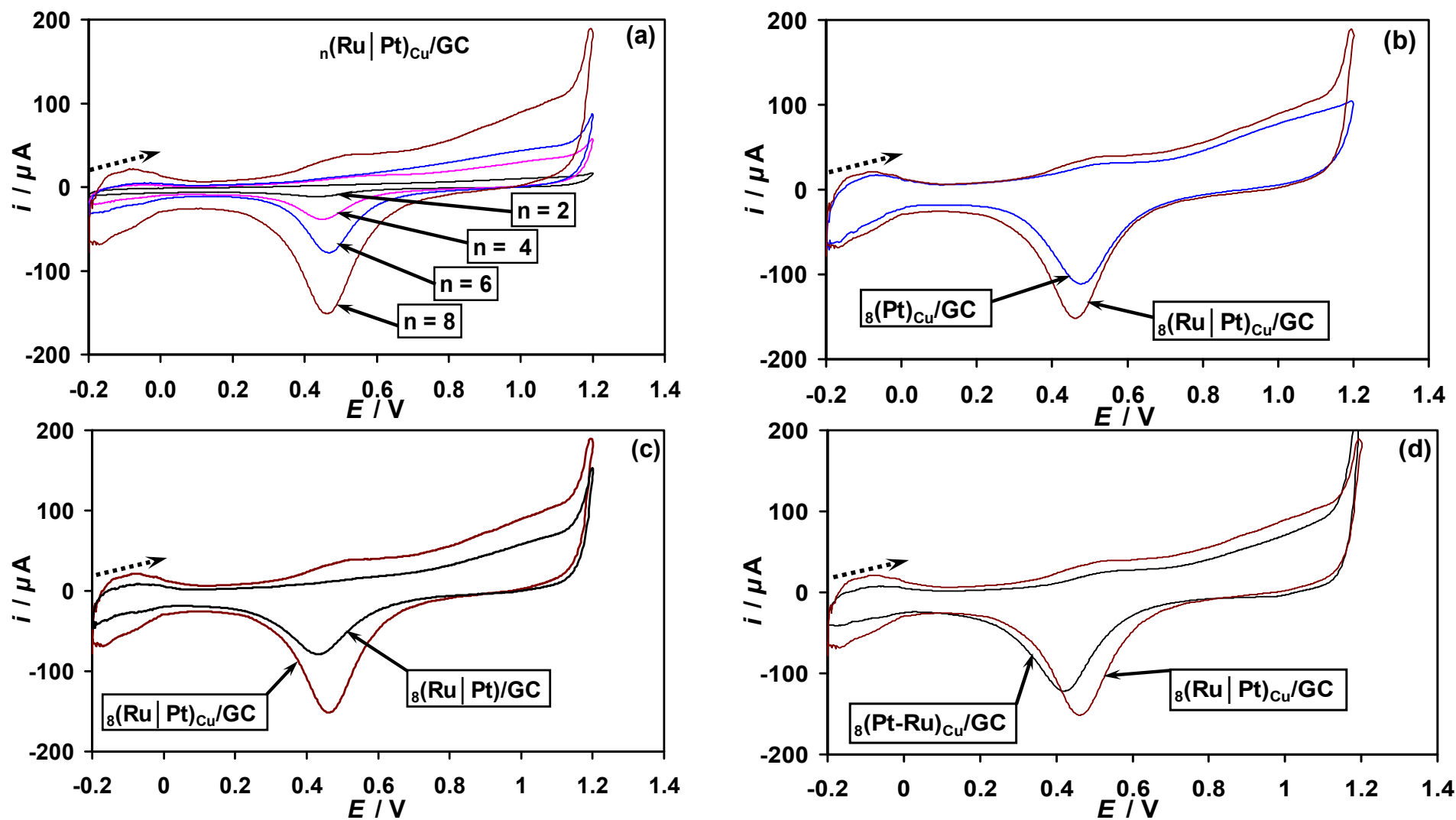


Figure 3.15: Comparison of CVs recorded in N_2 -saturated 0.1 M $HClO_4$ at 50 $mV s^{-1}$ for the as-prepared specified nanoclusters after indicated sequential deposition cycles. In all cases, the 5th scan is shown; the initial scan direction is indicated by the broken arrow.

3.4.7.2. Outer-sphere electrochemical activity

In an outer-sphere heterogeneous reaction the reactants, products, and intermediates do not strongly interact with the electrode material and electron transfer occurs by tunnelling across at least a monolayer of the solvation layer on the electrode surface, while in an inner-sphere heterogeneous reaction there is a strong chemical interaction of reactant, intermediate or product with the electrode surface [222,232]. Outer-sphere electron transfer property of the GC substrate and composite multilayered nanoclusters immobilized on it, were deduced from voltammetry of the redox couple $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ (Reaction 3.8, $E^0 = 0.358 \text{ V vs. SHE}$) using the perchloric solution of $\text{K}_4\text{Fe}(\text{CN})_6$ at pH 1. The dissociated K^+ ions are electrochemically inert in the acidic medium and potential range considered, consequently; electron-transfer (voltammetrically induced) only involves transformation of the core Fe^{2+} to Fe^{3+} and vice versa whilst the cyanide ligands maintain their complexing role (see Section 2.2.3, Chapter 2).



Figure 3.16 exhibits voltammograms resulting from the outer-sphere redox process on the bare GC substrate, $n(\text{Pt})_{\text{Cu}}/\text{GC}$, $n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Ru-Pt})_{\text{Cu}}/\text{GC}$.

Deconvolution of the voltammetric peaks revealed that the dependencies of the oxidation and reduction peak currents ($i_{\text{p,ox}}$ and $i_{\text{p,red}}$, respectively) on the potential scan rate (v) were linear (Figure 3.17); in effect, confirming that the overall electrode process was diffusion-controlled consistent with the Randles-Sevcik relationship (Equation 2.44, Chapter 2) Further representative results of electron-transfer diagnostic analysis (see Section 2.2.3, Chapter 2) emanating from CVs of Figure 3.16 are summarized in Table 3.1.

The voltammetric diagnostic results further revealed that the ratio of peak currents ($i_{\text{p,ox}}/i_{\text{p,red}}$), for all tested scan rates, was close to unity. To this effect, an ideal unit value is characteristic of a fully-reversible outer-sphere electron-transfer reaction (see Equation 2.47, Section 2.2.3.3, Chapter 2). Slightly larger departure from the theoretical value was exhibited by the unmodified glassy carbon, whereas the Pt-

based GC-supported nanostructured electrodes had values very close to 1 (Table 3.1).

Diagnostic tests for characteristic oxidation and reduction peak potentials, $E_{p,ox}$ and $E_{p,red}$, respectively, revealed values consistent, for all practical purposes, with reversible outer-sphere electron-transfer on the GC and GC-supported Pt-containing electrodes within the various time-scales of the voltammetric measurements performed (see Equations 2.45 -2.46 described in Chapter 2 where the theoretical value of 0.059 V is expected for a single-electron redox reaction). As was the case for the peak current ratio, only the bare GC electrode exhibited somewhat larger departure from ideality of $E_{p,ox}$ and $E_{p,red}$.

Figure 3.18a presents chronoamperometric results of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple, measured at diffusion-controlled potential regimes. The transformed $i-t^{1/2}$ plots for the various GC-based electrodes (Figure 3.18b) obeyed the linear Cottrell relationship of Equation 2.41 (see Chapter 2). From the slope and intercept of the linear trends (Figure 3.18b), the outer-sphere electrochemical surface area (A_{ES}) values were retrieved from the Cottrell equation, upon which the known values of diffusion coefficient and bulk concentration of the $Fe(CN)_6^{4-}$ complex were utilized (see Table 3.1). Notably, from several experiments (prior to electrodeposition and subsequent characterization tests) the evaluated outer-sphere A_{ES} of unmodified GC (disc-shaped), in relation to the geometric area (A_G), that is, the *roughness factor* (A_{ES}/A_G) [59,222], lied in the range 0.8 - 1.1. Therefore, for all practical purposes, the prepared glassy carbon electrode surfaces/substrates were electrochemically smooth. In comparison to the bare GC electrode, there was a modest increase (30 - 50%) in the outer-sphere electrochemical surface area A_{ES} of the metal-based working electrodes.

The foregoing tests strongly affirmed that the sequentially electrodeposited, multilayered Pt-containing electrodes had more facile outer-sphere electron-transfer properties than the unmodified GC; plausibly, attributable to the unique electron-tunneling dynamics across the multimetallic/carbon composite interface [222].

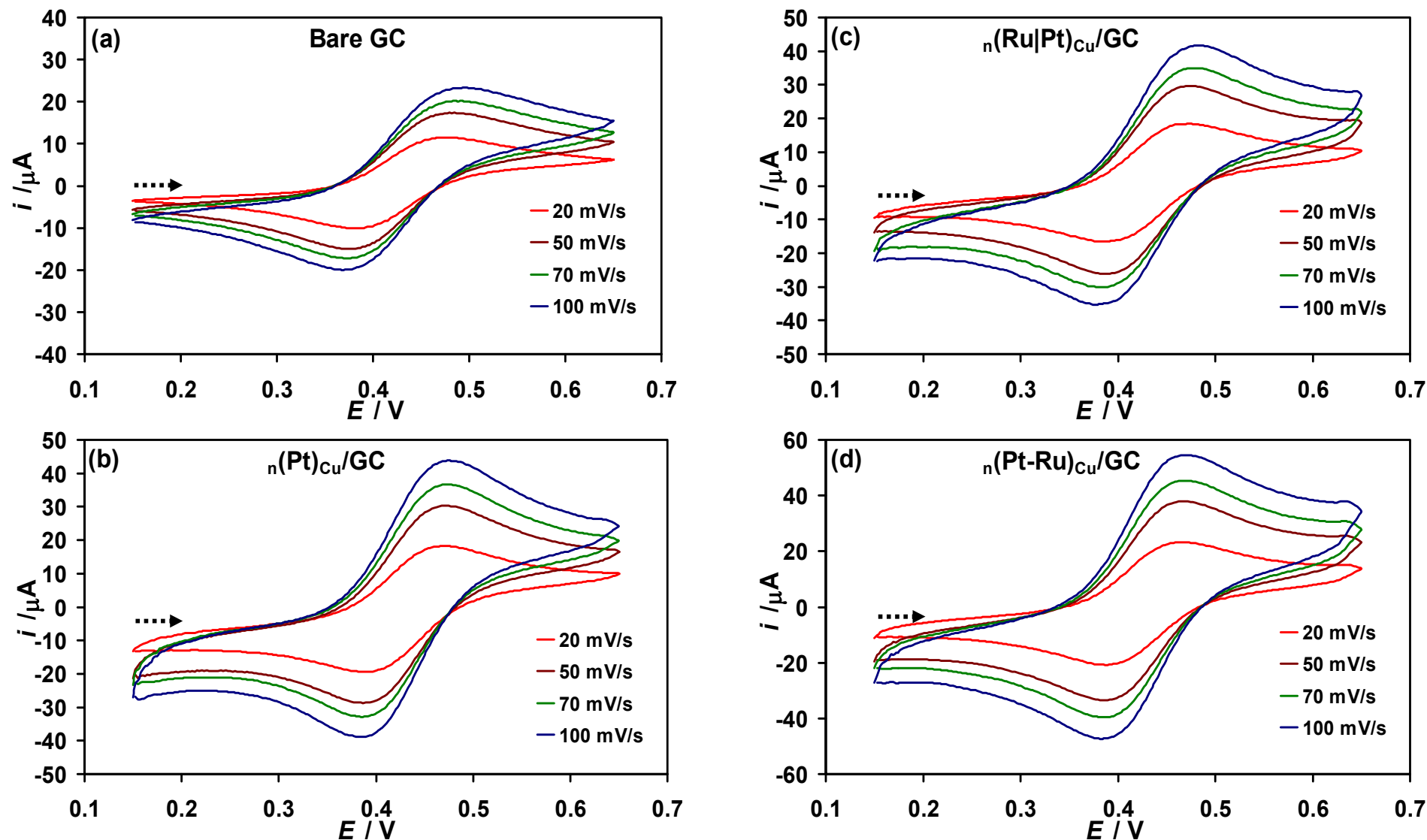


Figure 3.16: CVs of outer-sphere electron transfer on glassy carbon and various Pt-based nanocluster electrodes for variable potential scan rates. Electrolyte solution: 1 mM $K_4Fe(CN)_6$ in 0.1 M $HClO_4$. Arrows indicate initial potential and scan direction.

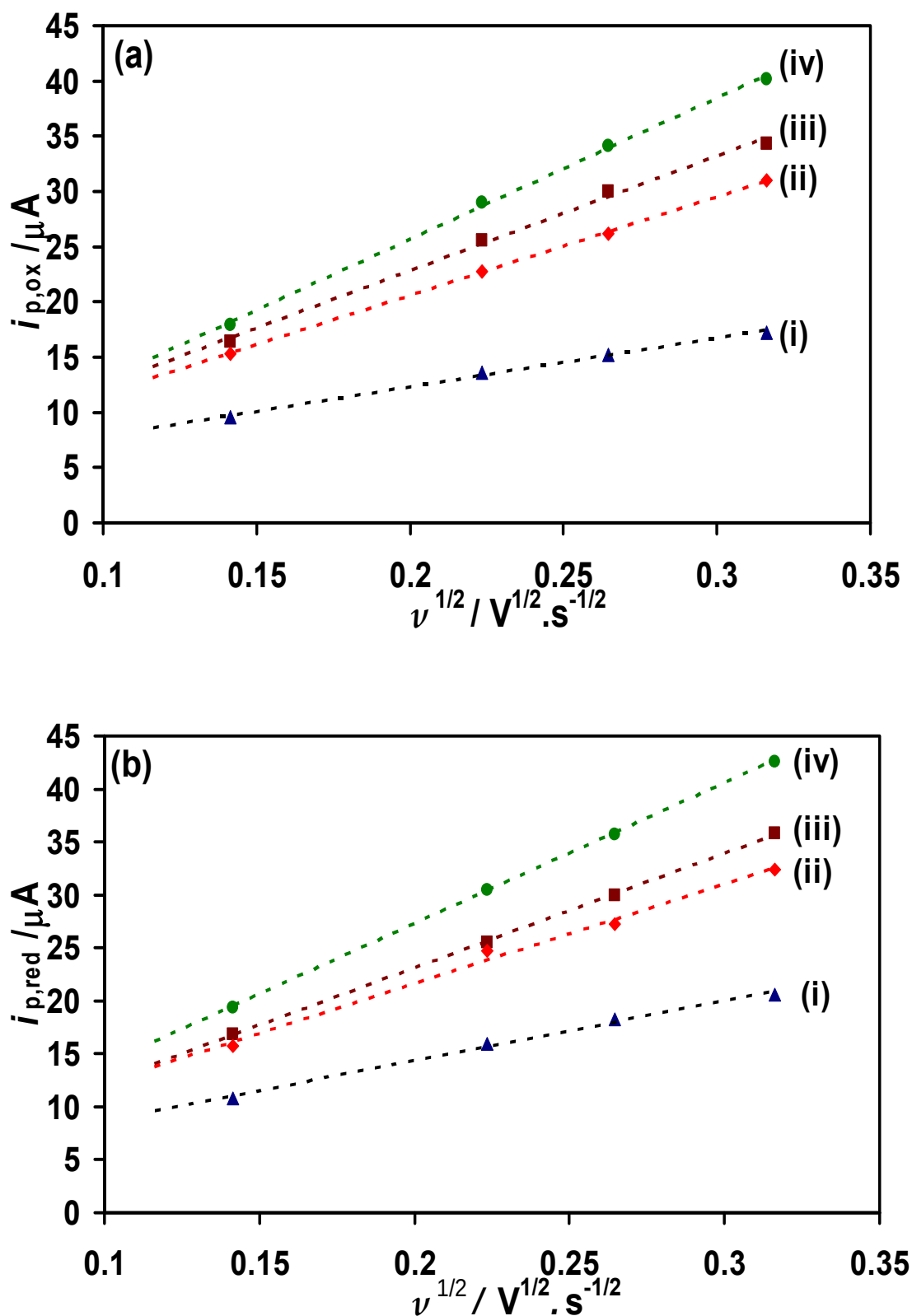


Figure 3.17: Dependence of voltammetric peak current, i_p - (a) oxidation, (b) reduction - on the potential scan rate, v . Analysis performed from curves of Figure 3.14 for the various electrodes: (i) unmodified GC, (ii) $s(Ru | Pt)_{Cu}/GC$, (iii) $(Pt)_{Cu}/GC$, and (iv) $s(Pt-Ru)_{Cu}/GC$.

Table 3.1. Representative electron-transfer and electrochemical surface activity parameters from voltammetry and chronoamperometry on glassy carbon and nanostructured platinum-based electrodes

Working electrode	Scan rate [*] (V/s)	$\frac{i_{p,ox}}{i_{p,red}}$ [*]	$\left E_{p,ox} - \frac{E_{p,ox}}{2} \right $ [*] (V)	$\left E_{p,red} - \frac{E_{p,red}}{2} \right $ [*] (V)	$\Delta E_p^{*,b}$ (V)	$A_{ES}^{**,c}$ (cm ²)	$A_{EAS}^{**,d}$ (cm ²)
Bare GC ^a	0.02	0.883	0.0596	0.0563	0.0804	0.15	-
	0.05	0.854	0.0582	0.0618	0.0879		
	0.07	0.835	0.0630	0.0587	0.0928		
	0.10	0.838	0.0617	0.0618	0.0977		
s(Pt) _{Cu} /GC	0.02	0.971	0.0514	0.0531	0.0635	0.24	0.77
	0.05	1.002	0.0530	0.0529	0.0659		
	0.07	1.002	0.0549	0.0551	0.0708		
	0.10	0.958	0.0557	0.0499	0.0684		
s(Ru Pt) _{Cu} /GC	0.02	0.974	0.0495	0.0571	0.0659	0.26	1.16
	0.05	0.922	0.0538	0.0593	0.0733		
	0.07	0.961	0.0537	0.0582	0.0757		
	0.10	0.957	0.0607	0.0560	0.0807		
s(Ru-Pt) _{Cu} /GC	0.02	0.922	0.0496	0.0527	0.0610	0.32	-
	0.05	0.950	0.0469	0.0577	0.0635		
	0.07	0.954	0.0543	0.0579	0.0708		
	0.10	0.943	0.0501	0.0530	0.0635		

^{*} Electrolyte solution: 1 mM K₄Fe(CN)₆ + 0.1 M HClO₄; ^{**} Electrolyte solution: 1 mM CuSO₄ + 0.1 M HClO₄; ^a Geometric area = 0.2 cm² (GC disc electrode)

^b Computed using Equation 2.45 (Chapter 2)

^c Determined from chronoamperometry at $E_{appl} = 0.6$ V, $t = 40$ s using the Cottrell relationship - Equation 2.41 (Chapter 2)

with diffusion coefficient, $D_{Fe(CN)_6^{4-}} = 6.30 \times 10^{-10}$ m²/s [222].

^d Determined from coulometric analysis of ASV curves employing Equation 2.61 (Chapter 2); underpotential $E_{dep} = +0.05$ V, $t = 90$ s; anodic stripping scan at 50mV/s up to 0.8V)

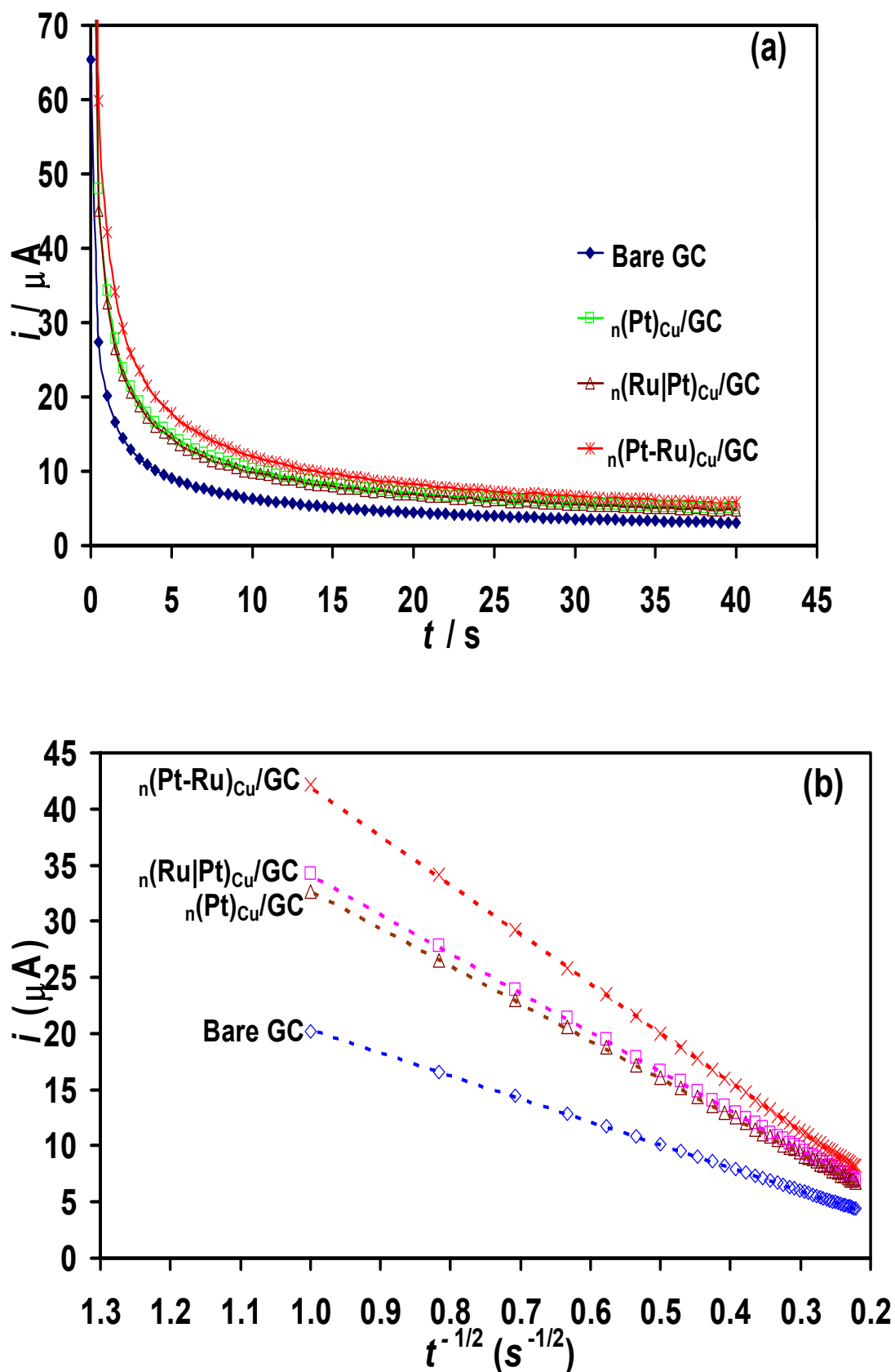


Figure 3.18: Chronoamperometric analysis of bare glassy carbon and electrochemically-generated Pt-based electrodes. (a) $i-t$ curves at $E_{app} = 0.6$ V. (b) $i - t^{-1/2}$ plots. Electrolyte solution: Nitrogen-saturated 1 mM $K_4Fe(CN)_6$ + 0.1 M $HClO_4$.

3.4.7.3. Inner-sphere electrochemical activity

Figure 3.19 displays representative CVs of bare GC substrate, together with those of Pt/GC and Ru|Pt /GC-supported electrodes (obtained using Cu SLRR templating reactions), measured in 0.1 M HClO₄ electrolyte solution in the absence and presence of Cu²⁺. The voltammetric scans on the bare GC (Figure 3.19a) show no features of Cu UPD, however, well-pronounced overpotential deposition of Cu (during cathodic scanning in the range +0.06 V to -0.2 V) was observed as previously noted (see Section 3.4.1). Furthermore, oxidative stripping of bulk Cu from the bare GC electrode effectively proceeded during the anodic scan (from -0.2 up to +0.15 V) with the characteristic peak maximum at +0.8 V (Figure 3.19a). In all the other cases (Figures 3.19b-c), involving monometallic Pt or bimetallic (Ru|Pt) supported on GC, both polycrystalline voltammetric features of inner-sphere UPD of Cu adlayers, essentially, on metallic active sites (at potential range +0.4 V to +0.045V) and OPD of Cu (at potentials < 0.045 V) during cathodic scans, respectively, were registered.

Distinguishable oxidative stripping (during anodic scanning) of both underpotentially-deposited and overpotentially-deposited Cu were observed for the metal-based electrodes in the potential ranges -0.2 V to +0.5 V (Figures 3.19b-c). The bimetallic (Ru|Pt) electrode had significantly enhanced Cu UPD features [251] than the corresponding monometallic Pt, observations that are in line with an enhanced active sites for the inner-sphere electrochemical mechanism (see Section 2.2.3.5, Chapter 2) on the bimetallic multilayered nanostructures.

Further probes of the inner-sphere electrochemical activity of the Pt-containing nanostructured electrodes were pursued with the UPD of Cu using linear sweep ASV, initiated at +0.05 V (which in principle did not involve Cu deposition on bare GC but metal centers) as shown in Figure 3.20. Such scans allowed deductions of the inner-sphere electrochemically-active surface area (A_{EAS}) (see Section 2.2.3.6, Chapter 2). The estimated A_{EAS} values (see Table 3.1) obtained were about four- to six-fold larger than the flat geometric area of the bare GC suggesting high-surface-area nanoclusters with high aspect ratios were generated.

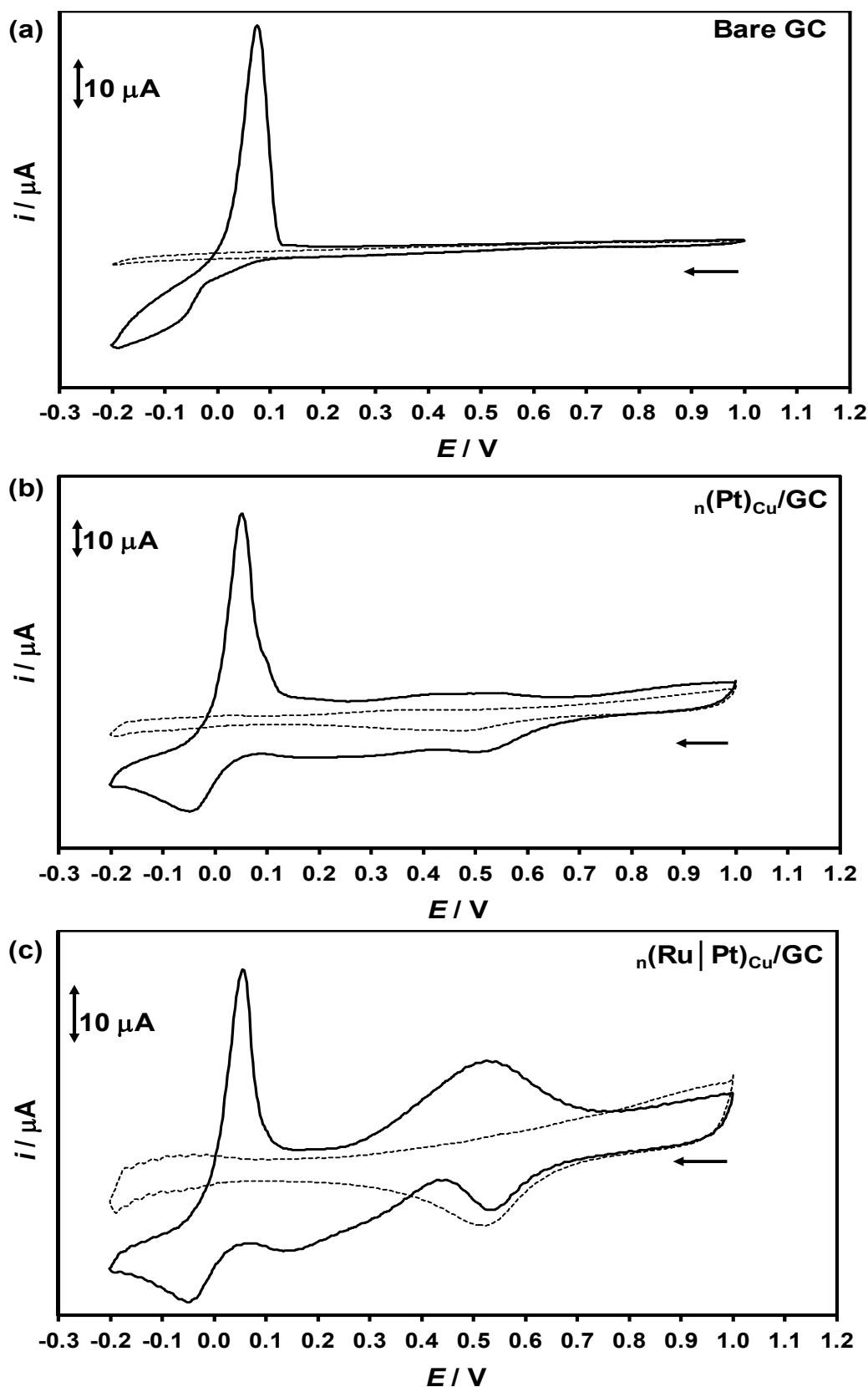


Figure 3.19: Cyclic voltammetric responses recorded with indicated glassy carbon-based working electrodes in nitrogen-saturated 0.1 M HClO_4 (dashed lines) and 1 mM $\text{CuSO}_4 + 0.1 \text{ M HClO}_4$ electrolyte solution (solid lines). Pt-containing electrodes were obtained after $n = 8$ deposition cycles via Cu SLRR sequential reactions. In all cases, scan rate was 5 mV/s; solid arrows indicate starting potential and initial scan direction.

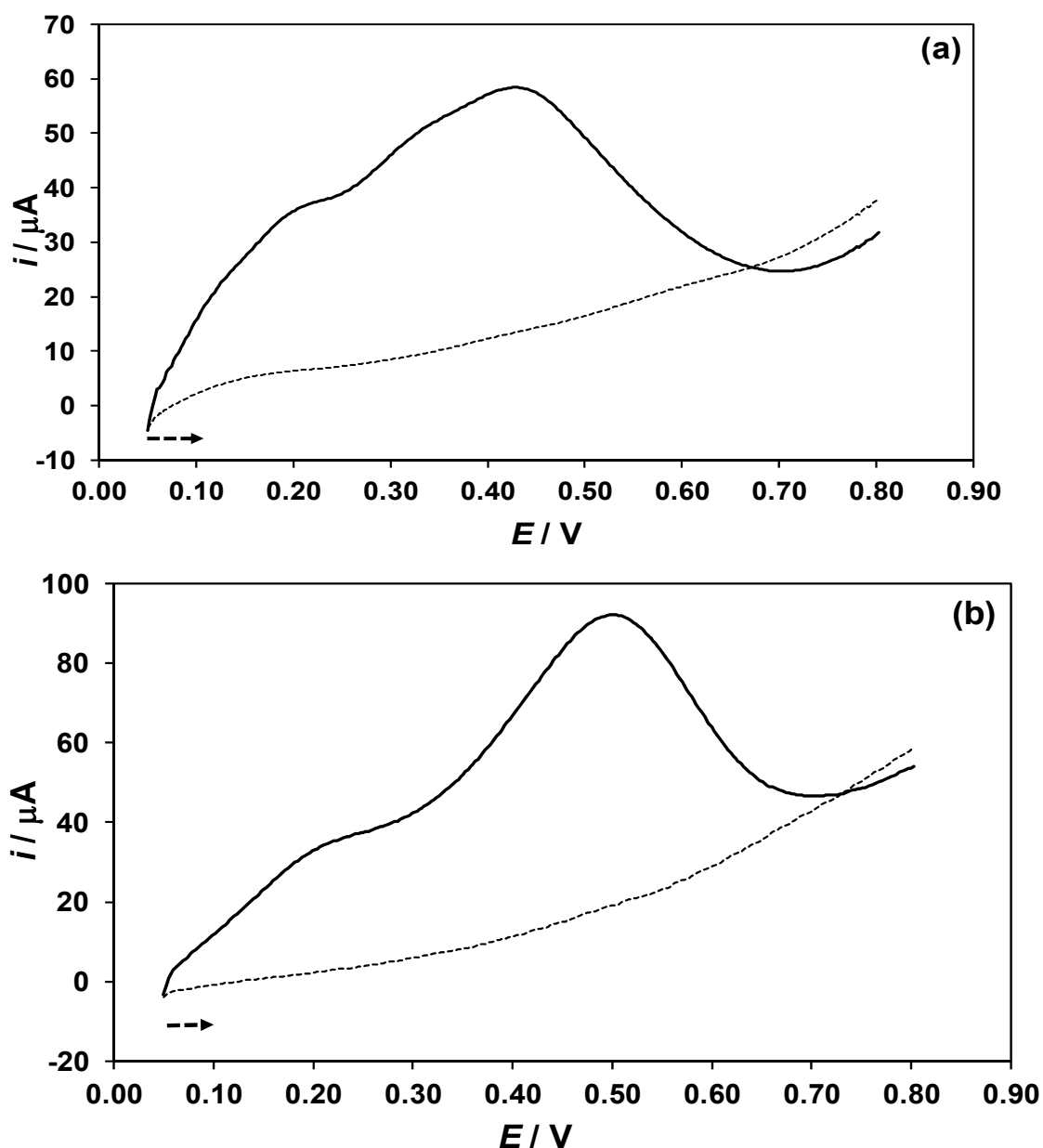


Figure 3.20: Anodic stripping voltammetry for Cu underpotentially deposited at +0.05 V for 90s on multilayered electrode systems (a) $n(\text{Pt})\text{Cu}/\text{GC}$ and (b) $n(\text{Ru}|\text{Pt})\text{Cu}/\text{GC}$. Solid lines are curves recorded in 1 mM Cu^{2+} + 0.1 M HClO_4 electrolyte solution; dashed lines are background curves separately recorded in neat nitrogen-saturated 0.1 M HClO_4 . In all cases, the stripping scan rate was 50 mV/s in the direction indicated by the broken arrow.

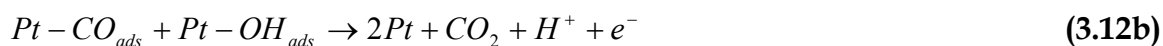
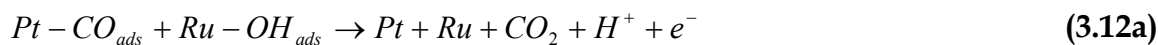
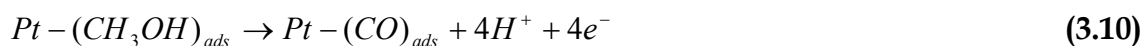
Comparatively, the bimetallic $\text{Ru}|\text{Pt}$ nanostructures were 75% electrochemically more active (considering the inner-sphere electrode surface) than the monometallic Pt. These observations were consistent with the morphological features for the apparent multilayered growth of densely packed bimetallic nanoclusters revealed earlier by AFM (see Figure 3.14b).

3.4.8. Electrocatalytic reactions on multilayered platinum-containing electrode systems

3.4.8.1. Methanol oxidation reaction

Representative CVs recorded on 0.5 M CH₃OH + 0.1 M HClO₄ solution for monometallic and bimetallic composed electrocatalysts are displayed in Figure 3.21a. The onset potentials on the CVs for the monometallic and bimetallic systems, electrochemically synthesized with the same deposition parameters, clearly shows a shift from about 0.45 V for the s(Pt)_{Cu}/GC electrode, to about 0.40 V for the s(Ru|Pt)_{Cu}/GC electrode. Qualitatively, the aforementioned onset potentials correlate with a significant decrease in the intrinsic overpotential (η , Equation 2.25, Chapter 2) and underlying exchange current density (Section 2.2.1, Chapter 2) for the electro-oxidation of methanol on the bimetallic systems as benchmarked to the electro-kinetic properties of the monometallic electrocatalyst (recall descriptions in Section 3). Also, a significant increase in current density of a methanol oxidation reaction (MOR) is observed for the bimetallic system (Ru|Pt) (trace (i), Figure 3.21a). However, the forward and reverse peak potentials appear to be very much the same for trace (i) and (ii) in Figure 3.21a, suggesting that the overall reaction mechanism of MOR is the same (with largely increased overall catalytic activity in case of Ru|Pt nanoclusters). Such observations are in line with the bifunctional mechanism of methanol oxidation involving promotional effects induced on Pt(s) by Ru(s) [213,280].

The generally accepted reaction mechanism for CH₃OH oxidation on bimetallic platinum-ruthenium catalysts may be described by Reactions 3.9 to 3.13 [51,53]. CH₃OH molecules are preferentially adsorbed on Pt(s) active sites (Reaction 3.10), followed by subsequent de-hydrogenation reactions (Reactions 3.11a-b). The interaction between CH₃OH and Ru(s) is a strongly activated process correlated with a high energy of adsorption of oxygen on Ru(s). However, water dissociates more easily on Ru(s) than on Pt(s) resulting in OH_{ads} (Reaction 3.11a). The species, CO_{ads} and OH_{ads}, adsorbed on adjacent Pt(s) and Ru(s) surface-active particles combine together forming CO₂ (Reaction 3.12) in a Langmuir-Hinshelwood (L-H) type of catalytic reaction mechanism [51].



The strikingly different morphology and composition of the sequentially codeposited Pt-Ru electrocatalyst (described in Sections 3.45 – 3.46, where RuO₂ was potentially formed during various deposition cycles) resulted in somewhat decreased activity towards the MOR (trace (ii), Figure 3.21a), when compared with monometallic Pt nanoclusters (trace (iii), Figure 3.21a) and largely decreased activity when compared with bimetallic Ru|Pt deposit (trace (i), Figure 3.21a) – the respective differences correlate well with literature reports of MOR catalysts [53]. Both forward and reverse peaks were registered in the various CVs (traces (ii) and (iii), Figure 3.21a), also suggesting that the overall mechanism of MOR was similar; however, the different ratio of their relative intensities was consistent with the enhanced bifunctional role of Ru|Pt active sites sequentially and uniquely generated in the n(Ru | Pt) electrocatalytic system.

Figure 3.21b shows representative electrochemical impedance spectroscopy (EIS) plots (in Nyquist format – see Section 2.2.4, Chapter 2) from studies involving the same set of electrodes and medium explored in CV studies of Figure 3.21a. Modelling of the EIS data was performed through Complex Non-Linear Least-Squares (CNLS) curve-fitting procedures involving *equivalent circuits* (Section 2.2.4, Chapter 2). CNLS fitting using equivalent circuits is used to extract relevant parameters of electrochemical processes with supposition that the electrode, and the processes occurring on it, behave like typical electrical elements in conventional circuits [253].

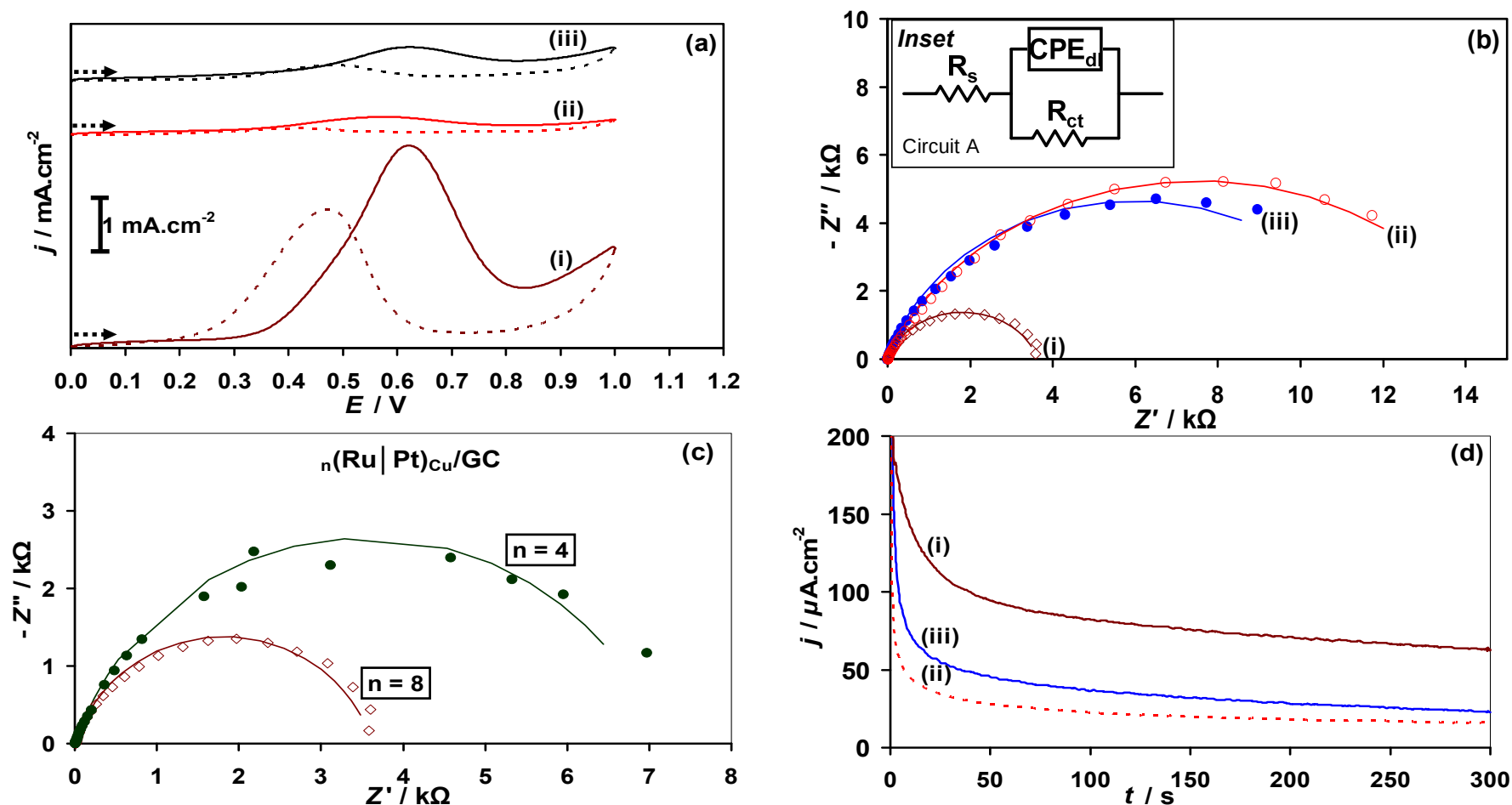


Figure 3.21: (a) CV curves recorded on 0.5 M CH_3OH + 0.1 M HClO_4 for (I) ${}_8(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$, (II) ${}_8(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$, and (III) ${}_8(\text{Pt})_{\text{Cu}}/\text{GC}$ at scan rate of 50 mV s^{-1} - forward scans (solid lines) and reverse scans (dotted lines) initiated as indicated by broken arrow; 5th scans shown. (b) EIS plots (electrolyte as in (a)) of (I) ${}_8(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$, (II) ${}_8(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$, and (III) ${}_8(\text{Pt})_{\text{Cu}}/\text{GC}$; Inset shows the equivalent circuit used in curve-fitting of the impedance responses (solid lines). (c) Comparison of EIS responses of ${}_n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$ after $n = 4$ and 8 deposition cycles; (d) CA responses of (i) ${}_8(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$, (ii) ${}_8(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$, and (iii) ${}_8(\text{Pt})_{\text{Cu}}/\text{GC}$, recorded at 0.4 V for 300 s. Current density (j) values in (a) and (d) are with respect to A_{EAS} .

Table 3.2: Representative electrochemical parameters obtained from EIS and HLSV measurements for methanol oxidation reaction (MOR) in 0.5 M CH₃OH + 0.1 M HClO₄ and oxygen reduction reaction (ORR) in 0.1 M HClO₄ of platinum-based electrodes.

Working electrode	Deposition Cycles (n)	MOR (EIS)				ORR (HLSV)	
		R_s/Ω	R_{ct}/Ω	CPE_{dl}/F	α	Computed number of electrons (z)	$k_c/\text{cm.s}^{-1}$
n(Pt) _{Cu} /GC	8	7.91	11.9×10^3	5.47×10^{-5}	0.84	3.1 ^a	
		(1.40 %)*	(3.07%)*	(2.04%)*	(0.42%)*	3.9 ^b	1.3×10^{-2}
n(Ru Pt) _{Cu} /GC	4	8.51	7.03×10^3	2.1×10^{-6}	0.82	–	–
		(5.01%)*	(5.63%)*	(9.48%)*	(1.38%)*		
n(Ru Pt) _{Cu} /GC	8	7.39	3.62×10^3	4.56×10^{-5}	0.86	1.6 ^a	
		(2.66 %)*	(3.37%)*	(4.61%)*	(0.86%)*	2.1 ^b	2.3×10^{-2}
n(Pt-Ru) _{Cu} /GC	8	8.62	15×10^3	1.9×10^{-6}	0.78	1.2 ^a	
		(2.17%)*	(4.04%)*	(3.45%)*	(0.86%)*	2.0 ^b	5.1×10^{-2}

^a) Analysis performed at $E = 0.502$ V, using electrochemical surface area;

^b) Analysis performed at $E = 0.502$ V, using geometric area;

* Relative errors of computed values.

Circuit A shown as *Inset* in Figure 3.21b (which is adopted here for its simplicity to model electrochemical impedances in accordance with literature reports of electrocatalysis in MOR [281]) was used in CNLS modelling of the EIS data. The equivalent circuit consisted of R_s (representing the solution resistance), CPE_{dl} (a constant-phase element associated with the double layer capacitance), and R_{ct} (as the overall charge-transfer resistance associated with underlying electrochemical process). Table C.1 (**Appendix C**) summarises appropriate mathematical expressions, and detailed descriptions of the total impedance (Z_T) as well as the corresponding real component (Z') and imaginary component (Z'') as functions of frequency (ω) for Circuit A. A complete and narrow semi-circular impedance spectrum was obtained for the $s(Ru|Pt)_{Cu}/GC$ electrode, whereas near-semicircular spectra were recorded for the $s(Pt)_{Cu}/GC$ and $s(Pt-Ru)_{Cu}/GC$ electrodes in the same frequency domain – the features were indicative of significantly different electrokinetic activity among the nanostructured electrodes. Qualitatively, the smallest impedance observed for the bimetallic $n(Ru|Pt)$ sets it as most electrocatalytically active.

Table 3.2 summarises the quantitative parameters extracted from the analysis of the EIS results. The consistency in the R_s values ($8.0 \Omega \pm 0.6$) reflects the fact that the electrochemical cell configurations (as well as electrolyte solution used) were the same for all systems investigated. Also, an acceptably small value of $\chi^2 = 0.1$ (a statistical parameter related to the overall fit) gave some sort of assurance when reliability of fitted parameters is of concern. The observed variation in the CPE_{dl} might be attributed to the morphology and size of the nanoparticulate deposits. It appears that for thinner layers the CPE_{dl} parameter is somewhat smaller, but at the same time the empirical constant α (extracted from EIS data and used to calculate CPE_{dl}) does not vary much (on average it was 0.82 ± 0.04). The R_{ct} parameter correlates very well with results obtained from the CV experiments; it is smallest for the $s(Ru|Pt)_{Cu}/GC$ electrode for which largest methanol oxidation currents were recorded, and largest for the electrode generated by the codeposition process. It is also interesting to note from Table 3.2 that with an increase in the number of deposition cycles n , an increase in the electrocatalytic activity for MOR is concurrently observed for the $n(Ru|Pt)_{Cu}/GC$ electrode (Figure 3.21c) – this

correlates very well with variation in electrochemical surface activity of the multilayered bimetallic nanoclusters (Figure 3.15a).

Chronoamperometry (CA) was independently employed to probe the time-based performance of the various nanostructured electrocatalysts (with respect to the MOR); aptly, the potential was stepped from open circuit to 0.4 V and held constant for 300 s (Figure 3.21d). The variation in the resulting current densities correlate very well with CV and EIS data discussed above; noticeably, the same order of electrocatalytic activity - $s(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC} > s(\text{Pt})_{\text{Cu}}/\text{GC} > s(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ - was observed.

3.4.8.2. Oxygen Reduction Reaction

The oxygen reduction reaction (ORR) is the topic of widespread investigations, both at fundamental and applied levels in fuel cells and electrochemical generation of hydrogen peroxide, among other applications [282,283]. The ORR is a complex process that involves two parallel reaction pathways in acidic medium. A direct 4-electron reaction in which O_2 is reduced to H_2O is represented by Equation 3.13



and the 2-electron pathway forming H_2O_2 shown in Equation 3.14:



The Pt, Ru|Pt and Pt-Ru nanoclusters were tested for their activity towards the ORR in the O_2 -saturated 0.1 M HClO_4 solution in separate experiments that used as-prepared nanoclusters (the synthetic procedures reported in this work proved to be reproducible). Figure 3.22a-c shows typical hydrodynamic linear sweep voltammetry (HLSV) curves (see Section 2.2.3.4, Chapter 2) recorded for the $s(\text{Pt})_{\text{Cu}}/\text{GC}$ electrode, $s(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ and $s(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ electrodes accordingly. Examples of superimposed HLSV curves recorded on all the electrodes at the flow rate of 10 mL/min are shown in Figure 3.22d.

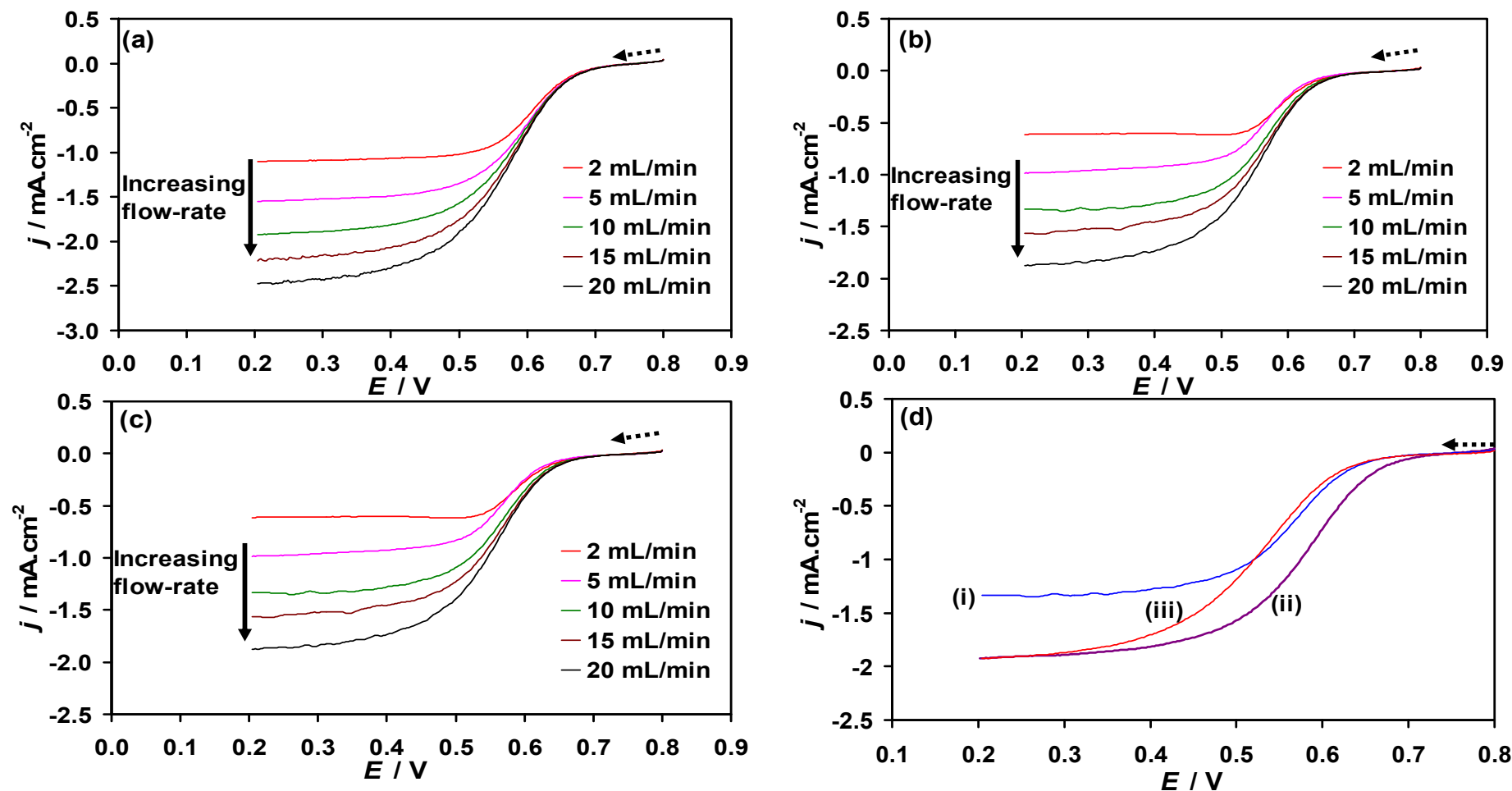


Figure 3.22: HLSV curves recorded in O_2 -saturated 0.1 M HClO_4 solution using (a) $s(\text{Pt})_{\text{Cu}}/\text{GC}$, (b) $s(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$, (c) $s(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ nanostructured electrodes, respectively, at scan rate of 50 mVs^{-1} and various solution flow-rates. (d) Comparison of the ORR HLSV curves for (i) $s(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$, (ii) $s(\text{Pt})_{\text{Cu}}/\text{GC}$, and (iii) $s(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ at flow-rate of $5 \text{ mL}/\text{min}$.

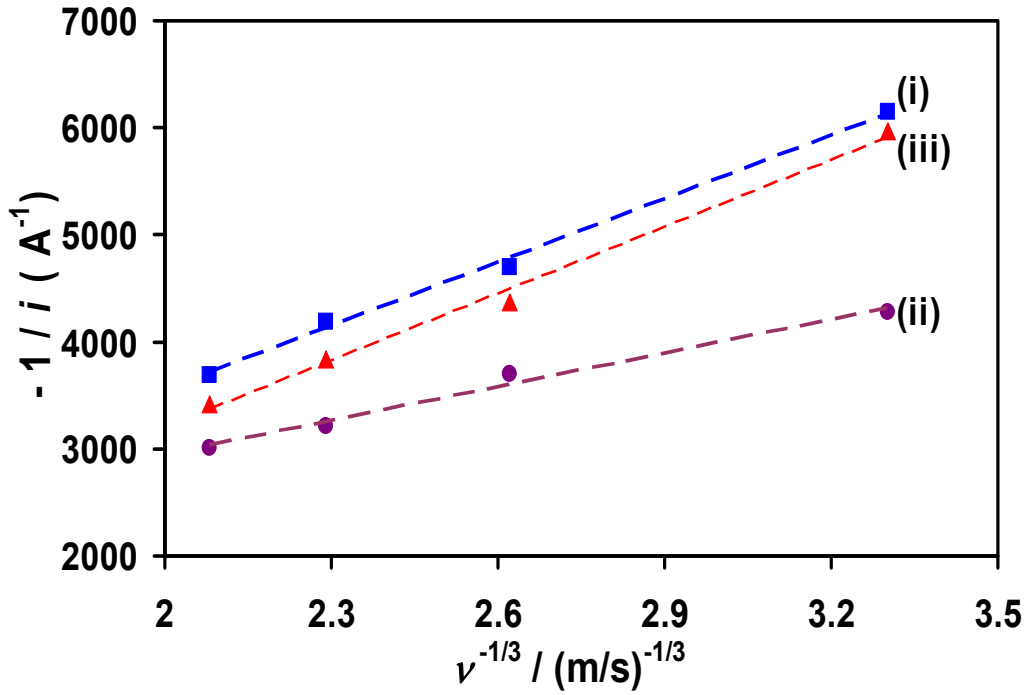


Figure 3.23: Plots of $1/i$ versus $1/v^{1/3}$ generated from the HLSV curves on (i) $s(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$, (ii) $s(\text{Pt})_{\text{Cu}}/\text{GC}$, and (iii) $s(\text{Pt-Ru})_{\text{Cu}}/\text{GC}$ nanostructured electrocatalysts.

Analysis of HLSV curves, to extract kinetic parameters related to ORR, involved the following expressions [270]:

$$-\frac{1}{i} = \frac{1}{i_k} + \frac{1}{zAFZ_{\text{O}_2}C_{\text{O}_2}v^{1/3}} \quad (3.15)$$

$$Z_{\text{O}_2} = 0.925D_{\text{O}_2}^{2/3}(hx_1)^{-1/3} \quad (3.16)$$

$$i_k = zAFk_cC_{\text{O}_2} \quad (3.17)$$

The equations are applicable to the mixed kinetic and diffusion controlled potential regions of the HLSV curves. Kinetic currents were computed using Equations 3.15–3.17, where i is the measured current at the applied potential E , v is the linear velocity (m s^{-1}) related to the volume flow rate by $v = v_f/hd$, v_f is the volume flow rate ($\text{m}^3 \text{s}^{-1}$), h is the half-height of the flow-channel ($0.5 \times 10^{-3} \text{ m}$), d is the width of the flow channel ($6 \times 10^{-3} \text{ m}$), x_1 is the diameter of the disc electrode in the direction along the flow, D_{O_2} is the diffusion coefficient of O_2 ($1.93 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$) [284], C_{O_2} is the saturation concentration of O_2 ($1.22 \times 10^{-6} \text{ mol.cm}^{-3}$) [284], z is the number of

electrons exchanged in the reduction reaction, k_c is the rate constant of the overall reaction, and A is the surface area of the electrode. The number of electrons was evaluated from Equation 3.15 by plotting $1/i$ vs. $1/\nu^{1/3}$ (Figure 3.23) and the data obtained using electrochemical as well as geometrical parameters are presented in Table 3.2. From the slopes seen in Figure 3.23, it is evident that similar ORR electrochemical processes take place in the bimetallic electrocatalysts (involving Pt and Ru) and distinct reaction proceeds on the monometallic Pt electrocatalyst.

The number of electrons, very close to the theoretically predicted value of 2, was obtained when geometrical rather than outer-sphere electrochemical surface area was used and the underlying hydrodynamic reason (mass transport effects) was explained in details by Van Brussel *et al* [285]. The 2-electron oxygen reduction (Reaction 3.10) observed for the two Ru-containing electrodes correlates well with the literature reports that suggest that surface oxides of ruthenium lower the activity of H_2O_2 decomposition to H_2O [286]. It is seen in Table 3.2 that the apparent electrokinetic reaction rate constant k_c obtained for the $s(Pt-Ru)_{Cu}/GC$ electrode is four times larger when compared with the $s(Ru | Pt)_{Cu}/GC$ electrode. Consequently, one might conclude that the $s(Pt-Ru)_{Cu}/GC$ electrodes could be more suitable for applications involving the ORR when predominant formation of peroxide is of main interest. The reaction path, in case of monometallic Pt-nanoclusters, follows the 4-electron direct reduction of O_2 to H_2O as described by Reaction 3.13 – the slope obtained for the $s(Pt)_{Cu}/GC$ electrode seen in Figure 3.23 is half of that retrieved for the other two electrodes.

3.5. Summary

In this chapter, it has been demonstrated that the use of successive OC SLRR reactions involving sacrificial Cu, when implemented to deposit multilayered $Ru | Pt$ nanoclusters, from separate Pt and Ru precursor solutions, leads to preferential formation of metallic states of both Pt and Ru after a few deposition cycles. The analysis of open-circuit potentials recorded during the various deposition experiments in combination with theoretical models (here thermodynamic data were used to model the $Pt-Cu-H_2O$, $Ru-Cu-H_2O$, and $Pt-Ru-H_2O$ systems) proved to be an excellent predictive tool of deposits generated during SLRR reactions

involving Cu. The use of a surface reducing agent, in this case Cu adlayers, has been shown to be a necessary condition for the sequential deposition methodology of metallic adlayers of Ru(s) on Pt(s). However, the direct spontaneous deposition of Pt followed by Ru, without SLRR steps, or codeposition of Pt and Ru involving SLRR, generates metallic Pt nanoclusters on which the spontaneous formation of ruthenium oxides most likely takes place. The generated nanostructures were characterized using CV, HLSV, CA, EIS, SEM, AFM, and EDX. The bimetallic nanoclusters electrode $n(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ is characterized by more positive onset potentials, lower charge-transfer resistances and higher oxidation currents when compared with monometallic Pt nanostructures and other bimetallic systems generated through codeposition and direct spontaneous deposition. In particular, codeposition of Pt-Ru system (via simultaneous SLRR steps) led to least active nanostructures, suggesting that formation of Ru oxides decreases the activity toward methanol oxidation. The mechanism of ORR was also investigated on the various nanocluster electrodes. The 4-electron pathway was favored by the monometallic Pt nanoclusters but the Ru-containing nanoclusters favored the 2-electron ORR pathway.

CHAPTER IV

Electrochemical Deposition and Electrocatalytic Properties of Multilayered Nanoclusters of Platinum and Gold

Content of this chapter has been published in journal articles:

- (I) T. S. Mkwizu, M. K. Mathe, and I. Cukrowski, *ECS Transactions*, Vol. 19, Issue 24, (2009) 97–113;
- (III) T. S. Mkwizu, M. K. Mathe, and I. Cukrowski, *Journal of the Electrochemical Society*, Vol. 160, Issue 9, (2013) H529-H546.

4.1. Introduction

In this chapter, an in-depth analysis is provided on the sequential electrochemical deposition strategies to generate the multilayered Pt and Au nanoclusters where focus has been placed on understanding the interplay of thermodynamics during growth of the nanoclusters, their resultant surface as well as bulk compositional properties, and their electrocatalytic activity with respect to CO adsorption-oxidation process and formic acid electro-oxidation.

A number of fundamental aspects were pursued including:

- What happens when repeated SLRR reactions involving Cu are implemented (in a sequential fashion) to grow deposits of two different highly noble metals, namely, Pt and Au?
- How different are deposits obtained by sequential spontaneous deposition (without using any SLRR steps)?
- What electrocatalytic properties do the various deposits impart on reactions that are structure-sensitive?
- Does the sequence of deposition, in case of multilayered nanocluster formation, have any effect on resultant electrocatalytic properties?

Accordingly, primary thermodynamic factors were investigated with respect to the effect of potential-pH on speciation under electrodeposition condition; moreover, morphological and surface features of monometallic Pt, monometallic Au, and their bimetallic counterparts were characterized.

Essentially, the chapter has focused on understanding the interplay of thermodynamics during growth of the nanoclusters, using Pt and Au deposits on glassy carbon as model system, their resultant surface as well as bulk compositional properties, and their electrocatalytic activity with respect to CO adsorption-oxidation process and formic acid electro-oxidation as probed using electrochemical methods on the various nanostructures. Moreover, the chapter provides systematic

comparisons between the monometallic and bimetallic noble metal nanostructured electrode systems.

4.2. Experimental Details

4.2.1. Materials

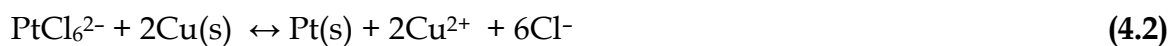
All solutions were prepared with high-purity demonized water obtained from a Milli-Q water purifier system (Millipore Inc. USA) at resistivity of 18 MΩ·cm. All electrochemical experiments were performed in air-conditioned laboratory environment at 25 (± 1) ° C. 1 × 10⁻³ mol/L precursor electrolyte solutions of Pt⁴⁺, Au³⁺, and Cu²⁺ – dissolved in 0.1 mol/L HClO₄ used as the blank electrolyte (BE) at pH 1 ± 0.05 – were prepared from H₂PtCl₆, HAuCl₄, and CuSO₄ salts obtained from SA Precious Metals (Pty) and Merck. All chemicals were of analytical grade with at least 99% purity.

4.2.2. Electrodeposition

Substrate-immobilized monometallic or bimetallic nanostructures were synthesized in a three-electrode flow-cell connected to a custom-developed automated instrumental setup described in details in Chapter 3; which consisted of; (i) a potentiostat/galvanostat (model PGSTAT30, Metrohm Autolab, Netherlands), (ii) a stainless steel counter electrode, (iii) the GC substrate under study (grade V-25, SPI Supplies, USA) as working electrode, and (iv) Ag/AgCl/3M KCl reference electrode (model 6.0727.000, Metrohm Autolab) – unless otherwise stated, potentials are reported versus (vs) this reference electrode. Nature of the noble-metal precursors was confirmed using UV-visible spectroscopy of the appropriate aqueous solutions using an Avaspec – 2048 (Avantes) spectrometer where bands due to typical ligand-to-metal charge transfer transitions in the PtCl₆⁻ and AuCl₄⁻ aquo complexes were used for confirmation of stability of the complexes in the HClO₄ medium (Figure C.3, **Appendix C**) according to appropriate literature [287,288].

Experiments were performed at pH 1 ± 0.05 using 0.1 mol/L HClO₄ as BE, in line with generally known aqueous chemistry of ClO₄⁻ anions as non-complexing anions in the presence of noble metal cations and their non-adsorbing nature on noble metal surfaces [30]. Pre-treatment procedures of the GC substrate were as per our

previous studies described in Chapter 3. We have utilized sequential deposition routes involving SLRR steps and voltammetric dealloying summarized in Reactions 4.1 – 4.3 and Figure 4.1.



Steps in synthesis of bimetallic nanoclusters $n(\text{M}|\text{N})_{\text{Cu}}/\text{GC}$ (M, N = Pt or Au) involved six-stage deposition cycles, whereas the monometallic systems $n(\text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Au})_{\text{Cu}}/\text{GC}$ as well as the sequentially-codeposited bimetallic system $n(\text{Au-Pt})_{\text{Cu}}/\text{GC}$ were generated utilizing three-stage cycles. Rinsing steps involved the BE at a fixed potential $E = +0.2$ V, followed by injection of the Cu^{2+} solution at the same potential. Given that the standard reduction potential of the $\text{Cu}^{2+}/\text{Cu(s)}$ redox couple is 0.340 V (vs SHE) – for a 1 mmol/L Cu^{2+} solution the Nernstian equilibrium potential is approximately 0.046 V (vs Ag/AgCl/3M KCl) – sacrificial Cu(s) deposition was carried out at $E_{\text{dep}} = -0.05$ V / $+0.05$ V, followed by rinsing with BE at E_{dep} . Injection of the PtCl_6^{2-} or AuCl_4^- precursor solutions was carried out at Open-Circuit (OC), followed by the OC SLRR at quiescent conditions according to Reaction 4.2 or 4.3, respectively. Inherent in the deposition cycles was the rinsing and dealloying step at $E_{\text{dep}} = +0.2$ V during Stages 1 and 4 after Cycle 2 (see Figure 4.1) – steps during which voltammetric dealloying of any remaining Cu(s) to Cu^{2+} was intended to proceed according to Reaction 4.1. It should be understood that, in the case of the use of Cu UPD (which does not happen on pristine GC for the experimental conditions employed in this work), spontaneously formed Pt or Au during the first cycle on fresh GC determined subsequent Cu UPD cycles. Cu(s) electrodeposition stages were the same as for per studies described in Chapter 3. Electrochemical flow-cells described in Chapter 3 were utilized and dedicated Labview virtual instruments, *AutolabPumpsMainControl.vi*, *Autolab-SeqDep-3pumps-Autorefill.vi*, and *Autolab-SeqDep-4pumps-Autorefill.vi* and associated instrumentation described in detail in Chapter 3 and **Appendix A** were used for the automated electrodeposition experiments.

All solution rinsing and injection stages were performed for 20 s at 5 mL/min and all OC SLRR steps were allowed for a maximum time of 180 s. Deposition steps were repeated up to $n = 8$ cycles with respect to: (a) stepwise increase of the size of nanostructures, and (b) stepwise growth of nanostructures in relation to tuning of their electrocatalytic properties. Current-potential-time (i - E - t) data were sampled in situ at 0.2 s intervals.

4.2.3. Thermodynamic Modelling

Equilibrium models of potential-pH (E -pH) – Pourbaix-type multicomponent models – for Pt-Cu-H₂O, Pt-Au-H₂O, and Pt-Cu-Cl-H₂O, and Au-Cu-Cl-H₂O systems were generated using the thermochemical software package FactSage™ version 5.5 or 6.0 [271] at 298.15 K and molality of all aqueous forms of Pt, Cu, Au incorporated in the models of 1×10^{-4} mol/kg and 1×10^{-3} mol/kg, and molality of Cl⁻ between 1×10^{-6} mol/kg and 1×10^{-1} mol/kg. Further details regarding thermodynamic modelling are documented in **Appendix B**.

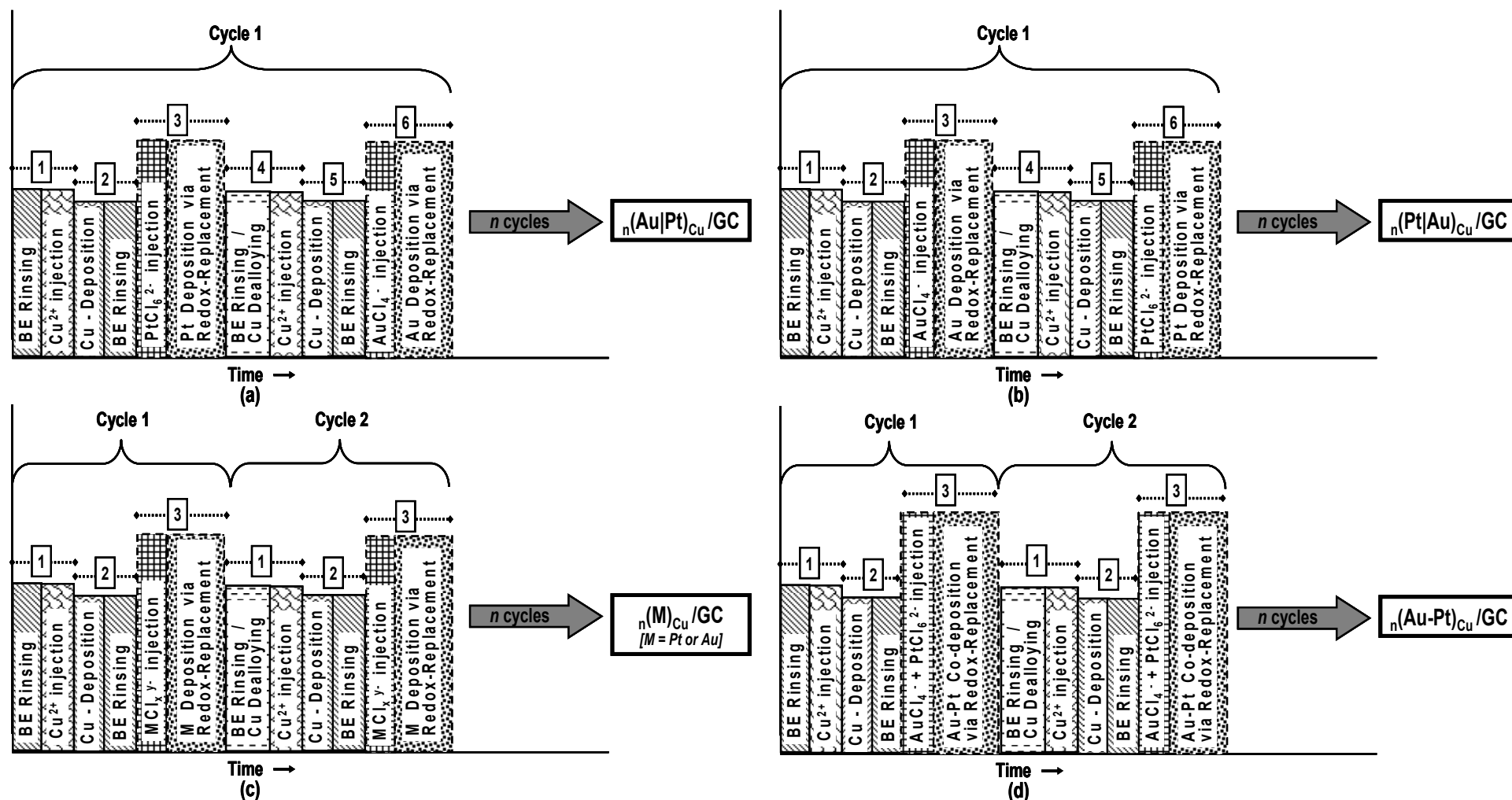


Figure 4.1: Schemes showing electrochemical deposition strategies explored to generate immobilized (a) – (b) bimetallic nanoclusters involving Au and Pt from separate precursors; (c) monometallic Pt or Au nanoclusters, and (d) codeposited bimetallic nanoclusters involving Au and Pt from mixed precursors.

4.2.3 Electrochemical Characterization

Post-synthesis electrochemical measurements involving Anodic Stripping Voltammetry (ASV), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were performed with the same potentiostat/galvanostat of the deposition instrumental setup described above, but utilizing commercial software packages GPES 4.9, FRA 4.9 and NOVA 1.6 (Metrohm Autolab, The Netherlands). Modelling of EIS, using equivalent circuits and complex nonlinear least-squares (CNLS) procedures, based on Boukamp's algorithms [255], was performed with built-in data analysis modules of FRA 4.9 and NOVA 1.6.

Electrochemically-active surface area (A_{EAS}) of a nanocluster electrode was estimated from ASV involving UPD Cu deposited at 0.05 V for 90s, using 1 mmol/L CuSO_4 (in 0.1 mol/L HClO_4) solution, anodically stripped at scan rate of 50 mV/s; A_{EAS} values were extracted using a conversion factor of $420 \mu\text{C cm}^{-2}$ by integration of ASV peaks, after appropriate baseline subtraction, following literature methods [289,290].

The electrochemical behaviour of the nanocluster electrodes was characterized by means of CV in N_2 -saturated 0.1 mol/L HClO_4 solution recorded at 50 mV/s from -0.2 V to +1.4 V, for 5 to 10 cycles. HCOOH electro-oxidation studies were carried out in quiescent N_2 -saturated 0.5 mol/L solutions (all prepared in 0.1 mol/L HClO_4) solutions injected to the electrochemical flow-cell containing the freshly prepared immobilized nanoclusters.

CV of HCOOH was ran at 50 mV/s for 5 cycles in the potential range 0 V - +1.0 V, followed by EIS measurements in freshly-injected solutions, at appropriate bias potentials between 0 and +0.4 V, using sine-wave signals of 10 mV amplitude in the frequency range 0.5 Hz - 100 kHz. CO adsorption-oxidation studies were performed using CO-saturated 0.1 mol/L HClO_4 solution, with saturation times of at least 1800 s, after which ASV was employed to strip the adsorbed CO at scan rates between 10 mV/s and 50 mV/s from 0 V to + 1.2 V in N_2 -saturated 0.1 mol/L HClO_4 solution; a single peristaltic pump (Model MINIPULS™ 3, GILSON, USA)

was used to direct the gas-saturated solution to the flow-cell as shown in the experimental setup displayed in Figure 4.2.

In between all electrochemical measurements the flow-cell was rinsed at OC with N_2 -saturated 0.1 mol/L $HClO_4$.

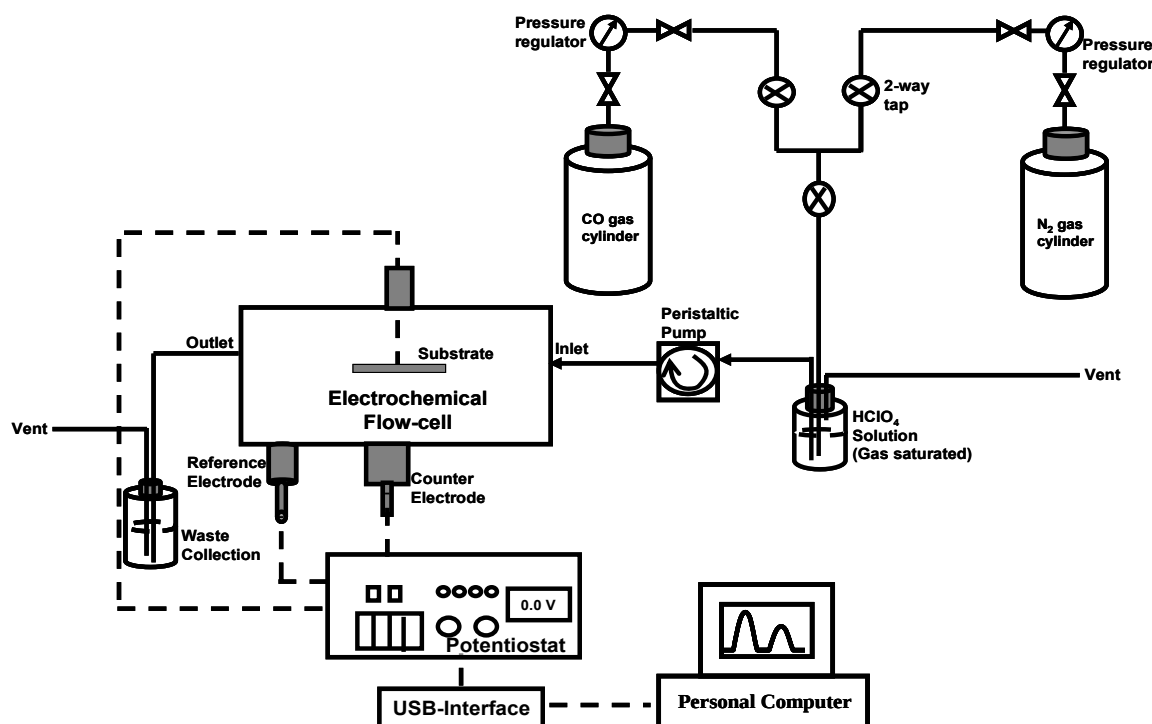


Figure 4.2: Experimental setup for carbon monoxide adsorption-oxidation studies using an electrochemical flow-cell.

4.2.4 Surface and Bulk Characterization

Freshly-prepared samples were subjected to various *ex-situ* characterisations. A JEOL model JSM-5800LV scanning electron microscope (operated at 10 kV for SEM imaging and 20 kV for EDX measurements) was employed to study the morphology and for elemental ‘fingerprinting’ of the synthesized nanoclusters. Atomic Force Microscopy (AFM) using a DI Nanoscope IVa (Digital Instruments, USA) in ambient tapping mode using a model RTESPW tip (Veeco Manufacturing, USA) provided additional in-depth morphological and topographical characteristics of the GC substrate and subsequent deposits.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed with a PHI spectrometer (model 5400), equipped with a non-monochromatic magnesium K_α X-ray source (1253.6 eV, operated at 15 kV and 300 W in ultra-high vacuum chamber

with base pressure $< 1 \times 10^{-8}$ Torr) and a concentric hemispherical sector analyzer. The spectra were recorded at scan rate of 0.16 eV s^{-1} (step-size of 0.05 eV) and take-off angle of 45° . The spectrometer was calibrated using Au and Cu standards' peaks of Au $4f_{1/2}$ (84.0 eV), Cu $2p_{1/2}$ (953 eV) and Cu $2p_{3/2}$ (933 eV). Corrections of binding energy scale for charging effects, for spectra recorded on the GC-supported samples, were done by using the C1s (C-H peak) at 284.8 eV as an internal standard. Spectra were recorded on as-received samples and after sputter-cleaning using argon ion beam of 2 keV for durations of between 180 s and 660 s . The publicly available software XPSPEAK version 4.1 [291] was employed for deconvolution of relevant multicomponent spectral regions into appropriate components using mixed Gaussian-Lorentzian functions and Shirley-type baseline subtraction.

Appropriate freshly-prepared electrodeposited samples were also subjected to analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [292,293] in order to determine their Total Metal Content; the electrodeposits were carefully dissolved in ultra-pure aqua-regia ($3 : 1 \text{ HCl} / \text{HNO}_3$ solutions) and suitably diluted (with $1\% \text{ HCl}$ and $3\% \text{ HNO}_3$ aqueous solutions) prior to final ICP-MS analysis. To this end, the spectrometer Model ELAN 6000 (Perkin Elmer) was employed for the ICP-MS trace analyses of Pt, Au, and Cu (Analytical service provider: Mintek, Randburg, South Africa).

4.3. Results and Discussion

4.3.1. Current-Potential-Time Variations and Thermodynamic Modelling

Rapid variations were observed at Stages 3 and 6 in current-potential-time (i - E - t) transients recorded during deposition of the nanocluster systems investigated in this work as presented in Figure 4.3a-c (and Figure C.4 in **Appendix C**). Such i - E - t signals revealed that as soon as open-circuit conditions were set rather steady open-circuit potential (OCP) values were observed within 40 s , strongly signifying sufficient time for occurrence of SLRR reactions and establishment of interfacial equilibrium conditions. Figure 4.3d-e presents variations in average OCP during SLRR reactions (averaged over the last 90 s at Stages 3 and 6 as shown in Figure 4.3a-c. After the second deposition cycle, the OCP during SLRR involving Pt (SLRR_{Pt}) reached a steady value of about $+0.7 \text{ V}$ (vs Ag/AgCl), approximately $+0.9$

V (vs SHE), whereas the OCP during SLRR involving Au (SLRR_{Au}) was steady at a value of about +1.0 V (vs Ag/AgCl), approximately +1.2V (vs SHE).

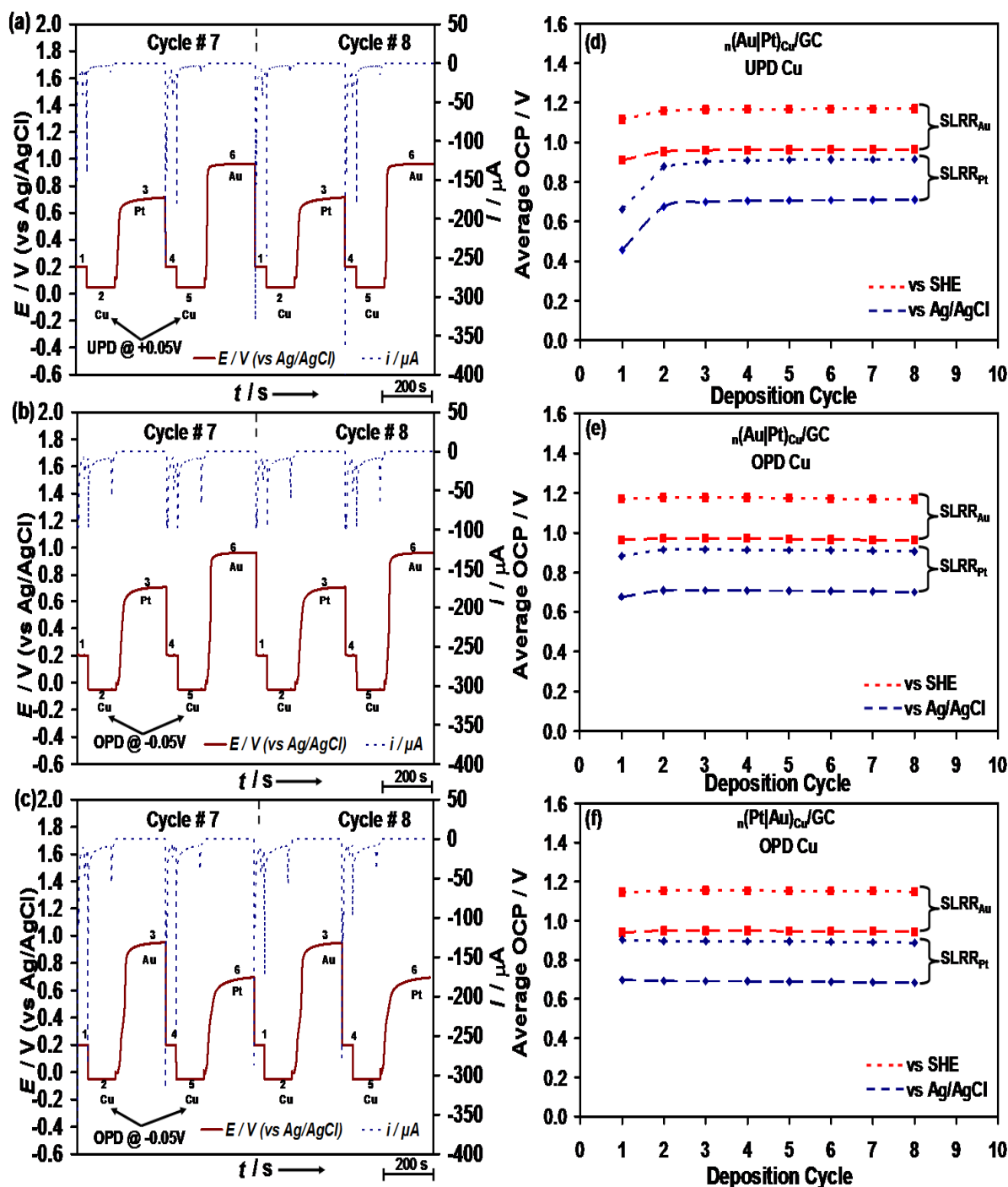


Figure 4.3: Current-potential-time (i - E - t) transients recorded during deposition of the bimetallic nanoclusters: (a) $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$, utilizing Cu UPD steps, (b) $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ involving Cu OPD steps, and (c) $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$, where Cu OPD steps were employed. (d) - (f) Variations in average open-circuit potential (OCP) during the final 90 s of SLRR stages.

The nature of E_{dep} invoked to electrodeposit sacrificial Cu (either UPD or OPD) had an effect only during the first deposition cycle, attributable to different mechanisms of nucleation and growth of metal clusters on the pristine substrate (see Figure 4.3d-e). Use of OPD Cu resulted in very steady OCP variations during SLRR stages throughout the deposition sequences as shown in Figure 4.3e-f. The steady nature of the OCP variations observed during SLRR stages strongly indicated some equilibrium situation was established involving solid Pt or Au nanoparticulate surfaces and their corresponding precursor ions and the liberated Cu^{2+} ions as implied by Reactions 4.2 - 4.3. Indeed, fast reaction kinetics have been systematically established for SLRR reaction involving Cu UPD and Pt on Au(111) substrate and the plateau of OCP transients during SLRR step is reflective of equilibrium attainment [193].

Further insights on expected speciation upon completion of SLRR stages were gained from comparison of OCP to thermochemical E -pH models (Figure 4.4), computed close to experimental concentrations of aqueous precursors used. Experimentally our main endeavour was utilization of separate redox reactions between Cu and the noble metals Pt and Au, hence E -pH models were independently optimized for Au-Cu- H_2O or Pt-Cu- H_2O (Figure 4.4a-b).

More appropriately, given that chloride-containing complexed ions were employed as the noble metal precursors, further models were generated for Au-Cu-Cl- H_2O and Pt-Cu-Cl- H_2O systems (Figure 4.4c-d). In all scenarios, thermodynamic modelling strongly suggested that hydrolyzed species and oxides of Cu, namely $\text{Cu}(\text{OH})_2(\text{s})$ and $\text{Cu}_2\text{O}(\text{s})$, were expected to exist above pH 4 and at potentials greater than about +0.2 V (vs SHE); giving strong support for the use of acidic electrolytes as precursors for SLRR reactions involving Cu. Moreover, the stability of AuCl_4^- and PtCl_6^{2-} is clearly revealed in the models inclusive of chloride-containing species (Figure 4.4c-d): when pH is less than 3 and E greater than 1.2 V (vs SHE), no possibility of the hydrolysed species $\text{Au}(\text{OH})_3(\text{s})$ is expected, whereas PtCl_6^{2-} is found to be very stable when pH less than 7 and E greater than 1.1 V (vs SHE). Pt(s) is found to be thermodynamically stable at E less than + 0.9 V (vs SHE) when pH is less than 7.

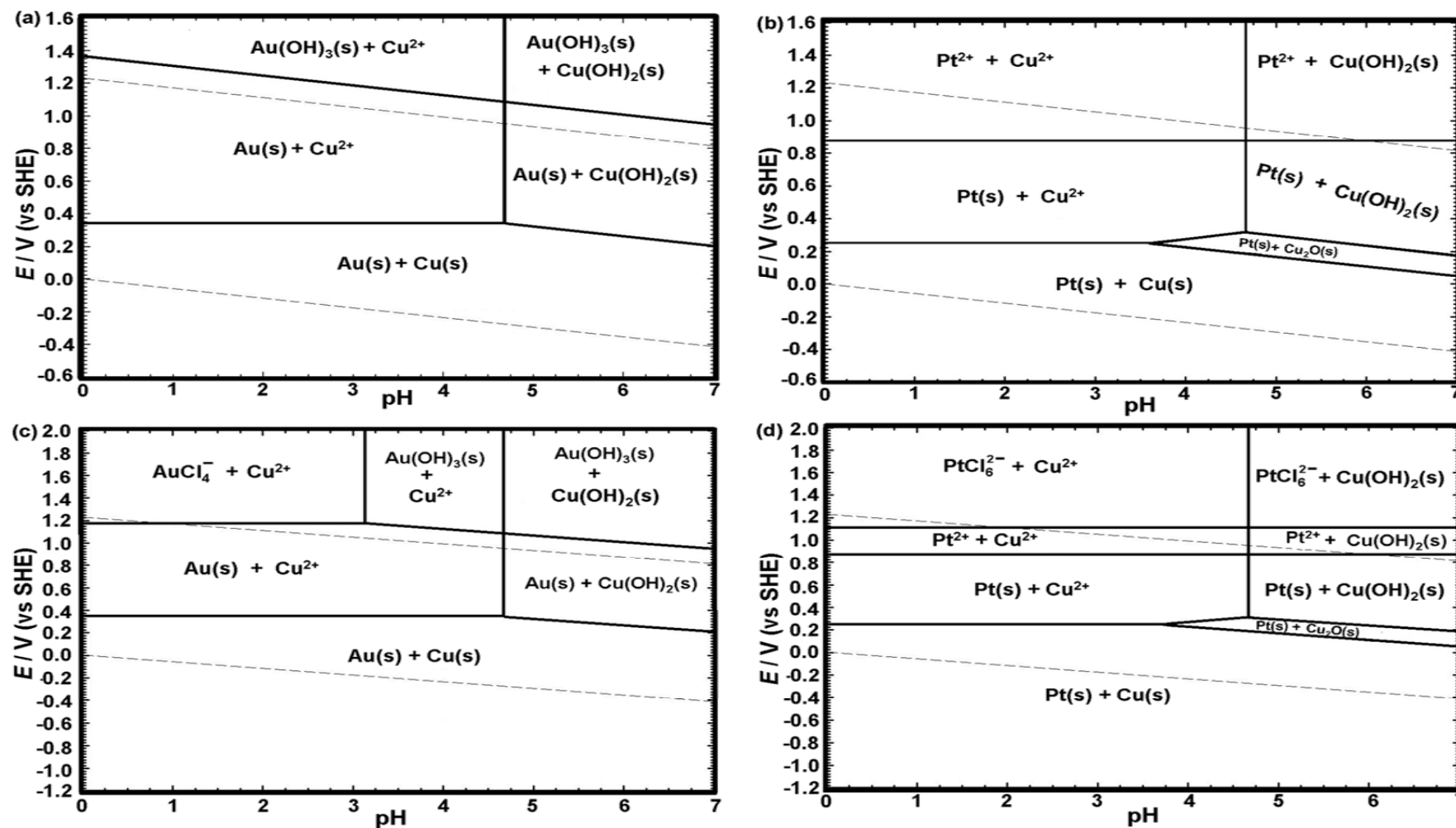


Figure 4.4: Thermochemical E - pH models for (a) Au-Cu-H₂O, (b) Pt-Cu-H₂O, (c) Au-Cu-Cl-H₂O and (d) Pt-Cu-Cl-H₂O systems at 298.15 K and molality for all aqueous forms of Pt, Au and Cu considered in the model set at 1×10^{-3} mol/Kg.

Au(s) is stable at more positive potentials as compared to Pt(s), for instance, at pH less than 3, it is stable when E is less than +1.1 V(vs SHE) (see Figure 4.3c). The E -pH models revealed that Cu^{2+} is predominant above +0.25 V (vs SHE) when considered with respect to Pt species and predominant above +0.35 V (vs SHE) when considered with respect to Au species.

Comparing the preceding E -pH scenarios to OCP variations during SLRR_{Pt} (Figure 4.3d-e) – where steady-state OCP of about +0.7 V (vs Ag/AgCl) (or +0.9 V (vs SHE)) was established – equilibria involving $\text{Pt}^{2+}/\text{Pt(s)}$ and Cu^{2+} were likely to have been responsible for the observed OCP steady-state. Moreover, the above observations indicated that the reduction pathway from PtCl_6^{2-} to Pt(s) during actual SLRR stages might have involved formation of thermodynamically-stable intermediate Pt^{2+} prior to further reduction to Pt(s) and the final equilibrium reached was that between, Cu^{2+} , Pt^{2+} and Pt(s). Recent work by Gokcen and co-workers [192], on the issue of stoichiometry of SLRR reaction between PtCl_6^{2-} and Cu(s), indicate that Cu^+ ions may also be involved. From thermodynamic point of view, the inference made was that during reduction of PtCl_6^{2-} , the liberated Cl^- ions could have sufficient local concentration on the electrode surface to influence the pathway of Cu adatoms oxidation to Cu(I) instead of Cu(II) ions with probable formation of some CuCl_x^y type of species resulting in apparent stoichiometry of Cu : Pt as 4 : 1 [192]. On the other hand, the reduction pathway from AuCl_4^- to Au(s) appeared to have proceeded spontaneously as per Reaction 4.3 as no intermediary Au species were observed in the E -pH models; the OCP during SLRR_{Au} in Figure 4.3 were very steady at about +1.2 V (vs SHE), the potential at which the species AuCl_4^- and Au(s) share an equilibrium stability boundary at pH 1 (see Figure 4.3c).

Figure 4.5 presents variation in total charge (uncorrected for background charge, here assumed not to be significant), determined from integration of current-time (i - t) curves at Stages 2 and 4 during Cu deposition to generate the bimetallic nanoclusters. There is a clear difference for the first cycle when E_{dep} of +0.05 V was employed (see Figure 4.5a); purely background charge developed as no discernible Cu deposition was expected to occur at the potential concerned.

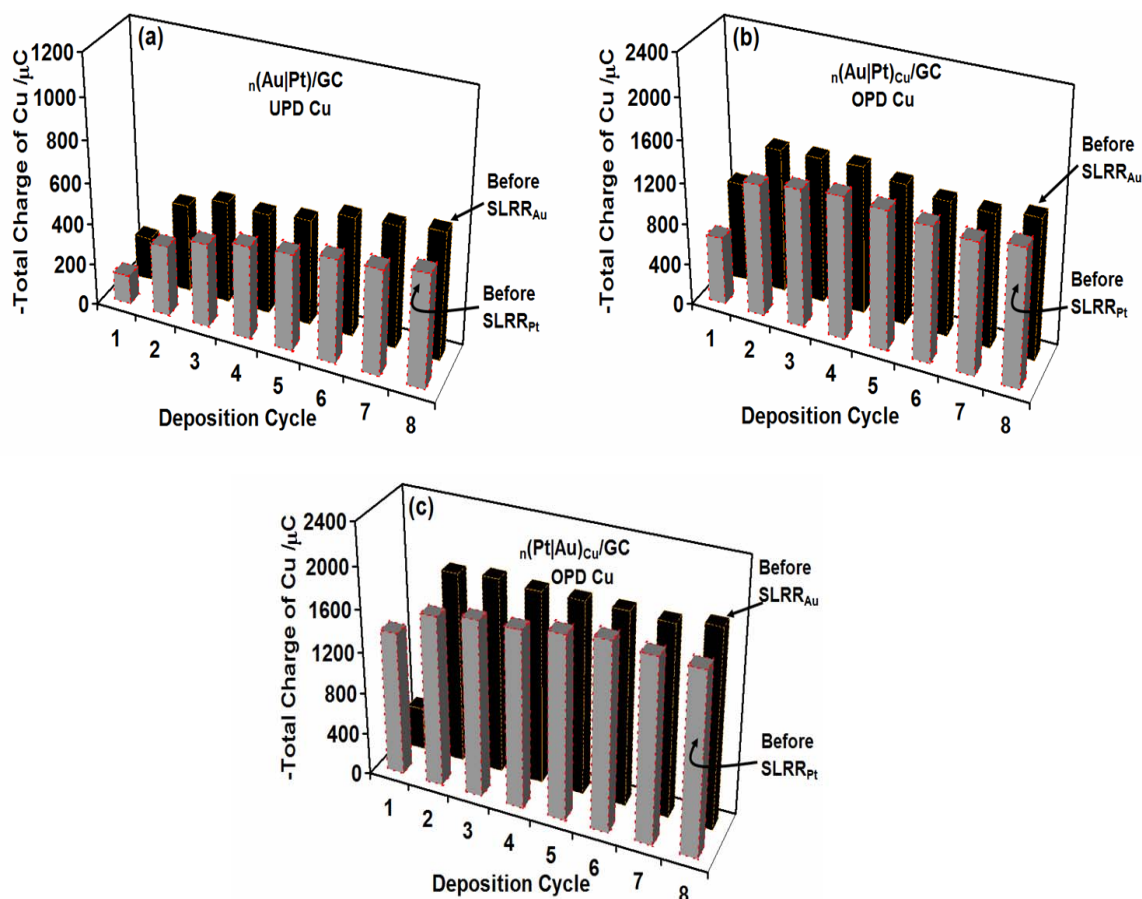


Figure 4.5: Variation in total charge developed during Cu deposition stages prior to redox-replacement reactions to generate bimetallic nanoclusters (a) $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ using UPD Cu at +0.05 V, (b) $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ nanoclusters using OPD Cu at -0.05 V, and (c) $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ using OPD Cu at +0.05 V.

This is in line with OCP observations discussed above as far as the first cycle is concerned. On the other hand, during the first cycle when E_{dep} was -0.05 V, a lesser charge developed indicative of nucleation and growth on pristine glassy carbon surface as compared to subsequent cycles for which Cu deposition proceeded on either existing Pt or Au nuclei (see Figure 4.5b). Moreover, with increasing number of cycles a gradual increase of the Cu deposition charge was observed with a tendency to a steady value after the first three cycles, most likely suggestive of a more uniform Cu deposition on the well-developed noble metal clusters. As expected larger values of Cu deposition charge developed when E_{dep} was -0.05 V (Cu OPD) was employed as compared to E_{dep} of +0.05 V (Cu UPD) plausibly due to formation of several adlayers of Cu on the growing noble metal clusters as

deposition cycles increased when the former E_{dep} was used; submonolayers are typically formed during UPD steps.

All subsequent characterization procedures were performed on the electrodic deposits obtained after eight deposition cycles ($n = 8$) as depicted in Figure 4.1.

4.3.2. Microscopic Analysis

Figure 4.6a-b presents representative SEM images and corresponding EDX spectra for the $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ decorated electrodes obtained either with Cu UPD or Cu OPD templating stages; Figure 4.6c shows the corresponding sequentially-codeposited $n(\text{Au-Pt})_{\text{Cu}}/\text{GC}$ nanoclusters. Elemental signatures for Pt and Au were clearly observed. It is seen from Figure 4.6 that reasonably uniform coverage of the GC substrate by deposited nanoparticles was obtained after 8 deposition cycles, with the GC surface providing electrochemically active sites for a preferential growth of the nanoclusters. Finely dispersed nanoclusters were formed in the case of Au|Pt sequentially generated using separate Cu SLRR steps for either Pt or Au (Figure 4.6a-b). The use of either Cu UPD or Cu OPD as templating adlayers led to much finer nanoclusters, especially in the case of Cu UPD. On the other hand, significant agglomerated particles were formed in the case of the sequentially-codeposited $n(\text{Au-Pt})_{\text{Cu}}/\text{GC}$ electrode system (see Figure 4.6c). The agglomerated morphology was also observed in the case of sequentially-codeposited (Ru-Pt) system described in Chapter 3, clearly providing further distinction between stepwise deposition of noble metals as opposed to their simultaneous deposition. Representative AFM micrographs for the bare GC electrode and the bimetallic $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ system obtained utilizing either SLRR reactions involving Cu UPD or Cu OPD and potentiostatic dealloying are shown in Figure 4.7. AFM revealed reasonably uniform coverage and dispersion on the GC substrate of the deposited nanoclusters consistent with Cu charge variations observed during actual deposition cycles (see Figure 4.5). Furthermore, AFM revealed – using more detailed 3D images – immobilized needle-like nanocluster morphology (see Figure 4.7d-e). The observed immobilized clusters varied in height between 5 nm to 40 nm when Cu UPD steps were used and between 10 nm to 80 nm when Cu OPD steps were involved.

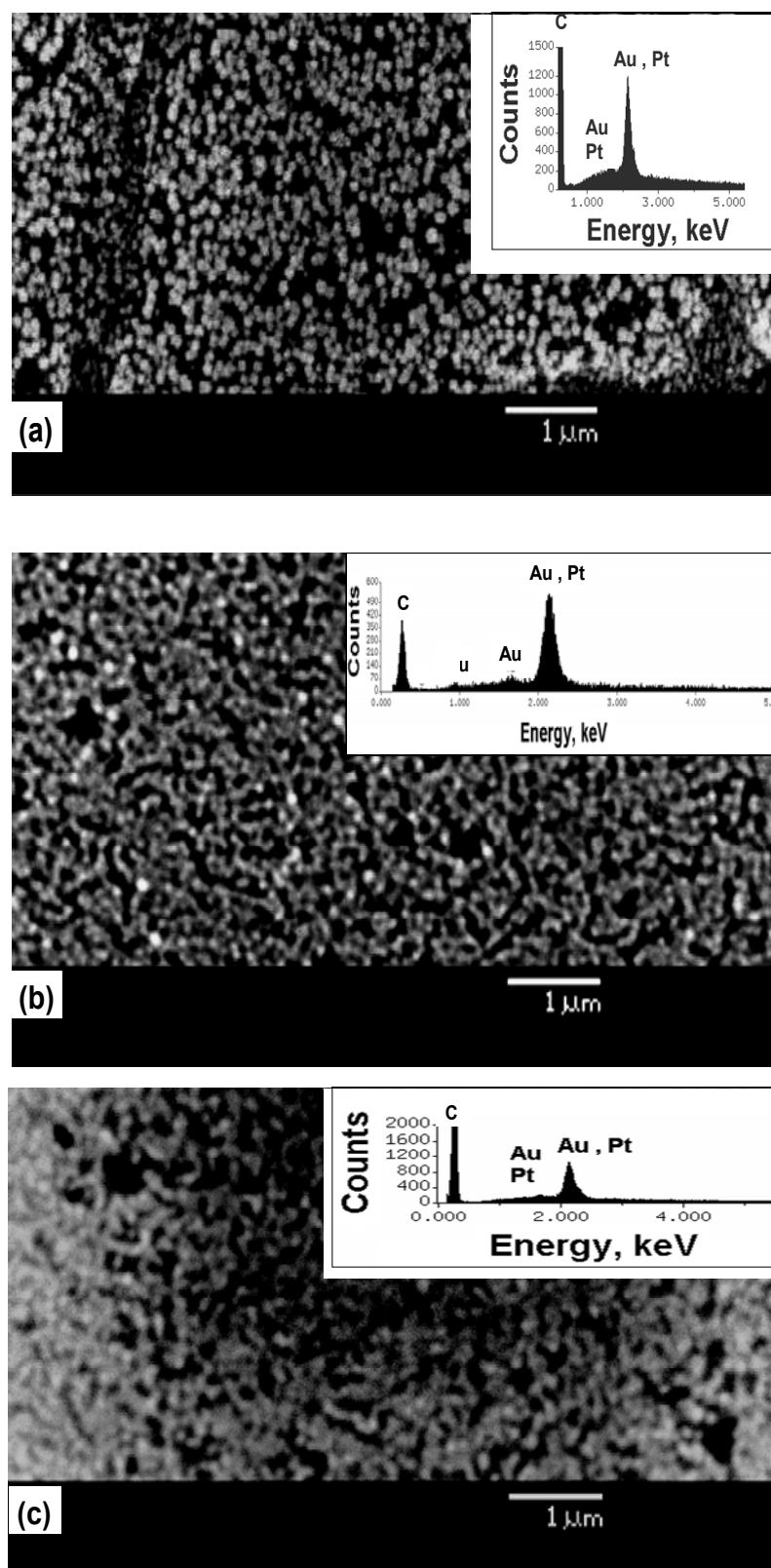


Figure 4.6: SEM micrographs and corresponding EDX spectra (insets) of: (a) bimetallic $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ nanoclusters with SLRR reactions involving Cu UPD; (b) bimetallic $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ nanoparticles with SLRR reactions involving Cu OPD; (c) sequentially-codeposited $n(\text{Au-Pt})_{\text{Cu}}/\text{GC}$ nanostructures obtained with simultaneous Cu OPD SLRR reactions. In all cases, the $n = 8$ deposition cycles.

Microscopic analyses presented in Figure 4.6 – 4.7 clearly revealed that the use of Cu UPD as templating adlayers led to much finer nanoclusters which were smaller in their average height and diameter as compared to their counterparts generated utilizing OPD steps. This is in line with the fact that multilayers of Cu most likely were generated when OPD steps were used and their subsequent redox-replacement and potentiostatic dealloying led to the morphology observed. On the other hand, the smaller number of adlayers (presumably monolayers or submonolayers) had to be replaced when Cu UPD steps were employed. Additional AFM surface plots (Figure 5e–g) clearly revealed growth of closely-neighboured nanoclusters, reaching almost similar heights and widths, these fused nanoclusters most likely developed due to the close proximity of electrochemically-active sites on which nucleation and growth of metallic nuclei were initiated on the heterogeneous glassy carbon surface. The fact that most of the proximal nanoclusters attained similar heights strongly suggests that their multilayer growth paths during the various deposition cycles were also independent.

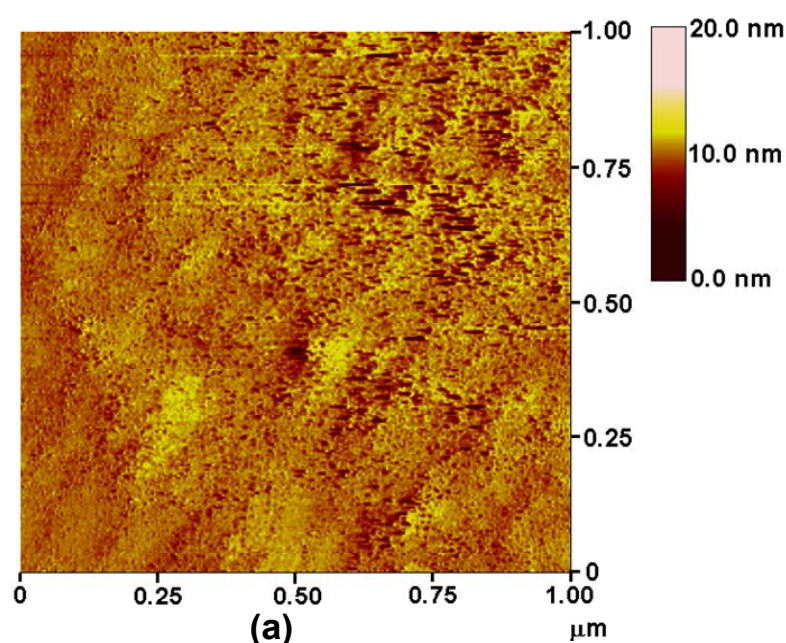


Figure 4.7: Tapping mode AFM images of glassy carbon surface before deposition of Au|Pt bimetallic nanoclusters: (a) A 1 μm x 4 μm top-viewed area of the bare GC;

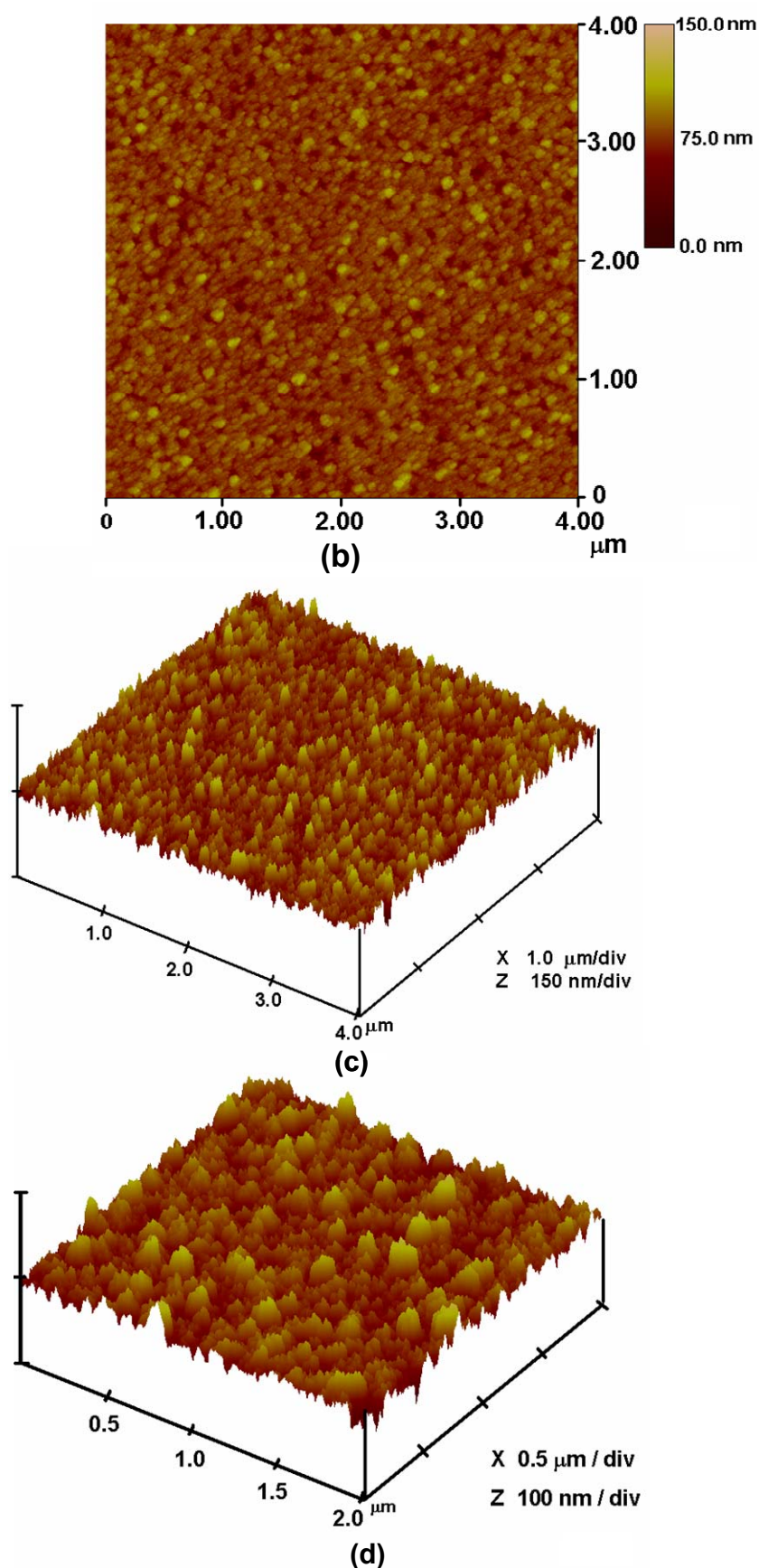


Figure 4.7 (Continued): Tapping mode AFM images of glassy carbon surface after deposition of Au|Pt bimetallic nanoclusters (obtained after eight deposition cycles): (b) A $4\ \mu\text{m} \times 4\ \mu\text{m}$ top-viewed area of nanoclusters generated via Cu UPD steps with corresponding (c) $4\ \mu\text{m} \times 4\ \mu\text{m}$ and (d) $2\ \mu\text{m} \times 2\ \mu\text{m}$ surface plots;

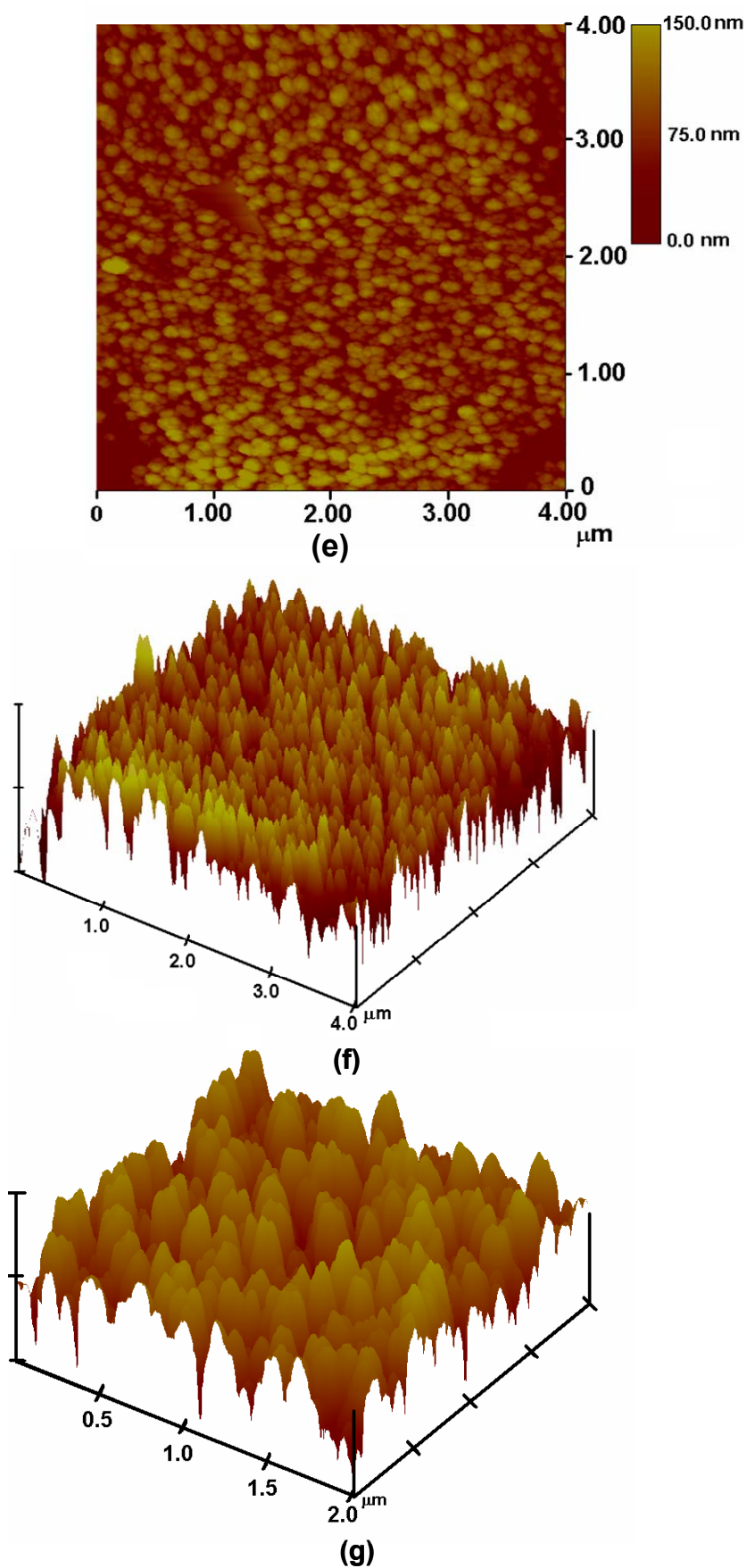


Figure 4.7 (Continued): Tapping mode AFM images of glassy carbon surface after deposition of Au|Pt bimetallic nanoclusters (obtained after eight deposition cycles). (e) A 4 $\mu\text{m} \times 4 \mu\text{m}$ top-viewed area of nanoclusters generated via Cu OPD steps with corresponding (f) 4 $\mu\text{m} \times 4 \mu\text{m}$ and (g) 2 $\mu\text{m} \times 2 \mu\text{m}$ surface plots.

4.3.3. Surface Electrochemistry

Results of cyclic voltammetry (CV) of the as-prepared nanoclusters (recorded in N₂-saturated 0.1 mol/L HClO₄) are presented in Figure 4.8; the obtained voltammograms depict typical surface electrochemical features of Au and Pt in an acidic environment. CV confirmed that Pt and Au electrochemically-active sites were generated on monometallic nanoclusters (Figure 4.8; traces *a* and *d*) as well as on the bimetallic nanoclusters (Figure 4.8; traces *b* and *d*); typical voltammetric features of electroreduction of surface-oxides of Pt (Peak I) and Au (Peak II) in acidic media were observed [222,248,294,295]. The overall electrochemical processes involving Pt can mainly be attributed to Reaction 4.4, whose standard reduction potential is 0.980 V (vs SHE), where during anodic scans surface electro-oxidation occurred forming PtO(s) films on the nanoclusters and during the cathodic scans electroreduction of the oxide films proceeded to the metallic state Pt(s).



Similarly, electrochemical processes involving Au could primarily be linked to formation of hydrated surface oxides according to Reaction 4.5, whose standard reduction potential is +1.45 V (vs SHE).



Voltammograms of bimetallic electrodes also exhibited slightly broader reduction peaks (Peaks I and II; Figure 4.8) when compared to the monometallic electrodes. This could be attributed to the effect of interfacial interactions between Au and Pt, leading to electronic changes on the Pt and Au electrochemically-active sites and electron-transfer properties. Similar effects have been observed by Obradovic and co-workers on CVs (in N₂-saturated 0.5 mol/L H₂SO₄) of Pt adlayers electrochemically deposited on polycrystalline Au electrodes [175]. For the bimetallic clusters, observation of both oxides of Pt and Au reduction peaks strongly indicated that the nanoclusters formed with incomplete top-most layers of a given noble metal, most likely in a multilayered fashion, resulting in presence of electrochemically-active sites of both Au and Pt.

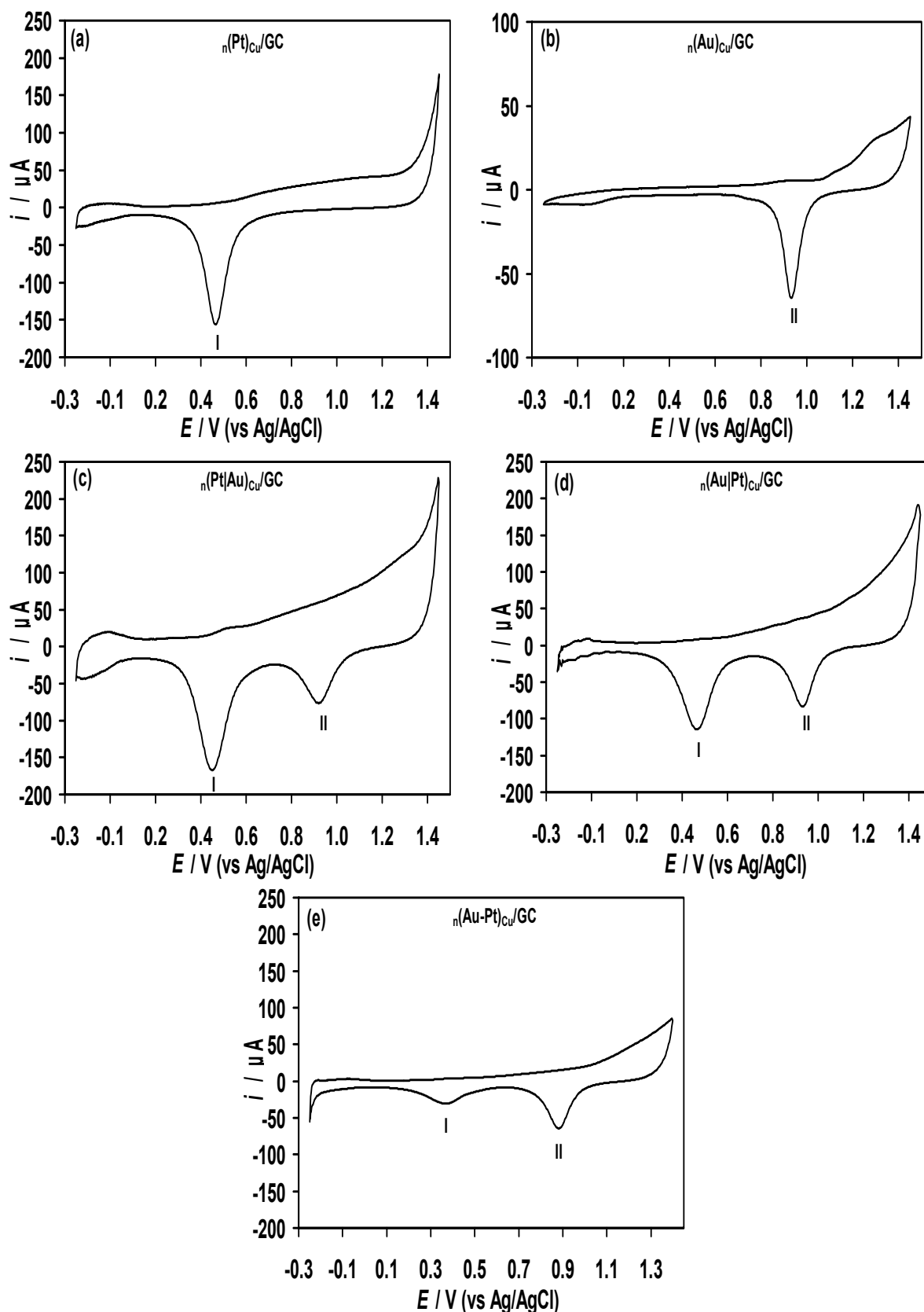


Figure 4.8: Cyclic voltammograms of the as-prepared monometallic and bimetallic nanoclusters recorded in N_2 -saturated 0.1 mol/L $HClO_4$ electrolyte. In all cases the scan rate was 50 mV/s and 5th cycles were taken for this analysis.

Moreover, CV showed that there was a significant suppression of the Pt surface oxide reduction feature (Peak I) relative to the Au surface oxide reduction feature (Peak II) in the case of the sequentially co-deposited bimetallic system $n(\text{Au-Pt})_{\text{Cu}}/\text{GC}$ (see Figure 4.8e).

4.3.4. Surface and Bulk Properties

4.3.4.1. Electrochemically-Active Surface Area

CV of bare glassy carbon (GC) electrode and those of the various Au and Pt nanostructured electrodes (recorded in 1 mmol/L CuSO_4 + 0.1 mol/L HClO_4 electrolyte solution) are presented in Figure C.5 (Appendix C). No discernible Cu UPD features were observed on the bare GC but distinguishable bulk Cu deposition from about 0.0 V to -0.2 V and corresponding oxidation (stripping of the bulk deposits) with peak maximum at about +0.08V were clearly observed (Figure C.5a) as described in our previous findings described in Chapter 3. In all the other cases (see Figures C.5b-e), which involved monometallic Pt, monometallic Au and their bimetallic counterparts, both deposition as well as stripping of UPD Cu and bulk Cu were observed in the potential range +0.5 V to -0.2 V, whereby during cathodic scans broad Cu UPD features were identifiable in the potential range +0.5 V to +0.05 V in agreement with known electrochemistry of Cu deposition on Pt and Au electrodes [289,296,297].

To further probe the active surfaces of the generated nanocluster electrodes, we utilized ASV involving UPD Cu (see Figure 4.9). The broad voltammetric features observed in Figure 4.9 were indicative of stripping of Cu adlayers from polycrystalline facets of the nanoclusters; on single-crystal surfaces sharp peaks are generally observed [159].

The ASV features (Figure 4.9) revealed that the electrochemically synthesized nanoclusters were polycrystalline in nature with various crystallographic facets electrochemically-active. Subsequently, the stripping charges (from integration of the ASV peaks) were used to estimate electrochemically-active surface area A_{EAS} (see Section 2.2.3.6, Chapter 2). The A_{EAS} data sets are summarized in Table 4.1.

Table 4.1: Metal contents and corresponding electrochemically-active surface area (A_{EAS}) of various Pt-based nanoclusters.

Electrode System	Metal Content ^a (At. %)		A_{EAS}^b (cm ²)	Normalized A_{EAS}^c (cm ² /g _{Pt})	Normalized A_{EAS}^d (cm ² /g _{TMC})
	Pt	Au			
n(Pt) _{Cu} /GC	100	–	0.77	1.65 × 10 ⁵	1.65 × 10 ⁵
n(Au Pt) _{Cu} /GC	34.0	66.0	0.82	1.69 × 10 ⁵	5.70 × 10 ⁴
n(Pt Au) _{Cu} /GC	48.5	51.5	0.71	7.17 × 10 ⁴	3.46 × 10 ⁴
n(Au–Pt) _{Cu} /GC	19.4	80.6	–	–	–

^a) Determined by ICP-MS;

^b) Obtained using anodic stripping voltammetry involving Cu UPD;

^c) With respect to Pt content; ^d) With respect to Total Metal Content (TMC).

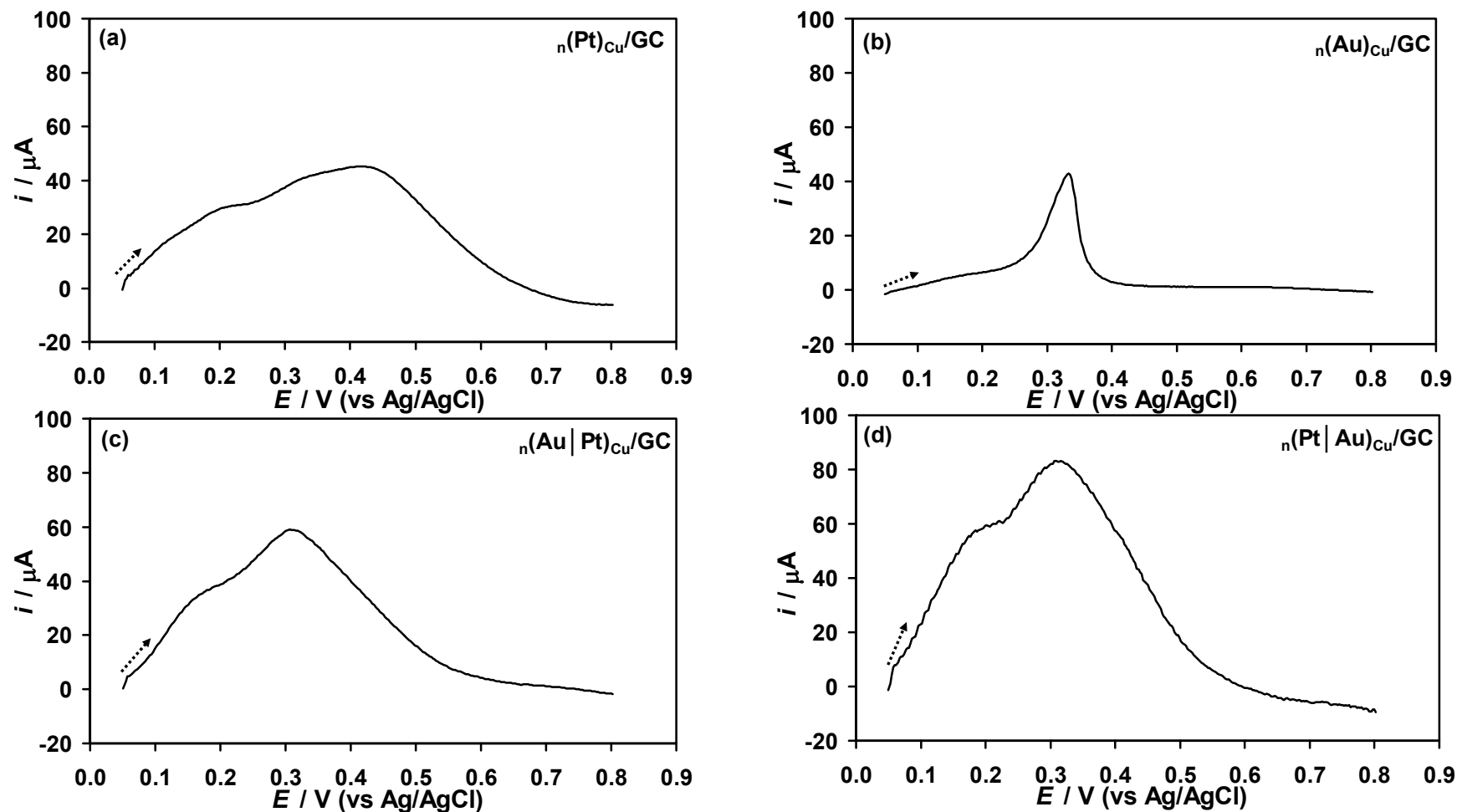


Figure 4.9: Anodic stripping voltammograms after Cu UPD at +0.05 V for 90s on various Pt and Au nanoclusters recorded from N_2 -saturated 1 mmol/L $CuSO_4$ in 0.1 mol/L $HClO_4$. In all cases, the scans were performed in the direction indicated by broken arrows at 50 mV/s. Background current correction was done by subtraction of voltammograms recorded in neat 0.1M $HClO_4$.

The estimated A_{EAS} values obtained were about four- to six-fold larger than the geometric area of the bare GC (ca. 0.2 cm²), strongly suggesting that high surface area nanoclusters, with high aspect ratios were generated. The most surface-active electrode was bimetallic $n(Pt | Au)_{Cu}/GC$ followed by $n(Au | Pt)_{Cu}/GC$ and the least active was monometallic $n(Pt)_{Cu}/GC$.

4.3.4.2. ICP- MS Analysis

Results of quantitative analyses of the bulk composition of various Pt-containing nanoclusters, determined using ICP-MS, are summarized in Table 4.1. $n(Au | Pt)_{Cu}/GC$ nanoclusters contained 66 at% Au and 34 at% Pt (or Au : Pt = 2 : 1); whereas the metal distribution in the $n(Pt | Au)_{Cu}/GC$ nanoclusters was 51.5 at% Au and 48.5 at% Pt (or Au : Pt $\approx$ 1 : 1). No detectable traces of Cu in the samples of digested nanoclusters could be found using ICP-MS. The observed metal contents indicated that the nature of the first deposited noble metal had influenced subsequent total metal distribution in the ultimate formed nanoclusters. The interplay of preferential deposition of the more noble Au during sequential codeposition of (Au-Pt) system was clearly revealed metal content was about 80.6 at% Au and 19.4 at % (approximately Au to Pt ratio of 4 : 1). Inspection of the $E-t$ transients during simultaneous SLRR stage involving competition between Pt and Au to replace Cu, there was a significant thermodynamic advantage towards Au deposition over Pt as the overall OCP attained was about +0.9 V (vs Ag/AgCl) or about +1.1 V (vs SHE) (see Figure 4.1e, Figure 4.4 and Figure C.4c in **Appendix C**). Clearly, sequential deposition of bimetallic noble metal nanosystems as opposed to sequential codeposition provides a unique set of degrees of freedom in tuning composition of resultant nanostructured deposits.

Using ICP-MS derived metal contents, further normalization of the A_{EAS} to account for any effect of total metal loading was carried out (see Table 4.1). Normalization of A_{EAS} with respect to Pt content showed that bimetallic $n(Au | Pt)_{Cu}/GC$ had slightly higher surface area compared to monometallic $n(Pt)_{Cu}/GC$ and the bimetallic $n(Pt | Au)_{Cu}/GC$ system had the least surface area. When total metal content (TMC) was used to normalize the A_{EAS} , the trend in normalized surface area changed to $n(Pt)_{Cu}/GC > n(Au | Pt)_{Cu}/GC > n(Pt | Au)_{Cu}/GC$.

4.3.4.3. XPS Analysis

XPS was employed *ex-situ* to probe surface to near-surface chemical composition of pristine glassy carbon electrode (the substrate in this work) and the Pt-based nanocluster electrodes. XPS is a powerful technique for surface characterization of materials generating chemical information from the outer few atomic layers of the probed material with typical depth range of 10 nm and lateral resolution of about 1 μm [262,298]. Samples were probed “as-received” and after sputtering with Ar^+ ions within the XPS chamber. Survey spectra involving extensive binding energy regions are presented in Figure C.6 (**Appendix C**). Qualitative analysis of characteristic photoelectron emission lines revealed that the bare substrate mainly contained carbon and oxygen, whereas the nanocluster systems probed contained carbon, oxygen, platinum, as well as gold (in the case of bimetallic systems). The qualitative XPS results were in line with observations made using surface electrochemistry as well as microscopy providing additional and independent evidence that the nanocluster growth pattern left some exposed carbonaceous spots on the substrate and the surface to near-surface composition of the nanoclusters were of the appropriate noble metals Pt and/or Au.

Figures 4.9 – 4.10 display detailed photoelectron spectra, recorded in relevant binding energy regions related to C 1s, O 1s, Pt 4f, and Au 4f orbitals (additional spectra of as-received and sputter-cleaned samples are presented in Figures C.6 – C.8 in **Appendix C**). Deconvolution of the C 1s photoelectron spectral curves, using non-linear curve-fitting procedures, revealed at least three spectral components, namely, C-1, C-2, and C-3 in Figure 4.10a–b and Table 4.2. Curve-fitting with three components resulted in most reasonable full-width-at-half-maximum (FWHM) value of about 1 eV; inclusion of one or two components resulted in much larger values of FWHM.

Guided by literature on XPS studies on glassy carbon and related carbonaceous materials and their expected chemical functionalities [219,299], particularly after undergoing electrochemical pretreatment as was done in this work prior to deposition of the nanoclusters, the following assignments were made to the deconvoluted C 1s spectra: (i) C-1 at 284.8 eV was assigned to graphitic carbon (in

C-H bonding environment) on the GC surface; (ii) C-2 at about 285.5 eV was assigned to expected phenolic surface functionalities such as -C-OH and -C-NH on the GC surface; and (iii) C-3 (B_E positions in the range 286.3 eV – 286.5 eV) was attributed to carbonyl (-C=O) groups, also mainly from the GC surface and possibly from traces of adventitious adsorbed species.

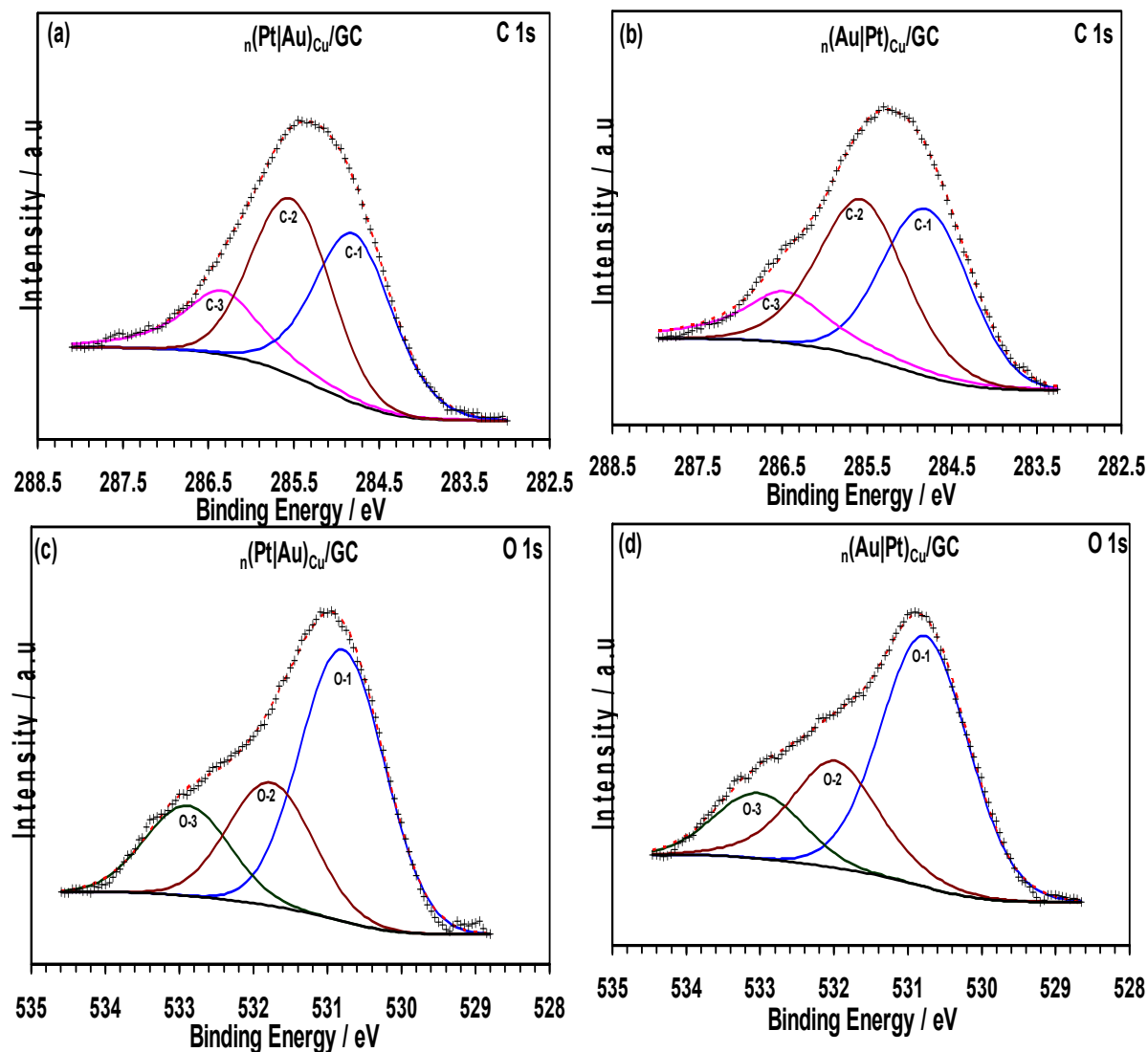


Figure 4.10: X-ray photoelectron spectra (points) and their corresponding deconvoluted spectral components (solid lines) of various bimetallic nanoclusters. Spectra correspond to photoelectrons from (a) – (b) C 1s; and (c) – (d) O 1s subatomic levels. Probed samples were sputtered with Argon ions.

The O 1s spectra (Figure 4.10c-d) were found to appropriately fit at least three components with overall FWHM value of 1.5 ± 0.2 eV: (i) O-1 (B_E positions in the range 530.6 – 530.8 eV), (ii) O-2 (B_E positions in the range 531.8 – 532.2 eV), and (iii) O-3 (B_E position about 533 – 533.6 eV). O-1 was mainly attributed to C=O groups on

the GC surface and probably some surface metal oxides on the nanoclusters, if they were formed at all. The B_E position of O-2 was typical of C-OH and/or C-O-C groups; O-3 was of the lowest intensity and perhaps was due to chemisorbed oxygen and/or some traces of adsorbed water [299]. The similarities in XPS binding energy positions of the carbon and oxygen components from the two types of bimetallic systems strongly indicated that the characteristics of the GC surface did not vary much from one sample to another, appropriately so given the fact that pre- and post-treatment procedures on the GC samples were the same and practically reproducible.

In the case of Pt 4f and Au 4f photoemission spectral regions (see Figure 4.11a-d) spectral doublets were observed as theoretically expected due to Spin-Orbit Splitting (S.O.S) phenomenon, a consequence of electron spin and angular momentum in the 4f orbitals, $4f_{7/2}$ and $4f_{5/2}$, respectively [262,298]. In particular, the Pt 4f spectral regions markedly indicated presence of multiple microstates of Pt as broad peaks with clearly discernible shoulders were observed; compared to the monometallic Pt system the peak features were more distinctly pronounced in the bimetallic systems, suggestive of a strong influence of Au on Pt XPS responses.

Deconvolution of the 4f doublets proceeded by fitting two symmetric mixed Gaussian-Laurentzian functions for every microstate component considered, applying theoretical constraints on the peak area ratios of $4f_{7/2}$ and $4f_{5/2}$ peaks at 4 : 3 with their B_E separations fixed at literature values of 3.30 eV and 3.67 eV for Pt and Au, respectively [262]. During optimization FWHM of all spectral components ($4f_{7/2}$ and $4f_{5/2}$ peak pairs) considered were set to remain equal. The presence of a single Au $5p_{1/2}$ peak in the same binding energy region of Pt 4f doublets had to be considered in deconvolution of Pt 4f spectral region by inclusion of one additional single peak during fitting procedures on the Pt 4f curves of the bimetallic systems; on XPS of bulk gold systems, the Au $5p_{1/2}$ photoelectron peak occurs at about 74 eV [262,298].

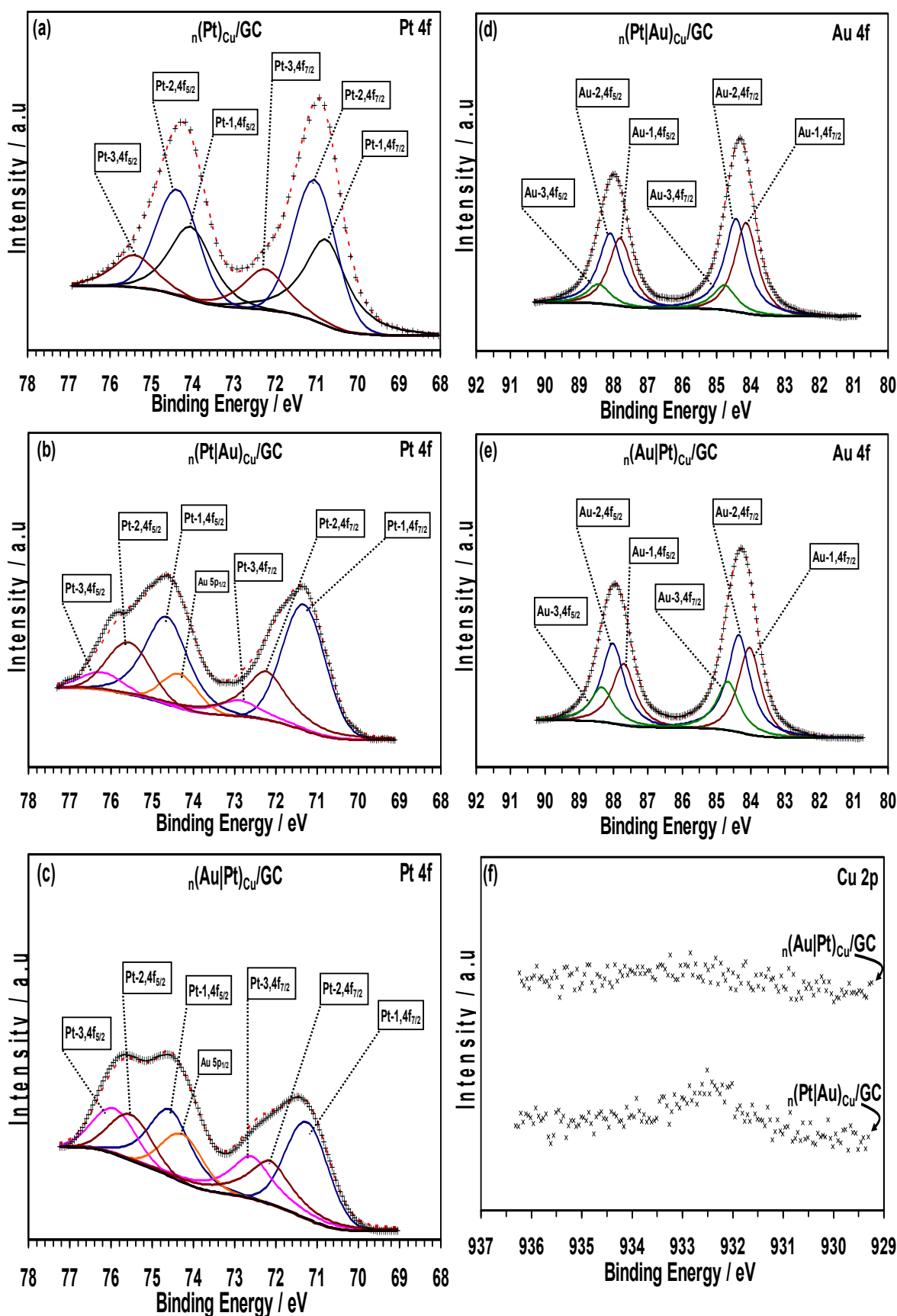


Figure 4.11: (Color Online) X-ray photoelectron spectra (points) and their corresponding deconvoluted spectral components (solid lines) recorded from as-received samples of mono- and bimetallic nanoclusters, in the binding energy regions corresponding to photoelectrons ordinarily from (a) – (c) Pt 4f, (d) – (e) Au 4f and (f) Cu 2p subatomic levels.

Initial attempts to fit the Pt 4f with only two sets of doublets resulted in unreasonably large FWHM values for Pt 4f, such large FWHM values are characteristic of presence of multiple Pt chemical microenvironments [300]. Three sets of doublets were used in deconvolution of Pt 4f signals in further fitting procedures which resulted in reasonable FWHM values. For consistency the same scenario was employed to fit the Au 4f spectra. Consequently, the Pt 4f and Au 4f spectra were resolved into three spectral components, namely, Pt-1, Pt-2, Pt-3, Au-1, Au-2, and Au-3 (each component was a doublet composed of 4f_{7/2} and 4f_{5/2} peaks as depicted in Figure 4.11).

Detailed Cu 2p XPS region (Figure 4.11f) did not reveal any analyzable peaks strongly suggesting effective redox-replacement reactions and dealloying steps of the sacrificial Cu used during deposition of the nanocluster systems.

Surface and near-surface content from XPS (that is, concentrations of observed components) were estimated using the relation:

$$C_{At\%_x} = \frac{\frac{PA_x}{ASF_x}}{\sum \frac{PA_i}{ASF_i}} \times 100 \quad (4.6)$$

where PA_x, PA_i denote the extracted peak areas of spectral component *x* or *i*, respectively; ASF_x, ASF_i denote the atomic sensitivity factors of elemental component *x* or *i* (here taken from the relevant literature) [301], respectively; C_{At%_x} denotes the atomic concentration of elemental component *x*.

Table 4.2 summarises the relevant XPS binding energy (*B_E*) values of deconvoluted Pt and Au 4f_{7/2} peaks, overall FWHM values and respective atomic concentrations (for simplicity, *B_E* values of 4f_{5/2} peaks are not shown as they can be deduced from above-mentioned S.O.S considerations). For bulk monometallic Pt systems standard reference literature provide *B_E* values of the Pt 4f_{7/2} peak related to Pt(0) in the range 70.8 – 71.2 eV and oxidized states of Pt have much higher *B_E* values. For example, *B_E* values of PtO_x (*x* =1,2) have been reported in the range 73.6 – 75.0 eV and for Pt(OH)₂ in the range 72.4 – 72.8 eV [262,298].

Table 4.2: Binding energy values of deconvoluted X-ray photoelectron spectral components of the Pt-containing nanoclusters

Electrode System	Binding Energy, B_E / eV											
	C 1s			O 1s			Pt 4f _{7/2}			Au 4f _{7/2}		
	C-1	C-2	C-3	O-1	O-2	O-3	Pt-1	Pt-2	Pt-3	Au-1	Au-2	Au-3
n(Pt) _{Cu} /GC ^a	284.8	285.4	286.5	–	–	–	70.8	71.0	72.2	–	–	–
	(FWHM = 1.2 eV)			–			(FWHM = 1.2 eV)			–		
n(Au Pt) _{Cu} /GC ^a	284.8	285.5	286.4	530.6	532.2	533.5	71.3	72.1	72.6	84.0	84.4	84.7
	(FWHM = 1.0 eV)			(FWHM = 1.6 eV)			(FWHM = 1.2 eV)			(FWHM = 0.8 eV)		
n(Au Pt) _{Cu} /GC ^s	284.8	285.1	286.5	530.8	532.0	533.0	71.2	72.2	72.7	84.3	84.6	84.9
	(FWHM = 1.2 eV)			(FWHM = 1.4 eV)			(FWHM = 1.1 eV)			(FWHM = 0.8 eV)		
n(Pt Au) _{Cu} /GC ^a	284.8	285.5	286.5	530.7	532.3	533.6	71.3	72.2	72.9	84.1	84.4	84.8
	(FWHM = 1.1 eV)			(FWHM = 1.4 eV)			(FWHM = 1.2 eV)			(FWHM = 1.0 eV)		
n(Pt Au) _{Cu} /GC ^s	284.8	285.5	286.3	530.8	531.8	532.9	71.3	72.3	72.8	84.2	84.5	84.9
	(FWHM = 1.1 eV)			(FWHM = 1.3)			(FWHM = 1.1 eV)			(FWHM = 0.9 eV)		

^a) As-received sample;

^s) Sample sputtered with Ar⁺

Table 4.3: Surface and near-surface composition of the bimetallic nanocluster electrodes as determined from XPS semi-quantitative analysis involving carbon, oxygen, platinum, and gold spectral components.

Electrode System	Content ^b (At %)											
	C			O			Pt			Au		
	C-1	C-2	C-3	O-1	O-2	O-3	Pt-1	Pt-2	Pt-3	Au-1	Au-2	Au-3
n(Au Pt) _{Cu} /GC ^a	19.9%	20.1%	5.8%	10.8%	10.8%	5.9%	2.2%	1.4%	1.4%	7.5%	9.7%	4.8%
	(Total C = 45.8%)			(Total O = 27.3%)			(Total Pt = 4.9%)			(Total Au = 22.0%)		
n(Au Pt) _{Cu} /GC ^s	19.3%	18.9%	8.5%	9.3%	4.1%	2.4%	5.7%	3.1%	1.9%	9.2%	12.0%	5.8%
	(Total C = 46.8%)			(Total O =15.8%)			(Total Pt =10.4%)			(Total Au = 27.0%)		
n(Pt Au) _{Cu} /GC ^a	22.0%	18.9%	4.9%	7.8%	6.9%	4.0%	6.5%	3.6%	1.2%	9.9%	11.4%	3.0%
	(Total C = 45.8%)			(Total O = 18.7%)			(Total Pt = 11.3%)			(Total Au = 24.2%)		
n(Pt Au) _{Cu} /GC ^s	14.2%	14.4%	6.2%	6.5%	3.0%	2.2%	7.1%	3.1%	1.4%	13.1%	22.7%	6.3%
	(Total C = 34.7%)			(Total O =11.6%)			(Total Pt =11.6%)			(Total Au = 42.5%)		

^a) As received;

^b) Content estimation inclusive of C, O, Pt, and Au;

^s) Sample sputtered with Ar⁺

Table 4.4: Surface and near-surface composition of Pt-containing nanoclusters electrodes as determined from XPS semi-quantitative analysis involving platinum and gold spectral components.

Electrode System	Content ^b / At %					
	Pt			Au		
	Pt-1	Pt-2	Pt-3	Au-1	Au-2	Au-3
n(Pt) _{Cu} /GC ^a	36.1%	48.2%	15.7%	–	–	–
	(Total Pt = 100%)				–	
n(Au Pt) _{Cu} /GC ^a	8.0%	5.1%	5.0%	27.9%	36.2%	17.7%
	(Total Pt = 18.2%)				(Total Au = 81.8%)	
				(Pt : Au = 1.0 : 4.5)		
n(Au Pt) _{Cu} /GC ^s	15.2%	8.4%	4.2%	24.6%	32.0%	15.6%
	(Total Pt = 27.8%)				(Total Au = 72.2%)	
				(Pt : Au = 1.0 : 2.6)		
n(Pt Au) _{Cu} /GC ^a	18.3%	10.1%	3.4%	27.9%	32.0%	8.4%
	(Total Pt = 31.8%)				(Total Au = 68.2%)	
				(Pt : Au = 1.0 : 2.1)		
n(Pt Au) _{Cu} /GC ^s	13.3%	5.8%	2.5%	24.3%	42.3%	11.8%
	(Total Pt =21.6%)				(Total Au = 78.4%)	
				(Pt : Au = 1.0 : 3.6)		

^{a)} As received; ^{b)} Content estimation inclusive of Pt and Au only; ^{s)} Sample sputtered with Ar⁺.

In typical nanoparticulate Pt systems, literature reports of the B_E of Pt(0) 4f_{7/2} peak are scattered in the range 71.2 – 72.3 eV and oxidized nanoparticulate forms of PtO and PtO₂ have B_E values between 72.6 – 75.6 eV [127,302-305]. Due to different coordination numbers surface atoms do not behave the same way as bulk atoms upon their interaction with incident X-ray beams, that is, surface potentials and bulk (or subsurface) potentials are quite distinct. Accordingly, a small shift in core electron binding energy (typically less than 1 eV) of surface atoms relative to bulk atoms can be observed from XPS spectra [306]. In terms of microstates of monometallic Pt nanoparticles (vapor deposited onto highly oriented pyrolytic graphite (HOPG), Zhang et al [303] resolved the Pt 4f XPS signals into three components at B_E values of 71.4 eV, 72.3 eV, and 73.2 eV, respectively, which were attributed to surface Pt(0) atoms, bulk Pt(0) atoms, and surface Pt oxide films (PtO_x) on the nanoparticles, respectively. In light of the above, it is clear that one oxidation state of Pt may generate multiple microstates that can be manifested by observation of multiple peaks in XPS investigations.

Pt spectral components of all nanocluster electrodes investigated in this work exhibited B_E values of Pt 4f_{7/2} peak in the range 70.8 – 72.9 eV (see Table 4.2). Observed B_E values strongly indicated presence of Pt(0), particularly for components Pt-1 and Pt-2. Moreover, Pt-3 could be related to some PtO_x or some Pt-substrate interaction as indicated by aforementioned literature information on Pt XPS characteristics. Furthermore, the B_E values of all the Pt spectral components of the bimetallic nanosystems, $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$, exhibited a general positive shift of between 0.5 eV and 1 eV when compared to the monometallic Pt system, $n(\text{Pt})_{\text{Cu}}/\text{GC}$. This observation strongly suggested either a significant electronic influence on Pt atoms by incorporation of Au atoms in the nanocluster systems or some nanocluster-substrate interaction [127,302,304]. In particular, the B_E of the Pt-2 component was the greatest at about 1 eV, whereas the corresponding shifts for Pt-1 and Pt-3 components were between 0.5 – 0.7 eV. Most likely Pt-1 was related to surface Pt atoms, Pt-2 was related to Au|Pt interactions in the subsurface of the bimetallic nanoclusters due to its strongest B_E shift when compared to monometallic Pt, and Pt-3 was associated with surface PtO_x and/or metal-substrate interactions involving surface oxygenated functional groups.

Accordingly, the B_E values of the Pt components in the two types of bimetallic systems did not differ much (the values were within 0.1 eV, regardless of the Ar^+ treatment). These observations strongly suggested that the nature of electronic properties of the Pt components in the bimetallic nanoclusters remained essentially the same from one type of nanocluster to the other.

The Au $4f_{7/2}$ B_E values of the spectral components Au-1, Au-2, and Au-3 of the bimetallic nanocluster electrodes ranged from 84.0 to 84.9 eV (see Table 4.2). Typical literature B_E values of Au in zero oxidation state in bulk monometallic Au are in the range of 83.8 – 84.2 eV [262,298,307]; B_E values of Au(0) in nanoparticulate systems have been reported between 83.9 to 84.7 eV, with attribution of more positive B_E values for nanoparticles (when benchmarked to bulk Au) due to nanostructuring effects and/or alloying effects [127,308,309]. Oxidized states of Au generate more positive Au $4f_{7/2}$ B_E values than Au(0), for example, Au(+1) states generate B_E values in the range 85.6 – 85.8 eV, whereas B_E values of Au(+3) range from 86.0 to 86.5 eV [307,309]. Therefore, the Au components observed in our work were essentially in the elemental oxidation state. Similar to XPS microstates observed for Pt, the component Au-1 was most likely due to non-interactive surface Au atoms whereas Au-2 and Au-3 components were related to embedded Au atoms with Au|Pt interfacial interactions as well as Au atoms interacting with surface functional groups of the substrate, respectively.

Semi-quantitative XPS analysis (inclusive of C, O, Pt, and Au components) using Equation 4.6 revealed a general decrease for the oxygen components of both $n(Au | Pt)_{Cu}/GC$ and $n(Pt | Au)_{Cu}/GC$ nanocluster electrodes upon Ar^+ sputtering. In particular, changes in the concentration of components O-2 and O-3 (decrease in both B_E values and content, see Tables 4.2, 4.3 and 4.4), strongly suggested these components were due to adventitious adsorbed oxygenated species, such as H_2O_{ads} , as well as carbonaceous oxygen-containing surface functional groups.

In the $n(Au | Pt)_{Cu}/GC$ system an increase of about 10% in total Pt was observed after Ar^+ -sputter treatment, whereas a decrease of about 10% was observed for total Au content. The trend for the Pt and Au contents in the $n(Pt | Au)_{Cu}/GC$ system was almost the converse (see Tables 4.3 and 4.4). The preceding observations were

consistent with the removal of a thin contamination layer upon Ar^+ sputtering, which subsequently led to availability of more surface-to-near-surface metal content during subsequent measurements. The trends in changes of Pt and Au contents before and after Ar^+ -sputtering were also consistent with multilayer growth pattern of sequentially-deposited nanoclusters which resulted in Au-rich surfaces on the $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ nanoclusters as opposed to the Pt-rich surfaces of the $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ nanoclusters. The Pt and Au contents obtained from XPS (see Table 4.4) for the two types of bimetallic nanoclusters somewhat differ from corresponding metal contents derived from ICP-MS (see Table 4.1). This is expectedly the case since ICP-MS essentially probed the metal contents of the entire nanocluster samples whereas XPS probed a few atomic layers of the nanoclusters' surface-to-near surface structures. Overall, ICP-MS and XPS results appropriately showed that the sequence of deposition, the different stoichiometry of SLRR reactions between Pt and Au and the sacrificial Cu (see Reactions 4.1 – 4.3), and potentiostatic dealloying of Cu from layers of either Pt or Au played significant roles in determining the final distribution of Au and Pt in the nanoclusters. It appears, if preferential growth of the nanoclusters was layer-by-layer, then the distribution of the first layer of either Au or Pt, during the first deposition cycle, determined the available sites for the growth of subsequent layers.

Based on B_E values and estimated concentrations of the deconvoluted spectral components from XPS, the following scenarios can aptly describe the surface-to-near surface composition of the nanoclusters as immobilized on glassy carbon: (i) presence of carbon and oxygen surface functional groups from bare areas on the GC surface and their possible interaction with the nanoclusters, (ii) presence of only zerovalent states of Pt and Au in the nanoclusters, (iii) occurrence of mixed microstates of Pt and Au, due to interfacial interactions between Pt and Au atoms in the bimetallic nanoclusters, and (iv) existence of metal-substrate interactions between first few layers of the nanoclusters where some electronic interplay of exposed Pt and Au surface atoms and oxygenated and carbonaceous surface functional groups of the glassy carbon surface took place. Furthermore, the plausible metal-substrate interactions could be playing a stabilizing role. These deductions are schematically presented in Figure C.9 (**Appendix C**).

4.3.5. Electrocatalysis of Formic Acid Oxidation Reaction and Carbon Monoxide Adsorption-Oxidation Process

4.3.5.1. Voltammetric Studies

Electrocatalysis of FAOR (Reaction 4.7; $E^\circ \approx -0.25$ V (vs SHE)) [310] on the Pt and Au-containing nanostructured electrodes was carried out in 0.5 mol/L HCOOH (in 0.1 mol/L HClO₄) primarily to investigate any differences in the electrocatalytic properties of the nanosystems of interest, as this particular structure-sensitive reaction is technologically and fundamentally very important in applications such as fuel cells. The mechanisms of FAOR electrocatalysis on Pt-based systems are complex and have been a subject of interest for several decades [47,129,311,312].



Recent works [313-315] on molecular-level mechanisms of the formic acid oxidation on metal-based catalytic surfaces point out that the reaction should be considered as involving at least three distinct pathways, each commencing from adsorbed HCOOH as schematically shown in Figure 4.12a. In particular, the direct (or dehydrogenation) pathway to CO₂ likely operates via a weakly-bound reactive HCOOH intermediate and is initiated by C-H bond activation; the indirect (or dehydration) pathway proceeds through strongly-adsorbing intermediates, mainly CO_{ads}, and to a lesser extent COH_{ads}, and HCO_{ads}; the formate pathway takes place via a HCOO intermediate and is thought to be initiated by O-H bond activation [313-315].

Figure 4.12b-c show CV scans of the HCOOH irreversible electro-oxidation process on the various nanoclusters that were recorded in gentle flowing solutions at 2mL/min (CV in stationary solutions led to significant bubbles in the cell, in line with formation of CO₂ - Reaction 4.7 - at high anodic overpotentials). Monometallic Au nanoclusters revealed the lowest current density and exhibited some small activity toward electro-oxidation of HCOOH at high overpotentials. Indeed, FAOR on monometallic Au electrodes, investigated by Surface-enhanced Raman Spectroscopy and electrochemistry [312], showed that the main reaction occurs via the dehydrogenation pathway with negligible CO_{ads} formation. Monometallic Pt

nanoclusters exhibited approximately a ten-fold increase in oxidation peak current density as compared to forward scan oxidation peak of monometallic Au (see Peak I in Figure 4.12b). The onset of oxidation was also observed at a much more negative potential in the case of monometallic Pt, revealing that these nanoclusters were relatively more electrocatalytically-active than the counterpart monometallic Au nanoclusters toward FAOR. Moreover, the FAOR on monometallic Pt appeared to have proceeded in multiple steps as the broad peak observed in the forward scan (Peak I) was somewhat split into two features (Peak I_a and I_b in Figure 4.12b), most likely through the indirect and/or formate pathway (see Figure 4.12a) involving multiple adsorbed intermediates that were oxidized in parallel [129,314].

Figure 4.12c shows CV responses of the HCOOH electro-oxidation process on the bimetallic nanoclusters. Compared to the monometallic systems voltammograms recorded on the bimetallic nanoclusters had sharper, more intense peaks suggestive of enhanced overall kinetics of the electro-oxidation process; with the $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ exhibiting the highest current densities for the FAOR.

Direct electro-oxidation of CO on the nanocluster electrodes was probed by anodic adsorptive stripping voltammetry (Figure 4.12d); adsorption was carried out in CO-saturated 0.1 mol/L HClO₄ and to eliminate any role of Pt and/or Au oxides formation in the same potential window during CO oxidative stripping the recorded voltammograms were corrected for any background current from independent voltammograms recorded in neat N₂-saturated 0.1 mol/L HClO₄ solutions. In Figure 4.12d, a very broad, low-intensity voltammogram (peak maximum at about 0.58 V) was observed for the $n(\text{Au})_{\text{Cu}}/\text{GC}$ electrode; the peak was characteristic of diffusion-controlled oxidation voltammograms, indicative of the weak nature of Au to adsorb CO, hence, its oxidation proceeded readily on the monometallic Au sites. On the other hand, a sharp, high intensity stripping peak (peak maximum at 0.63 V) was observed for the $n(\text{Pt})_{\text{Cu}}/\text{GC}$ electrode; the peak is characteristic of CO_{ads} oxidation from monometallic Pt surface [175,316]. For bimetallic cases, $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ had its peak maximum at 0.65 V and the maximum for $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ was at about 0.68 V (see Figure 4.12d). In addition, the stripping peaks exhibited some shoulders at about 0.8 V and 1.15 V, respectively, features that could be attributed to the polycrystalline nature of the nanoclusters which led to adsorption of CO (and its subsequent stripping) from energetically different crystallographic facets.

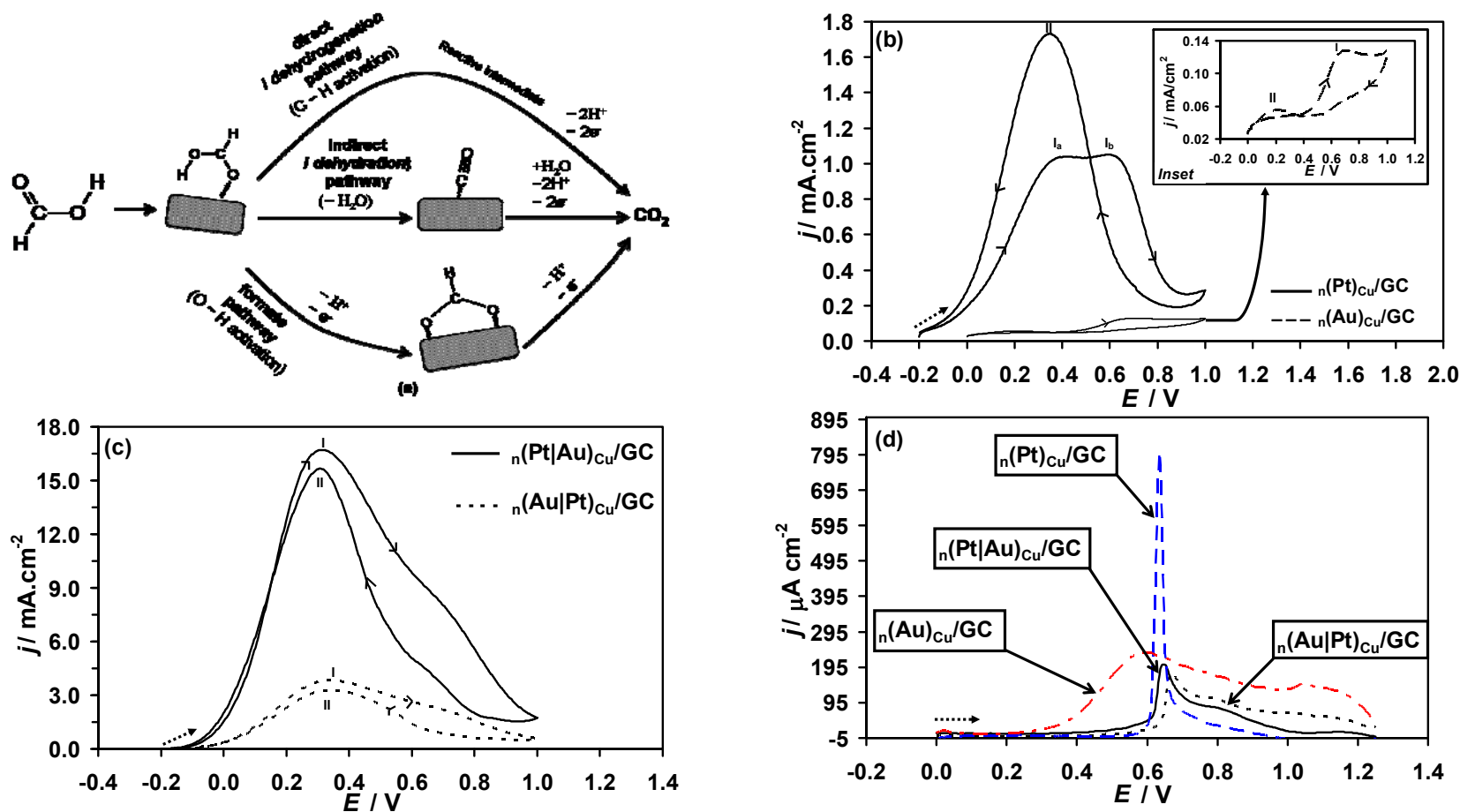
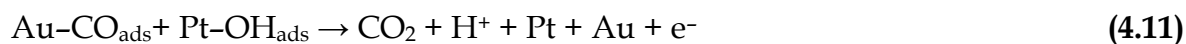
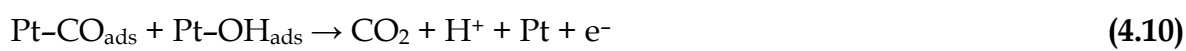
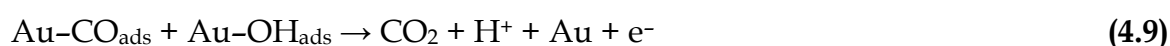
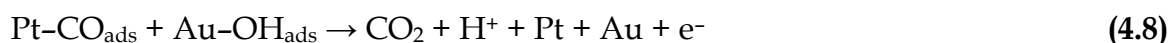


Figure 4.12: (a) Scheme showing plausible mechanistic aspects of formic acid electro-oxidation. (b)-(c) Cyclic voltammograms related to formic acid oxidation reaction (FAOR) on monometallic and bimetallic nanoclusters of Pt and Au; scans were carried out in N_2 -saturated 0.5 mol/L HCOOH (in 0.1 mol/L HClO_4) in the anodic direction to +1 V (as indicated by the dotted arrows), followed by cathodic direction; 5th cycles were taken for this analysis. (d) Linear sweep voltammograms of CO electro-oxidation after CO-saturation in 0.1 mol/L HClO_4 on the monometallic and bimetallic systems. In all cases, the scan rate was 50 mV/s and $n = 8$.

The CO_{ads} ASV observations were similar to those of ASV involving Cu UPD (Recall Figure 4.9). The observed CO electro-oxidation suppression on the bimetallic systems relative to monometallic Pt, as evidenced by the drastic change in intensity and shape of the peaks, strongly indicate the influence of Au in the bimetallic systems. Indeed, the positive potential shifts in CO_{ads} stripping peaks of the bimetallic systems relative to monometallic Pt have been observed on Au-Pt alloy and Pt-decorated Au nanoparticles and attributed to oxidation of CO through Langmuir-Hinshelwood mechanism with strong adsorption of CO [316,317]. On the basis of the bifunctional mechanism, DFT studies on the oxidation of adsorbed CO_{ads} indicate that the process may take place through one of the pathways shown in Reactions 4.8 to 4.11, where the oxygen source to form OH_{ads} required is considered to mainly originate from dissociated water on the metallic sites [318]:



DFT calculations on trimers of the type Au₃, Pt₃, Au₂Pt, and AuPt₂ showed that the surface reaction of CO_{ads} with OH_{ads} is energetically more favourable on the alloy trimers than the pure metals.[318] Further DFT models on CO oxidation on Pt_mAu_n (m + n = 4) clusters by Wang and co-workers [216] indicated that the interaction of CO with Pt in bimetallic clusters is stronger than that with Au. The preceding computational models also revealed that Au atoms play a binary role, that is; to avoid excessive adsorption around the catalytically active Pt centers and to electronically stabilize the active centers [216].

The voltammetric results of Figure 4.12 strongly suggest that FAOR on the bimetallic nanoclusters investigated in this work proceeded more preferentially through the dehydrogenation pathway than the other FAOR pathways, which appeared to have been favoured on the monometallic Pt nanoclusters. Since in acidic electrolytes, Au is not as effective as Pt in producing surface oxygenated

species to facilitate oxidation of CO_{ad} , and therefore the bifunctional effect alone could not be responsible for the enhanced electrocatalytic activity of the bimetallic surfaces in the FAOR [175]; ensemble and electronic effects between Au and Pt interfacial sites, uniquely generated in our synthetic protocols, are likely to be at play in promotion of the FAOR on the bimetallic systems. The subtle differences in CO oxidation on the $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ and $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ systems most likely arose due to the slight changes in surface-sensitive synergistic effects on uniquely positioned active sites of the respective nanocluster systems and/or due to their compositional differences as confirmed by XPS and ICP-MS.

4.3.5.2. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) [253] was deployed to further probe interfacial charge-transfer and adsorptive properties related to the FAOR on the various nanocluster-type electrodes. Impedance responses were obtained in N_2 -saturated stationary solutions of 0.5 mol/L HCOOH in 0.1 mol/L HClO_4 at E_{appl} of 0.0 V and 0.1 V, respectively; the potentials were chosen so that the electro-oxidation process was expected to proceed with initial adsorption of reactants or intermediates, high degree of kinetic-control and without much perturbation from formation of CO_2 – conditions that ensured high extent of linearity in the EIS measurements [253]. Modelling of the EIS data was performed through Complex Non-Linear Least-Squares (CNLS) curve-fitting procedures involving equivalent circuits. CNLS fitting using equivalent circuits is used to extract relevant parameters of electrochemical processes with supposition that the electrode and the processes occurring on it behave like typical electrical elements in conventional circuits [253]. Moreover, it is known that equivalent circuits for electrodic processes with adsorbed species generally should contain at least one capacitor (C) or inductor (L) in addition to the double-layer capacitance (C_{dl}), the charge-transfer resistance (R_{ct}) and solution resistance (R_{s}) [319].

In this work equivalent circuits (Circuits A, B, and C; in Figure 4.13a) consisted of elements R_{s} , R_{ct} , a constant-phase element (CPE_{dl}) to account for electrode double-layer, pseudo-capacitance related to adsorption (C_{ads}) and the corresponding resistor element associated with any resistance due to adsorptive processes (R_{ads}).

Table C.1 in **Appendix C** summarizes appropriate mathematical expressions of the total impedance (Z_T) and the corresponding real component (Z') and imaginary component (Z'') as functions of frequency (ω) for Circuits A, B, and C. Near-semicircular Nyquist plots and their corresponding fitted curves using Circuits A, B, and C (that is, complex plots of Z' versus Z'') are shown in Figure 4.13b-d.

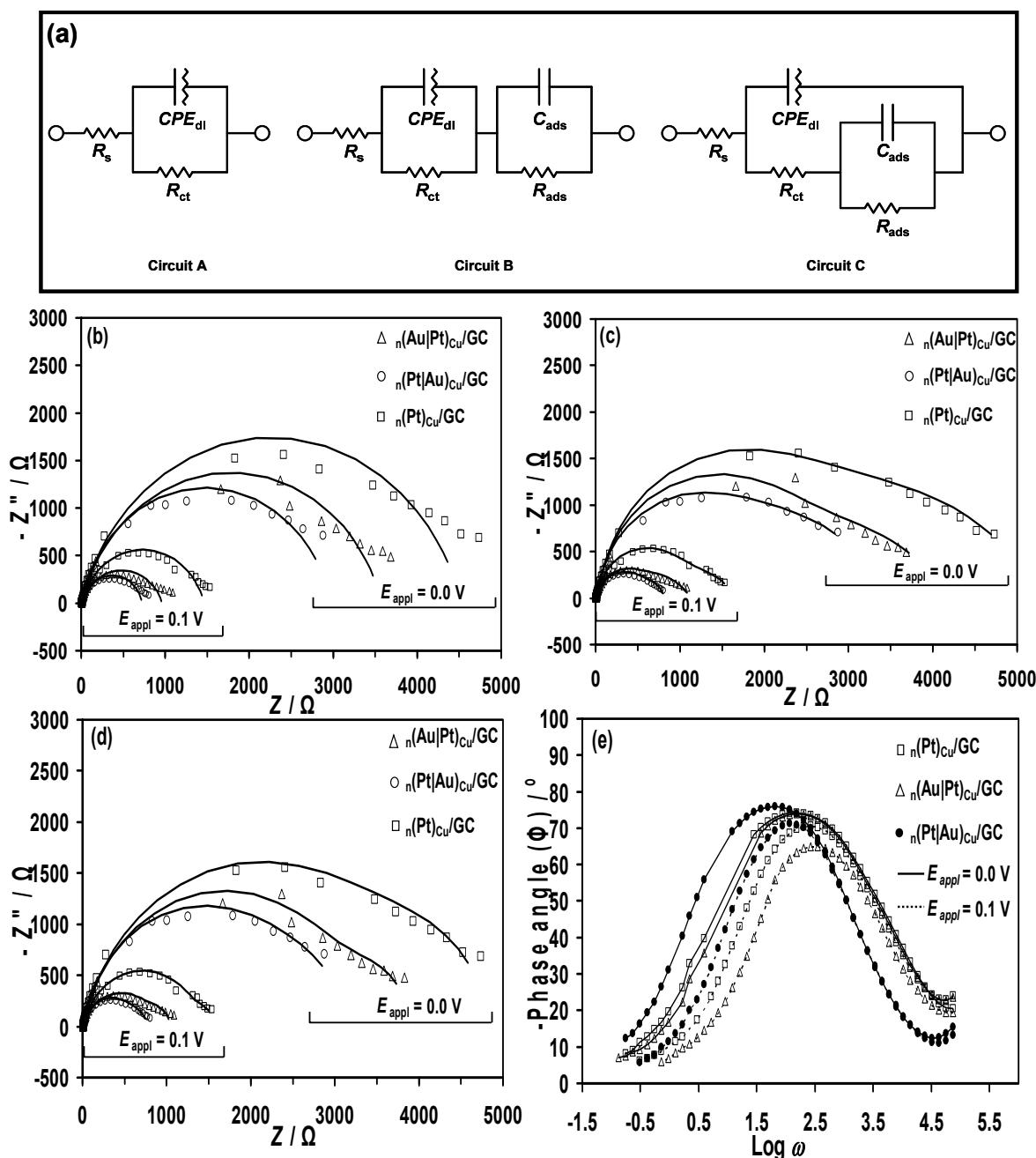


Figure 4.13: (a) Equivalent circuits used for modelling electrochemical impedance responses of the Pt-based electrocatalysts. (b) - (d) Complex plane impedance plots (Nyquist plots) fitted using (b) Circuit A, (c) Circuit B, and (d) Circuit C; points are experimental data and solid lines correspond to fitted curves. (e) Bode plots of impedance responses. All measurements were performed from N_2 -saturated 0.5 mol/L $HCOOH$ (in 0.1 mol/L $HClO_4$) solutions.

Qualitatively, the near-semicircular plots decreased with increasing E_{appl} , indicating less charge-transfer resistance at higher E_{appl} , consistent with accelerated rate of the FAOR at the more positive potential. Furthermore, the $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ electrode exhibited the smallest semicircular Nyquist plots, indicating the least charge-transfer resistance on the nanocluster electrode. The Bode plots, that is, graphical representations of the variation in phase angle (Φ), defined by Equation 4.12, as a function of the frequency of the EIS perturbation signal are shown in Figure 4.13e.

$$\Phi = \tan^{-1} \left(\frac{Z''}{Z'} \right) \quad (4.12)$$

The broad nature of the Bode plots, with amplitudes extending more than one frequency decade were indicative of multiple processes on the nanocluster electrodes with various time constants [281]. At E_{appl} of 0.0 V the Bode plots of the monometallic $n(\text{Pt})_{\text{Cu}}/\text{GC}$ and bimetallic $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ systems exhibited almost the same phase angles at the high frequency regions; this was indicative of very similar initial resistive behaviours on the $n(\text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ nanocluster electrodes. Furthermore, the Bode plot for the bimetallic $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ electrode exhibited the narrowest peak, and distinct phase angle response at the high frequency region (negatively shifted as compared to the $n(\text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ systems) – possibly due to the least resistive behaviour and least number of adsorptive species on the $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ electrode. Increasing E_{appl} to 0.1 V led to a general decrease and a shift to higher frequencies in the phase angle maxima, consistent with the increase in the overall reaction rate of the FAOR at more positive applied potentials.

Table C.2 (**Appendix C**) summarises extracted parameters from CNLS curve-fitting of EIS spectra of FAOR on the various nanostructured electrodes under consideration. In general, better fits were obtained utilizing either Circuit B or C (Figure 4.13c-d) – scenarios which included simulation of adsorptive processes – as compared to fits obtained with Circuit A (Figure 4.13a) which excluded circuit elements simulating adsorption. These observations strongly suggested that adsorptive processes were occurring in parallel to the charge-transfer processes. In the series of measurements on the various nanocluster electrodes computed R_s

values observed were in the range of 4 – 7 Ω showing that the solution conductivity was excellent and the electrolyte properties had inconsequential variations during various EIS measurements. For both EIS measurements (at 0.0 V and 0.1 V), R_{ct} values decreased in the order $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC} > n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC} > n(\text{Pt})_{\text{Cu}}/\text{GC}$, firmly indicating that the overall reaction rate of the FAOR was highest on the bimetallic electrode $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ and lowest on the monometallic $n(\text{Pt})_{\text{Cu}}/\text{GC}$.

In the case of parameters related to CPE_{dl} (see Table C.2 in **Appendix C**), the empirical parameter α was in the range 0.6 – 0.8, due to surface inhomogeneities of the nanocluster electrodes as a result of their characteristic morphologies as was observed above using microscopy.

The average double-layer capacitance (C_{dl}) values were estimated for the various nanocluster electrodes using mathematical relationships involving the constant Q , α , R_s , and R_{ct} detailed in Table C.1 (**Appendix C**). In the cases of monometallic electrode $n(\text{Pt})_{\text{Cu}}/\text{GC}$ and bimetallic $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ electrode systems, for both EIS measurements at 0.0 V and 0.1 V, the C_{dl} values, for a given equivalent circuit, were comparable within the range 2.7 – 4.5 μF . On the other hand, the bimetallic system $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ markedly exhibited higher C_{dl} values in the range 16 – 25 μF . For all nanocluster electrodes, there was a general decrease in the magnitude of R_{ads} as the perturbation potential increased from 0.0 V to 0.1 V, irrespective of the equivalent circuit used; this trend was consistent with an accelerated reaction at the more positive potential which was probably accompanied by faster rate of removal of adsorbed reactant molecules and formed intermediate species off the nanocluster surfaces. Furthermore, the lowest R_{ads} values were observed for the $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ electrode. Highest C_{ads} values were also obtained for the bimetallic $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ electrode as a result to its most electroactive characteristics and unique distribution of surface and near-surface Pt and Au atoms as was that led to it having most pronounced adsorptive properties related to the FAOR.

4.4. Summary

This chapter described detailed studies on multilayered Pt and/or Au-containing nanoclusters (as monometallic or bimetallic systems) were effectively prepared

utilizing multistage electrochemical deposition strategies involving templating Cu adlayers (generated by potentiostatic electrodeposition at underpotential or overpotential about the equilibrium potential of the $\text{Cu}^{2+}/\text{Cu(s)}$ redox couple) and SLRR reactions of such adlayers involving PtCl_6^{2-} and AuCl_4^- , with intermediate steps of *in situ* potentiostatic dealloying of any subsurface Cu. *E*-pH models and open-circuit potential variations observed experimentally strongly indicated that Pt(s) and Au(s) were the main forms expected after completion of SLRR reactions at various deposition stages. The resulting nanocluster-like multilayered electrodic systems obtained were subjected to various characterizations for their bulk composition, surface area, near-surface atomic distribution topographic and morphological features using microscopic, spectrophotometric, spectroscopic, and electrochemistry techniques.

Microscopy revealed well-dispersed nanoclusters, where close proximity of electrochemically-active sites on the glassy carbon surface led to some fused nanoclusters with similar heights and diameters, most likely as a consequence of independent multilayer growth paths on the various active sites where nucleation was initiated. Surface electrochemical studies of the nanoclusters revealed Pt and Au electrochemically-active sites, in their monometallic forms, and both Pt and Au active sites in the corresponding bimetallic forms. Anodic stripping voltammetric studies on the nanoclusters exhibited typical features of polycrystalline electrodes indicating that the growth pattern of the nanoclusters, whether monometallic or bimetallic, resulted in formation of various electrochemically-active crystallographic facets. Total metal content analysis using inductively-coupled plasma spectrophotometry informed us that sequential codeposition, to generate the alloy-type bimetallic system (Au-Pt), led to preferential deposition of the nobler Au, in which case the content of Pt was greatly suppressed. X-ray photoelectron spectroscopic studies showed typical features of glassy carbon surface functionalities, mainly involving multiple forms of carbon and oxygen such as carbonyl and hydroxyl groups and their plausible interactions with the noble metal nanoclusters, effectively stabilizing them. Moreover, XPS investigations showed that mixed microstates of Pt and Au were clearly generated in the nanoclusters due to interfacial bimetallic interactions consistent with multilayer growth pattern of the

deposited nanoclusters which were predominantly zero-valent Pt and Au forms whose surface to near-surface distribution depended on the sequence of their deposition.

The most electrochemically-active Pt-based nanocluster electrode system was the bimetallic form $n(\text{Pt} | \text{Au})_{\text{Cu}}/\text{GC}$ followed by $n(\text{Au} | \text{Pt})_{\text{Cu}}/\text{GC}$ and the least active was the monometallic $n(\text{Pt})_{\text{Cu}}/\text{GC}$. Electrocatalytic studies on the nanocluster electrodes, for the test reactions involving direct formic acid oxidation and carbon monoxide oxidation, firmly revealed that the Pt-rich $n(\text{Pt} | \text{Au})_{\text{Cu}}/\text{GC}$ appeared to have superior electrocatalytic activity followed by $n(\text{Au} | \text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Pt})_{\text{Cu}}/\text{GC}$; the monometallic system $n(\text{Au})_{\text{Cu}}/\text{GC}$ exhibited the least electrocatalytic activity. The direct (or dehydrogenation) pathway of formic acid was likely predominant on the bimetallic systems, whereas either the indirect or formate pathways most likely occurred preferentially on the monometallic Pt systems.

CHAPTER V

Kinetics and Thermodynamics of Phase Formation via Surface-Limited Reactions in Electrosynthesis of Multilayered Platinum on Gold

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5.1. Introduction

In the previous chapters we explored various aspects related to the influence of deposition pathways, equilibrium speciation, surface as well as bulk properties of electrocatalytic multilayered nanocluster electrodes fabricated through multistage deposition routes involving stepwise SLRR reactions.

In a typical SLRR reaction (Reaction 5.1), an adlayer of a metal M formed electrochemically through underpotential deposition (UPD) [159,160] on a substrate S (M_{UPD}/S ; Reaction 5.2), is spontaneously re-oxidized by open-circuit (OC) contact with ions $N^{\text{P}+}$ of a more noble metal N ; the overall process culminates in formation of an adlayer of metal N on S [170,193].



This chapter systematically scrutinises the underlying reaction kinetics and thermodynamics of multistep SLRR reaction involving underpotentially deposited Cu adlayers (Cu_{UPD}) as employed in formation a multilayered Pt system. Our approach adopts general electrochemical adsorption models within the Langmuir, Temkin and Frumkin isotherm frameworks [193,196,198,203]. The chapter probes quantitatively the underlying adlayer phase formation kinetics as well as thermodynamics via Cu_{UPD} and sequentially-implemented SLRR reaction involving PtCl_6^{2-} ions and the adlayers. An in-depth exploration of the interplay of substrate heterogeneity effects, mass-transport, phase formation kinetics and thermodynamics of SLRR reactions as implemented through successive deposition cycles of Reaction (5.1) carried out *in situ*. By implication, the substrate S is initially a crystalline Au film (Au_{film}) and upon successive deposition cycles it is gradually changed to a layered Pt system.

The findings reported herein underpin applicability and generality of submonolayer potential formalism to probe SLRR phase formation processes, whereby not only electrodic monolayered Pt, but also sequentially-generated multilayered Pt nanostructures are involved. Trends in the modelled adatom interactions involved

during Cu_{UPD} and associated SLRR process are also deduced. In general, the chapter will shed fundamental light on the role of various physico-chemical phenomena that occur in electrochemical synthetic routes for noble metal adlayers via sequentially-implemented surface-limited reactions from a distinct Au crystalline substrate with respect to the stepwise formed layered Pt.

5.2. Experimental Details

5.2.1. Materials

All solutions were prepared with high-purity deionised water obtained from a Milli-Q water purifier (Millipore Inc., USA) operated at resistivity of $18 \text{ M}\Omega\cdot\text{cm}$. All electrochemical experiments were performed in air-conditioned laboratory environment of about 25°C . $1 \times 10^{-3} \text{ mol/L}$ aqueous precursor electrolyte solutions of PtCl_6^{2-} and Cu^{2+} were made in 0.1 mol/L HClO_4 ; they were prepared from analytical grade H_2PtCl_6 and CuSO_4 reagents and ultra-pure concentrated HClO_4 supplied by SA Precious Metals (Pty) and Merck, respectively. The 0.1 mol/L HClO_4 solution, at $\text{pH } 1 \pm 0.05$, was used as the background electrolyte (BE).

5.2.2. Electrochemical deposition

The custom-developed Labview virtual instruments and instrumentation described in Chapter 4 (with additional details in **Appendix A**) were used for all electrochemical deposition experiments. The setup consisted of piston pumps with electrolyte reservoirs in digitally-controlled exchange units (765 Dosimat, Metrohm Autolab, Netherlands), potentiostat/galvanostat (model PGSTAT30, Metrohm Autolab, Netherlands), and a three-electrode flow-cell using Ag/AgCl/3M KCl reference electrode (model 6.0727.000, Metrohm Autolab) – unless otherwise stated, potentials are reported versus this reference electrode. The deposition substrate (connected as the working electrode of the flow-cell – see Figure 5.1) was a piece of 300 nm vapour-deposited Au thin-film coated on a glass slide with a Ti adhesion layer as per preparations reported elsewhere [177]. Prior to flow-cell assembly for electrochemical deposition, the substrate Au_{film} was cleaned in concentrated HNO_3 by immersion for 120 s , rinsed with ultra-pure deionized water and, upon assembly in the flow-cell, by electrochemical cycling in the blank electrolyte.

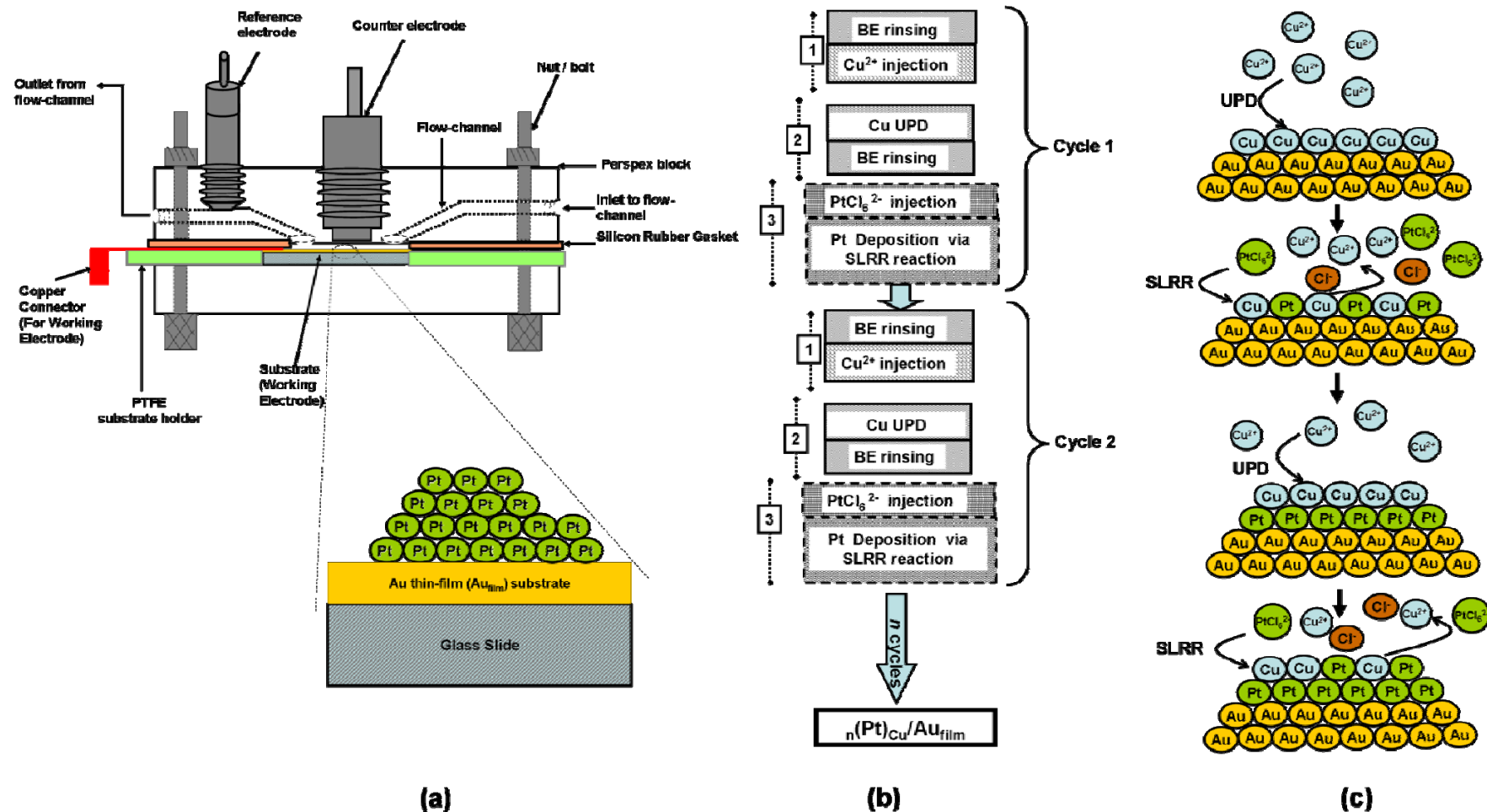


Figure 5.1: (a) Flow-cell assembly for electrochemical deposition on a gold thin-film substrate. (b) - (c) Schemes showing the sequential electrodeposition routes to form monometallic Pt multilayers on Au_{film} substrate via surface-limited redox-replacement reactions involving UPD of Cu.

Electrochemical experiments involving Anodic Stripping Voltammetry (ASV) and Cyclic Voltammetry (CV) were performed with the PGSTAT30 electrochemical workstation utilizing the software packages GPES 4.9 and NOVA 1.6 (Metrohm Autolab). Experiments on electrochemical characterization of the substrate Au_{film} as well as UPD of Cu on the substrate Au_{film} ($\text{Cu}_{\text{UPD}}/\text{Au}_{\text{film}}$) and subsequent oxidative dissolution of the Cu adlayer were carried out utilizing CV and ASV potentiostatic modes as applicable. All electrolyte solutions used during various experiments were nitrogen-saturated. Between the measurements the electrochemical cell was rinsed at open-circuit (OC) with the BE solution. Electrosynthesis of a multilayered Pt on Au_{film} – denoted as $n(\text{Pt})_{\text{Cu}}/\text{Au}_{\text{film}}$ – proceeded by repetition of n deposition cycles as depicted in Figure 5.1; the virtual instrument software module *Autolab-SeqDep-3pumps-Autorefill.vi* (**Appendix A**) was engaged, where a single cycle employed in formation of an adlayer of Pt involved three stages: (i) rinsing with the BE solution and injection of the sacrificial metal electrolyte, 1×10^{-3} mol/L Cu^{2+} , (ii) deposition of Cu adlayers at UPD followed by BE rinsing, and (iii) OC stage involving injection of 1×10^{-3} mol/L PtCl_6^{2-} electrolyte solution and allowance of SLRR reaction in quiescent solution. Injection of electrolyte solutions was carried out at flow-rate of 5 mL/min throughout all deposition cycles. Current-time (i - t) and potential-time (E - t) transients were simultaneously captured *in situ* during the various deposition stages at intervals of 0.2s.

5.2.3. Physical characterization

Field Emission Gun Scanning Electron Microscopy (FEG-SEM) was used for *ex situ* analysis of unmodified Au_{film} substrate using model ULTRA PLUS microscope with in-lens capabilities (CARL ZEISS, Germany) operated at 0.5 – 1 kV. X-ray Diffraction (XRD) analysis of the Au_{film} was performed with a model X'Pert PRO powder diffractometer (PANalytical B.V., The Netherlands) equipped with an X'Celerator detector with variable divergence and receiving slits utilizing iron-filtered cobalt- K_{α} radiation; the phases were identified using X'Pert Highscore plus software.

5.3. Theoretical basis

The relationship between surface coverage of adlayers generated by UPD (θ_{UPD}) and the activity of the depositing species in the coverage range $0 \leq \theta_{\text{UPD}} \leq 1$, may be approximated in terms of a thermodynamic formalism based on the concept of “submonolayer equilibrium potential” [196], formulated within the framework of equal electrochemical potentials of the parent species in solution and in the corresponding substrate phases. Effectively, the submonolayer equilibrium potential during a UPD process (Reaction (5.2)) can be defined as

$$E_{\text{UPD}} = E_{\text{UPD}}^{\circ} + \frac{RT}{zF} \ln \frac{a_{\text{M}^{z+}}}{a_{\text{M,UPD}}} \quad (5.3)$$

where R , T , z and F have their usual meaning; $a_{\text{M,UPD}}$ is the activity of adlayer of metal M at coverage θ_{UPD} (the latter is described by an appropriate potential-coverage isotherm); E_{UPD}° is the standard submonolayer potential which is related to the standard Gibbs free energy of the underlying UPD process by $\Delta G_{\text{UPD}}^{\circ} = -zFE_{\text{UPD}}^{\circ}$. Considering the Langmuir-type isotherm, E_{UPD} dependence on the submonolayer coverage can be described by Equation 5.4 [196,198]:

$$E_{\text{UPD}} = E^{\theta=0.5} - \frac{RT}{zF} \left[\ln \left(\frac{\theta_{\text{UPD}}}{1 - \theta_{\text{UPD}}} \right) \right] \quad (5.4)$$

where $E^{\theta=0.5}$ corresponds to the potential of surface coverage of 0.5 at unit solution activity.

More complex processes can be modelled through a generalized Temkin-Frumkin-type electrochemical isotherm given by Equation 5.5 [196,198,201]:

$$E_{\text{UPD}} = E^{\theta \rightarrow 0} - \frac{RT}{zF} \left[\ln \left(\frac{\theta_{\text{UPD}}}{1 - \theta_{\text{UPD}}} \right) + f\theta_{\text{UPD}} + g\theta_{\text{UPD}}^{3/2} \right] \quad (5.5)$$

where the parameter $E^{\theta \rightarrow 0}$ represents the potential where UPD monolayer formation approaches zero-coverage at unit solution activity; f is an interaction parameter which accounts for (i) heterogeneity effects, (ii) induced work-function changes

accompanying surface adlayer formation, and (iii) adatom–substrate interactions; g is an interaction parameter which accounts for lateral adatom–adatom interactions (of electrostatic dipole–dipole nature) that may arise due to charge polarization between the adatoms [196,201]. Additionally, the f and g parameters largely determine the change of the Gibbs free energy of adlayer formation (ΔG_{UPD}) with coverage θ_{UPD} which can be approximated by Equation 5.6:

$$\Delta G_{\text{UPD}} = \Delta G^{\theta \rightarrow 0} + RTf\theta_{\text{UPD}} + RTg\theta_{\text{UPD}}^{3/2} \quad (5.6)$$

where $\Delta G^{\theta \rightarrow 0} = -zFE^{\theta \rightarrow 0}$.

Focusing on the SLRR process involving phase formation of an adlayer of the more noble metal N (Reaction 5.1), its overall rate (r_{SLRR}) can be described by Equation 5.7 as either a time-dependent incremental change of surface concentration of the UPD metal adlayer ($C_{\text{M,UPD}}$) or the change in the surface coverage $\theta_{\text{M,UPD}} = \Gamma_{\text{i,UPD}}/C_{\text{M,UPD}}$ (where $\Gamma_{\text{i,UPD}}$ is the initial surface concentration at $t = 0$) [193]. By linking the potential dependency of UPD coverage (Equation 5.5) with appropriate rate equations resulting from Equation 5.7, potential-coverage-time kinetic models (Equations 5.8 – 5.10)[193] can be deduced. Such potential-coverage-time relationships were tacitly demonstrated to be useful for describing phenomenological reaction kinetics and phase formation properties of a single-step SLRR reaction - employed to form a monolayer Pt system on single-crystal Au(111) substrate [193]:

$$r_{\text{SLRR}} = -\frac{dC_{\text{M,UPD}}}{dt} = -\Gamma_{\text{i,UPD}} \frac{d\theta_{\text{M,UPD}}}{dt} \quad (5.7)$$

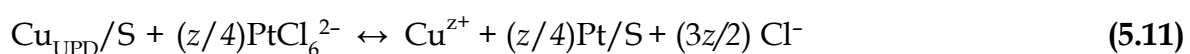
$$E_{\text{SLRR}} = E^{\theta \rightarrow 0} - \frac{RT}{zF} \left[\ln \left(\frac{1 - k_{\text{o}}t}{k_{\text{o}}t} \right) + f(1 - k_{\text{o}}t) + g(1 - k_{\text{o}}t)^{3/2} \right] \quad (5.8)$$

$$E_{\text{SLRR}} = E^{\theta \rightarrow 0} - \frac{RT}{zF} \left[-(k_{\text{r1}}t + \ln(1 - \exp(-k_{\text{r1}}t))) + f(\exp(-k_{\text{r1}}t)) + g(\exp(-k_{\text{r1}}t))^{3/2} \right] \quad (5.9)$$

$$E_{\text{SLRR}} = E^{0 \rightarrow 0} - \frac{RT}{zF} \left[\ln \left(\frac{(1 + k_{\text{r}}t)^{1/(1-N_{\text{or}})}}{1 - (1 + k_{\text{r}}t)^{1/(1-N_{\text{or}})}} \right) + f(1 + k_{\text{r}}t)^{1/(1-N_{\text{or}})} + g(1 + k_{\text{r}}t)^{3/(2-2N_{\text{or}})} \right] \quad (5.10)$$

where $E^{0 \rightarrow 0}$, f , g , R , T , z , and F have their usual meaning; N_{or} is the order of the reaction with respect to M_{UPD} adlayer; and E_{SLRR} is an open-circuit potential during adlayer formation through an SLRR reaction. k_0 in Equation 5.8 is a rate constant resulting from the limiting case involving transport-limited redox-replacement of UPD adlayers and a zero-order reaction mechanism ($N_{\text{or}} = 0$). In the case where a diffusional transport of noble metal ions $N^{\text{p}+}$ to the substrate's surface does not limit reaction kinetics, Equations 5.9 – 5.10 apply. In particular, Equation 5.9 is applicable for a first-order reaction mechanism with respect to M_{UPD} and the phenomenological rate constant $k_{\text{r1}} = k(C_{\text{N}^{\text{p}+}}^{\text{s}})^{J_{\text{or}}}(\Gamma_{\text{i,UPD}})^{N_{\text{or}}-1}$ where J_{or} stands for the order of reaction with respect to noble metal ions $N^{\text{p}+}$; k is the fundamental rate constant of the SLRR reaction; and $C_{\text{N}^{\text{p}+}}^{\text{s}}$ is the surface concentration of $N^{\text{p}+}$ ions. Equation (10) applies for $N_{\text{or}} \neq 0$ and $N_{\text{or}} \neq 1$; the phenomenological rate constant $k_{\text{r}} = k(C_{\text{N}^{\text{p}+}}^{\text{s}})^{J_{\text{or}}}(\Gamma_{\text{i,UPD}})^{N_{\text{or}}-1}(N_{\text{or}} - 1)$ [193].

This work embarked on such systematic investigation of phase formation involving, as a model system, consecutive SLRR reactions between Cu_{UPD} and PtCl_6^{2-} complex ion (Reaction 5.11).



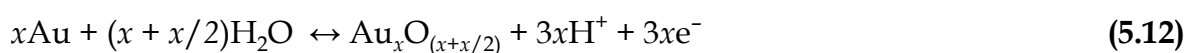
The interplay of substrate heterogeneity effects, mass-transport, phase formation kinetics and thermodynamics of SLRR reactions, as implemented through successive deposition cycles of Reaction (5.11) carried out *in situ*, is quantitatively modelled. By implication, the substrate S is initially a crystalline Au thin-film (Au_{film}) and upon successive deposition cycles it is gradually changed to a layered Pt system. The findings reported herein underpin applicability and generality of submonolayer potential formalism to probe SLRR phase formation processes, whereby not only electrodic monolayered Pt, but also sequentially-generated multilayered Pt nanostructures are involved.

5.4. Results and discussion

5.4.1. Characteristics of the Au_{film} substrate and thermodynamics of surface coverage by UPD of Cu

The morphology of the substrate Au_{film} is shown by FEG-SEM micrograph in Figure 5.2a; clear Au crystallites with distinct grain boundaries are visible. The XRD pattern (see Figure 5.2b) confirmed that the substrate had somewhat polycrystalline characteristics with prominent composition of (111)-oriented crystallites. The corresponding surface electrochemical behaviour of Au_{film} substrate is exhibited in representative cyclic voltammograms, CVs (Figure 5.2c); they are consistent with surface electrochemistry of a polycrystalline Au electrode in acidic medium in the potential window +0.5 V to +1.6 V.

In this regard, the general surface electrochemistry of Au is described by Reaction 5.12 [242,294], where gold can be transformed from oxidation state of 0 to +3:



The CVs of bare Au_{film} were obtained with maximum anodic potentials between +1.4 V and +1.6 V at various scan rates as shown in Figure 5.2c. Chronocoulometric analysis of the surface oxide reduction peak (Peak A; Figure 5.2c), upon scanning to +1.4 V, was consistent with surface adlayer coverage of about 1:1 oxygen-gold structure obtainable below this potential in accordance with known surface electrochemistry of Au electrodes [198,241,294,320].

Figure 5.2d depicts a typical CV involving the Cu²⁺/Cu(s) redox process in 0.1 mol/L HClO₄ on the Au_{film}; characteristically it shows the potential ranges where UPD and OPD of Cu occur in the vicinity of E_{eq} of the Cu²⁺/Cu redox couple (calculated at about 0.046 V using the Nernst equation taking the bulk concentration of Cu²⁺ ions as 1 × 10⁻³ mol/L). Surface coverage of Cu_{UPD}/Au_{film} was probed utilizing ASV at deposition potential (E_{dep}) of +0.05 V for variable deposition time (t_{dep}) as shown in Figure 5.3a; the broad doublet stripping peaks observed were consistent with the polycrystalline nature of Au_{film} used.

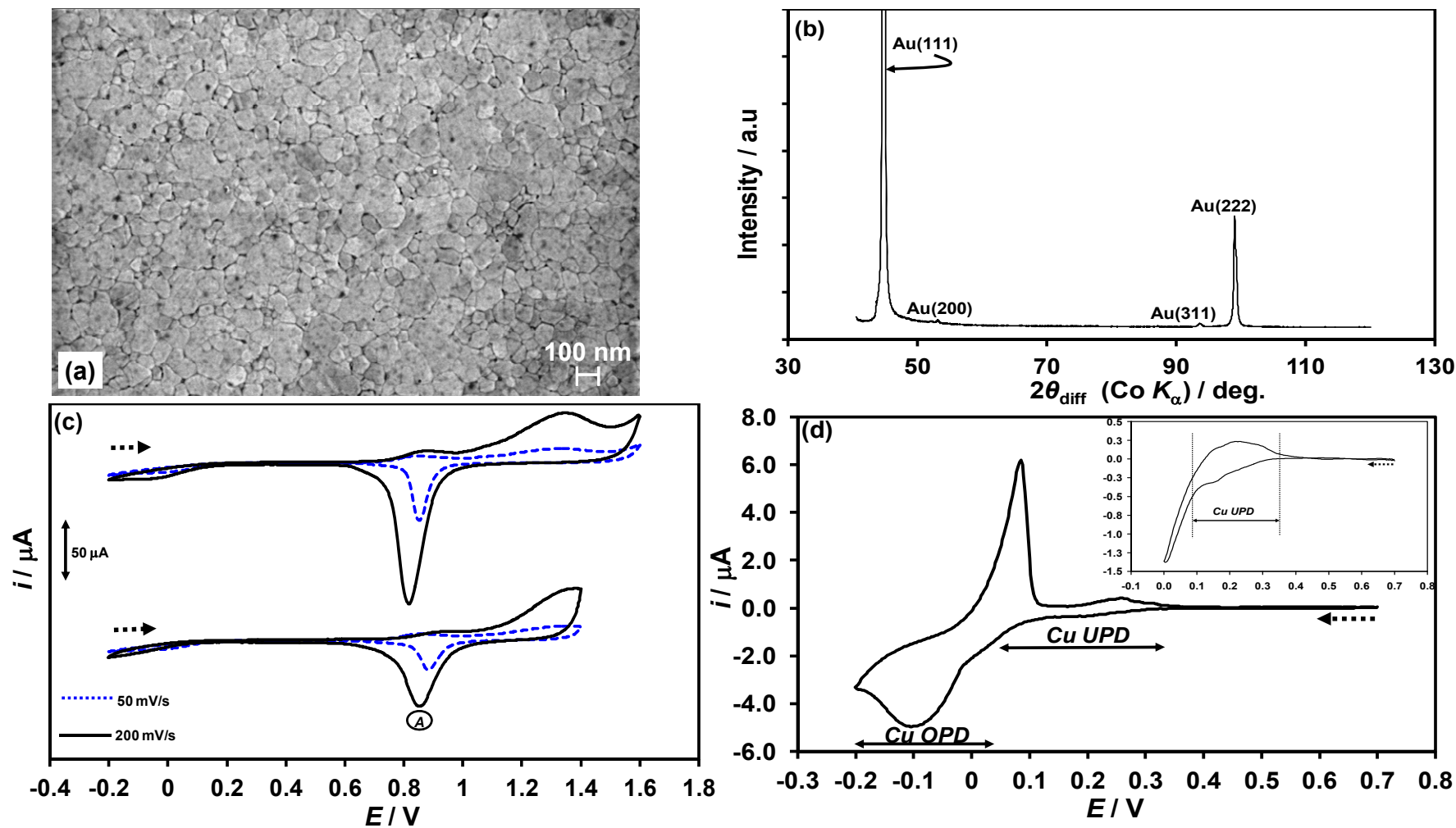


Figure 5.2: (a) FEG–SEM micrograph showing the morphology of a typical bare Au_{film} substrate. (b) XRD pattern of Au_{film}. (c) Representative CVs recorded on Au_{film} in 0.1 mol/L HClO₄ at indicated scan rates, showing Au surface oxide features (Peak A) – see text for details. (d) Representative CVs recorded on Au_{film} at a scan rate of 5 mV/s in 1 x 10⁻³ mol/L Cu²⁺ in 0.1 mol/L HClO₄ solution showing UPD and OPD of Cu; the inset is a CV recorded in narrower potential range. In all CVs the initial scanning was carried out in the direction indicated by the broken arrow.

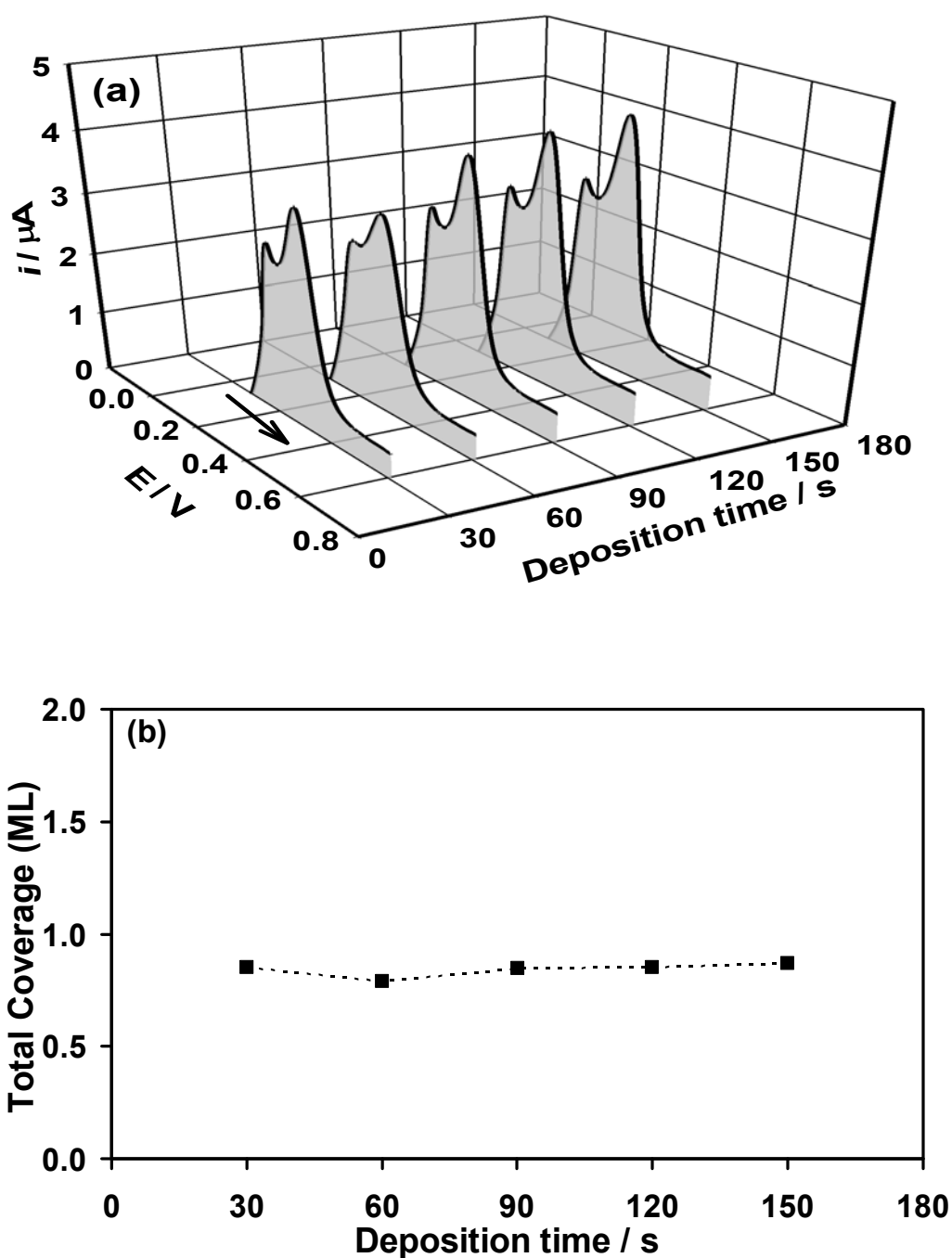


Figure 5.3: (a) ASV curves after UPD of Cu at +0.05 V for the indicated deposition time. (b) Trend in the total coverage in monolayer-equivalents for the $\text{Cu}_{\text{UPD}}/\text{Au}_{\text{film}}$ system derived from ASV for the applicable deposition time.

From the ASV study, the monolayer (ML) equivalent trend in the total coverage of Cu on Au_{film} was established as shown in Figure 5.3b, whereby the surface science convention was adopted, that is, one adatom for every substrate surface atom corresponds to one ML.

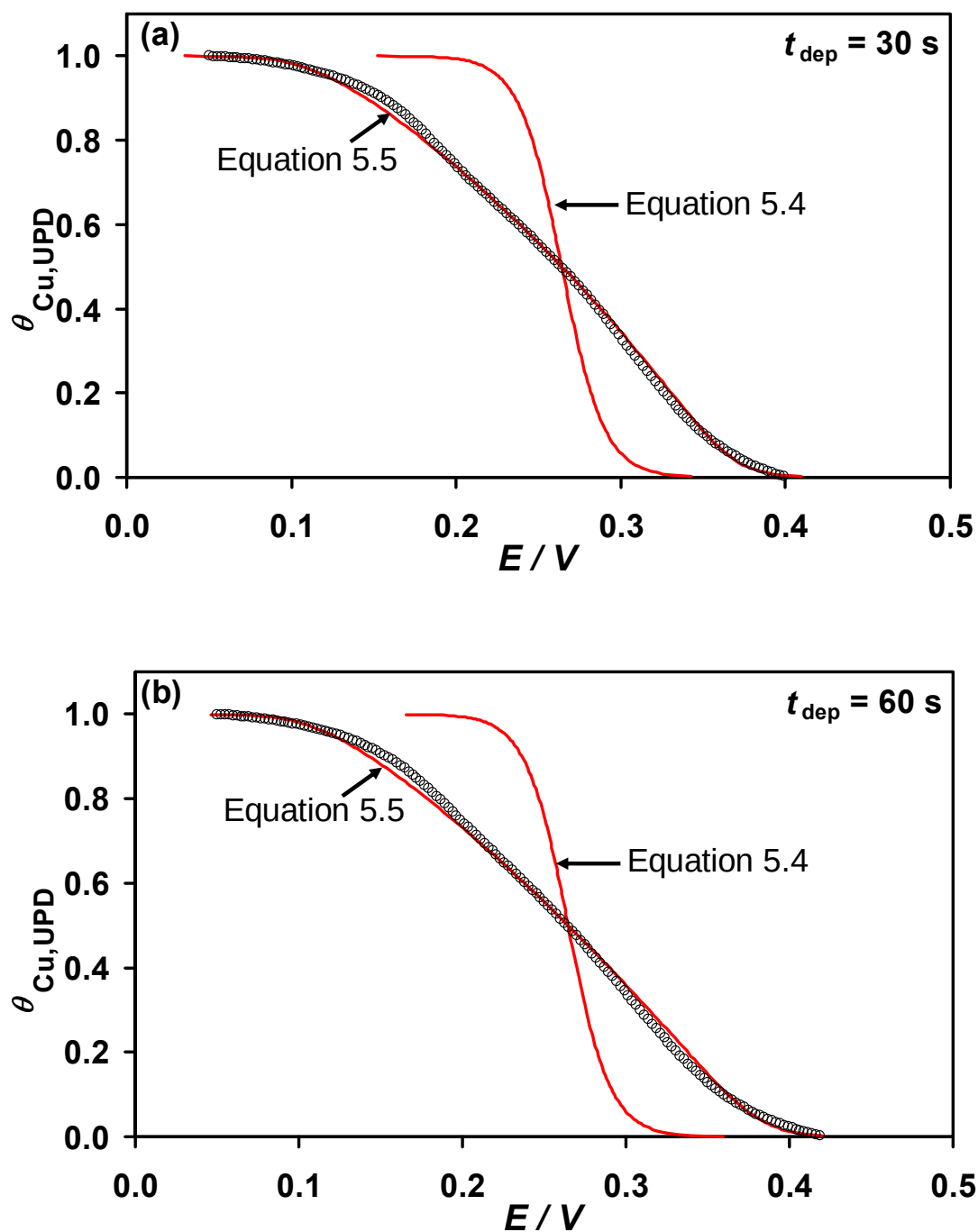


Figure 5.4: Representative electrochemical isotherms for Cu_{UPD}/Au_{film} obtained from analysis of ASV after deposition at 0.05 V for the indicated t_{dep} ; circles are experimentally-derived data and solid lines are fitted curves based on designated model isotherms.

The ML -equivalent coverage was derived from the total charge of the UPD process (Q_{UPD}), obtainable from integration of the corresponding stripping peaks, taking the area of the electrode as the electrochemical surface area A_{EAS} . In this regard, A_{EAS} was determined separately from CV recorded immediately prior to ASV measurements essentially by integration of the gold oxide reduction peak (peak A in

Figure 5.2c). Considering a presumable 1:1 oxygen/gold ratio of the surface oxide generated on the pristine Au_{film} in a neat nitrogen-saturated 0.1 mol/L HClO₄ solution, a nominal charge of 400 μC/cm² was taken as the conversion factor corresponding to the charge required for full 1:1 monolayer coverage on the crystalline Au film [160,198,222,248]. A reasonably steady total maximum coverage of about 0.8 was estimated in this way for t_{dep} between 30 and 150 s as shown in Figure 5.3b. Surface coverage of Cu_{UPD}/Au_{film} was probed utilizing ASV at deposition potential (E_{dep}) of +0.05 V for variable deposition time (t_{dep}). Surface coverage of Cu, as generated by UPD ($\theta_{\text{Cu,UPD}}$) on Au_{film}, was estimated by numerical integration using Equation 5.13 from the corresponding stripping voltammetric data.

$$\theta_{\text{Cu,UPD}} = \frac{Q_{\text{Cu,str}}}{Q_{\text{Cu,max}}} = \frac{\int_{t_j}^{t_q} i dt}{Q_{\text{Cu,max}}} = \frac{\frac{1}{v} \int_{(E_j - E_0)/v}^{(E_q - E_0)/v} i dE}{Q_{\text{Cu,max}}} \quad (5.13)$$

where v is the potential sweep scan rate (dE/dt), E_0 is the starting potential of ASV scan, $Q_{\text{Cu,str}}$ is the total charge from oxidative stripping of Cu from the time t_j at potential E_j to a final time t_q at potential E_q ; the maximum possible charge, $Q_{\text{Cu,max}}$, was determined from the corresponding A_{EAS} of the pristine Au_{film} described above.

Analysis of potential-coverage ($\theta_{\text{Cu,UPD}} - E_{\text{UPD}}$) relationship for Cu_{UPD}/Au_{film} system, employing Equations 5.4 – 5.5, was carried out by multivariate nonlinear curve-fitting for various deposition times, with $E^{\theta \rightarrow 0}$, f , g , and z as fitting parameters. A representative Cu_{UPD} surface coverage plot (circles) and fitted curves (solid lines) are shown in Figure 5.4; noticeably, the Langmuirian model of Equation 5.4 resulted in inadequate description of the $\theta_{\text{Cu,UPD}} - E_{\text{UPD}}$ data. From fitting operations using Equation 5.5, $E^{\theta \rightarrow 0}$ was systematically found to be in the range 0.330 ± 0.030 V for fitted $\theta_{\text{Cu,UPD}} - E_{\text{UPD}}$ data sets; remarkably, corresponding to the maximum peak potential of the ASV curves (shown in Figure 5.3a) where complete electro-oxidation of Cu⁰ adatoms to Cu²⁺ ions is expected to take place. Moreover, in cases when all isotherm fitting parameters were varied, an average z value of about 1.5 (± 0.2) was obtained; a value indicative of an overall two-electron redox process involving Cu adlayer dissolution from the Au_{film} substrate (Cu⁰/Cu²⁺ couple).

Moreover, the f parameter, obtained from analysis of $\theta_{\text{Cu,UPD}} - E_{\text{UPD}}$ with Equation 5.5, was found to be rather sensitive to t_{dep} . In this regard, for t_{dep} 30 and 60 s the generated f values varied between 1 and 5, whereas for t_{dep} 90 to 150s they varied between -9 and -13. Markedly, regardless of t_{dep} , consistent positive g values (in the range 10 - 24) were retrieved. Since the f value, in addition to accounting for substrate-adatom interactions and crystalline heterogeneities, could also be indicative of some variations in the substrate's work function upon Cu UPD and its adlayer coverage depletion [196,198]. Hence, longer deposition times (> 90s) might have induced some surface reconfiguration and/or surface alloying between Cu and Au resulting in negative f values observed. Since Cu and Au have atomic radii of 0.145 nm and 0.174 nm, respectively, and both metals have cubic-close packed lattice structures, adatom-substrate interactions were expected to be less significant due to the intrinsic heterogeneities of the polycrystalline substrate and the relatively small lattice mismatch between Cu adatoms and Au surface atoms [31,157,159,198].

However, the consistent large positive g value, obtained with Equation 5.5, was strongly suggestive of prevalent Cu adatom-adatom lateral repulsive interactions. Considerable electronegativity differences between Cu and Au, which in the Pauling scale are 1.9 for the former and 2.4 for the latter [31] plausibly effected some significant charge polarization on the Cu adatoms leading to formation of surface dipoles. In addition, positive values of lateral Frumkin-type interaction parameter involving voltammetric Cu_{UPD} on polycrystalline Pt substrate in acidic medium have also been interpreted to involve Cu-H interactions, in addition to Cu-Cu neighbouring adatoms interactions, where the H-atoms are derived from adsorbed water in the vicinity of the surface active sites of deposition [202].

The contributions of f and g on the monolayer free energy variation with Cu_{UPD} coverage were clearly observed in plots of ΔG_{UPD} vs. $\theta_{\text{Cu,UPD}}$ from Equation 5.6 (results not shown); the ΔG_{UPD} trend confirmed the spontaneous Cu_{UPD} phase formation where energetics favour the diminishing surface coverage [196,198].

Having inspected direct Cu_{UPD} monolayer phase formation features on the Au_{film} as a base substrate, it was of great interest and importance to interrogate the trends in the underlying parameters for the Cu_{UPD} adlayer involvement in successive SLRR

reactions with PtCl_6^{2-} (employed to generate multilayered Pt). The systematic analysis of kinetics and thermodynamics of these layer-by-layer phase-forming processes is discussed in the following sections.

5.4.2. Physico-chemical analysis of deposition processes of the multilayered $\text{n(Pt)}_{\text{Cu}}/\text{Au}_{\text{film}}$ electrode system

Figure 5.5a shows typical potential transients corresponding to various deposition stages as recorded *in situ* during the stepwise formation of the multilayered Pt system $\text{n(Pt)}_{\text{Cu}}/\text{Au}_{\text{film}}$. The potential transients (Figure 5.5a) clearly show pre-treatment steps involving rinsing with the background electrolyte (BE) solution (Stage 1) at +0.2 V, phase formation of Cu_{UPD} (Stage 2) at +0.05 V for 90 s, and open-circuit (OC) injection of PtCl_6^{2-} electrolyte solution followed by Pt deposition via SLRR reaction (SLRR_{Pt} , Stage 3) where replacement of the Cu_{UPD} with Pt adlayers took place. Typical CV signatures prior to and after carrying out the multistage deposition are shown in Figure 5.5b. The disappearance of the Au electrochemical surface feature [294] on the $\text{n(Pt)}_{\text{Cu}}/\text{Au}_{\text{film}}$ electrode system - Au surface oxide reduction process (Peak A in Figure 5.5b), as per Reaction 5.12, was confirmation of successful Pt adlayer coverage on the Au_{film} . Moreover, Pt surface electrochemistry [222] is clearly observed on the $\text{n(Pt)}_{\text{Cu}}/\text{Au}_{\text{film}}$ by: (i) recognition of well-pronounced reduction feature of Pt surface oxide layer (Peak B with maximum at 0.4 V), proceeding mainly via Reaction 5.14, and (ii) typical hydrogen UPD features on polycrystalline Pt described in Chapter 2 involving the hydrogen adsorption-desorption reaction (Reaction 5.15) in the potential range between 0.0 V and -0.2 V (Potential Region C in Figure 5.5b).



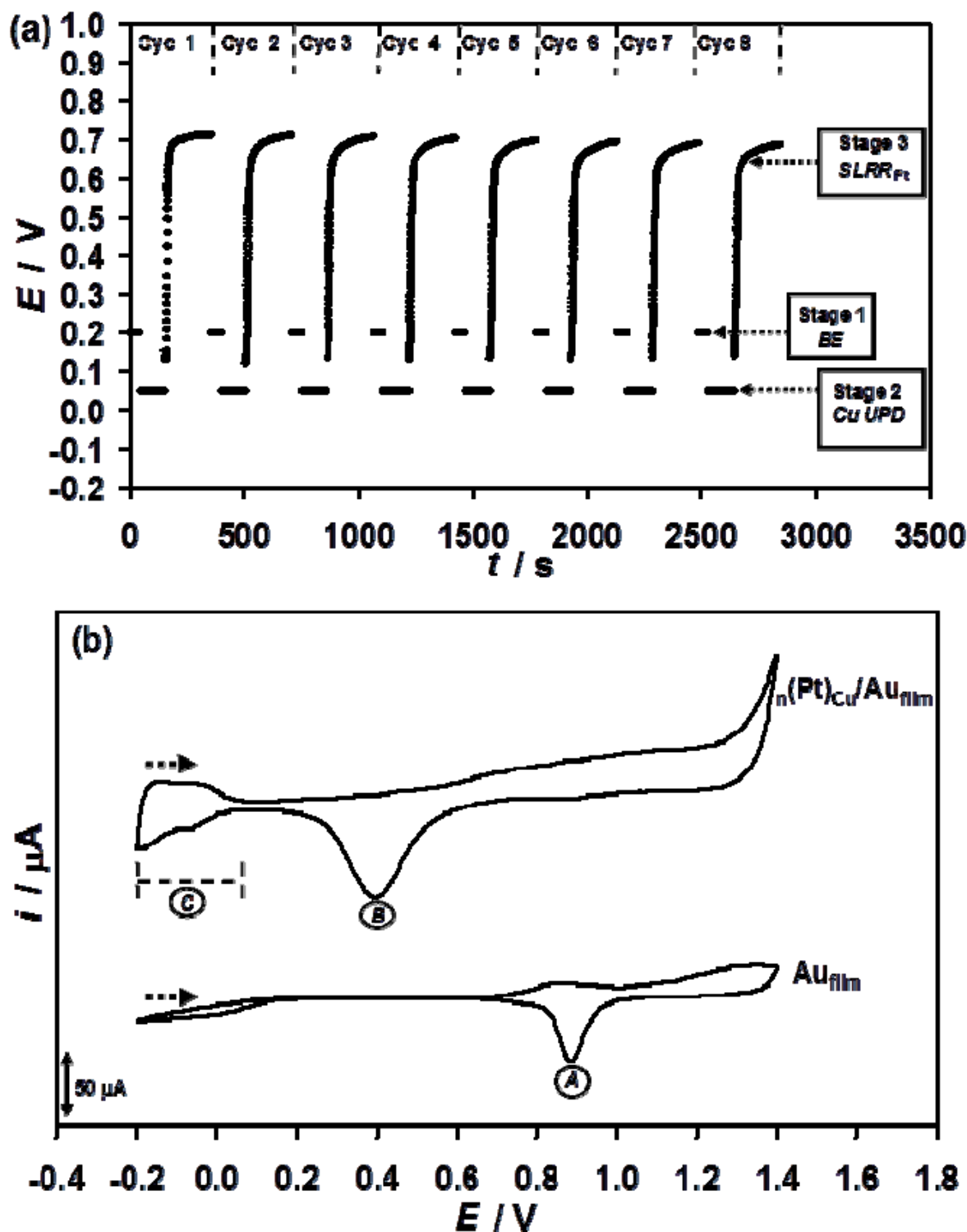


Figure 5.5. (a) Potential transients recorded *in situ* during multistage deposition of the multilayered Pt electrode system $n(Pt)_{Cu}/Au_{film}$ via SLRR reaction involving Cu_{UPD} and $PtCl_6^{2-}$ (SLRR_{Pt}). 0.1 M $HClO_4$ was the background electrolyte used for preconditioning and rinsing purposes between UPD of Cu and SLRR_{Pt}; Cyc = deposition cycle. (b) CVs of bare Au_{film} and $n(Pt)_{Cu}/Au_{film}$ after eight deposition cycles recorded in 0.1 M $HClO_4$ at scan rate of 50 mV/s. The initial scanning direction is indicated by broken arrows.

5.4.3. Modelling adlayer phase formation during SLRR_{Pt}

Having confirmed formation of Pt adlayers on Au_{film}, an investigation of the kinetics and thermodynamics during formation of such adlayers involving Reaction 5.11 for various deposition cycles was undertaken. To this effect, general analytical models of Equations 5.8 – 5.10 were systematically tested to describe the time-dependent SLRR phase formation through regression analysis performed on E_{SLRR} transients (Stage 3, Figure 5.5a). In this case, besides the phase formation parameters f , g , and $E^{\theta \rightarrow 0}$, the phenomenological reaction kinetic parameters (k_o , k_{r1} , k_r and N_{or}) were also optimized for consecutive deposition stages. With neither presumption of the underlying nature of transport-limitations of ionic species involved nor imposing the reaction order N_{or} , the overall modelling approach was such that the analytical models of Equations 5.8 – 5.10 were separately tested to describe the E_{SLRR} transients.

Employing either Equation 5.8 or 5.9, to fit the appropriate potential transients, resulted in non-convergence; this strongly suggested that during respective deposition cycles (i) the diffusion flux of PtCl_6^{2-} ions from the solution phase to the substrate surface was much larger than the rate of SLRR reaction, and (ii) reaction mechanisms with non-zero N_{or} occur [193], regardless of z being set at either 1 or 2 (considering possible stable oxidation states of Cu). Consequently, the analysis of E_{SLRR} transients was then focused on the parameters determined by use of Equation 5.10. The aforementioned model yielded best-fit solutions, but only when z was constant at the value of 2 (representative fitted transients are shown in Figure 5.6 and fitting results given in Table 5.1). Hypothetical fitted potential curves, where z was set at 1, are shown in *Insets* of Figure 5.6; markedly, for all the cycles tested, the scenario of z being unity was implausible. Modelling results of phase formation of SLRR_{Pt} revealed a distinct decrease in the value of k_r (the phenomenological overall reaction constant in this model) between the first deposition cycle (which exclusively involved Pt adlayer formation on the Au substrate) and the second deposition cycle involving Pt deposition on pre-existing Pt sites (Figure 5.7a). Eventually, with further Pt deposition (Cycles ≥ 2), k_r attained a remarkable constancy.

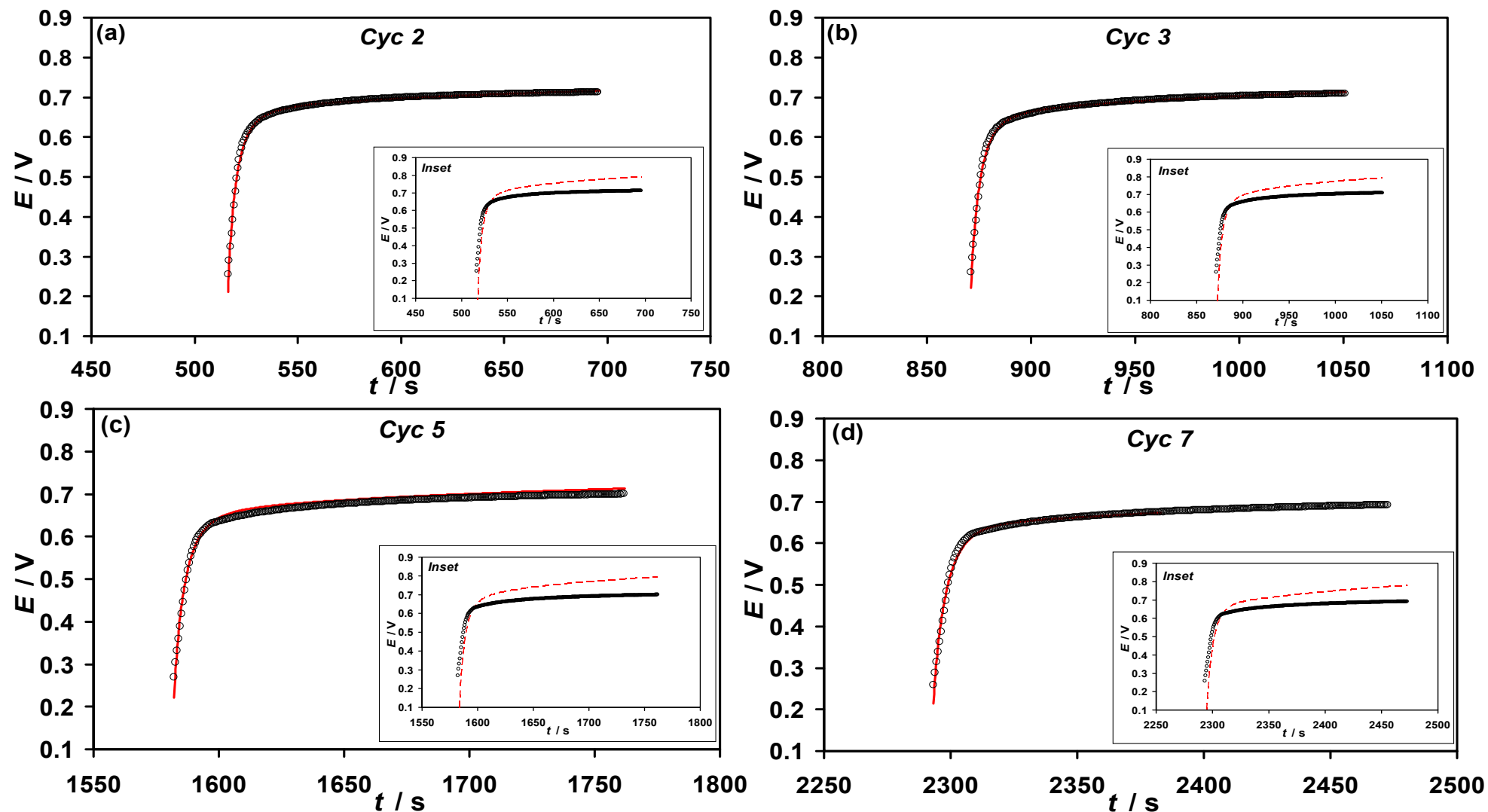


Figure 5.6: Representative potential transients for various deposition cycles during multilayer Pt deposition on Au_{film} involving Cu_{UPD} redox-replacement by Pt (SLRR_{Pt}). Circles are experimental data and solid lines are best-fit curves using the analytical model of Eq. (10) where $E^{\theta \rightarrow 0}$, f , g , k_r , and N_{or} were simultaneously optimized whilst z was kept constant at a value of 2. *Insets:* hypothetical curves (dotted lines), computed with z kept constant at a value of 1.

Furthermore, the evaluated N_{or} was computed at about 1.8 for the first deposition cycle that took place on bare Au_{film} and decreased to about 1.3 after the third cycle (See Figure 5.7b).

The trends in k_r and N_{or} for various deposition cycles categorically showed the dissimilarity between the reaction mechanism of Pt phase formation through SLRR on the initial crystalline Au_{film} substrate and gradually formed layered Pt deposits. Indeed, k_r and N_{or} are intricately linked to the fundamental rate constant k of the SLRR reaction and collision frequency between surface $PtCl_6^{2-}$ ions, Cu_{UPD} adatoms, and the activation energy of their activated complexes (intermediate states) during the redox-replacement reaction [193,321]. Hence, the observed variations in k_r and N_{or} might be understood from the variable activation complexes formed as a result of surface changes induced by the growing Pt nanocluster array-like system on Au_{film} .

The changing surface properties, charge-polarization, and overall activation energetics of transitional states on the pristine $Au|Au$ surface, mixed substrate involving $Au|Pt$ surface sites, and eventual involvement of layered $Pt|Pt$ interfaces, could have effects on the observed decrease of reaction rate and somewhat involved reaction mechanism of the $SLRR_{Pt}$.

The trend in the fitting $E^{0 \rightarrow 0}$ (Figure 5.7c), for the Cu_{UPD} depletion and resultant Pt phase formation through SLRR, is such that it became somewhat more negative with increasing Pt deposition (the initial $E^{0 \rightarrow 0}$ value of 0.65 V for the first deposition cycle on fresh Au_{film} smoothly decreases throughout the process and approaches a value of ≈ 0.61 V for the final deposition cycle). This decreasing trend could also be attributed to the changing substrate properties, in particular, the work function of the respective surfaces [196,198]. The variation in $E^{0 \rightarrow 0}$ also suggest more favourable energetics, from a thermodynamic point of view, of depletion of Cu_{UPD} adlayer coverage upon redox-replacement with Pt adlayers on Au_{film} in contrast to the Cu_{UPD} coverage diminishment on pre-existing Pt nanocluster array.

Table 5.1. Reaction kinetics and surface coverage parameters^a incorporating both adatom-substrate and adatom-adatom lateral interactions from analysis of potential transients involving SLRR reaction of Cu_{UPD} and PtCl₆²⁻ during generation of n(Pt)_{Cu}/Au_{film}.

Cycle	k_r / s^{-1}	N_{or}	$E^{\theta \rightarrow 0} / \text{V}$	f	g
1	0.39 ± 0.02	1.85 ± 0.02	0.651 ± 0.001	-20.6 ± 0.7	56.0 ± 0.5
2	0.067 ± 0.003	1.44 ± 0.01	0.641 ± 0.001	-15.6 ± 0.9	47.2 ± 0.7
3	0.052 ± 0.002	1.37 ± 0.01	0.632 ± 0.001	-13.8 ± 0.9	43.5 ± 0.7
4	0.049 ± 0.002	1.36 ± 0.01	0.627 ± 0.001	-16.8 ± 0.8	46.3 ± 0.7
5	0.045 ± 0.002	1.35 ± 0.01	0.621 ± 0.001	-18.4 ± 0.8	46.5 ± 0.7
6	0.039 ± 0.002	1.32 ± 0.01	0.616 ± 0.001	-19.9 ± 0.8	47.8 ± 0.7
7	0.032 ± 0.001	1.29 ± 0.01	0.612 ± 0.001	-22.3 ± 0.8	50.5 ± 0.7
8	0.029 ± 0.001	1.28 ± 0.01	0.609 ± 0.001	-22.7 ± 0.8	50.1 ± 0.7

^a) Cycle = deposition cycle as shown in Figure 5.1; k_r = the overall reaction rate constant; N_{or} = order of SLRR reaction determined with respect to Cu_{UPD} coverage; $E^{\theta \rightarrow 0}$ = electrode potential in the limit of zero-coverage during a SLRR reaction; f = Temkin-type isotherm adatom-substrate interaction parameter; g = Frumkin-type isotherm adatom-adatom interaction parameter; z = number of electrons in a redox reaction. All parameters were obtained from curve-fitting analysis using analytical model of Equation 5.10; z was fixed at the value of 2 during fitting operations; potential range of data sets was 0.25 V – 0.7 V.

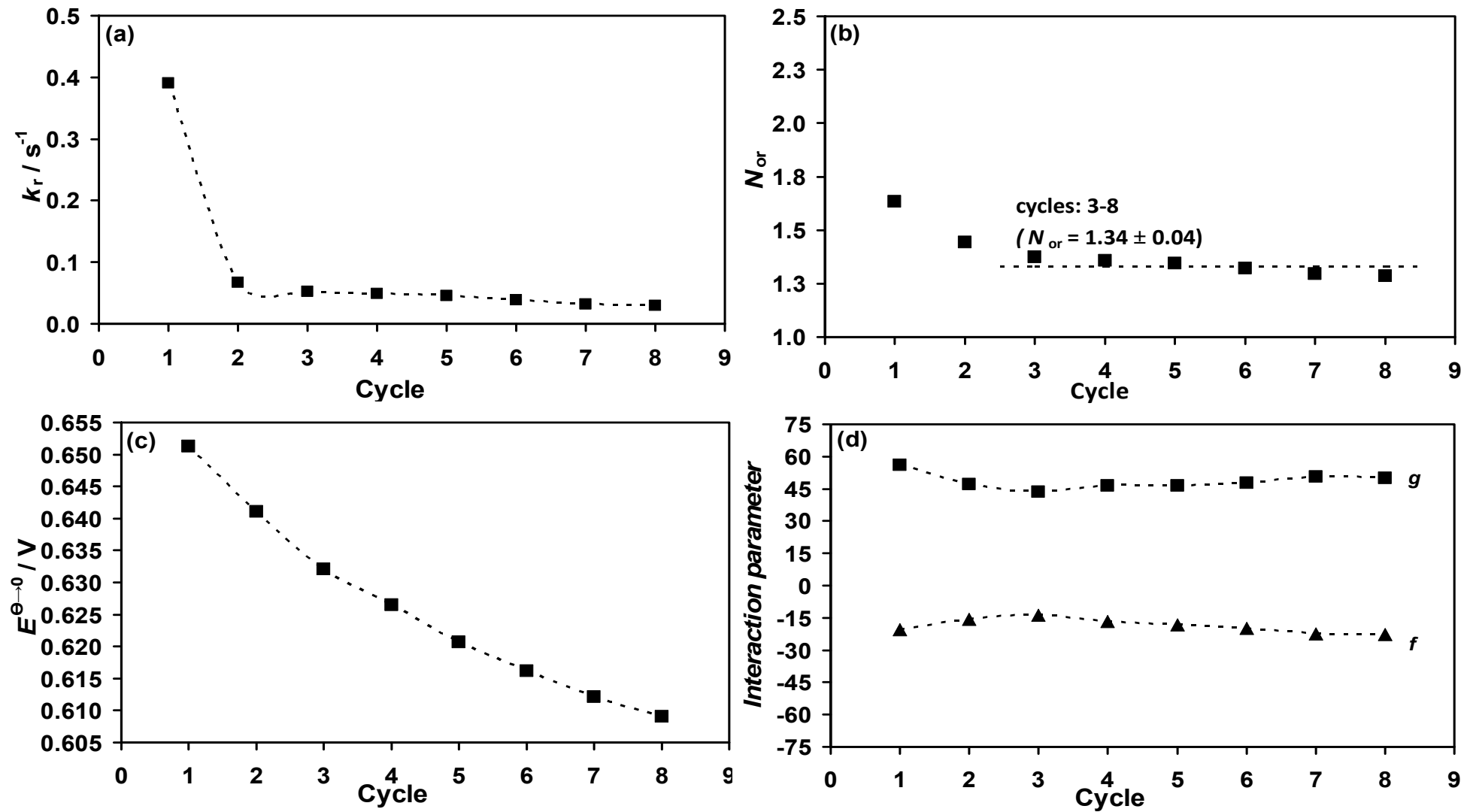


Figure 5.7: Trends of the parameters (a) k_r , (b) N_{or} , (c) $E^{0 \rightarrow 0}$, and (d) variations in interaction parameters f and g obtained from modelling with Equation 5.10 for various deposition cycles during electrochemical generation of the multilayered electrode system $n(\text{Pt})_{\text{Cu}}/\text{Au}_{\text{film}}$.

Figure 5.7d exhibits the variations in simultaneously optimized parameters f and g . Both types of interaction parameters show small variations for the first three cycles or so, and almost constant values of $f = -19 (\pm 3)$ and $g = 47 (\pm 3)$ thereafter. The steady values obtained after the third cycle might suggest minimal changes in underlying substrate surface and nature of adatom interactions properties after predominant formation of Pt deposits. In particular, the observed $f < 0$ could be indicative of cumulative effects involving distinctive interactions amongst the adatoms, induced changes in the polycrystalline surface work functions, and overall heterogeneity of the deposition sites [196,198,202].

The consistently positive trend in the g parameter during consecutive SLRR reactions, from progressively changed Au substrate to Pt layered deposits, might also indicate some interplay of charge polarization effects that led to distinct surface dipoles when Cu adlayers and their subsequent replacement took place solely on Au as compared to their formation and replacement on gradually formed Pt centres (electronegativity value for Cu is 1.9 whereas Pt and Au have values of 2.2 and 2.4, respectively, in the Pauling scale) [31]. The variations in f and g parameters could also suggest some overcoming of the weak repulsive forces of dipole–dipole nature probably through two–dimensional nucleation and formation of some band structures leading to condensed phase formation [196,198]. Moreover, the parameters f and g might also be attributable to characteristic geometric factors, enhancing promotion of nearest adatom–adatom neighbours within the adlayers as well as two-dimensional coordination of the Cu surface arrays on Pt adlayers as opposed to Au_{film} surface [196,198].

From above modelling results, essentially generating z as 2, the overall SLRR reaction, in integer stoichiometry, that most likely took place is given by Reaction 5.16 below



where S is Au_{film} which gradually changed to Pt during formation of the multilayered $\text{n(Pt)}_{\text{Cu}}/\text{Au}_{\text{film}}$ system.

Re-oxidation Cu_{UPD} by PtCl_6^{2-} might in principle proceed to Cu^+ [192,193], essentially generating z as 1; perhaps this scenario is plausible only when conditions for significant formation of CuCl_2^- exist or free Cl^- ions availability persist. The nature of the substrate might also have an effect on formation of different activated complexes during redox-replacement, with consequences on observed stoichiometry.

5.4.4. Gibbs free energy variations during successive SLRR reactions

The underlying kinetics of phase formation involving SLRR reactions in growth of Pt multilayers through replacement of Cu_{UPD} adlayers, are deductable from models of potential dependency, such as that of Equation 5.10, as demonstrated and discussed in the preceding section. Overall thermodynamic driving force and its underlying variation upon such phase formation phenomena can be appreciated from time-dependent Gibbs free energy changes. From $E_{\text{SLRR}} - t$ relationship of Equation 5.10 and the relationship $\Delta G = zFE$, we phenomenologically introduce the Gibbs free energy change of adlayer formation via SLRR reaction (ΔG_{SLRR}) as function of reaction time t as shown in Equation 5.17:

$$\Delta G_{\text{SLRR}} = \Delta G^{\theta \rightarrow 0} + RT \left[\ln \left(\frac{(1 + k_r t)^{1/(1-N_{\text{or}})}}{1 - (1 + k_r t)^{1/(1-N_{\text{or}})}} \right) + f(1 + k_r t)^{1/(1-N_{\text{or}})} + g(1 + k_r t)^{3/(2-2N_{\text{or}})} \right] \quad (5.17)$$

where R , T , f , g , k_r and N_{or} have their usual meaning; $\Delta G^{\theta \rightarrow 0} = -zFE^{\theta \rightarrow 0}$.

Representative ΔG_{SLRR} curves for Reaction 5.16, at various deposition cycles, as evaluated employing Equation 5.17 using best-fit parameters obtained from regression analysis of $E_{\text{SLRR}} - t$ data sets described above, are plotted in Figure 5.8. In all cycles, the negatively decreasing ΔG_{SLRR} with increasing reaction time is consistent with thermodynamically favoured spontaneous Cu_{UPD} adatom depletion and concomitant replacement by Pt adatoms. The role of thermodynamics of phase formation involving SLRR reactions performed on an interfacial substrate (that is a substrate composed of two distinct metal adlayers) is clearly discernible from the trend of ΔG_{SLRR} as a function of deposition cycles in generation of $n(\text{Pt})_{\text{Cu}}/\text{Au}_{\text{film}}$.

Notably, there is an overall positive change in the ΔG_{SLRR} as Pt centres are formed away from the base Au_{film} upon increasing deposition cycles (Figure 5.8).

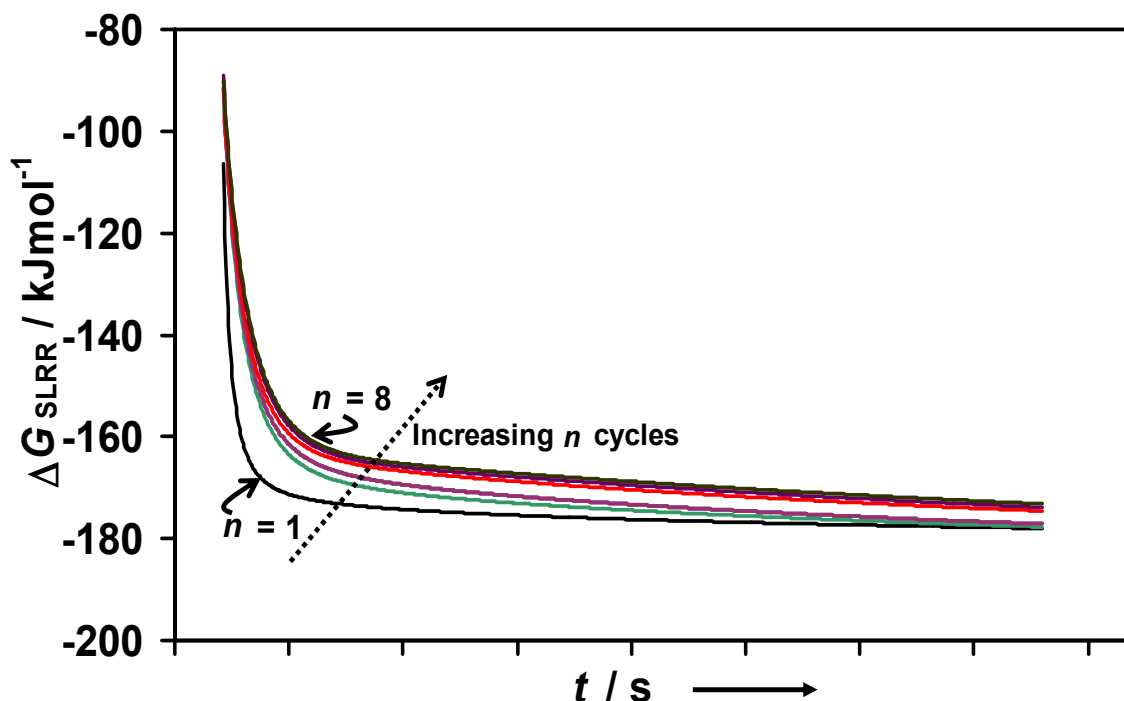


Figure 5.8: Gibbs free energy variations of the SLRR reaction (Reaction 16) computed using Eq. (17) at various deposition cycles to generate $n(\text{Pt})_{\text{Cu}}/\text{Au}_{\text{film}}$.

Overall, the trends of phenomenological surface coverage parameters during successive SLRR steps as well as variations in ΔG_{SLRR} strongly suggest that the $\text{Pt}|\text{Au}_{\text{film}}$ interface during the first two deposition cycles or so influence the fastest SLRR reaction kinetics and overall favourable thermodynamics as compared to the exclusive replacement of Cu_{UPD} adlayers proceeding at layered Pt-on-Pt sites which were formed in subsequent deposition stages. The quantitative trends deduced in this work are in agreement with recent qualitative findings from *in situ* scanning tunnelling microscopy of UPD on Au (111) and Pt clusters generated via successive SLRR reactions [179], where a somewhat bimetallic mixed substrate between Au and Pt was suggested to form during initial UPD/SLRR cycles on Au(111) substrate. Moreover, the models explored here also cement our earlier observations [194] on unique electrocatalytic properties of bimetallic and multilayered nanostructured electrode systems generated via sequential electrodeposition involving SLRR reactions.

5.5. Summary

This chapter analytically explored applicability of models describing UPD phase formation within the framework of adlayer adsorption-desorption electrochemical isotherms and surface-limited redox-replacement involving Cu_{UPD} and Pt to quantify the underlying reaction kinetics during various stages of formation of a multilayer Pt system on a crystalline Au film substrate (Au_{film}). Analytical models, based on electrochemical adsorption isotherms describing variation of Cu_{UPD} surface coverage with applied electrode potential, have been explored to deduce kinetic and thermodynamic parameters of adlayer phase formation on Au_{film} as well as multistage-implemented SLRR reactions of Cu_{UPD} and PtCl_6^{2-} in deposition of a multilayered Pt system. The models took into account heterogeneity effects, adatom-substrate interactions as well as adatom-adatom lateral interactions within the adlayers. Physico-chemical insights on underlying stoichiometry of the SLRR reaction, the order of the reaction, rate of the reaction, and phenomenological Gibbs free energy during various stages of deposition of the multilayered Pt nanofilm were divulged.

CHAPTER VI

Conclusions and Perspectives

6.1. Introduction

The aim of this final chapter of the thesis is three-fold. Firstly, the main deductions and conclusions of the original works presented in this thesis are presented. Secondly, details on some perspectives stemming from the findings are presented. Finally, general recommendations in the direction of plausible avenues for further research and areas of potential technological adoption are outlined.

6.2. Main deductions and general conclusions

Overview

Multilayered platinum, ruthenium and/or gold-containing nanoclusters (as monometallic or bimetallic systems) were effectively prepared utilizing multistage electrochemical deposition strategies consisting of sequentially-implemented cyclical steps involving formation of templating Cu adlayers by potentiostatic electrodeposition, an electroless deposition stage involving SLRR reaction of Cu by the nobler metals Pt, Ru and/or Au, and final potentiostatic dealloying of any subsurface Cu. The templating Cu nanoclusters were generated using either UPD or OPD about the equilibrium potential of the $\text{Cu}^{2+}/\text{Cu(s)}$ redox couple in an acidic, perchlorate medium.

The resulting nanocluster-like multilayered electrodic systems obtained were subjected to various characterizations for their bulk composition, surface area, near-surface atomic distribution topographic and morphological features using microscopic, spectrophotometric, spectroscopic, and voltammetric- and impedance-based electrochemical techniques. Novel thermodynamic and kinetic models were developed to complement interpretation of experimental observations and provide in-depth physico-chemical insights of the underlying deposition processes explored.

Thermochemical E-pH modelling and analysis of open-circuit potential transients

The analysis of open-circuit potentials recorded during the various deposition experiments in combination with theoretical models (here thermodynamic data were used to model the E -pH predominance relationships involving the Pt-Cu- H_2O , Ru-Cu- H_2O , Pt-Ru- H_2O , Au-Cu- H_2O , Pt-Au- H_2O , Pt-Cu-Cl- H_2O , and Au-Cu-

Cl-H₂O systems) proved to be an excellent predictive tool of deposits generated during SLRR reactions involving Cu. The use of a surface reducing agent, in this case Cu adlayers, has been shown to be a necessary condition for the sequential deposition of adlayers of the noble metals in their metallic states, especially for Ru which is susceptible to spontaneous ruthenium oxide formation. The *E*-pH models and open-circuit potential variations observed experimentally clearly showed that zero-valent Pt, Au, or Ru were the main forms expected after a few cycles of independent SLRR stages where Cu was oxidatively-replaced to Cu²⁺ by the noble metal precursor ions, respectively. In the case of sequential codeposition, with concomitant SLRR reactions of mixed noble metals' precursors, the observed potentials were thermodynamically more in favour of the more noble metal between the pairs considered in generation of bimetallic deposits.

Surface and bulk properties: Microscopy, surface electrochemistry, spectroscopy and spectrophotometry

Ex situ microscopic investigations with SEM and AFM revealed well-dispersed needle-like nanoclusters on the deposition substrate when SLRR reactions of Cu adlayers and intermediate dealloying processes were carried out sequentially and independently for respective deposition of multilayers of noble metals (Pt, Au, or Ru). Close proximity of electrochemically-active sites on the carbonaceous glassy carbon surface appeared to have influenced formation of fused nanoclusters, with similar heights and diameters, most likely as a consequence of independent multilayer growth paths on the various active sites where nucleation was initiated. Furthermore, morphological features of the sequentially-codeposited (alloy-type) bimetallic systems were found to involve significantly agglomerated structures on the carbonaceous substrates, strongly revealing the advantageous sequential deposition from separate precursors of noble metals when their multilayer nanostructures are sought.

Surface electrochemical studies by voltammetry on the sequentially deposited nanoclusters, performed *in situ* immediately after deposition involving SLRR reaction, revealed electrochemically-active sites of the constituent noble metals in their monometallic forms, and both Pt and Au active sites in the bimetallic forms.

Total metal content analysis using *ex situ* inductively-coupled plasma spectrophotometry informed us that sequential codeposition to generate the alloy-type bimetallic systems, led to preferential deposition of the nobler metal such as Au, in which case the content of the less noble metal was greatly suppressed. Such analysis also revealed the overall noble metal content is highly dependent on the order of their sequential deposition, accounting for stoichiometric effects of the underlying SLRR reactions imposed by the oxidation state of the precursor ions.

Further *in situ* voltammetric studies on the final multilayered deposits exhibited typical features of polycrystalline electrodes. Thus, the growth pattern of the nanoclusters whether monometallic or bimetallic resulted in formation of various crystallographic facets which were electrochemically-active.

X-ray photoelectron spectroscopic characterization of the various nanostructured deposits (performed *ex situ*) showed typical features of the carbonaceous surface functionalities of the glassy carbon substrate, mainly involving multiple forms of carbon and oxygen, such as carbonyl and hydroxyl groups, and their plausible interactions with the noble metal nanoclusters, effectively stabilizing them. The surface-to-near surface spectroscopic probe also revealed that the nanoclusters contained zero-valent forms of the highly noble Pt and Au, whose surface to near-surface distribution depended on the sequence of their deposition; Pt-rich surface could be obtained, for instance in the case of $n(\text{Pt} | \text{Au})_{\text{Cu}}/\text{GC}$ system, where Au was deposited prior to Pt, and Au-rich ones could be generated on the corresponding $n(\text{Au} | \text{Pt})_{\text{Cu}}/\text{GC}$ system, with all other deposition parameters remaining constant. Such simplicity in tuning composition of the desired nanoclusters, confirm the versatility of the sequential deposition methodology explored in this work. Furthermore, mixed microstates of Pt and Au were clearly generated in the nanoclusters due to interfacial bimetallic interactions consistent with multilayer growth pattern of the deposited nanoclusters, in line with their desired electrocatalytic properties summarized hereafter.

Electrocatalysis

Elaborate electrocatalytic studies using structure-sensitive test reactions of direct methanol, formic acid oxidation and carbon monoxide oxidation, as well as oxygen reduction reaction on the nanocluster systems firmly informed us that the route used to nanostructurally-preorganise monometallic and bimetallic active sites had consequential effects on subsequent electrocatalysis on the nanostructured systems generated as outlined below:

Methanol oxidation reaction

The bimetallic nanocluster electrode $n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$ was characterized by lower electro-oxidation overpotentials, lower charge-transfer resistances and higher oxidation currents when benchmarked to characteristics of monometallic Pt nanostructures (and other bimetallic systems generated through codeposition and direct spontaneous deposition). In particular, codeposition of alloy-type Pt-Ru system (via simultaneous SLRR steps) or direct spontaneous deposition of (Ru | Pt) – without involvement of SLRR reactions – led to least active nanostructures, suggesting that significant formation of Ru oxides in the resultant deposits decrease the activity toward methanol oxidation via the bifunctional mechanism.

Oxygen reduction reaction

The mechanism of the fundamentally and technologically important oxygen reduction reaction was also investigated on the various nanocluster electrodes. The four-electron pathway was favored by the monometallic Pt nanoclusters but the equivalent bimetallic Ru-containing nanoclusters favored the two-electron ORR pathway, where fastest rate of the heterogeneous reaction was observed for the sequentially-deposited nanoclustered systems utilizing SLRR reactions as opposed to the codeposited counterparts or spontaneously formed agglomerates. This tuning of electrocatalytic properties from preorganisation of the nanostructures by way of electrodeposition pathways underpins the inherent advantages in these types of electrosynthetic protocols for potential use in electrocatalysis applications, for instance, in fabrication of fuel cell cathodes where the ORR is of necessity.

Formic acid oxidation reaction

In the case of the formic acid oxidation, the Pt-rich $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ had superior electrocatalytic activity followed by $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$, $n(\text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Au})_{\text{Cu}}/\text{GC}$ as the least active system. The direct (or dehydrogenation) pathway of formic acid was likely predominant on the bimetallic systems and the indirect or formate pathways with adsorbed CO as intermediate and catalyst poisoning species most likely occurred preferentially on the monometallic Pt systems as confirmed by direct CO adsorption-oxidation studies on the respective nanostructured electrodes.

Kinetics and thermodynamics of adlayer formation and dissociation via UPD and SLRR reactions

In Chapter 5, this research work analytically explored applicability of models describing UPD phase formation of Cu adlayers, within the framework of adlayer adsorption-desorption electrochemical isotherms, and SLRR reaction involving such adlayers with hexachloroplatinate in order to quantify the underlying reaction thermodynamics and kinetics during various stages of formation of a multilayer Pt system on a crystalline Au film substrate.

Modelling of the direct UPD process on crystalline Au film, utilizing electrochemical isotherms of Temkin- and Frumkin-type, successfully described the potential dependency of the surface coverage of the UPD layers and their subsequent dissolution to Cu^{2+} . Through multivariate regression analysis of potential transients during sequentially-implemented SLRR reaction between Cu adlayers, generated by UPD, and PtCl_6^{2-} , reaction kinetics, phenomenological Gibbs free energy variations and stoichiometric aspects were deduced for each deposition cycle during multilayer growth of Pt nanoclusters.

The SLRR reaction involving Cu adlayers and the aqua hexachloroplatinate complex was derived as second-order with respect to Cu adlayers when the reaction took place on pristine Au substrate and significantly fractional on subsequent cycles involving the gradually formed Pt centres. Furthermore, the magnitude of the phenomenological SLRR reaction rate constant was also found to decrease gradually with multiplication of Pt adlayers, observations that were indicative of faster

reaction on bare crystalline Au film as opposed to its dispensation on subsequently formed Pt adlayers. The trend in the apparent Gibbs free energy of the SLRR reaction also exhibited increasing spontaneity with reaction time towards steady-state.

Moreover, the analytical models employed to scrutinise the UPD adlayers and associated SLRR process, at various deposition stages, revealed that the adatom-substrate and adatom-adatom interactions involved in generation of Pt adlayers (via the open-circuit SLRR reaction) proceeded in a distinct manner as compared to direct fixed-potential UPD of Cu on Au. In the former case, the interactions were predominantly found to be attractive and in the latter case they were found to be generally repulsive. Furthermore, the gradual change of substrate effects from predominantly Au to Au|Pt and subsequently Pt|Pt interfacial characteristics appeared to influence the interplay of kinetics and thermodynamics of the UPD-based SLRR reaction. The physico-chemical properties systematically investigated in this work and reported here [322] can be useful in design of multilayered systems where SLRR reactions form an integral part in their fabrication. The reaction kinetic and thermodynamic modelling performed in this work, clearly provided hitherto little understood, that SLRR reactions are substrate-sensitive.

6.3. Perspectives

In this work our focus was on sequential electrodeposition of multilayered active surfaces enhanced with a number of atomic contacts between the component noble metals such as Pt and Ru. The original work presented in this thesis (Chapters 3 – 5) demonstrated automated synthesis of multilayered monometallic and bimetallic Pt-based nanoclusters (with Ru or Au as Pt counterpart noble metals) using SLRR cycles involving Cu for deposition of each noble metal with variable electrocatalytic activity toward oxygen reduction reaction (ORR), methanol oxidation reaction (MOR) and formic acid oxidation reaction (FAOR) in acidic media [190,194,323]. To this effect, a large number of 3D bimetallic nanoclusters (rather than flat and large surface monolayers deposited on top of each other) were generated on carbonaceous and crystalline metallic substrates that significantly enhanced the number of active sites where bifunctional catalytic mechanisms could take place. Figure 6.1

schematically summarizes the deposition steps involving successive templating Cu adlayer replacement by the nobler Pt and Ru that led to unique bimetallic Ru|Pt nanoclusters.

Given the effects of either Ru or Au, upon insertion to Pt, to form bimetallic multilayers using SLRR synthetic strategies as observed with studies reported here [190,194,323], further exploration of the sequential electrodeposition methodology can be extended to formation of trimetallic $n(\text{Au}|\text{Ru}|\text{Pt})$ nanostructured electrode system (where Pt is deposited first, followed by Ru and finally Au) or $n(\text{Ru}|\text{Au}|\text{Pt})$ nanoclusters (where Pt is deposited first, followed by Au and finally Ru), for variable n cycles. Preliminary work to this effect was carried out. Typical deposition cycles to generate trimetallic multilayers, by extension of deposition of bimetallic systems as explored in this work, involve nine main steps: filling the cell with sacrificial metal solution, followed by deposition at a pre-set fixed potential. The cell was then rinsed with the BE, filled with the first noble metal precursor and redox-replacement allowed at open circuit (OC). The cell was rinsed with BE and Cu deposition proceeded again, followed by rinsing with the second noble-metal and redox-replacement at OC. Rinsing with BE and Cu deposition as previous steps, followed by introduction of the third metal and its deposition at OC, completed one cycle of forming a trimetallic nanostructure. The instrumental setup utilizing at least five dedicated electrolyte reservoirs, pumps, multi-valve and computer-control details (with the *Autolab-SeqDep-5Pumps-Autorefill.vi*) are given in **Appendix A**.

Representative $E-t$ transients recorded during deposition of trimetallic $n(\text{M}|\text{Y}|\text{Pt})_{\text{Cu}}/\text{GC}$, where metals M and Y were either Au or Ru, are shown in Figure 6.2. The OC potentials observed during Stage 3 and 6, corresponding to either Ru or Au SLRR reaction with Cu, correlated well with OC potentials of the same reactions during deposition of bimetallic Ru|Pt or Au|Pt nanoclusters described in Chapters 3 - 4; formation of adlayers of Pt(s), Ru(s) and Au(s) were thermodynamically viable as predicted from relevant $E\text{-pH}$ equilibrium models. *Ex situ* microscopic investigations using AFM (Figure 6.3) of the $n(\text{Ru}|\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ show distinct immobilized needle-like clusters well-dispersed on the GC substrate.

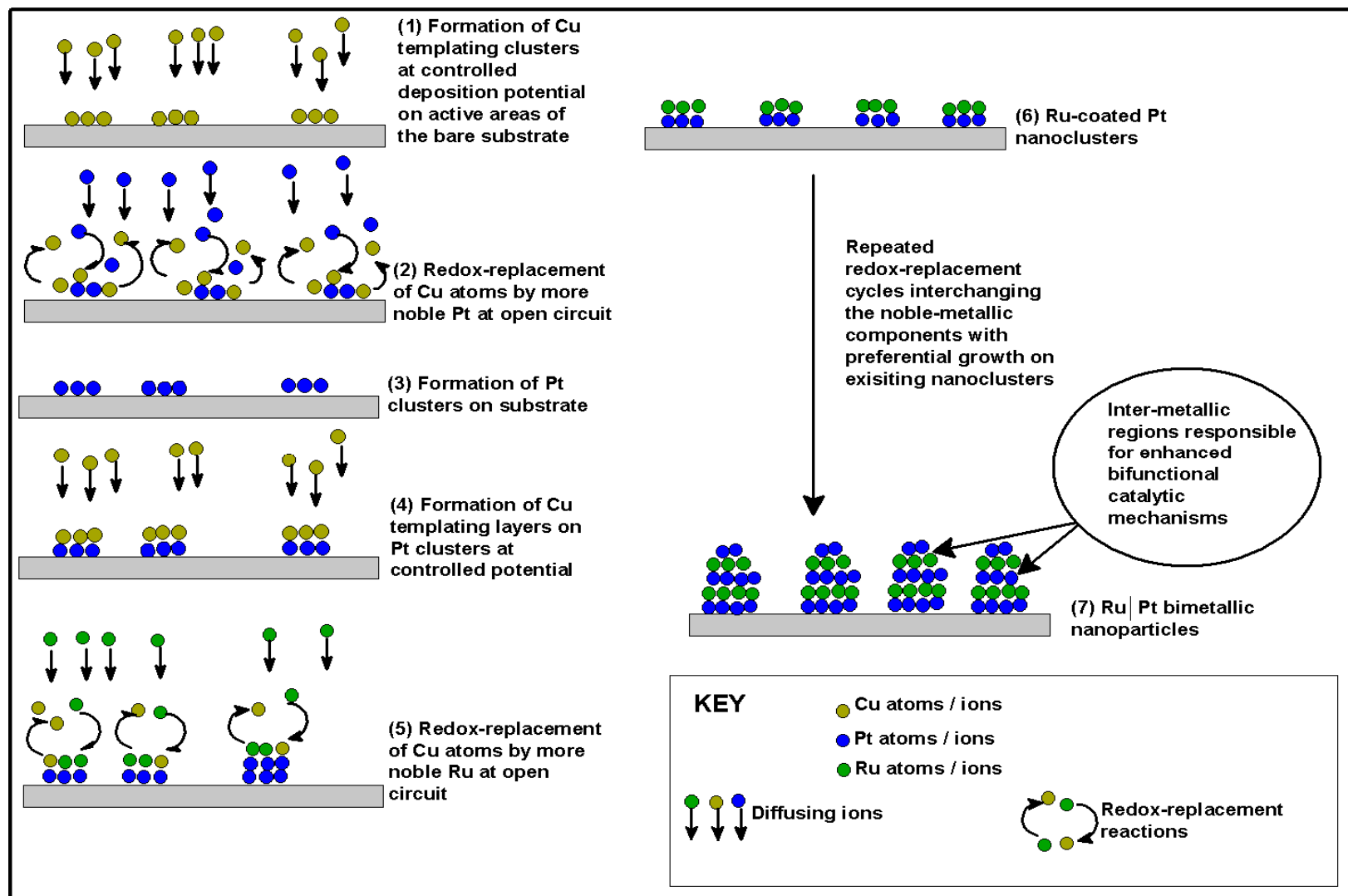


Figure 6.1: Schematic of the electrochemical synthetic protocols used to obtain bimetallic Ru|Pt nanoclusters via SLRR reactions and the proposed resultant active sites that lead to their enhanced bifunctional electrocatalytic activity (Ref. [190]).

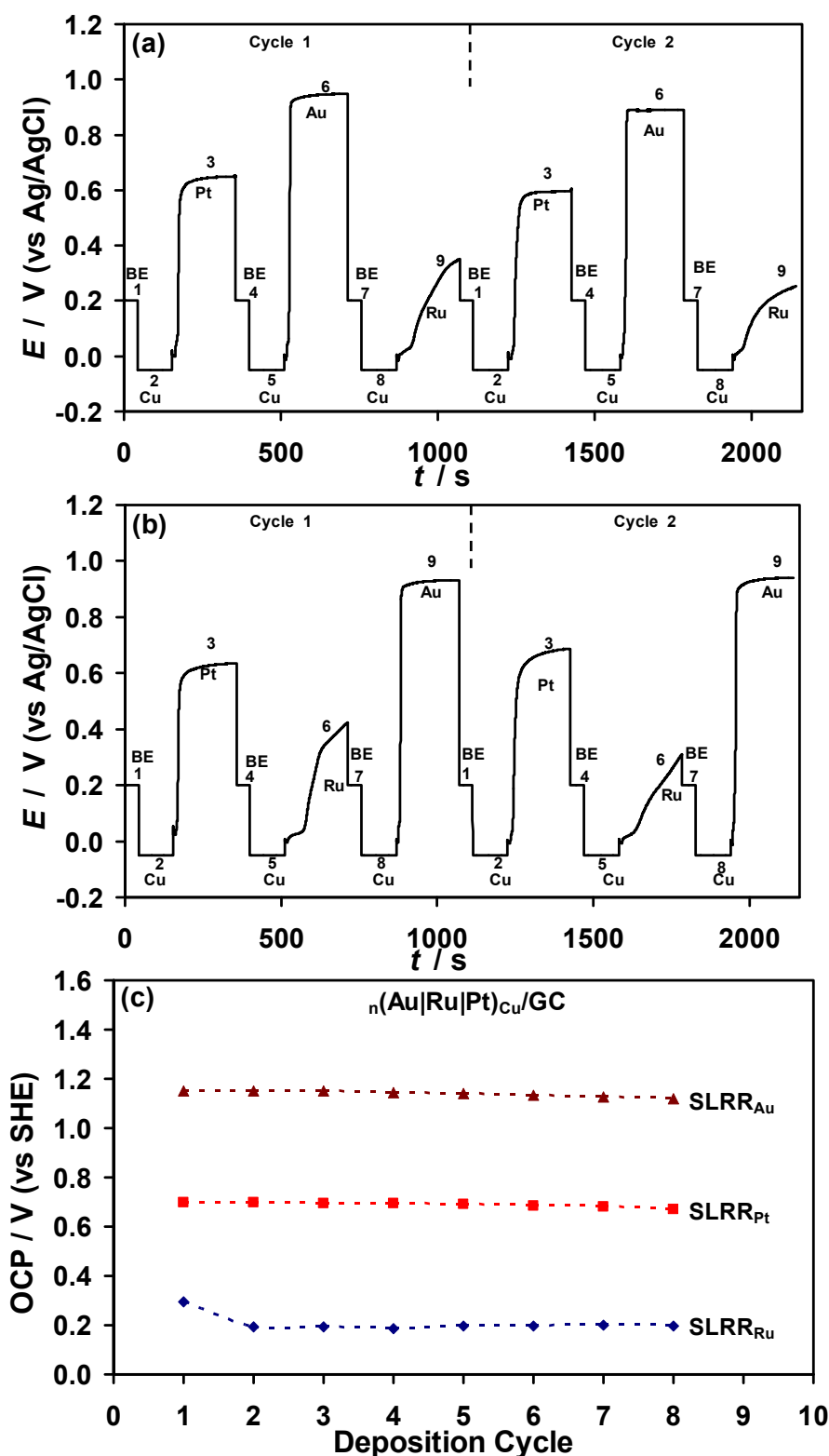
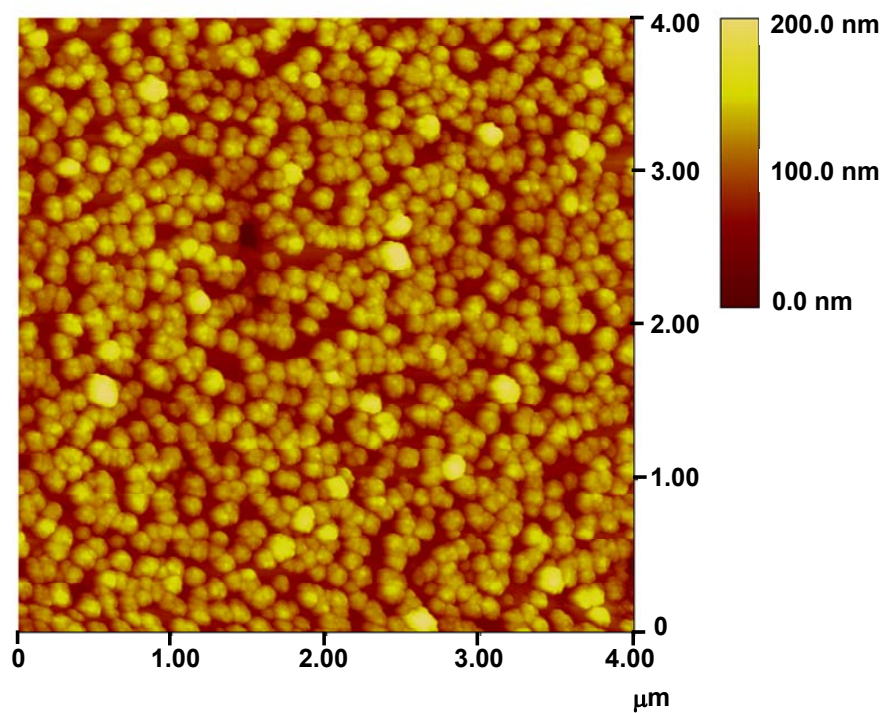
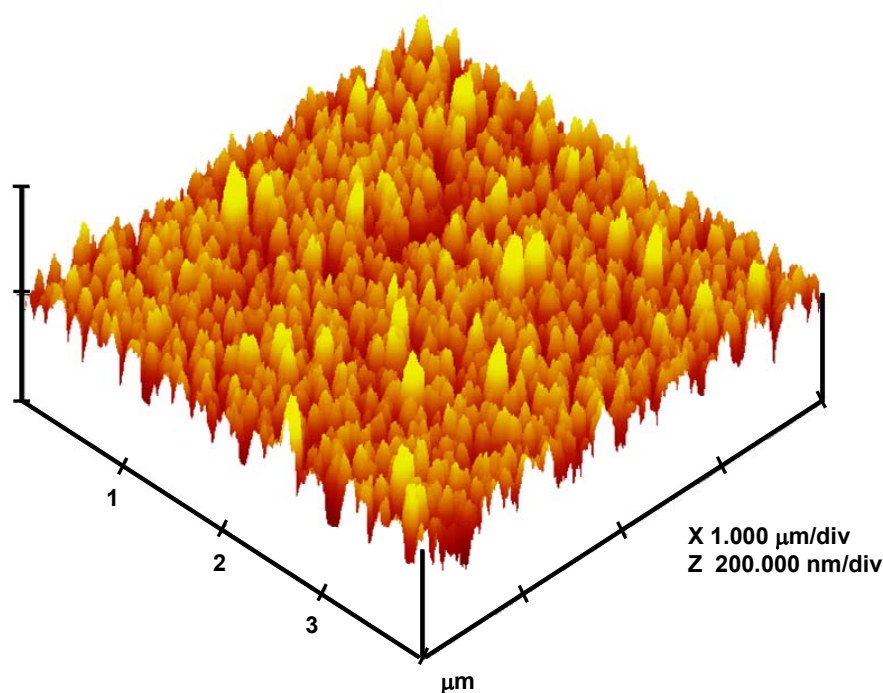


Figure 6.2: Representative potential-time traces recorded *in situ* during deposition of trimetallic systems (a) $n(\text{Ru}|\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ and (b) $n(\text{Au}|\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ involving Cu OPD templates generated at -0.05 V. (c) OCP variation with increasing deposition cycles during SLRR reactions (Stages 3, 6, and 9 in (b)); OCP values averaged during last 90 s.



(a)



(b)

Figure 6.3: Representative tapping mode AFM images; (a) top-view and (b) 3D surface plot of the trimetallic nanostructured electrode $n(\text{Ru}|\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ obtained after four deposition cycles ($n = 4$).

The trimetallic clusters $n(\text{Ru}|\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ were similar in morphology to the bimetallic ones $n(\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ (studied in detail in Chapters 3 -

4), but much larger in height and breadth after only a few deposition cycles. The preceding observation is expected due to deposition of three distinct noble metals in the case of $n(\text{Ru}|\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$. Surface electrochemical features of representative trimetallic systems were probed with cyclic voltammetry *in situ* immediately following their deposition (Figure 6.4). The typical surface oxides formation and reduction voltammetric signatures were discernible as identified by Peaks **I**, **II**, and **III** in Figure 6.4 corresponding to Pt, Ru, and Au surface oxides reduction, respectively. The voltammetric studies strongly support the successful generation of distinct active sites of the three noble metals. Furthermore, the surface electrochemistry observed also revealed the effect of order of deposition of such trimetallic multilayered systems, where the pronouncement of Ru oxide reduction feature (Peak **II**) was clear when the overall deposition was truncated with Ru adlayers on Au (Figure 6.4a); this feature was masked as shoulder to Peak **I** when the order of deposition between Ru and Au was reversed with Au adlayers formed last on Ru sublayers (Figure 6.4b-c). Similar observations with the effect of sequence of deposition in generation of bimetallic multilayered systems involving only Pt and Au were observed as discussed in Chapters 3 – 4.

Electrocatalytic studies on the representative trimetallic systems were performed for the methanol oxidation reaction (MOR) in 0.5 M CH_3OH in 0.1 M HClO_4 acidic medium; similar to tests carried out for the bimetallic systems discussed in Chapter 3. Typical cyclic voltammetric curves related to the electrocatalysis of MOR, as performed on the $n(\text{Ru}|\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Au}|\text{Ru}|\text{Pt})_{\text{Cu}}/\text{GC}$ multilayered electrode systems, are shown in Figure 6.5. The CVs recorded indicated that interchanging the sequence of depositing Au and Ru appears to have significant effects on the electrocatalytic activity of the final trimetallic nanoparticles. Detailed electrochemical studies might be carried out in further works to ascertain adsorption-desorption characteristics of reaction intermediates of the MOR on the trimetallic multilayered systems in a similar manner to detailed studies reported in Chapters 3 - 4 for electrocatalysis of monometallic and bimetallic Pt-based systems.

Effect of sequence of deposition on composition of the trimetallic systems, the electrochemical surface area and interfacial surface chemistry with techniques such as XPS may yield more in-depth understanding of the underlying properties of the trimetallic systems generated via sequential electrodeposition methodologies involving SLRR reactions.

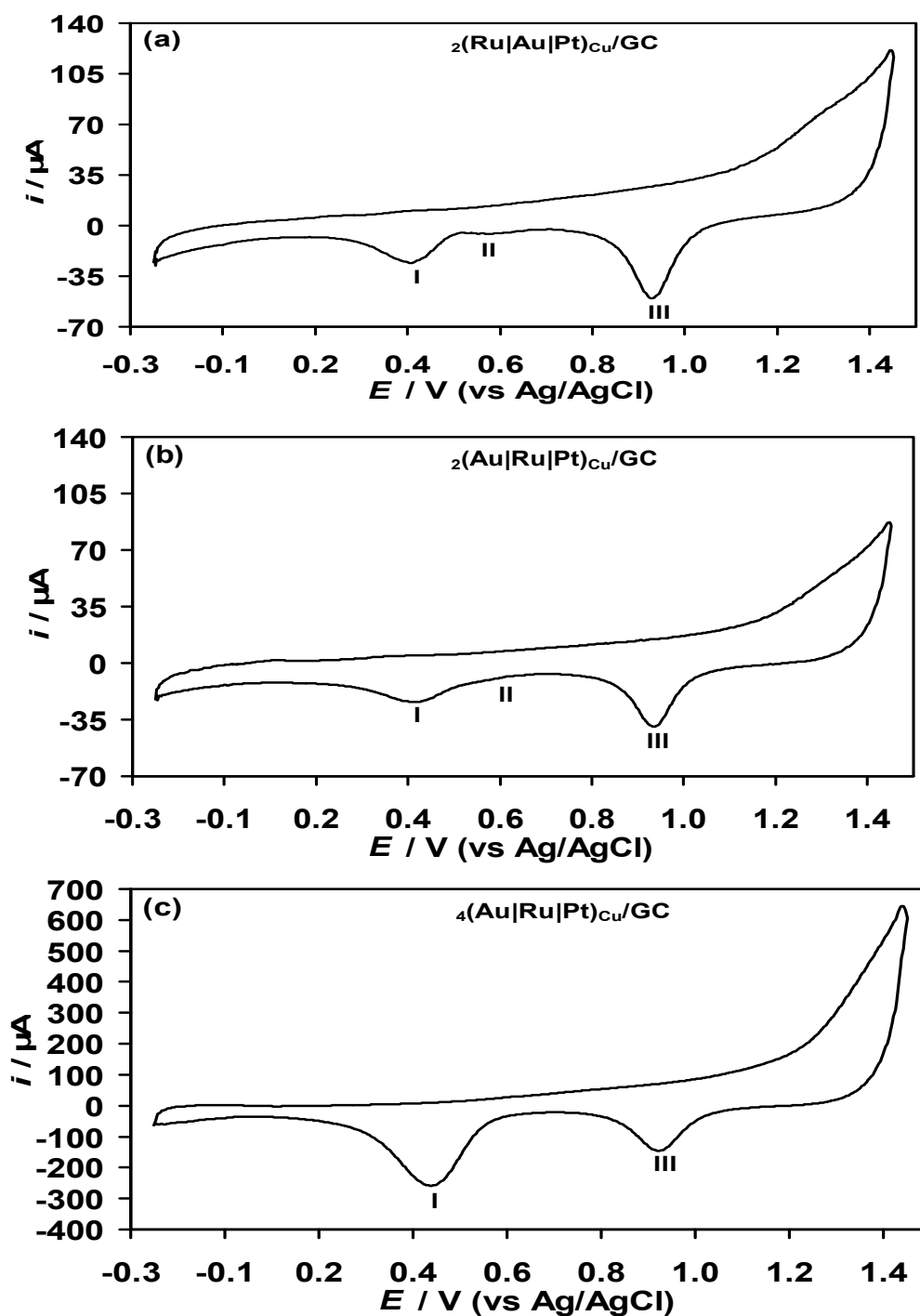


Figure 6.4: Cyclic voltammograms in N_2 -saturated in 0.1 M HClO_4 of various trimetallic nanostructured electrode systems.

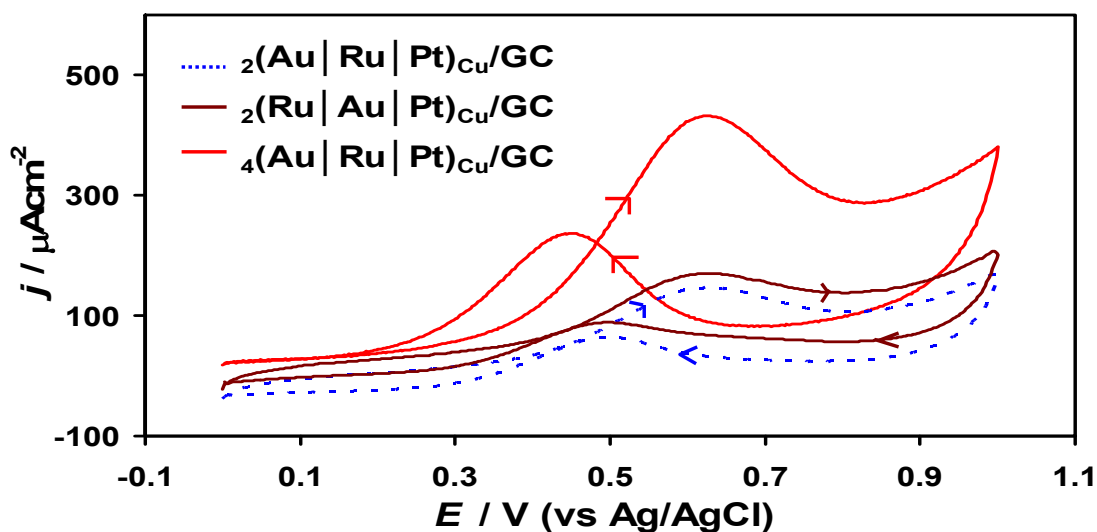


Figure 6.5: Cyclic voltammograms in N_2 -saturated 0.5 M CH_3OH in 0.1 M $HClO_4$ for various trimetallic nanoparticles— $n(M|Y|Pt)_{Cu}/GC$, sequentially deposited via Cu redox-replacement for n cycles on glassy carbon (GC), $M, Y = (Au \text{ or } Ru)$. Scan rate = 50 mV/s.

6.4. Recommendations

Indeed, the methodology explored in this work allows unique fabrication of multilayered nanostructured electrodes with highly surface-active multimetallic composition. We explored sequential electrodeposition of noble metals Au, Pt and Ru as monometallic, bimetallic, or trimetallic systems, and effectively investigated their various surface, bulk, compositional, and electrocatalytic properties using a range of physical and chemical characterization techniques. Further research can be carried out; since, it is the nature of research that, ‘opening one door leads to discovery of many others’! The scope of this research can indeed be extended to discover more about the properties of the multilayered nanostructured systems, from the fundamental viewpoint as well as technological applications.

General recommendations as extrapolated from the research works of this thesis are outlined below:

- (i) Deposition of mixed-state nanostructured systems composed of metallic forms and oxide forms of constituent noble elements that might have unique electrocatalytic properties for a specific reaction of interest can be explored further.

- (ii) Dedicated studies may delve on systematic adjustment of composition and properties of multimetallic deposits generated through
- adjustment of precursor electrolyte composition involving variable concentrations and pH,
 - application of organic additives in the deposition baths, use of non-aqueous media,
 - exploration of cationic and anionic complexed precursors, and deposition reaction stoichiometry adjustment by using various oxidation states of precursor ions.

Such studies may shed more light on fundamental insights related to the inherent rates of mass transport to the sites of cluster growth, the role of concentration of precursors used, the influence of electrolytes used, kinetics of the deposition reactions, in particular the rates of reduction of the templating metal on the more noble metals, and influence of thermodynamic properties of the metals of interest during deposition.

- (iii) Further *in situ* microscopic characterization of the sequential deposition processes investigated in this work may be carried out by way of coupling electrochemistry to other microscopic and spectroscopic techniques. Dedicated flow-cells may be designed allowing for such *in situ* studies, for instance utilizing Electrochemical Atomic Force Microscopy (EC-AFM) or Electrochemical Scanning Tunneling Microscopy (EC-STM) modes [324], which allow for structural insights of surfaces in solution. Such studies may lead to in-depth structural understanding of the nature of nucleation and growth of adlayer formation of noble metals and dissociation of sacrificial templating layers employed when SLRR reactions are used in sequential deposition of multilayered nanoclusters.
- (iv) Coupling a electrochemical flow-cells to synchrotron radiation techniques such as Grazing Angle X-ray Diffraction (GR-XRD) and X-ray Absorption Near-Edge Spectroscopy (XANES) have been

demonstrated for studying (*in situ*) electrocrystallization phenomena and composition of electrode surfaces [325,326]. One may extend such studies to sequential electrodeposition in flow-cells as explored in this work to ascertain the nature of crystallization at various deposition stages of multilayers and resultant composition without removing the deposited material from its natural electrochemical environment.

- (v) Dedicated studies may be undertaken towards further insights on electrocatalysis of multilayered nanoclusters as electrosynthesized in this work. In particular, coupling electrochemical techniques to spectroscopy (spectroelectrochemical techniques) may be useful. A range of analytical spectroscopic and spectrophotometric techniques such as Fourier-Transformed Infrared Spectroscopy and Raman Spectroscopy and Mass Spectrophotometry may be coupled to electrochemical cells and directly used to study *in situ* the electrocatalytic intermediates and products formed during actual reactions on electrodes employed [327].
- (vi) The sequential electrodeposition methodologies may be extended further to include generation of templating adlayers through other electrochemical modes such as pulsed electrodeposition and galvanostatic deposition as opposed to potentiostatic modes solely explored in this work. These types of studies may shed more light on the nature of nucleation and growth and any inherent advantages of the electrochemical modes over the ones investigated in this thesis.
- (vii) Extension of influence of substrate on the electrodeposition pathways investigated can be explored further through dedicated studies using single-crystalline substrates of various noble metals, in addition to Au as was investigated in this work; other noble metals such as Rh, Ir, and Os may be explored as substrate materials.
- (viii) Combination of different noble metals such as Rh, Ir, Pd, Au, and Os in multilayer nanostructures through extensions of methodologies

developed in this work may be explored further towards potential applications in catalysis and electrocatalysis of the precious metals, a research direction for the expansion in beneficiation of these metals for industrial and technological applications.

- (ix) Electrochemical deposition on carbonaceous substrates such as carbon fibres, cloths, and papers of ubiquitous use in emerging electrochemical technologies such as polymer electrolyte fuel cells, may be explored further towards catalyst fabrication for such assemblies through methodologies developed in this work and their plausible extensions and optimization. Electrochemical functionalization of such substrates, for instance, through combination of multimetallic deposition and electropolymerization of conductive polymers, is a plausible avenue of sequential deposition methodology in fabrication of technologically important electrodes for applications in electrochemical or photochemical energy-converting devices as well as biosensors.

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APPENDICES

APPENDIX A

Supplementary Information: Electrochemical techniques and instrumentation

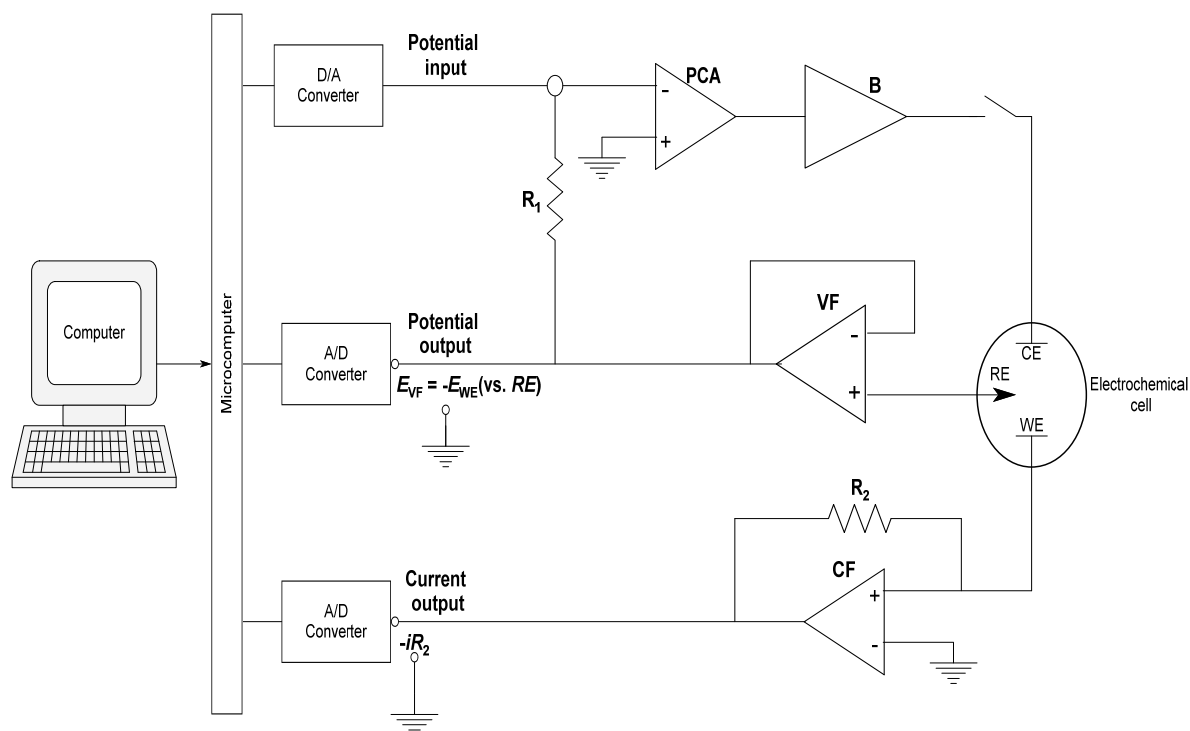


Figure A.1: A typical computer-controlled potentiostatic electrochemical system based on a potential control amplifier (PCA) with a booster (B) to improve the voltage range coupled with voltage follower (VF) and current follower (CF) circuits for measurement of i - E signals from the electrochemical cell employing Analog-to-Digital (A/D) and Digital-to-Analog (D/A) converters.

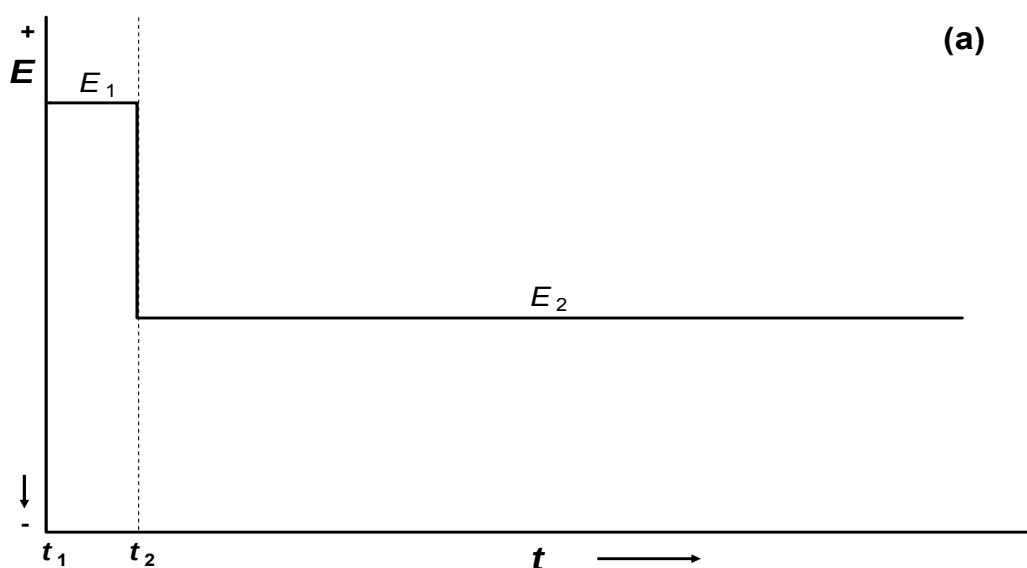


Figure A.2: (a) Potential stepping waveform in a typical experiment in which a species of interest is electroinactive at E_1 , but is reduced at a diffusion-controlled rate at E_2 .

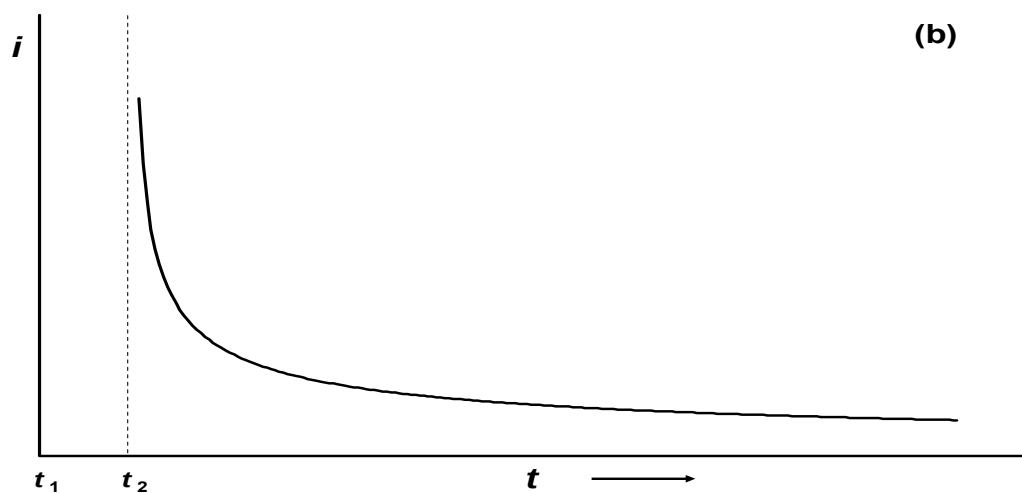


Figure A.2 (Continued): (b) chronoamperometric response as a result of the waveform perturbation described in (a).

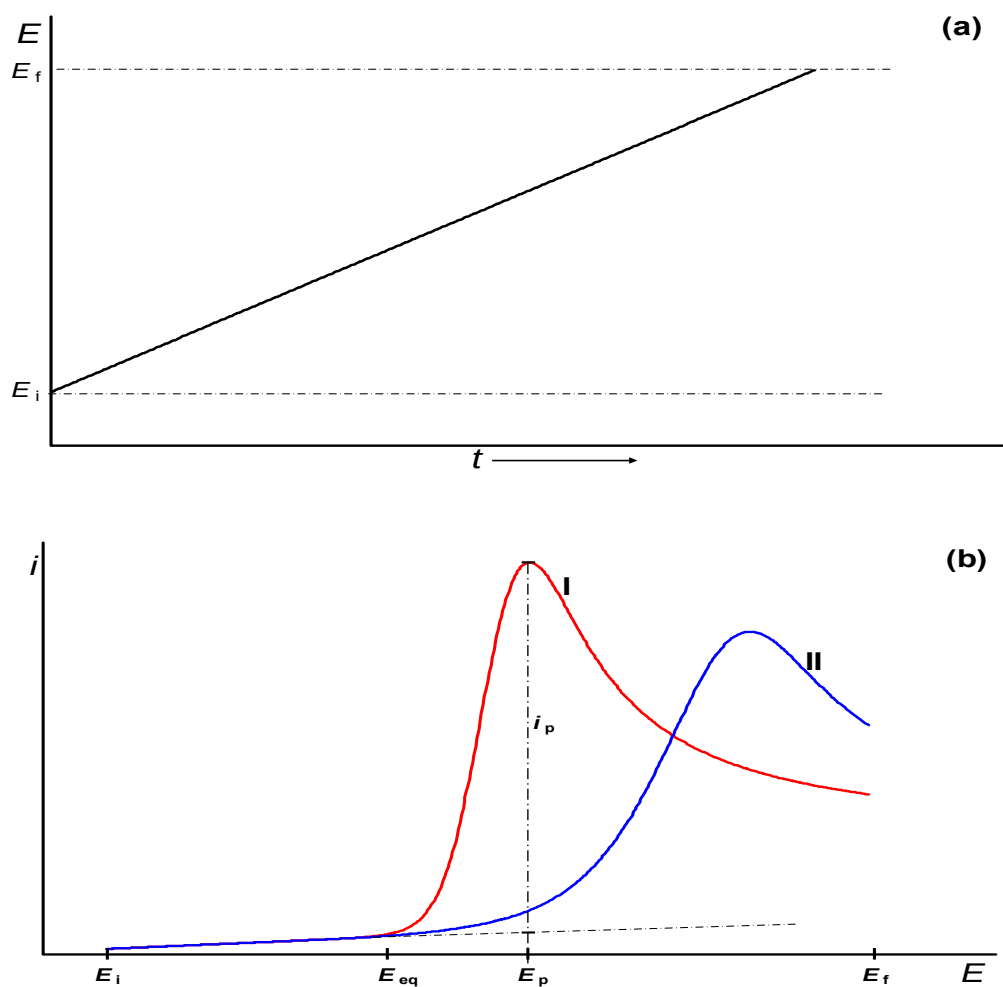


Figure A.3: Linear sweep voltammetry. (a) Applied potential ramp as a function of time. (b) Typical voltammograms with diffusion as core mode of mass-transport of electroactive species for (I) a reversible electron-transfer reaction and (II) an irreversible electrode reaction.

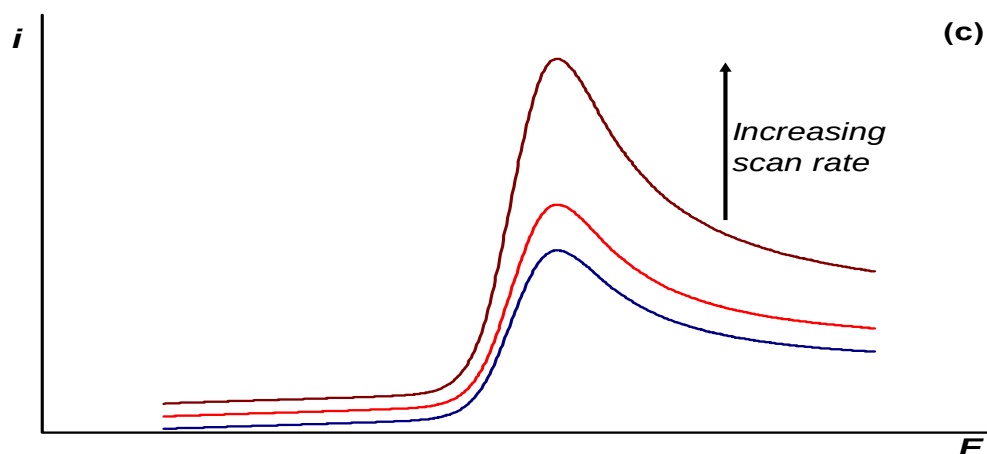


Figure A.3(Continued): (c) Effect of linear sweep scan rate variation on i - E response. A general oxidation reaction $R \rightarrow O + e^-$ is implied (Adapted from: Fischer, A.C., *Electrode Dynamics*, ed. R.G. Compton. 1996, New York: Oxford University Press).

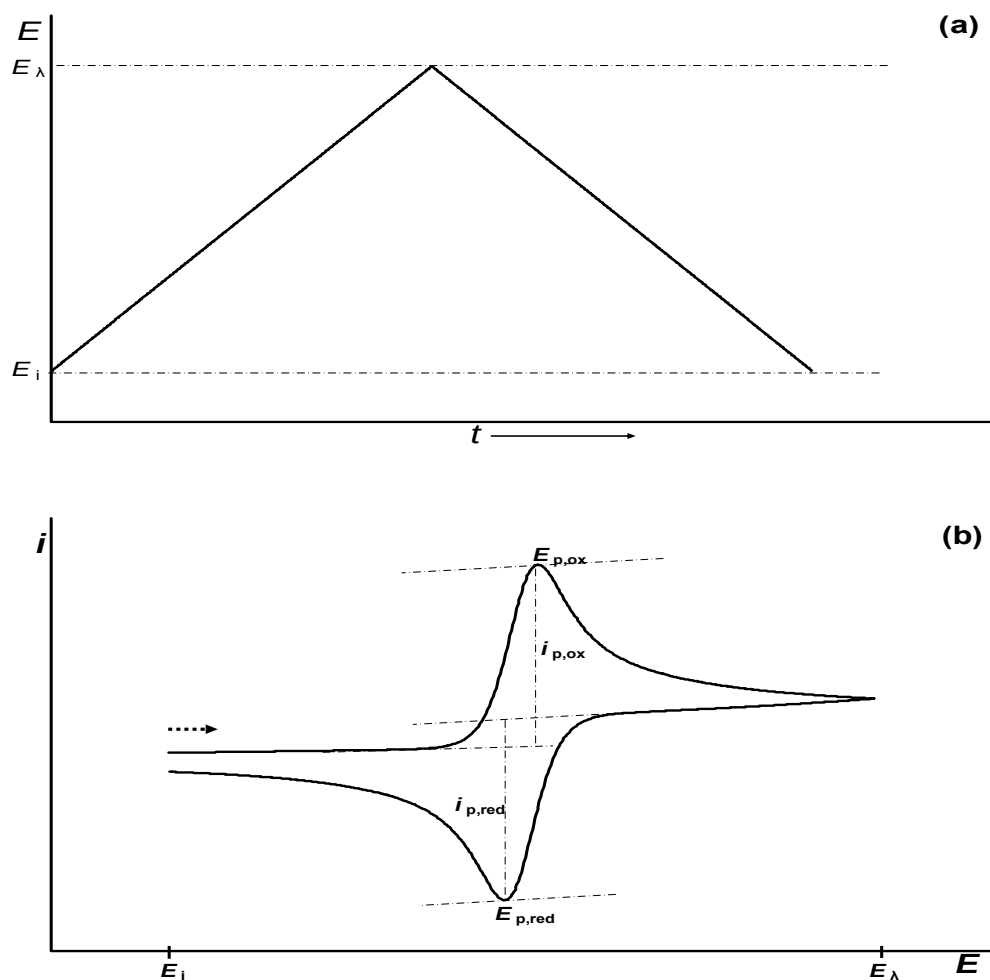


Figure A.4: Cyclic voltammetry. (a) Applied potential ramp as a function of time. (b) Typical cyclic voltammograms for a diffusion-controlled redox reaction involving a general reversible O/R couple.

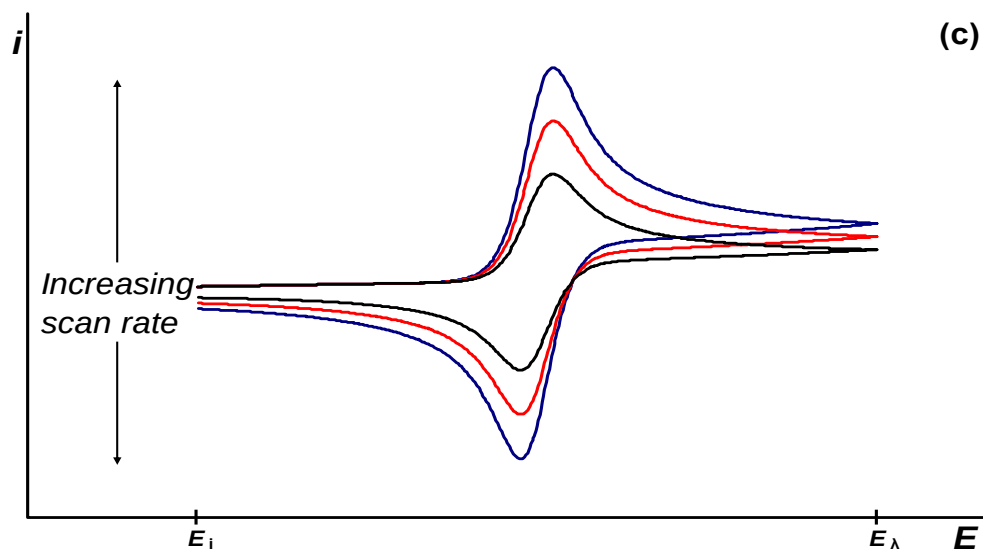


Figure A.4(Continued): (c) A series of voltammograms obtained at several potential scan rates for the reversible electron-transfer reaction.

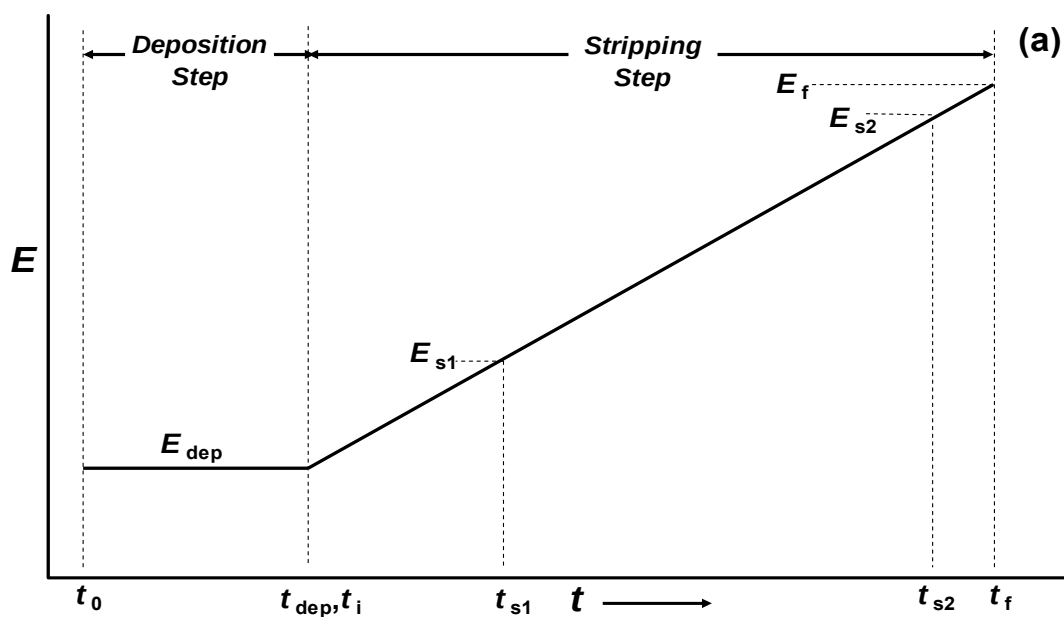


Figure A.5: (a) Potential ramp in anodic stripping voltammetry.

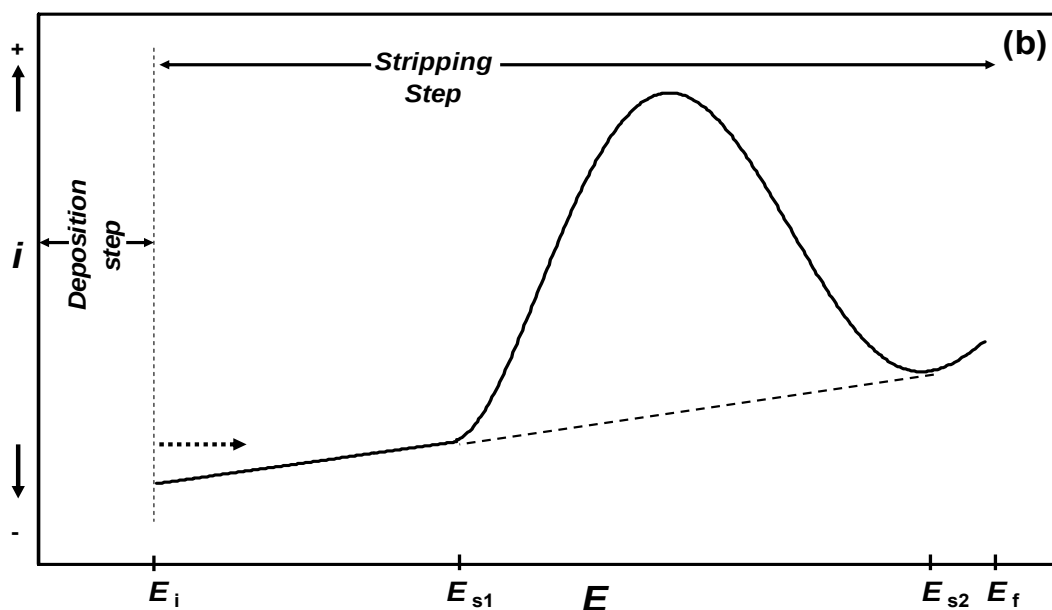


Figure A.5 (Continued): (b) Typical anodic stripping voltammogram.

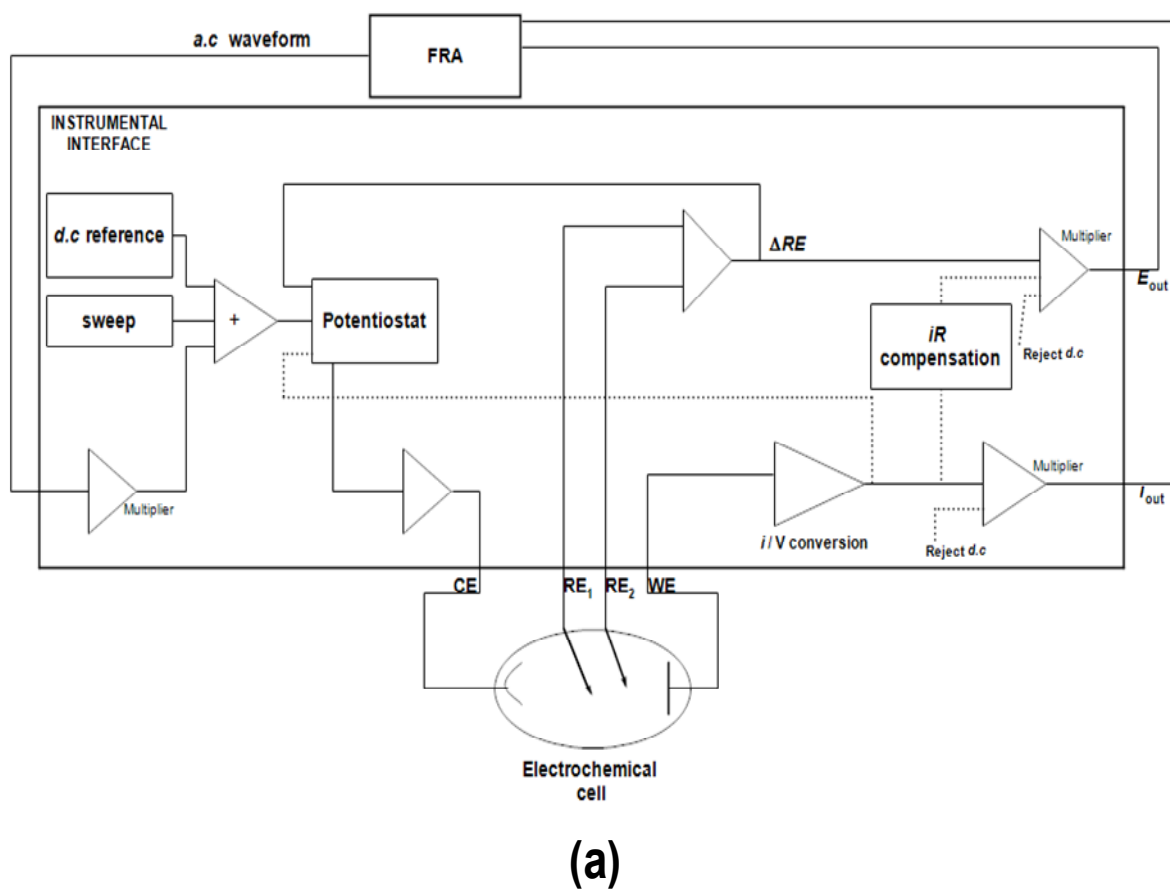


Figure A.6: (a) Electrochemical impedance spectroscopy measurement setup using a Potentiostat coupled to a Frequency Response Analyzer (FRA).

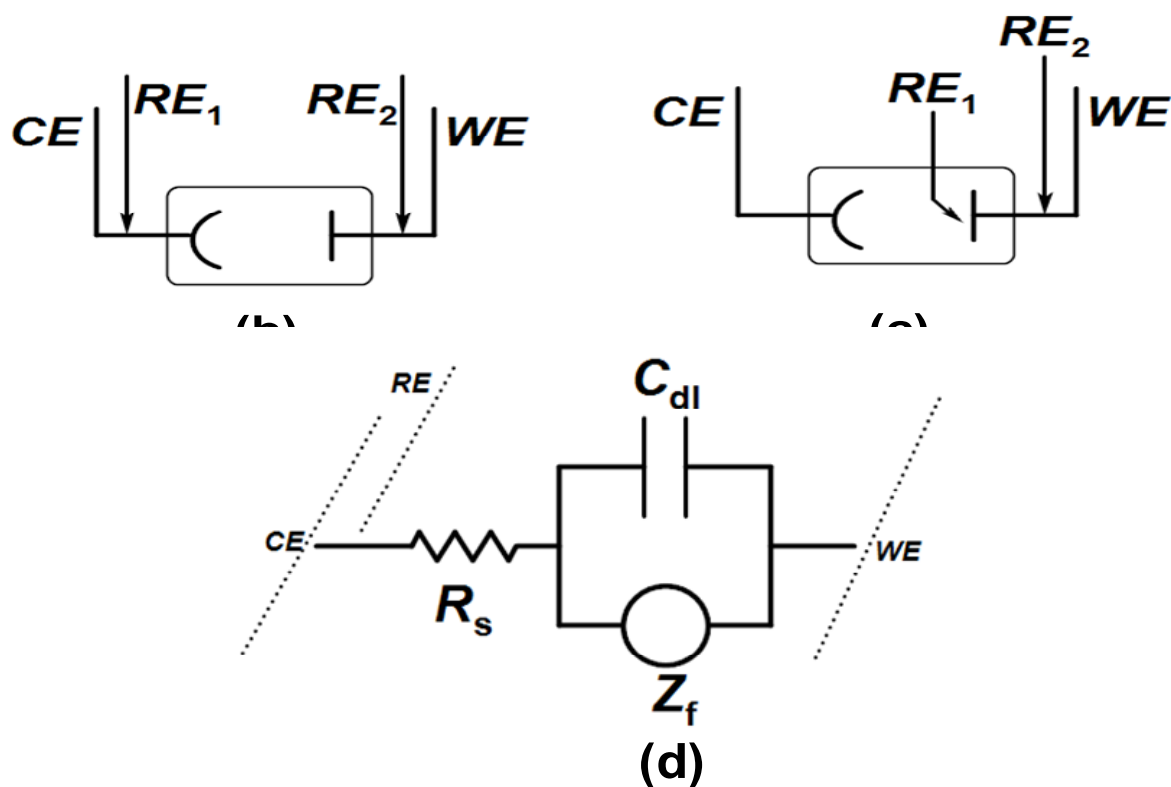


Figure A.6 (Continued): (b) Two-electrode cell and (c) three-electrode cell arrangement during impedance measurements. (d) Equivalent circuit for a general electrochemical cell. (Adapted from: Krause, S., *Impedance Methods*, in *Encyclopedia of Electrochemistry*, A.J. Bard and M. Stratmann, Editors. 2003. p. 196-229.).

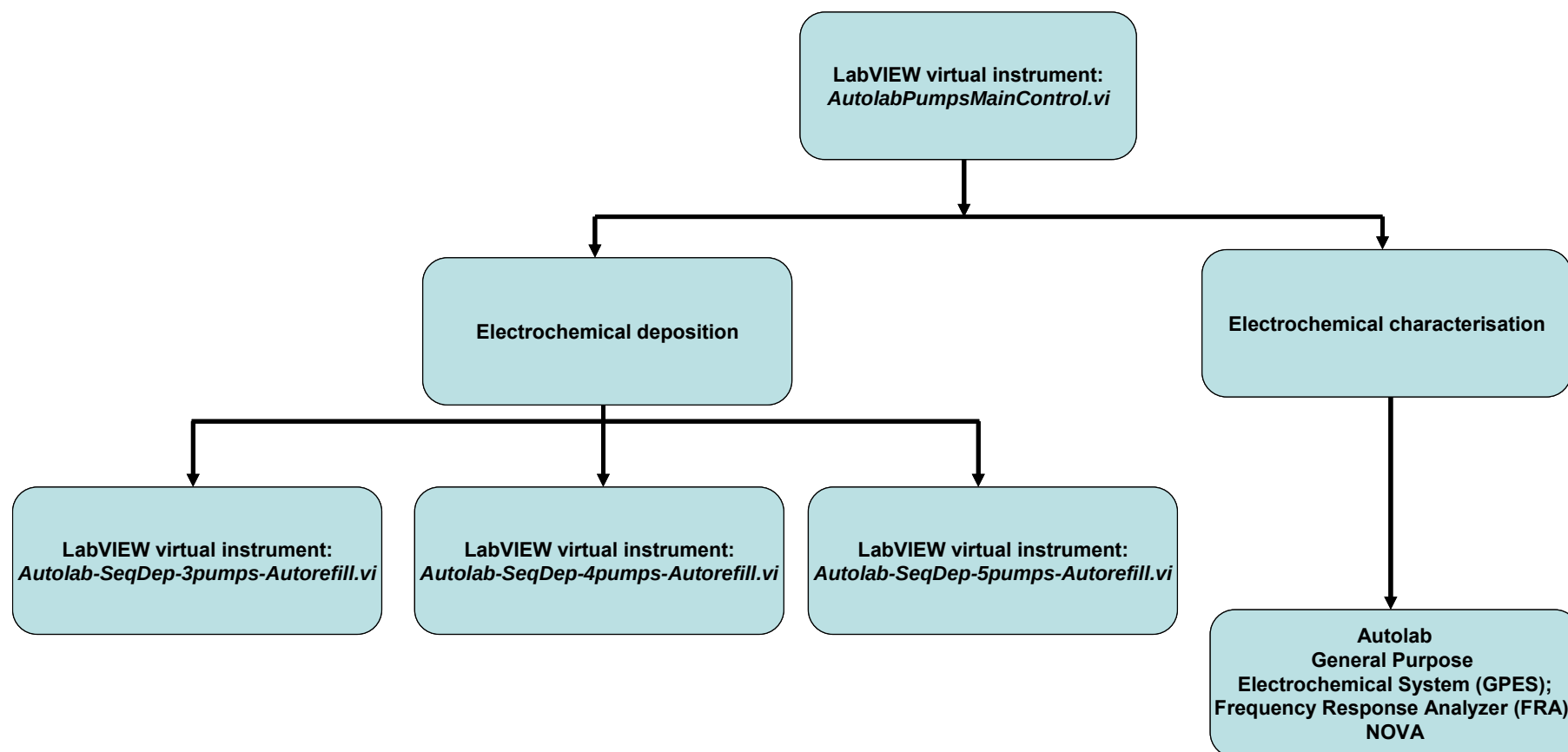


Figure A.7: Main software modules used in this work for automated electrochemical deposition and electrochemical characterisation.

A.1. Program for automated operation of potentiostat, multi-valve and piston pumps: *AutolabPumpsMainControl.vi*

Description

This software module (front panel shown in Figure A.8) controls up to six independent digital burettes (model 765 DOSIMAT, Metrohm, Switzerland), hereby used as pumps to deliver various electrolyte solutions from solution reservoirs (exchange units of the DOSIMATS), a Hamilton serial multi-valve positioner (Figure A.9) and an electrochemical measurement system (model PGSTAT 30(2), EcoChemie, Metrohm Autolab, The Netherlands), operated in potentiostatic mode. The program is used to initialize the remote control mode of the various hardware components prior to execution of any of the other computer-control modules utilising the instrumental setup schematically shown in Figure A.10.

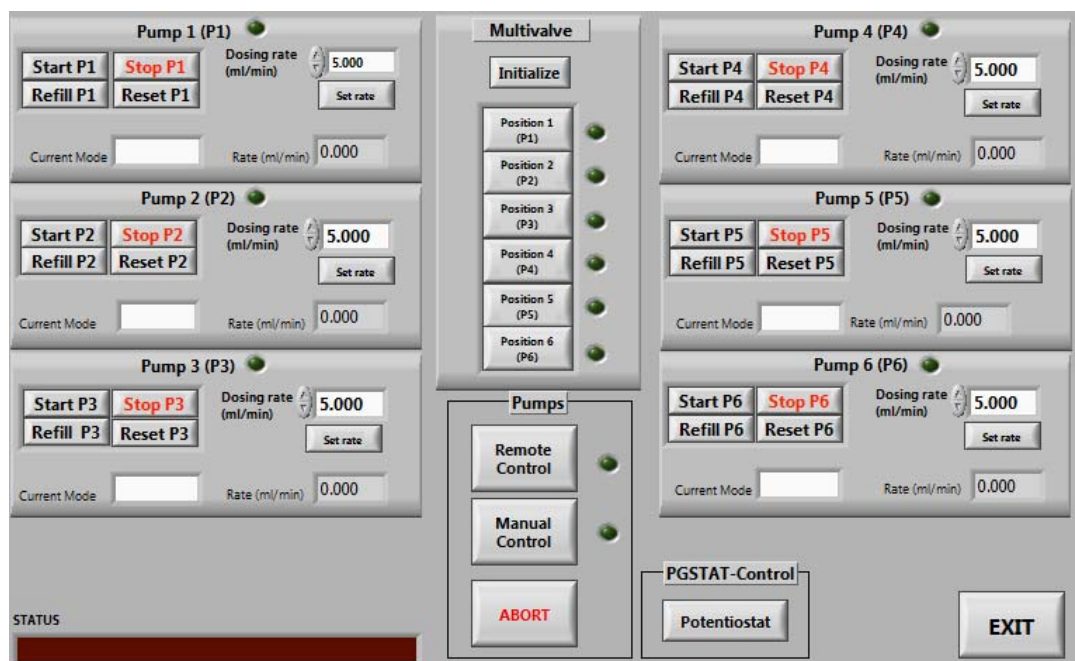


Figure A.8: Front panel of the *AutolabPumpsMainControl.vi* software module.

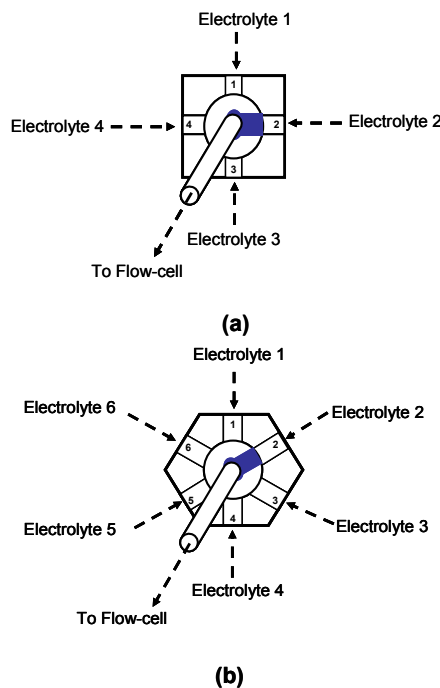


Figure A.9: Diagrams of electrolyte flow distribution from: (a) a five-way Hamilton serial Multivalve Positioner (Model HVXM R36781 valve head) with four inlet ports positioned at 90° and one central outlet to a flow-cell, (b) a seven-way Hamilton serial Multivalve Positioner (Model HVXM 36760 valve head) with six inlet ports at 60° and one central outlet.

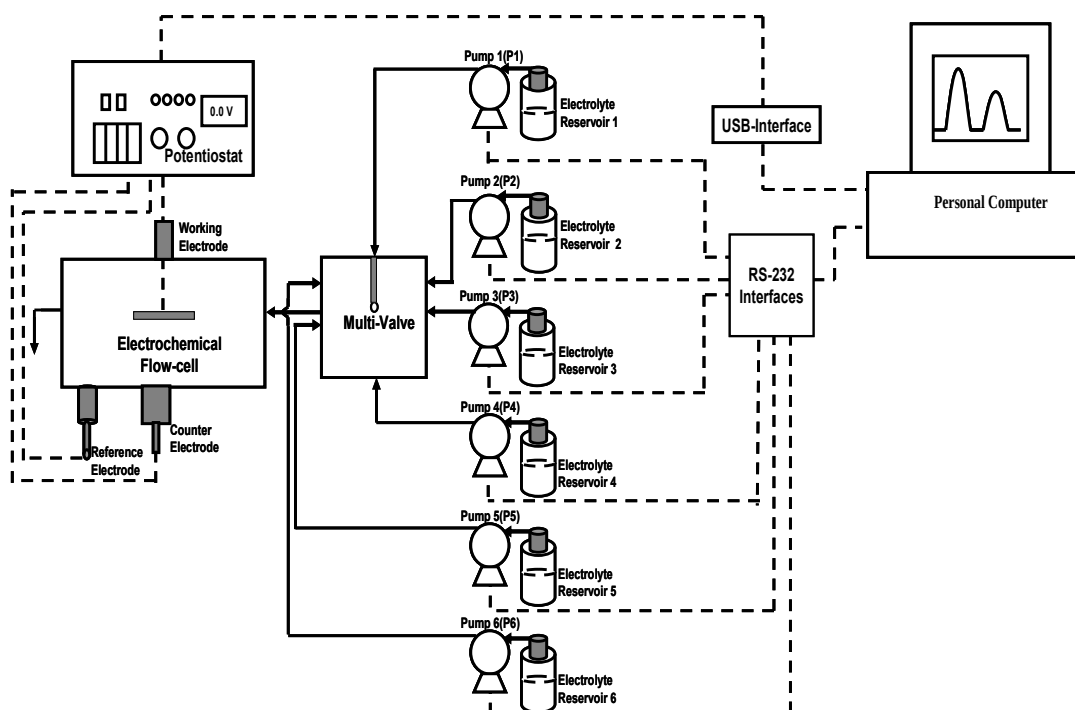


Figure A.10: Schematic of automated instrumentation setup for use with the *AutolabPumpsMainControl.vi*

A2. Automated sequential electrodeposition program: *Autolab-SeqDep-3Pumps-Autorefill.vi*

Description

This program (front panel shown in Figure A.11, general sequential steps shown in Figure A.12, typical equipment setup shown in Figure A.13 and flow-chart of execution presented in Figure A.14) controls three independent pumps (model 765 DOSIMATS, Metrohm) and a Hamilton serial multivalve positioner (Figure A.9) and an Autolab PGSTAT30(2) electrochemical workstation operated in potentiostatic mode. The *Autolab-SeqDep-3Pumps-Autorefill.vi* software module was developed with capabilities to essentially sequentially electrodeposit layered metal-based systems on suitable conductive substrate, that serves as a working electrode in a three-electrode flow-cell, either (i) composed of metals M1 and M2 from their respective precursor electrolytes with intermediate rinsing steps from an inert electrolyte or (ii) metal M2 through redox-replacement of adlayers of predeposited less noble metal M1. During execution of *Autolab-SeqDep-3Pumps-Autorefill.vi*, the sequence of deposition is carried out by applying either a series of controlled potentials or allowing open-circuit (OC) conditions to prevail. Precursors are sourced from three separate electrolyte reservoirs, electrolyte solutions of the two metals M1 and M2 and an inert electrolyte (the background electrolyte (BE)).

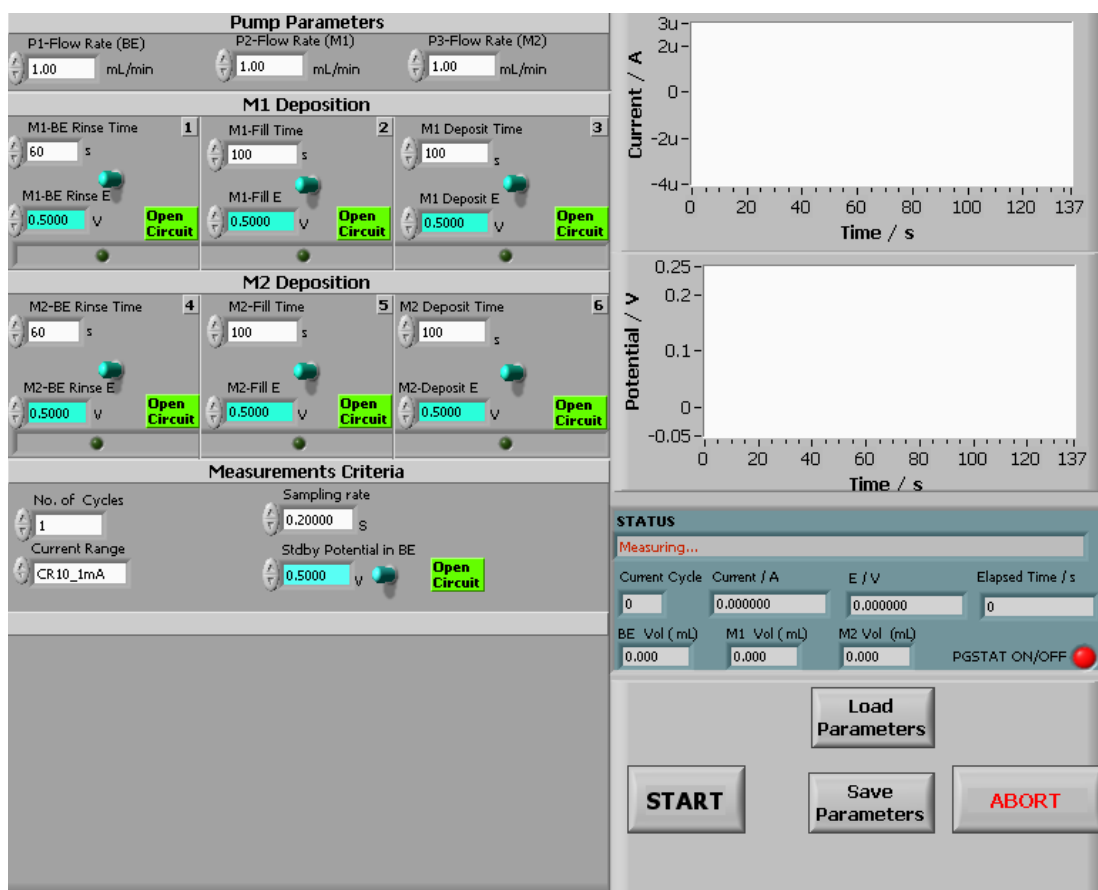


Figure A.11: Front panel of the software module *Autolab-SEQDEP-3PUMPS.vi*

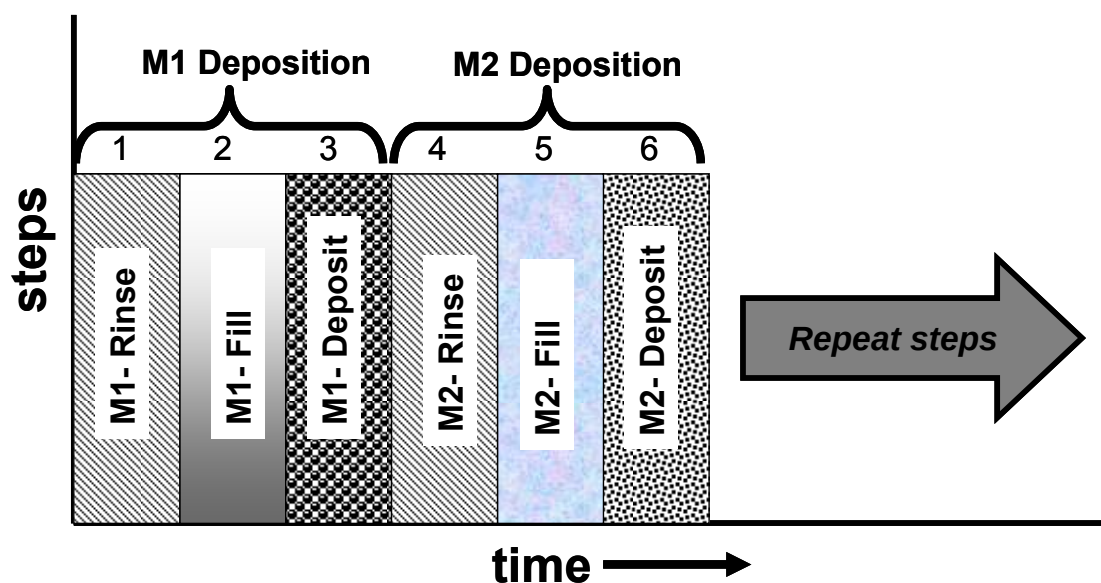


Figure A.12: Sequence of events executed by the electrodeposition program *Autolab-SeqDep-3Pumps-Autorefill.vi* involving two metal electrolyte solutions (M1 and M2) as well as a background electrolyte (BE) solution.

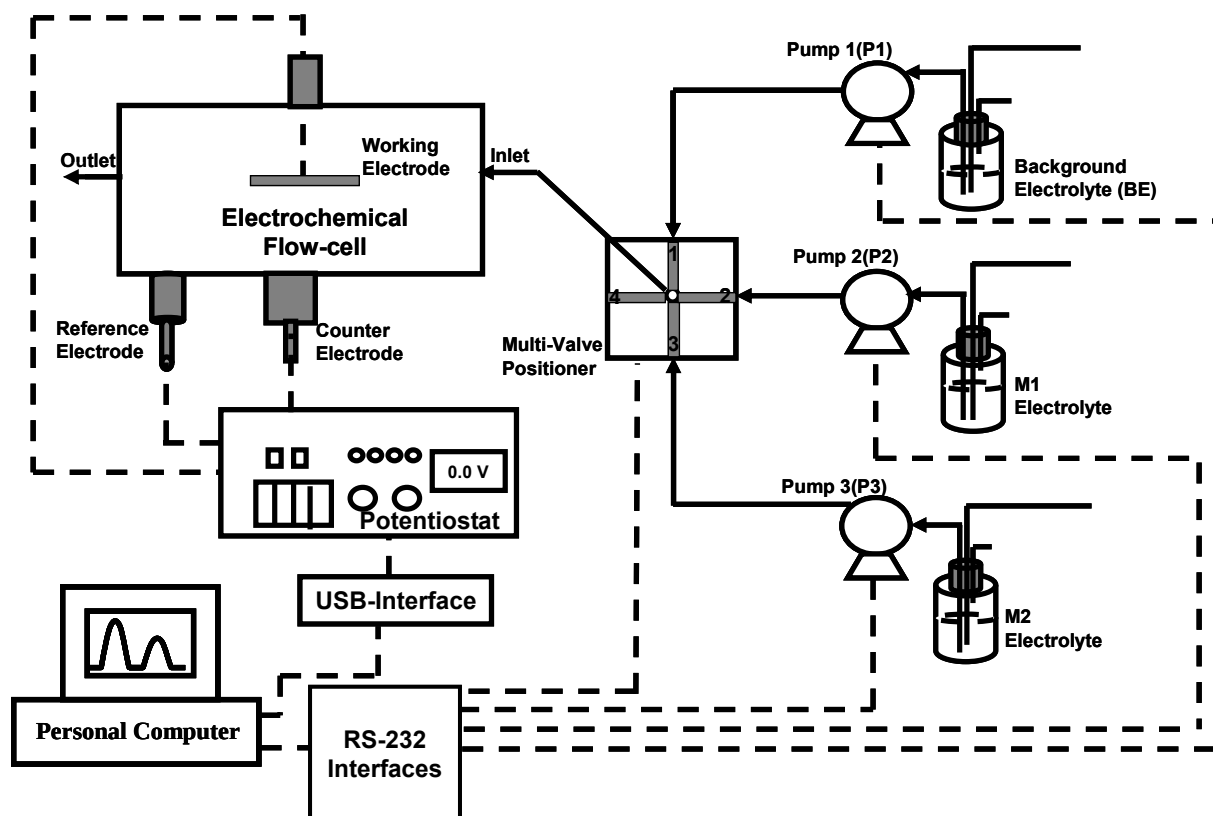


Figure A.13: Schematic of automated electrodeposition setup for use with the *Autolab-SeqDep-3Pumps-Autorefill.vi*



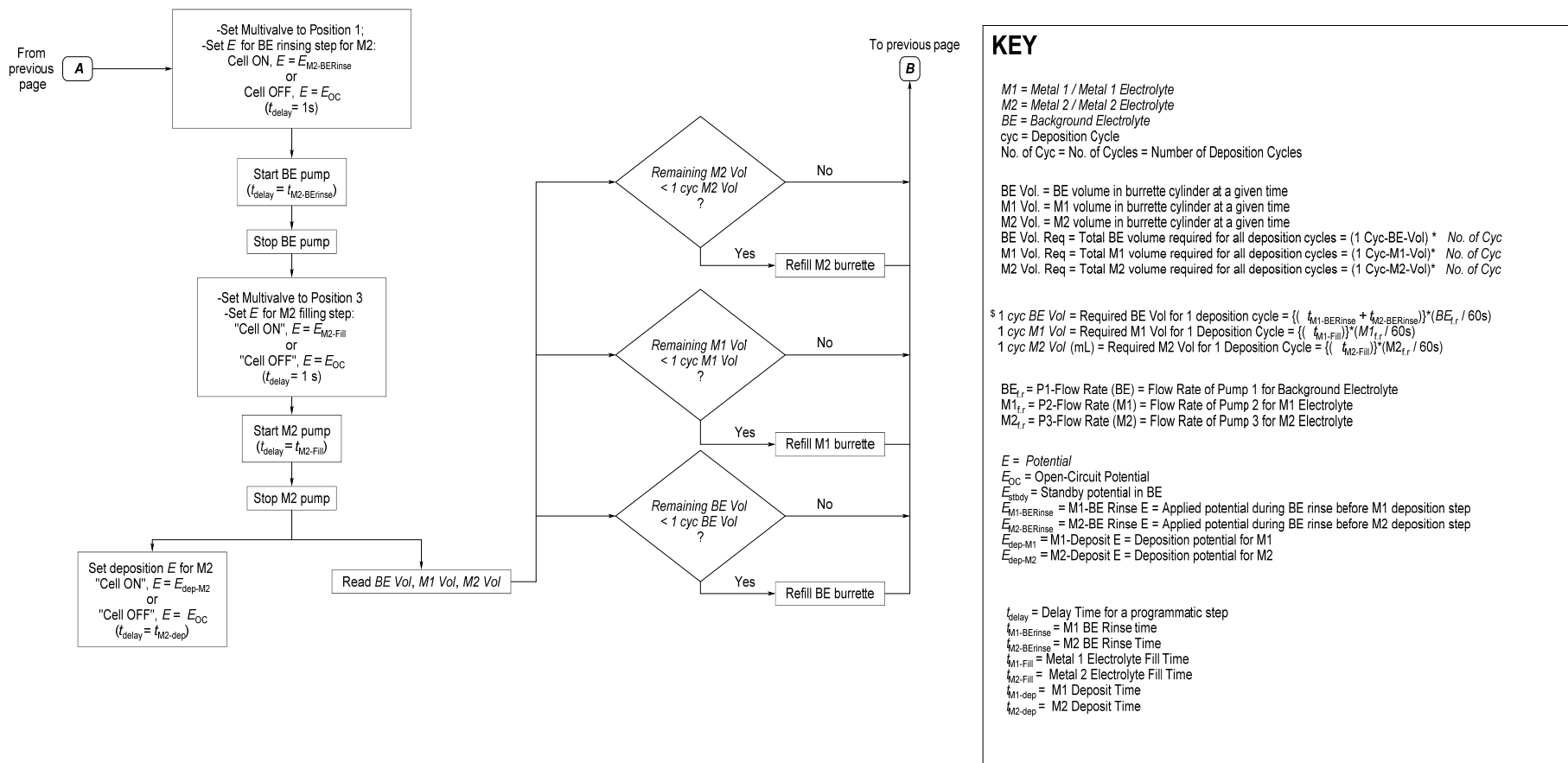


Figure A.14 (Continued): Flow-chart depicting execution of Autolab-SEQDEP-3PUMPS.vi

A.3. Program for automated electrodeposition:

Autolab-SeqDep-4Pumps-Autorefill.vi

Description

This program (front panel shown in Figure A.15, general sequential steps shown in Figure A.16, typical equipment setup shown in Figure A.17 and flow-chart of execution presented in Figure A.18) controls four independent pumps (model 765 DOSIMATS, Metrohm) and a Hamilton serial multivalve positioner (Figure A.9) and an Autolab PGSTAT30(2) electrochemical workstation operated in potentiostatic mode. The *Autolab-SeqDep-4Pumps-Autorefill.vi* software module was developed with capabilities to essentially sequentially electrodeposit layered metal-based systems on suitable conductive substrate, that serves as a working electrode in a three-electrode flow-cell, either (i) composed of metals M1, M2 and M2 from their respective precursor electrolytes with intermediate rinsing steps from an inert electrolyte or (ii) metals M2 and M3 through redox-replacement of adlayers of predeposited less noble metal M1. During execution of *Autolab-SeqDep-4Pumps-Autorefill.vi*, the sequence of deposition is carried out by applying either a series of controlled potentials or allowing open-circuit (OC) conditions to prevail. Precursors are sourced from four separate electrolyte reservoirs of the three metals M1, M2 and M3 and the BE solution.

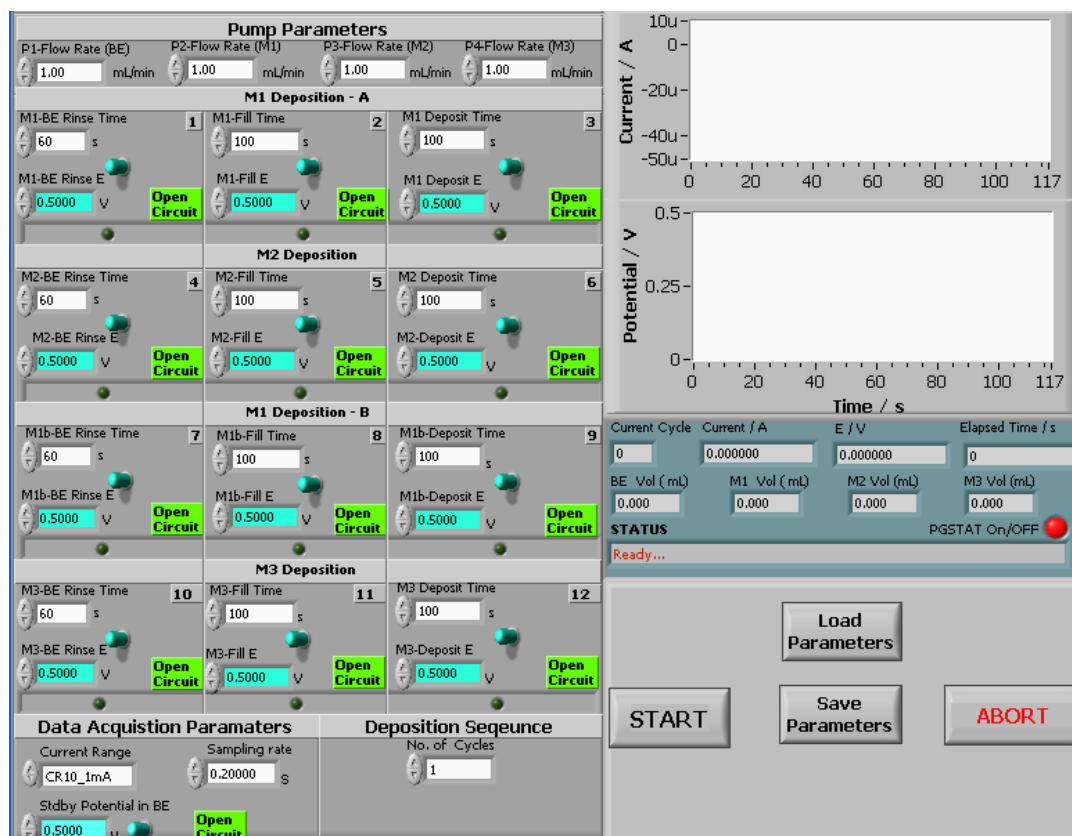


Figure A.15: Front panel of the software module *Autolab-SeqDep-4PUMPS.vi*

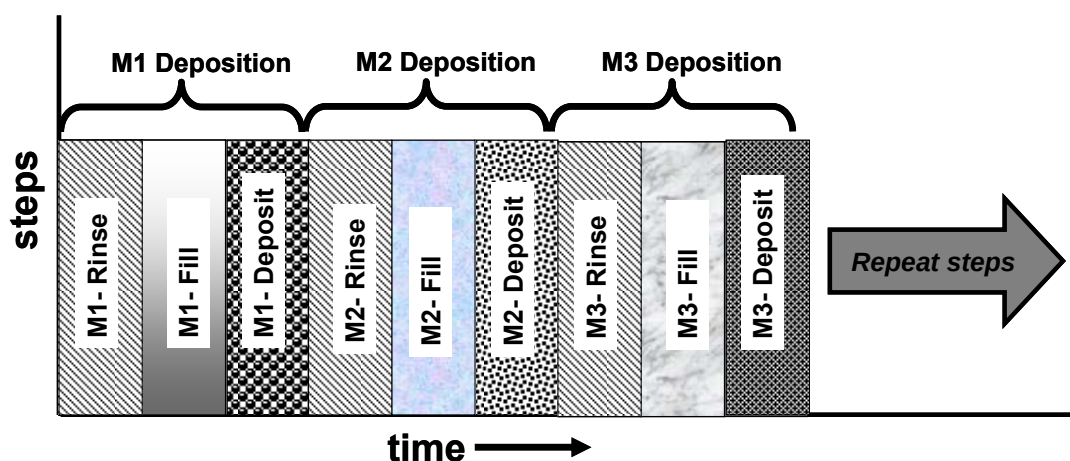


Figure A.16: Sequence of events executed by the electrodeposition program *Autolab-SeqDep-4Pumps-Autorefill.vi* involving three metal electrolyte solutions (M1, M2, and M3) as well as a background electrolyte (BE) solution.

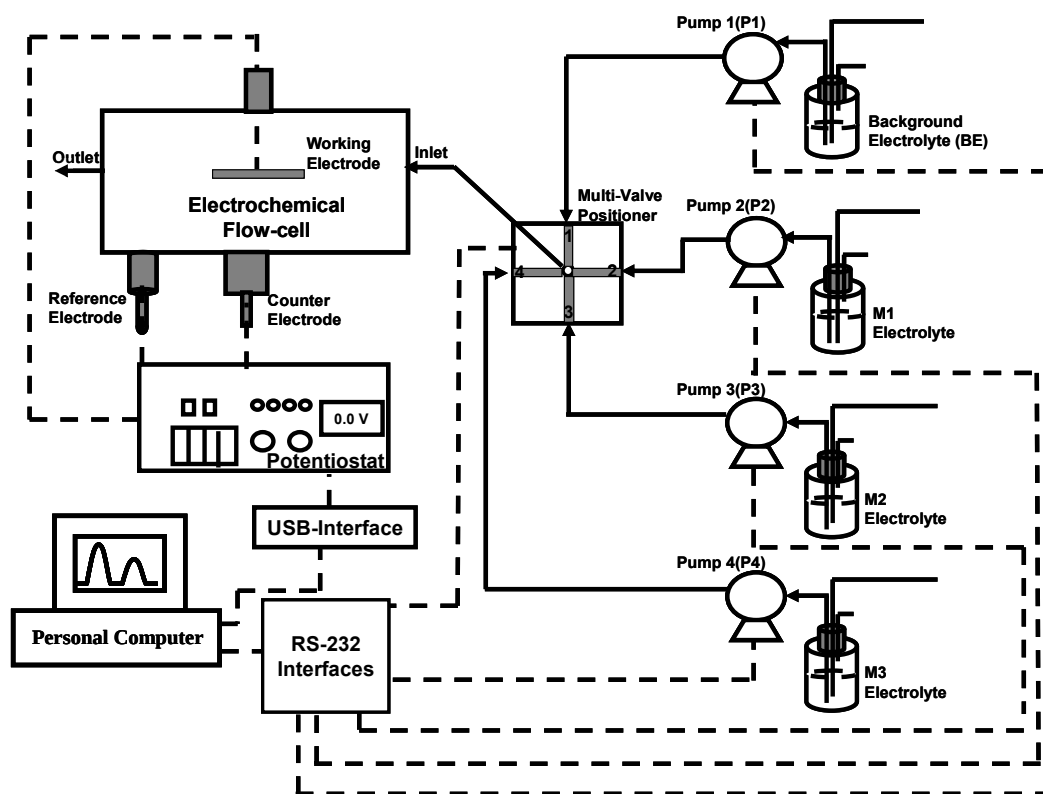


Figure A.17: Schematic of automated electrodeposition setup for use with the *Autolab-SeqDep-4Pumps-Autorefill.vi*

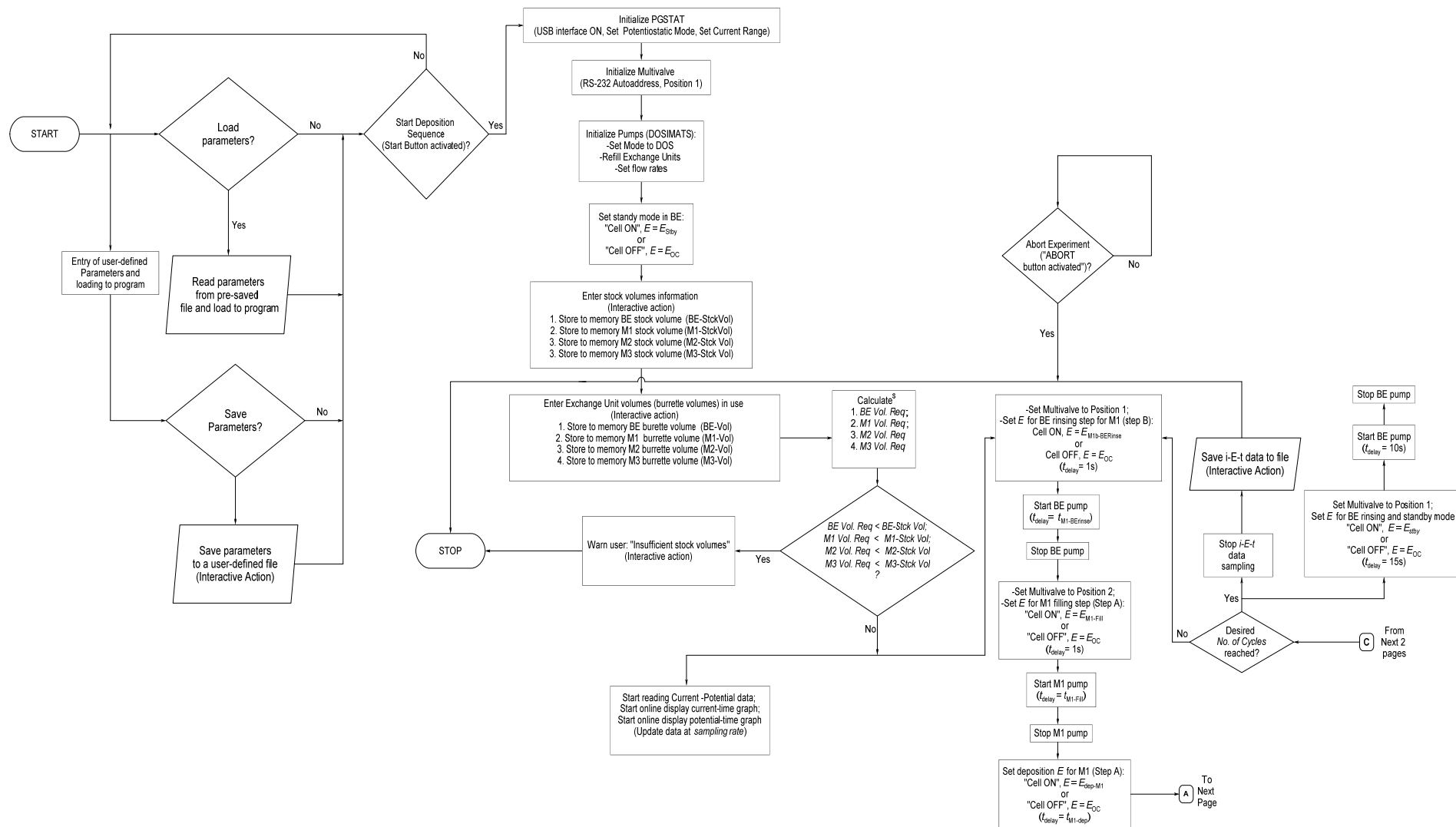


Figure A.18: Flow-chart depicting execution of *Autolab-SEQDEP-4PUMPS.vi*

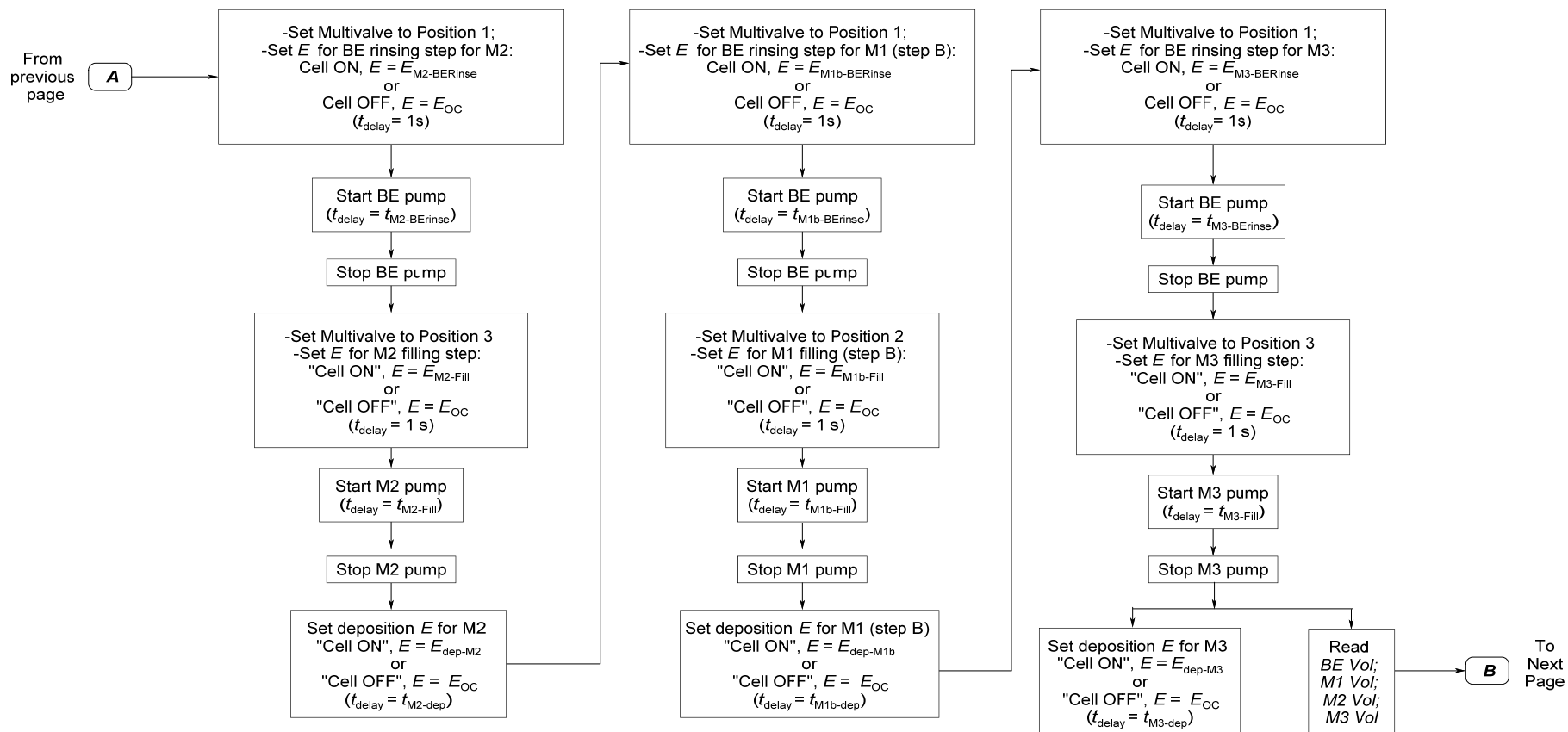
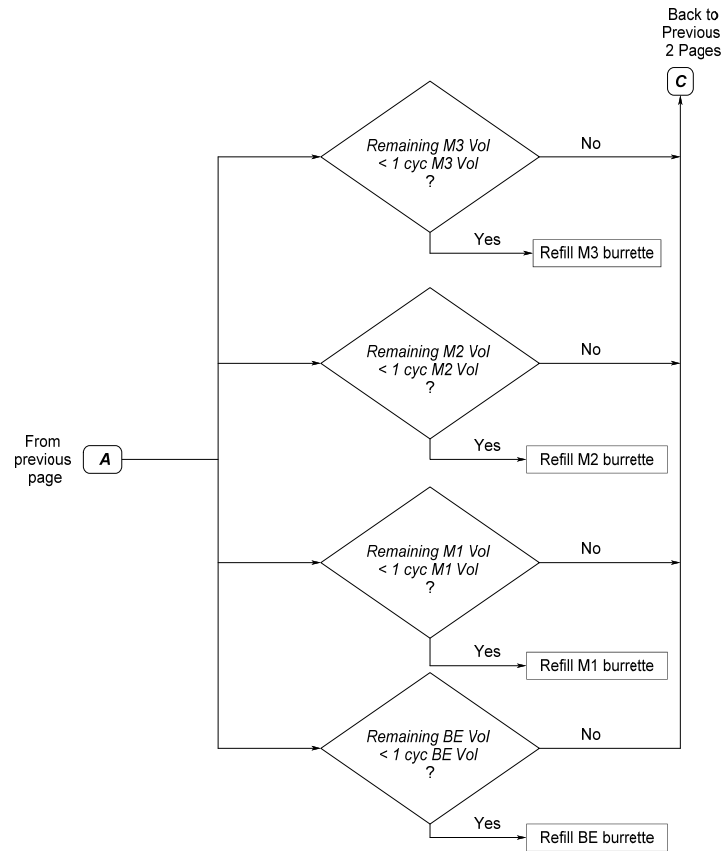


Figure A.18 (Continued): Flow-chart depicting execution of *Autolab-SEQDEP-4PUMPS.vi*



KEY

M1 = Metal 1 / Metal 1 Electrolyte
M2 = Metal 2 / Metal 2 Electrolyte
M3 = Metal 3 / Metal 3 Electrolyte
BE = Background Electrolyte
cyc = Deposition Cycle
No. of Cyc = No. of Cycles = Number of Deposition Cycles

BE Vol. = BE volume in burette cylinder at a given time
M1 Vol. = M1 volume in burette cylinder at a given time
M2 Vol. = M2 volume in burette cylinder at a given time
M3 Vol. = M3 volume in burette cylinder at a given time

BE Vol. Req = Total BE volume required for all deposition cycles = (1 Cyc-BE-Vol) * No. of Cyc
M1 Vol. Req = Total M1 volume required for all deposition cycles = (1 Cyc-M1-Vol) * No. of Cyc
M2 Vol. Req = Total M2 volume required for all deposition cycles = (1 Cyc-M2-Vol) * No. of Cyc
M3 Vol. Req = Total M3 volume required for all deposition cycles = (1 Cyc-M3-Vol) * No. of Cyc

\$1 cyc BE Vol = Required BE Vol for 1 deposition cycle = $\{(\frac{t_{M1-BERinse}}{60s} + \frac{t_{M2-BERinse}}{60s} + \frac{t_{M1b-BERinse}}{60s} + \frac{t_{M4-BERinse}}{60s})\} * (BE_{fr} / 60s)$
1 cyc M1 Vol = Required M1 Vol for 1 Deposition Cycle = $\{(\frac{t_{M1-Fill}}{60s})\} * (M1_{fr} / 60s)$
1 cyc M2 Vol (mL) = Required M2 Vol for 1 Deposition Cycle = $\{(\frac{t_{M2-Fill}}{60s})\} * (M2_{fr} / 60s)$
1 cyc M3 Vol (mL) = Required M3 Vol for 1 Deposition Cycle = $\{(\frac{t_{M3-Fill}}{60s})\} * (M3_{fr} / 60s)$

BE_{fr} = P1-Flow Rate (BE) = Flow Rate of Pump 1 for Background Electrolyte
M1_{fr} = P2-Flow Rate (M1) = Flow Rate of Pump 2 for M1 Electrolyte
M2_{fr} = P3-Flow Rate (M2) = Flow Rate of Pump 3 for M2 Electrolyte
M3_{fr} = P4-Flow Rate (M3) = Flow Rate of Pump 4 for M3 Electrolyte

E = Potential

E_{OC} = Open-Circuit Potential

E_{stbdy} = Standby potential in BE

E_{M1-BERinse} = M1-BE Rinse E = Applied potential during BE rinse before M1 deposition (step A)

E_{M1b-BERinse} = M1b-BE Rinse E = Applied potential during BE rinse before M1 deposition (step B)

E_{M2-BERinse} = M2-BE Rinse E = Applied potential during BE rinse before M3 deposition step

E_{M3-BERinse} = M4-BE Rinse E = Applied potential during BE rinse before M4 deposition step

E_{dep-M1} = M1-Deposit E = Deposition potential for M1 (step A)

E_{dep-M1b} = M1b-Deposit E = Deposition potential for M1 (step B)

E_{dep-M2} = M2-Deposit E = Deposition potential for M2

E_{dep-M3} = M3-Deposit E = Deposition potential for M3

t_{delay} = Delay Time for a programmatic step

t_{M1-BERinse} = M1 BE Rinse time (step A)

t_{M1b-BERinse} = M1 BE Rinse Time (step B)

t_{M2-BERinse} = M2 BE Rinse Time

t_{M3-BERinse} = M3 BE Rinse Time

t_{M1-Fill} = Metal 1 Electrolyte Fill Time (step A)

t_{M1b-Fill} = Metal 1 Electrolyte Fill Time (step B)

t_{M2-Fill} = Metal 2 Electrolyte Fill Time

t_{M3-Fill} = Metal 3 Electrolyte Fill Time

t_{M1-dep} = M1 Deposit Time (step A)

t_{M1b-dep} = M1 Deposit Time (step B)

t_{M2-dep} = M2 Deposit Time

t_{M3-dep} = M3 Deposit Time

Figure A.18 (Continued): Flow-chart depicting execution of Autolab-SEQDEP-4PUMPS.vi

A.4. Program for automated electrodeposition:

Autolab-SeqDep-5Pumps-Autorefill.vi

Description

This program (front panel shown in Figure A.19, general sequential steps shown in Figure A.20, typical equipment setup shown in Figure A.21 and flow-chart of execution presented in Figure A.22) controls five independent pumps (model 765 DOSIMATS, Metrohm) and a Hamilton serial multivalve positioner (Figure A.9) and an Autolab PGSTAT30(2) electrochemical workstation, operated in potentiostatic mode. The *Autolab-SeqDep-5Pumps-Autorefill.vi* software module was developed with capabilities to essentially sequentially electrodeposit layered metal-based systems on suitable conductive substrate, that serves as a working electrode in a three-electrode flow-cell, either (i) composed of metals M1, M2, M3 and M4 from their respective precursor electrolytes with intermediate rinsing steps from an inert electrolyte, (ii) distinct layers of metals M2, M3, and M4 through intermediate steps involving redox-replacement of adlayers of predeposited less noble metal M1, or (iii) distinct layers of M2 and M4 through intermediate steps involving redox-replacement of adlayers of less noble metals M1 and M2, respectively. During execution of *Autolab-SeqDep-5Pumps-Autorefill.vi*, the sequence of deposition is carried out by applying either a series of controlled potentials or allowing open-circuit (OC) conditions to prevail. Precursors are sourced from five separate electrolyte reservoirs; electrolyte solutions of the metals to be deposited and BE solution.

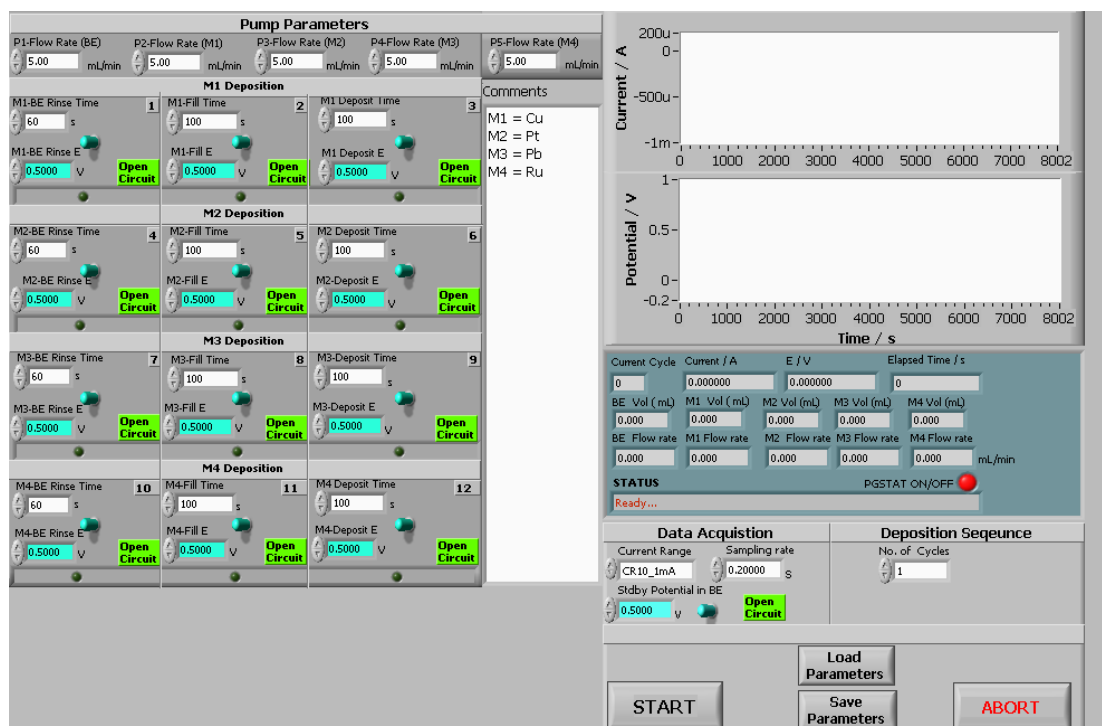


Figure A.19: Front panel of the software module *Autolab-SeqDep-5Pumps.vi*

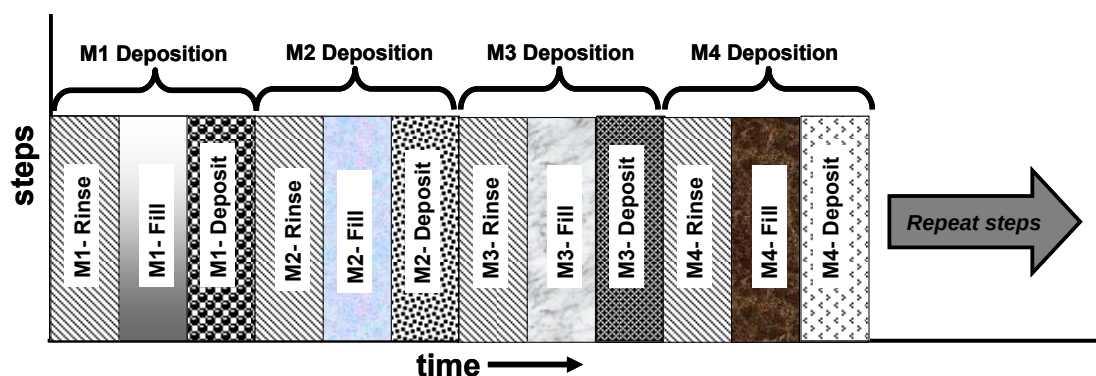


Figure A.20: Sequence of events executed by the electrodeposition program *Autolab-SeqDep-5Pumps-Autorefill.vi* involving four metal electrolyte solutions (M1, M2, M3 and M4) as well as a background electrolyte (BE) solution.

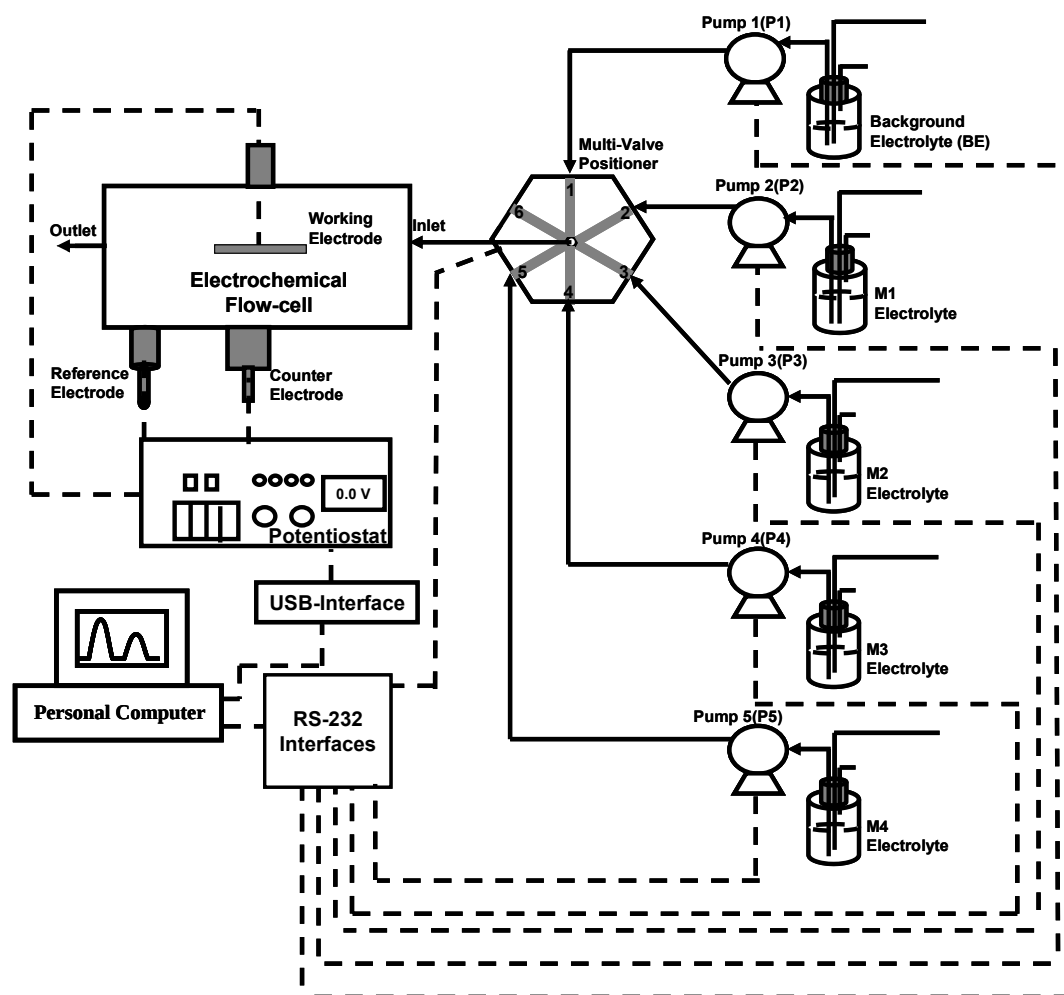


Figure A.21: Schematic of automated electrodeposition setup for use with the *Autolab-SeqDep-5Pumps-Autorefill.vi*.

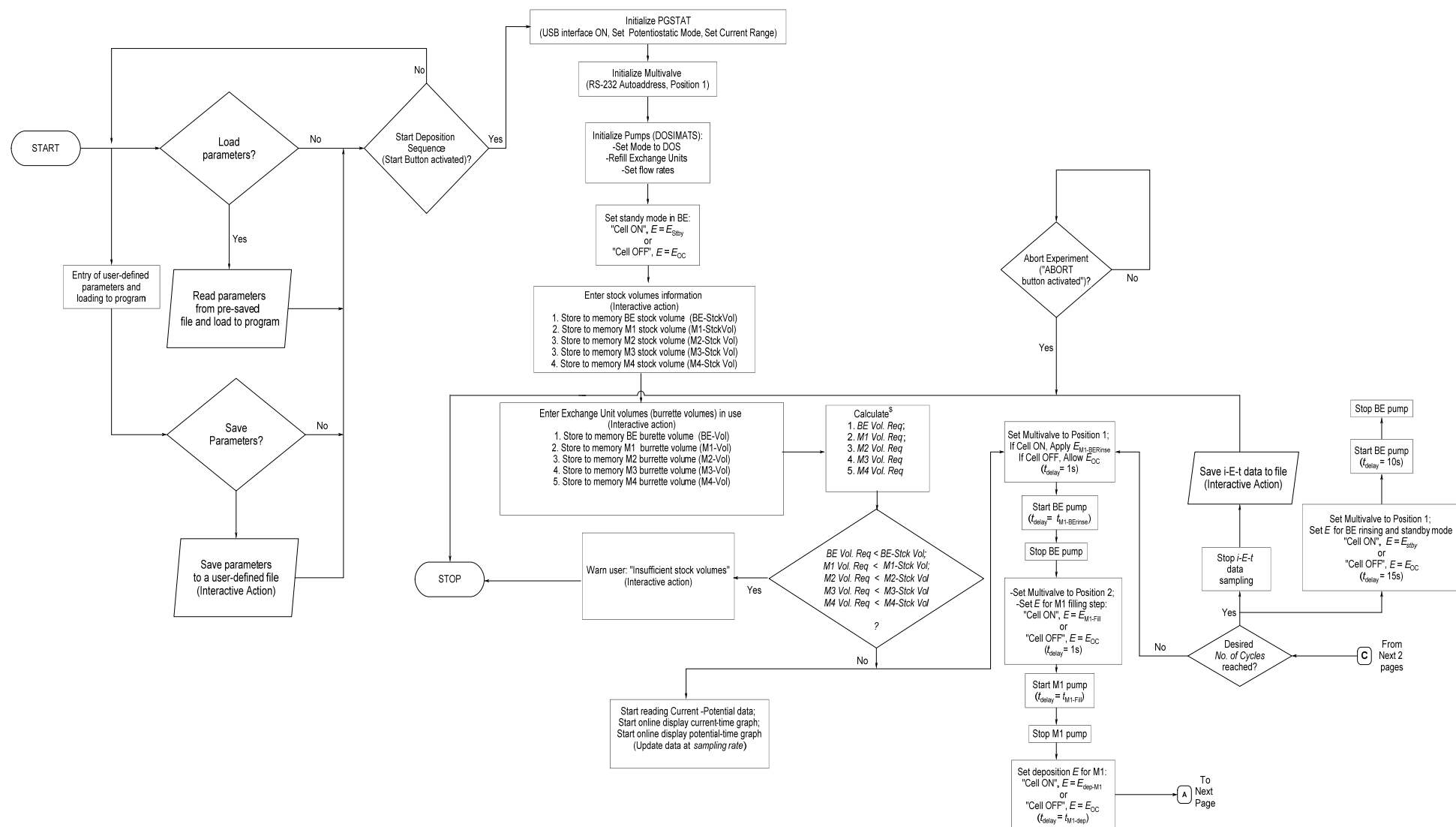


Figure A.22: Flow-chart depicting execution of *Autolab-SeqDep-5Pumps.vi*

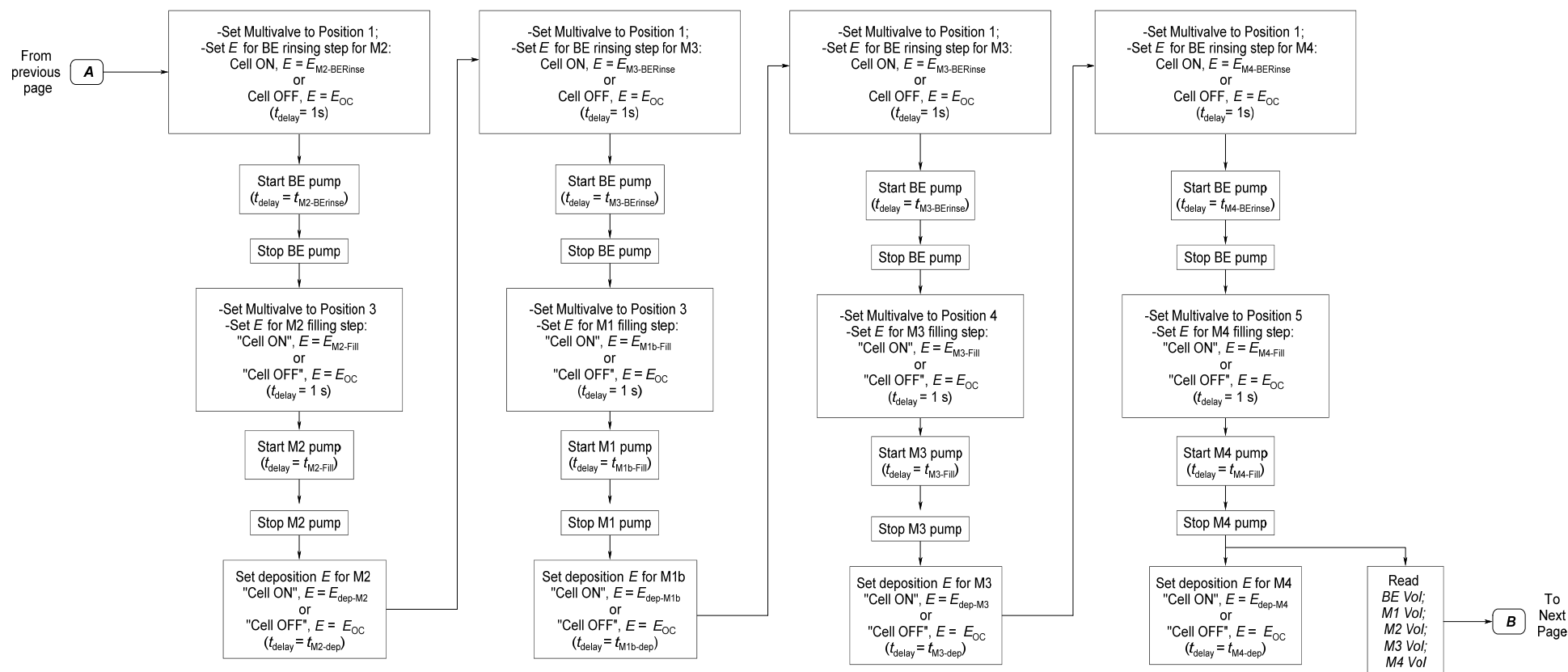


Figure A.22 (Continued): Flow-chart depicting execution of *Autolab-SEQDEP-5PUMPS.vi*

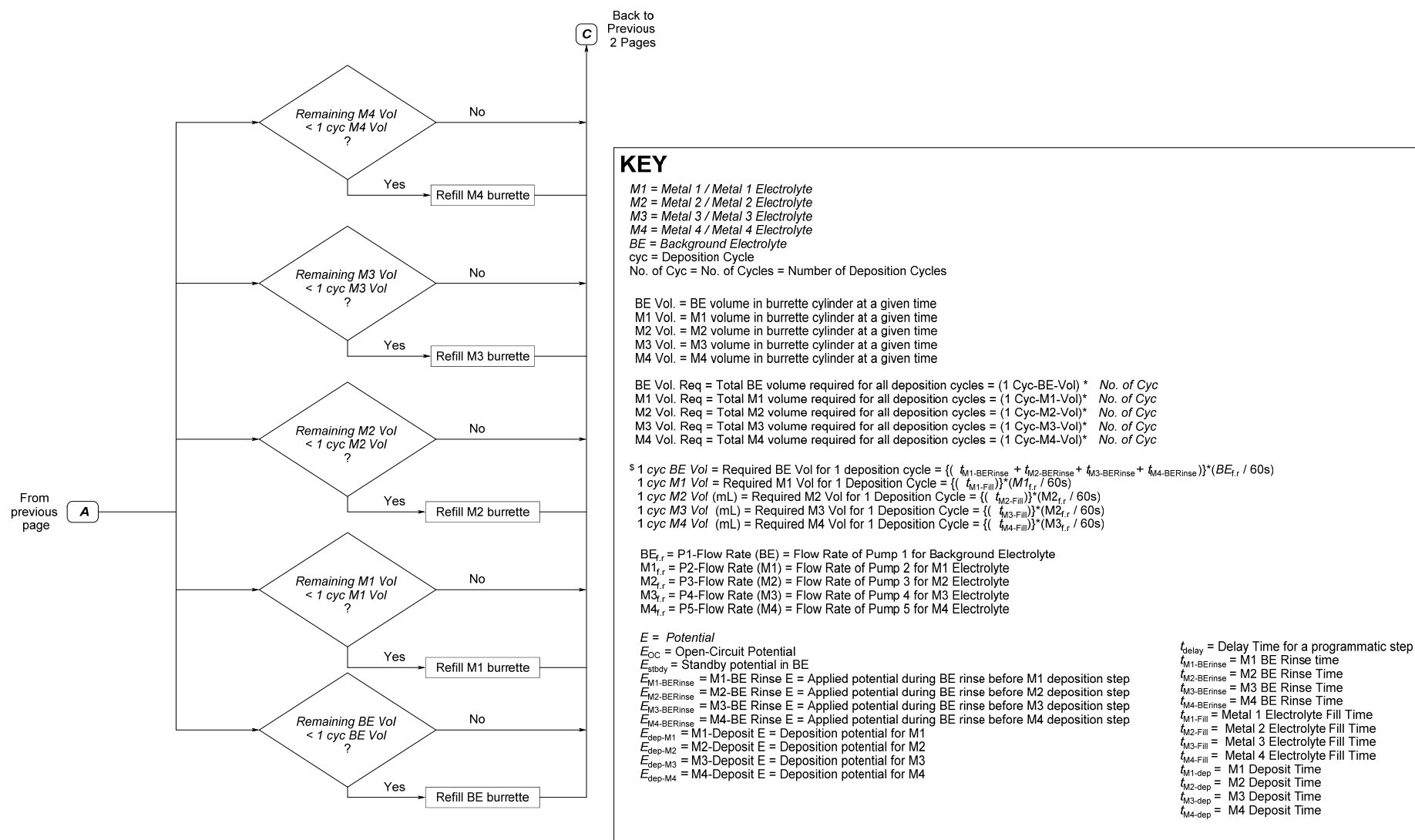


Figure A.22 (Continued): Flow-chart depicting execution of *Autolab-SEQDEP-5PUMPS.vi*

APPENDIX B

Supplementary Information: potential-pH thermochemical modelling

B.1. Potential-pH Thermochemical Modelling: Theoretical background

Thermodynamic analysis is an important and powerful tool in predicting and rationalizing the stability relations in redox reaction systems such as those involving transformation of metal ions to metallic forms via electrochemical deposition techniques. In particular, in the ubiquitous aqueous solutions employed to carry out electrochemical reactions, the influence of pH and electrochemical potential (E) on chemical stabilities of species, at their various oxidation states, is especially useful. Conventionally, the E - pH stability or predominance diagrams - commonly known as the Pourbaix diagrams - are consulted.^[1] The early works (established in the 1960s) were restricted to graphs of single elements in aqueous systems at 25 °C.^[1] In recent times, as a result of advances in computer technologies, methods of evaluation of thermodynamic stabilities of chemical species have been forthcoming and they provide visualization of thermodynamic stabilities with consideration of multiple chemical reaction systems at a range of temperature and system composition. To predict, comprehend and rationalize the stability relations in redox reaction systems, the relations are typically analyzed by plotting the stability fields of the chemical species as a function of the variables that determine the position of the electrochemical equilibrium.^[2,3]

A thermodynamic system can be considered to contain a number of phases. Phases are categorized into three groups: the gaseous phases, solution phases, and pure stoichiometric solid phases. Phases can have one or more species or phase constituents. The phase constituents have compositions expressed as amounts of a number of system components. Typically, the system components are elements, but they can also be stoichiometric combinations of elements. The Gibbs energy, G , is the focal state function in thermodynamic models; however, the relevant thermodynamic data of pure phase constituents is customarily stored in the form of enthalpy of formation and entropy at standard conditions (Temperature, $T = 298.15$ K and Pressure, $P = 1$ bar) as well as a

^[1] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*. NACE International: Houston, Texas, 1974.

^[2] C. W. Bale, P. Chartrand, S. A. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melançon, A. D. Pelton, and S. Petersen, *FactSage thermochemical software and databases*, *Calphad*, **26** (2), pp. 189-228 (2002).

^[3] I. Fishtik, *Thermodynamic Stability of Chemical Species in Multiple Reaction Systems*, *Journal of Physical Chemistry B*, **109**, pp. 3851-3859 (2005).

temperature function of the heat capacity at constant P. In this work the computer software package for thermochemical modelling FactSage and its associated databases^[2] was employed. In FactSage there are two types of thermochemical databases; (i) compound (pure substances) databases, and (ii) solution databases. Compound databases are for stoichiometric solid, liquid, and gaseous species. Depending upon the type of phase (solid, liquid, or gas) and data availability, the stored properties include enthalpy of formation at 298.15 K, ΔH°_{298} , entropy, S°_{298} , heat capacity at constant pressure, $C_p(T)$, molar volumes at 298.15 K, magnetic data, and other relevant thermochemical data. Infinitely dilute aqueous solution data and non-ideal gas properties are also stored in the compound databases. In particular, regarding heat capacity data, the coefficients of appropriate polynomial C_p functions are stored for appropriate temperature ranges for solid, liquid, and gaseous phases of the pure substances. Solution databases are for solid and liquid alloys, carbides, nitrides, and concentrated aqueous solutions, salts, etc.^[2]

The basic data ΔH°_{298} , S°_{298} , and $C_p(T)$ can be used to derive the temperature dependencies (Equations B.1 – B.3) of the enthalpy, $H(T)$, entropy, $S(T)$, and most important, the thermodynamic state function Gibbs energy, $G(T)$, through combination of $H(T)$ and $S(T)$ from the well-known Gibbs-Helmholtz relationship (Equation B.3):

$$H(T) = \Delta H^\circ_{298} + \int_{298}^T C_p(T) dT \quad (\text{B.1})$$

$$S(T) = S^\circ_{298} + \int_{298}^T \frac{C_p(T)}{T} dT \quad (\text{B.2})$$

$$G(T) = H(T) - T.S(T) \quad (\text{B.3})$$

For pure substances, that is, solids, liquids, and gases, the heat capacity, C_p , is expressed as an empirical polynomial function of the absolute temperature, T (Equation B.4):

$$C_p(T) = \sum_{i=1}^n C_{(i)} T^{P(i)} \quad (\text{B.4})$$

where $C_{(i)}$ are relevant empirical coefficients, and $p(i)$ are associated polynomial coefficients that are determined from thermochemical experiments and are critically evaluated for inclusion in the FactSage databases.

The Gibbs energy of a phase is defined as a function of temperature, pressure, and amounts of phase constituents:

$$G^P = G^P(T, P, n_i) \quad (\text{B.5})$$

The Gibbs energy of a mixture is given as:

$$G^P = \sum_i n_i \mu_i = \sum_i \mu_i^0 + RT \ln a_i = \sum_i \mu_i^0 + RT \ln \lambda_i x_i \quad (\text{B.6})$$

where μ_i is the chemical potential of a phase constituent i and n_i is the molar amount of the phase constituent i , μ_i^0 is the standard (reference) chemical potential, R is the gas constant, T stands for temperature, a_i is the activity of phase constituent i , λ_i is the activity coefficient and x_i is the effective concentration of phase constituent i .

For a general system comprising a set of m chemical species S_i ($i = 1, 2, \dots, m$) at temperature T , pressure P and species activities a_{S_i} ($i = 1, 2, \dots, n$), the stability fields between species in a thermodynamic system are determined based on Gibbs energy changes (ΔG_j) of individual reactions described by:

$$\Delta G_j = \Delta G_j^0 + RT \ln \prod_{i=1}^m a_{S_i}^{v_i} \quad (j = 1, 2, \dots, m) \quad (\text{B.7})$$

where v_i is the stoichiometric coefficient of species S_i in a particular reaction.

The reactions considered are compiled, to involve in a combinatorial manner, all pairs of a given subset of species in various phases. Each phase constituent is composed of one or more system components. The species stability boundaries are determined by satisfying the equilibrium conditions of Gibbs free energy of each of these reactions (*Gibbs energy minimization*),^[2] imposing that at equilibrium the chemical potential μ_i of each system component at each phase is equal such that the equations of mass balance, mass

action, and conservation of electrons should be satisfied. Gibbs energy of the thermodynamic system (of one or more phases, α) is given as:

$$G = \sum_{\alpha} \sum_i n_{i,\alpha} (\mu_{i,\alpha}^0 + RT \ln \lambda_{i,\alpha} x_{i,\alpha}) \quad (\text{B.8})$$

where $\mu_{i,\alpha}^0$ is the standard potential of constituent i in phase α , $n_{i,\alpha}$ is the molar amount of the constituent i in phase α , λ_i^α is the activity coefficient of the constituent i and x_i^α its corresponding concentration in phase α , R and T have their usual meaning.

From an initial state of the system with partial Gibbs energy $G'(T, P, n_i')$, the species are systematically tested to react with one another in a combinatorial manner until conditions for equilibrium of a closed thermodynamic system are established (the state of the system in which the partial Gibbs free energies of the system no longer decrease). At constant T and P , the equilibrium Gibbs energy of the species $G(T, P, n_i)$ is the minimum value reached when the following condition is satisfied:

$$G'(T, P, n_i') \leq G(T, P, n_i) \quad (\text{B.9})$$

Strictly, the minimum value of Gibbs energy is computed with mass-balance constraint (the masses of the system components must remain constant):

$$m_j = \sum_{\alpha} \sum_i n_{i,\alpha} v_{ij,\alpha} \quad (\text{B.10})$$

where m_j is the molar amount of the system component j , $n_{i,\alpha}$ is the molar amount of the constituent i in phase α , and $v_{ij,\alpha}$ is the stoichiometric coefficient of the system component j in constituent i .

Evaluation of stability conditions of species involves solving the ΔG_j equations for the variables of interest, such as activities $a_1, a_2, \dots, a_m$, and they are analyzed for stable and unstable species in accordance with relevant thermodynamic criteria. Unstable species are eliminated from further consideration and the analysis is focused only on the stability boundaries between dominant species.^[2,3]

The effect of potential E and species activities, in particular, pH is amenable from thermodynamic principles. Deducing stability of species in the E - pH coordinates involves testing whether a set of redox reactions are thermodynamically spontaneous or otherwise (depending on the sign of the Gibbs free energy change, ΔG , associated with the reactions). The products of a redox reaction are stable if ΔG is negative. On the contrary, if the ΔG is positive, the reactants are stable. Thus, the equilibrium line separates the stability fields of the reactants and products. This simple thermodynamic principle, valid for one redox reaction, is generalized to multiple redox reaction systems by applying it simultaneously to a special set of redox reactions involving, in a combinatorial manner, a certain number of species comprising the system. For instance, for systems comprising species of one element, the redox reactions are generated for all possible pairs of species while the electrons, hydrogen ions, and water molecules are the species used to balance the reactions. Finally, a set of rules is formulated aimed to determine the stable lines and triple points.^[4]

Generally, in computation of E -pH stability diagrams, a thermodynamic system is defined to contain elements of interest in gas phase, aqueous (solution) phase and stoichiometric condensed phase. An electron (e^-) with negative charge and hydrogen ions, $H^+(aq)$, are also explicitly considered as system components. This helps to set the charge balances in the equilibrium calculation, that is, at equilibrium the charge of the aqueous phase must be zero (electroneutrality) as it must be the initial composition.^[2,3]

In FactSage^[2] (the computer-package employed in thermodynamic modelling in this work) the built-in Gibbs energy minimization algorithm is invoked for evaluation of stable/metastable species which eventually determine the stability fields and intersections in the E -pH plane. Within this method a set of linearly independent chemical reactions, such that electrons (e^-), H^+ and H_2O are also considered as system components with remaining species S_i selected as most stable allotropic forms under standard conditions. Essentially, the ΔG are numerically evaluated for stability boundaries of the dominant species as a function of E and pH according to Equation B.11 for ideal aqueous solution ($a_{H_2O} = 1$, $pH = -\log a_{H^+}$).

^[4] I. Fishtik, *Thermodynamic Stability Relations in Redox Systems*, Environmental Science and Technology, Vol. 40 (2006), p. 1902-1910.

$$\Delta G = \Delta G^\circ - zFE - 2.303v_{H^+}RTpH + \sum_q^i v_q RT \ln a_{s_{qj}} - \sum_j^k v_j RT \ln a_{s_j} \quad (\text{B.11})$$

At a particular point in the plane E -pH, the species involved in the reaction with the lowest Gibbs free energy change is considered to be stable. The stability fields of two species, say S_p and S_q in coordinates E - pH at given T , P and species activities are separated by a straight line described by

$$\Delta G_{(S_p, S_q)}(E, pH) = 0 \quad (\text{B.12})$$

whilst the triple points (intersection of three equilibrium lines separating the stability of three species, S_p , S_q , and S_r) are evaluated by solving simultaneously a linear systems of equations described by

$$\Delta G_{(S_p, S_q)}(E, pH) = \Delta G_{(S_p, S_r)}(E, pH) = \Delta G_{(S_q, S_r)}(E, pH) = 0 \quad (\text{B.13})$$

In the analysis of possible chemical and electrochemical equilibria in the system under consideration, the stability boundaries in coordinates E - pH will be horizontal, vertical or sloping:^[1]

- A reaction involving a solid substance, a dissolved substance, and $H^+_{(aq)}$ without free electrons gives a vertical straight line; that is, the equilibrium is independent of potential E ;
- A reaction involving solid substance and a dissolved substance in water, plus free electrons but without $H^+_{(aq)}$ gives a horizontal straight line, that is, the equilibrium is independent of pH;
- A reaction involving a solid substance, a dissolved substance, free e^- , and $H^+_{(aq)}$ will result in a sloping straight line.

Table B.1: Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Pt-Cu-H₂O system

Species	Temperature range of heat capacity, <i>C_p</i> , (K)	Δ <i>G</i> (kJ)	Δ <i>G</i> (kcal)
Pt gases:			
Cu(g)	298 - 6000	297.909	71.202
Cu ₂ (g)	298 - 6000	433.083	103.509
CuO(g)	298 - 6000	276.804	66.158
Pt(g)	295 - 300	520.337	124.364
PtO ₂ (g)	298 - 2000	165.877	39.646
Pt, Cu liquids:			
Cu(l)	298 - 4000	9.336	2.231
Cu ₂ O(l)	298 - 2000	-100.398	-23.996
Pt(l)	2043 - 4097	12.711	3.038
Pt, Cu aqueous species:			
Cu ⁺	298 - 573	49.869	11.919
Cu ²⁺	298 - 573	65.500	15.655
CuO ₂ ²⁻	298 - ****	-183.678	-43.900
HCuO ₂ ⁻	298 - ****	-258.571	-61.800
Pt ²⁺	298 - ****	185.770	44.400
Pt, Cu solids:			
Cu(s)	298 - 2001	0.000	0.000
CuO(s)	298 - 2000	-128.309	-30.666
Cu ₂ O(s)	298 - 2000	-147.902	-35.350
Cu(OH) ₂ (s)	298 - 1500	-372.726	-89.084
Pt(s)	298 - 2043	0.000	0.000
Other gases:			
H(g)	298 - 6000	203.294	48.588
H ₂ (g)	298 - 6000	0.000	0.000
O(g)	298 - 6000	231.752	55.390
O ₂ (g)	298 - 6000	0.000	0.000
O ₃ (g)	298 - 6000	163.167	38.998
OH(g)	298 - 6000	34.278	8.193
H ₂ O(g)	298 - 6000	-228.607	-54.638
HOO(g)	298 - 6000	14.413	3.445
HOOH(g)	298 - 1500	-105.478	-25.210

Table B.1(Continued). Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Pt-Cu-H₂O system

Species	Temperature range of heat capacity, <i>C_p</i> , (K)	Δ <i>G</i> (kJ)	Δ <i>G</i> (kcal)
Other liquids:			
H ₂ O(l)	298 - 500	-237.190	-56.690
HOOH(l)	298 - 431	-119.922	-28.662
Other aqueous species:			
H ⁺	298 - 500	0.000	0.000
H ₂ (aq)	289 - 573	17.531	4.190
O ₂ (aq)	298 - 400	16.359	3.910
OH ⁻	298 - 573	-157.248	-37.583
HO ₂ ⁻	298 - 573	-67.296	-16.084
HOOH(aq)	298 - 1500	-134.060	-32.041
e ⁻ (aq)	298 - 6000	0.000	0.000
Other solids:			
H ₂ O(s)	250 - 273	-236.597	56.548

Table B.2: Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Ru-Cu-H₂O system

Species	Temperature range of heat capacity, <i>C_p</i> , (K)	Δ <i>G</i> (kJ)	Δ <i>G</i> (kcal)
Ru, Cu gases:			
Cu(g)	298 - 6000	297.909	71.202
Cu ₂ (g)	298 - 6000	433.083	103.509
CuO(g)	298 - 6000	276.804	66.158
Ru(g)	295 - 300	595.596	142.351
RuO(g)	298 - 3000	342.902	81.956
RuO ₂ (g)	298 - 3000	125.905	30.092
RuO ₃ (g)	298 - 1900	-60.368	-14.428
RuO ₄ (g)	298 - 2000	-139.985	-33.457
RuOH(g)	298 - 2000	305.932	73.12
RuO ₂ H ₂ (g)	298 - 3000	9.633	2.302
RuO ₃ OH(g)	298 - 2000	-295.855	-70.711
Ru, Cu liquids:			
Cu(l)	298 - 4000	9.336	2.231
Cu ₂ O(l)	298 - 2000	-100.398	-23.996
Ru(l)	2523 - 3700	7.664	1.832
RuO ₄ (l)	298 - 310	-152.314	-36.404
Ru, Cu aqueous species:			
Cu[+]	298 - 573	49.869	11.919
Cu[2+]	298 - 573	65.5	15.655
CuO ₂ [2-]	298 - ****	-183.678	-43.9
HCuO ₂ [-]	298 - ****	-258.571	-61.8
RuO ₄ [2-]	298 - ****	-303.758	-72.6
RuO ₄ [-]	298 - ****	-245.601	-58.7
RuO ₄ (aq)	298 - 298	-147.643	-35.287
Ru(OH) ₂ [2+]	298 - ****	-213.384	-51
Other gases:			
H(g)	298 - 6000	203.294	48.588
H ₂ (g)	298 - 6000	0.000	0.000
O(g)	298 - 6000	231.752	55.39
O ₂ (g)	298 - 6000	0.000	0.000
O ₃ (g)	298 - 6000	163.167	38.998

Table B.2 (Continued): Thermochemical data of species included in FactSage™ models to generate E -pH diagrams at $T = 298.15$ K for Ru-Cu-H₂O system

Species	Temperature range of heat capacity, C_p , (K)	ΔG (kJ)	ΔG (kcal)
OH(g)	298 - 6000	34.278	8.193
H ₂ O(g)	298 - 6000	-228.607	-54.638
HOO(g)	298 - 6000	14.413	3.445
HOOH(g)	298 - 1500	-105.478	-25.21
Other liquids:			
H ₂ O(l)	298 - 500	-237.19	-56.69
HOOH(l)	298 - 431	-119.922	-28.662
Other aqueous species:			
H[+]	298 - 500	0.000	0.000
H ₂ (aq)	289 - 573	17.531	4.19
O ₂ (aq)	298 - 400	16.359	3.91
OH[-]	298 - 573	-157.248	-37.583
HOO[-]	298 - 573	-67.296	-16.084
HOOH(aq)	298 - 473	-134.06	-32.041
e[-](aq)	298 - 6000	0.000	0.000
Other solids:			
H ₂ O(s)	250 - 273	-236.597	-56.548

Table B.3: Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Pt-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, C _p , (K)	ΔG(kJ)	ΔG(kcal)
Pt, Cu gases:			
Cu(g)	298 - 6000	297.909	71.202
Cu ₂ (g)	298 - 6000	433.083	103.509
CuO(g)	298 - 6000	276.804	66.158
CuCl(g)	298 - 6000	63.522	15.182
(CuCl) ₃ (g)	298 - 6000	-257.22	-61.477
Pt(g)	295 - 300	520.337	124.364
PtO ₂ (g)	298 - 2000	165.877	39.646
Cl ₃ Pt ₃ (g)	298 - 2000	78.452	18.75
Cl ₁₂ Pt ₆ (g)	298 - 2000	-400.525	-95.728
Pt, Cu liquids:			
Cu(l)	298 - 4000	9.336	2.231
Cu ₂ O(l)	298 - 2000	-100.398	-23.996
CuCl(l)	298 - 3000	-116	-27.725
Pt(l)	2043 - 4097	12.711	3.038
Pt, Cu aqueous species:			
Cu[+]	298 - 573	49.869	11.919
Cu[2+]	298 - 573	65.5	15.655
CuO ₂ [2-]	298 - ****	-183.678	-43.9
HCuO ₂ [-]	298 - ****	-258.571	-61.8
CuCl[+]	298 - ****	-68.199	-16.3
CuCl ₂ [-]	298 - 573	-242.356	-57.924
CuCl ₂ (aq)	298 - ****	-197.903	-47.3
CuCl ₃ [-]	298 - ****	-376.56	-90
Pt[2+]	298 - ****	185.77	44.4
PtCl ₂ (aq)	298 - ****	-76.567	-18.3
PtCl ₃ [-]	298 - ****	-228.446	-54.6
PtCl ₄ [2-]	298 - 573	-368.517	-88.078
PtCl ₆ [2-]	298 - 573	-489.719	-117.046
PtCl ₂ (OH) ₂ [2-]	298 - ****	-477.813	-114.2
PtCl ₂ (OH)(H ₂ O)[-]	298 - ****	-525.092	-125.5
PtCl ₂ (H ₂ O) ₂ (aq)	298 - ****	-554.38	-132.5
PtCl ₃ (OH)[2-]	298 - ****	-425.931	-101.8
PtCl ₃ (H ₂ O)[-]	298 - ****	-465.679	-111.3

Table B.3 (Continued): Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Pt-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, <i>C_p</i> , (K)	Δ <i>G</i> (kJ)	Δ <i>G</i> (kcal)
Pt, Cu solids:			
Cu(s)	298 - 2001	0.000	0.000
CuO(s)	298 - 2000	-128.309	-30.666
Cu ₂ O(s)	298 - 2000	-147.902	-35.35
Cu(OH) ₂ (s)	298 - 1500	-372.726	-89.084
CuCl(s)	298 - 1500	-120.892	-28.894
CuCl ₂ (s)	298 - 1500	-161.712	-38.65
CuCl ₂ (H ₂ O) ₂ (s)	298 - 310	-655.86	-156.754
Cu ₄ (OH) ₆ Cl ₂ (s)	298 - ****	-1339.5	-320.148
Pt(s)	298 - 2043	0.000	0.000
PtCl ₂ (s)	298 - 700	-70.657	-16.887
PtCl ₃ (s)	298 - 500	-106.209	-25.385
PtCl ₄ (s)	298 - 400	-152.571	-36.465
Other gases:			
H(g)	298 - 6000	203.294	48.588
H ₂ (g)	298 - 6000	0.000	0.000
O(g)	298 - 6000	231.752	55.39
O ₂ (g)	298 - 6000	0.000	0.000
O ₃ (g)	298 - 6000	163.167	38.998
OH(g)	298 - 6000	34.278	8.193
H ₂ O(g)	298 - 6000	-228.607	-54.638
HOO(g)	298 - 6000	14.413	3.445
HOOH(g)	298 - 1500	-105.478	-25.21
Cl(g)	298 - 6000	105.323	25.173
Cl ₂ (g)	298 - 6000	0.000	0.000
HCl(g)	298 - 6000	-95.3	-22.777
ClO(g)	298 - 6000	97.482	23.299
ClO ₂ (g)	298 - 6000	122.311	29.233
Cl ₂ O(g)	298 - 6000	105.049	25.107
HOCl(g)	298 - 6000	-61.686	-14.743

Table B.3 (Continued): Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Pt-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, C _p , (K)	ΔG(kJ)	ΔG(kcal)
Other liquids:			
H ₂ O(l)	298 - 500	-237.19	-56.69
HOOH(l)	298 - 431	-119.922	-28.662
Other aqueous species:			
H[+]	298 - 500	0.000	0.000
H ₂ (aq)	289 - 573	17.531	4.19
O ₂ (aq)	298 - 400	16.359	3.91
OH[-]	298 - 573	-157.248	-37.583
HOO [-]	298 - 573	-67.296	-16.084
HOOH(aq)	298 - 473	-134.06	-32.041
Cl[-]	298 - 573	-131.236	-31.366
Cl ₂ (aq)	298 - 298	6.872	1.642
Cl ₃ [-]	298 - ****	-83.68	-20
ClO[-]	298 - 573	-36.733	-8.779
ClO ₂ [-]	298 - 573	17.122	4.092
ClO ₂ (aq)	298 - 298	120.136	28.713
ClO ₃ [-]	298 - 573	-3.16	-0.755
ClO ₄ [-]	298 - 573	-8.582	-2.051
HOCl(aq)	298 - 473	-80.062	-19.135
HClO ₂ (aq)	298 - 473	5.819	1.391
e[-](aq)	298 - 6000	0.000	0.000
Other solids:			
H ₂ O(s)	250 - 273	-236.597	-56.548

Table B.4: Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Ru-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, C _p , (K)	ΔG(kJ)	ΔG(kcal)
Ru, Cu gases:			
Cu(g)	298 - 6000	297.909	71.202
Cu ₂ (g)	298 - 6000	433.083	103.509
CuO(g)	298 - 6000	276.804	66.158
CuCl(g)	298 - 6000	63.522	15.182
(CuCl) ₃ (g)	298 - 6000	-257.22	-61.477
Ru(g)	295 - 300	595.596	142.351
RuO(g)	298 - 3000	342.902	81.956
RuO ₂ (g)	298 - 3000	125.905	30.092
RuO ₃ (g)	298 - 1900	-60.368	-14.428
RuO ₄ (g)	298 - 2000	-139.985	-33.457
RuOH(g)	298 - 2000	305.932	73.12
RuO ₂ H ₂ (g)	298 - 3000	9.633	2.302
RuO ₃ OH(g)	298 - 2000	-295.855	-70.711
RuCl ₃ (g)	298 - 1500	45.782	10.942
RuCl ₄ (g)	298 - 1500	-63.486	-15.174
Ru, Cu liquids:			
Cu(l)	298 - 4000	9.336	2.231
Cu ₂ O(l)	298 - 2000	-100.398	-23.996
CuCl(l)	298 - 3000	-116	-27.725
Ru(l)	2523 - 3700	7.664	1.832
RuO ₄ (l)	298 - 310	-152.314	-36.404
Ru, Cu aqueous species:			
Cu[+]	298 - 573	49.869	11.919
Cu[2+]	298 - 573	65.5	15.655
CuO ₂ [2-]	298 - ****	-183.678	-43.9
HCuO ₂ [-]	298 - ****	-258.571	-61.8
CuCl[+]	298 - ****	-68.199	-16.3
CuCl ₂ [-]	298 - 573	-242.356	-57.924
CuCl ₂ (aq)	298 - ****	-197.903	-47.3
CuCl ₃ [-]	298 - ****	-376.56	-90
RuO ₄ [2-]	298 - ****	-303.758	-72.6
RuO ₄ [-]	298 - ****	-245.601	-58.7
RuO ₄ (aq)	298 - 298	-147.643	-35.287

Table B.4 (Continued): Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Ru-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, <i>C_p</i> , (K)	Δ <i>G</i> (kJ)	Δ <i>G</i> (kcal)
Ru(OH) ₂ [2+]	298 - ****	-213.384	-51
RuCl ₅ (OH)[2-]	298 - ****	-705.841	-168.7
Ru, Cu solids:			
Cu(s)	298 - 2001	0.000	0.000
CuO(s)	298 - 2000	-128.309	-30.666
Cu ₂ O(s)	298 - 2000	-147.902	-35.35
Cu(OH) ₂ (s)	298 - 1500	-372.726	-89.084
CuCl(s)	298 - 1500	-120.892	-28.894
CuCl ₂ (s)	298 - 1500	-161.712	-38.65
CuCl ₂ (H ₂ O) ₂ (s)	298 - 310	-655.86	-156.754
Cu ₄ (OH) ₆ Cl ₂ (s)	298 - ****	-1339.5	-320.148
Ru(s)	298 - 2523	0.000	0.000
RuO ₂ (s)	298 - 1300	-253.044	-60.479
RuO ₄ (s)	298 - 310	-152.214	-36.38
RuCl ₃ (s)	298 - 1000	-182.954	-43.727
Other gases:			
H(g)	298 - 6000	203.294	48.588
H ₂ (g)	298 - 6000	0.000	0.000
O(g)	298 - 6000	231.752	55.39
O ₂ (g)	298 - 6000	0.000	0.000
O ₃ (g)	298 - 6000	163.167	38.998
OH(g)	298 - 6000	34.278	8.193
H ₂ O(g)	298 - 6000	-228.607	-54.638
HOO(g)	298 - 6000	14.413	3.445
HOOH(g)	298 - 1500	-105.478	-25.21
Cl(g)	298 - 6000	105.323	25.173
Cl ₂ (g)	298 - 6000	0.000	0.000
HCl(g)	298 - 6000	-95.3	-22.777
ClO(g)	298 - 6000	97.482	23.299
ClO ₂ (g)	298 - 6000	122.311	29.233
Cl ₂ O(g)	298 - 6000	105.049	25.107
HOCl(g)	298 - 6000	-61.686	-14.743

Table B.4 (Continued): Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Ru-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, <i>C_p</i> , (K)	Δ <i>G</i> (kJ)	Δ <i>G</i> (kcal)
Other liquids:			
H ₂ O(l)	298 - 500	-237.19	-56.69
HOOH(l)	298 - 431	-119.922	-28.662
Other aqueous species:			
H[+]	298 - 500	0.000	0.000
H ₂ (aq)	289 - 573	17.531	4.19
O ₂ (aq)	298 - 400	16.359	3.91
OH[-]	298 - 573	-157.248	-37.583
HO ₂ [-]	298 - 573	-67.296	-16.084
HOOH(aq)	298 - 473	-134.06	-32.041
Cl[-]	298 - 573	-131.236	-31.366
Cl ₂ (aq)	298 - 298	6.872	1.642
Cl ₃ [-]	298 - ****	-83.68	-20
ClO[-]	298 - 573	-36.733	-8.779
ClO ₂ [-]	298 - 573	17.122	4.092
ClO ₂ (aq)	298 - 298	120.136	28.713
ClO ₃ [-]	298 - 573	-3.16	-0.755
ClO ₄ [-]	298 - 573	-8.582	-2.051
HOCl(aq)	298 - 473	-80.062	-19.135
HClO ₂ (aq)	298 - 473	5.819	1.391
e[-](aq)	298 - 6000	0.000	0.000
Other solids:			
H ₂ O(s)	250 - 273	-236.597	-56.548

Table B.5: Thermochemical data of species included in FactSage™ models to generate E-pH diagrams at $T = 298.15$ K for Au-Cu-H₂O system

Species	Temperature range of heat capacity, C_p , (K)	$\Delta G(\text{kJ})$	$\Delta G(\text{kcal})$
Au, Cu gases:			
Cu(g)	298 - 6000	297.909	71.202
Cu ₂ (g)	298 - 6000	433.083	103.509
CuO(g)	298 - 6000	276.804	66.158
Au(g)	3130 - 4000	325.451	77.785
AuH(g)	295 - 300	265.675	63.498
Au, Cu liquids:			
Cu(l)	298 - 4000	9.336	2.231
Cu ₂ O(l)	298 - 2000	-100.398	-23.996
Au(l)	1336 - 3130	8.308	1.986
Au, Cu liquids:			
Cu(l)			
Cu ₂ O(l)			
Au(l)			
Au, Cu aqueous species:			
Cu[+]	298 - 573	49.869	11.919
Cu[2+]	298 - 573	65.5	15.655
CuO ₂ [2-]	298 - ****	-183.678	-43.9
HCuO ₂ [-]	298 - ****	-258.571	-61.8
AuO ₃ [3-]	298 - ****	-51.882	-12.4
HAuO ₃ [2-]	298 - ****	-142.256	-34
H ₂ AuO ₃ [-]	298 - ****	-218.405	-52.2
Au(OH) ₃ (aq)	298 - ****	-283.466	-67.75
Au, Cu solids:			
Cu(s)	298 - 2001	0.000	0.000
CuO(s)	298 - 2000	-128.309	-30.666
Cu ₂ O(s)	298 - 2000	-147.902	-35.35
Cu(OH) ₂ (s)	298 - 1500	-372.726	-89.084
Au(s)	298 - 1336	0.000	0.000
Au ₂ O ₃ (s)	298 - 500	77.731	18.578
Au(OH) ₃ (s)	298 - 310	-316.932	-75.749
AuCu(s)	295 - 300	-18.438	-4.407
AuCu ₃ (s)	298 - 298	-29.328	-7.01

Table B.5 (Continued): Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Au-Cu-H₂O system

Species	Temperature range of heat capacity, <i>C_p</i> , (K)	Δ <i>G</i> (kJ)	Δ <i>G</i> (kcal)
Other gases:			
H(g)	298 - 6000	203.294	48.588
H ₂ (g)	298 - 6000	0.000	0.000
O(g)	298 - 6000	231.752	55.39
O ₂ (g)	298 - 6000	0.000	0.000
O ₃ (g)	298 - 6000	163.167	38.998
OH(g)	298 - 6000	34.278	8.193
H ₂ O(g)	298 - 6000	-228.607	-54.638
HOO(g)	298 - 6000	14.413	3.445
HOOH(g)	298 - 1500	-105.478	-25.21
Other liquids:			
H ₂ O(l)	298 - 500	-237.19	-56.69
HOOH(l)	298 - 431	-119.922	-28.662
Other aqueous species:			
H[+]	298 - 500	0.000	0.000
H ₂ (aq)	289 - 573	17.531	4.19
O ₂ (aq)	298 - 400	16.359	3.91
OH[-]	298 - 573	-157.248	-37.583
HO ₂ [-]	298 - 573	-67.296	-16.084
HOOH(aq)	298 - 473	-134.06	-32.041
e[-](aq)	298 - 6000	0.000	0.000
Other solids:			
H ₂ O(s)	250 - 273	-236.597	-56.548

Table B.6: Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Au-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, C _p , (K)	ΔG(kJ)	ΔG(kcal)
Au, Cu gases:			
Cu(g)	298 - 6000	297.909	71.202
Cu ₂ (g)	298 - 6000	433.083	103.509
CuO(g)	298 - 6000	276.804	66.158
CuCl(g)	298 - 6000	63.522	15.182
(CuCl) ₃ (g)	298 - 6000	-257.22	-61.477
Au(g)	3130 - 4000	325.451	77.785
AuH(g)	295 - 300	265.675	63.498
Au, Cu liquids:			
Cu(l)	298 - 4000	9.336	2.231
Cu ₂ O(l)	298 - 2000	-100.398	-23.996
CuCl(l)	298 - 3000	-116	-27.725
Au(l)	1336 - 3130	8.308	1.986
Au, Cu aqueous species:			
Cu[+]	298 - 573	49.869	11.919
Cu[2+]	298 - 573	65.5	15.655
CuO ₂ [2-]	298 - ****	-183.678	-43.9
HCuO ₂ [-]	298 - ****	-258.571	-61.8
CuCl[+]	298 - ****	-68.199	-16.3
CuCl ₂ [-]	298 - 573	-242.356	-57.924
CuCl ₂ (aq)	298 - ****	-197.903	-47.3
CuCl ₃ [-]	298 - ****	-376.56	-90
AuO ₃ [3-]	298 - ****	-51.882	-12.4
HAuO ₃ [2-]	298 - ****	-142.256	-34
H ₂ AuO ₃ [-]	298 - ****	-218.405	-52.2
Au(OH) ₃ (aq)	298 - ****	-283.466	-67.75
AuCl ₂ [-]	298 - ****	-151.168	-36.13
AuCl ₄ [-]	298 - 573	-235.173	-56.208
Au, Cu solids:			
Cu(s)	298 - 2001	0.000	0.000
CuO(s)	298 - 2000	-128.309	-30.666
Cu ₂ O(s)	298 - 2000	-147.902	-35.35

Table B.6 (Continued): Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Au-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, <i>C_p</i> , (K)	Δ <i>G</i> (kJ)	Δ <i>G</i> (kcal)
Cu(OH) ₂ (s)	298 - 1500	-372.726	-89.084
CuCl(s)	298 - 1500	-120.892	-28.894
CuCl ₂ (s)	298 - 1500	-161.712	-38.65
CuCl ₂ (H ₂ O) ₂ (s)	298 - 310	-655.86	-156.754
Cu ₄ (OH) ₆ Cl ₂ (s)	298 - ****	-1339.5	-320.148
Au(s)	298 - 1336	0.000	0.000
Au ₂ O ₃ (s)	298 - 500	77.731	18.578
Au(OH) ₃ (s)	298 - 310	-316.932	-75.749
AuCl(s)	298 - 443	-15.02	-3.59
AuCl ₃ (s)	298 - 527	-45.341	-10.837
AuCu(s)	295 - 300	-18.438	-4.407
AuCu ₃ (s)	298 - 298	-29.328	-7.01
Other gases:			
H(g)	298 - 6000	203.294	48.588
H ₂ (g)	298 - 6000	0.000	0.000
O(g)	298 - 6000	231.752	55.39
O ₂ (g)	298 - 6000	0.000	0.000
O ₃ (g)	298 - 6000	163.167	38.998
OH(g)	298 - 6000	34.278	8.193
H ₂ O(g)	298 - 6000	-228.607	-54.638
HOO(g)	298 - 6000	14.413	3.445
HOOH(g)	298 - 1500	-105.478	-25.21
Cl(g)	298 - 6000	105.323	25.173
Cl ₂ (g)	298 - 6000	0.000	0.000
HCl(g)	298 - 6000	-95.3	-22.777
ClO(g)	298 - 6000	97.482	23.299
ClO ₂ (g)	298 - 6000	122.311	29.233
Cl ₂ O(g)	298 - 6000	105.049	25.107
HOCl(g)	298 - 6000	-61.686	-14.743
Other liquids:			
H ₂ O(l)	298 - 500	-237.19	-56.69
HOOH(l)	298 - 431	-119.922	-28.662
Other aqueous species:			
H[+]	298 - 500	0.000	0.000

Table B.6 (Continued): Thermochemical data of species included in FactSage™ models to generate *E*-pH diagrams at *T* = 298.15 K for Au-Cu-Cl-H₂O system

Species	Temperature range of heat capacity, C_p , (K)	ΔG (kJ)	ΔG (kcal)
H ₂ (aq)	289 - 573	17.531	4.19
O ₂ (aq)	298 - 400	16.359	3.91
OH[-]	298 - 573	-157.248	-37.583
HO ₂ [-]	298 - 573	-67.296	-16.084
HOOH(aq)	298 - 473	-134.06	-32.041
Cl[-]	298 - 573	-131.236	-31.366
Cl ₂ (aq)	298 - 298	6.872	1.642
Cl ₃ [-]	298 - ****	-83.68	-20
ClO[-]	298 - 573	-36.733	-8.779
ClO ₂ [-]	298 - 573	17.122	4.092
ClO ₂ (aq)	298 - 298	120.136	28.713
ClO ₃ [-]	298 - 573	-3.16	-0.755
ClO ₄ [-]	298 - 573	-8.582	-2.051
HOCl(aq)	298 - 473	-80.062	-19.135
HClO ₂ (aq)	298 - 473	5.819	1.391
e[-](aq)	298 - 6000	0.000	0.000
Other solids:			
H ₂ O(s)	250 - 273	-236.597	-56.548

APPENDIX C

Supplementary Data

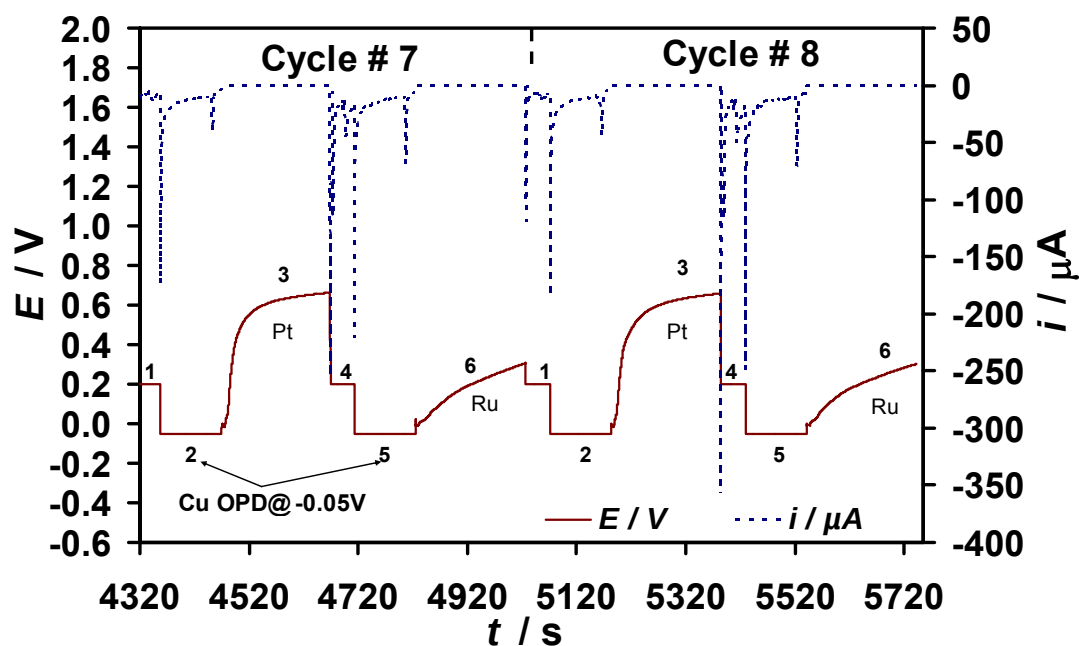


Figure C.1: Representative current-potential-time (i - E - t) transients recorded during indicated deposition cycles to generate $n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$.

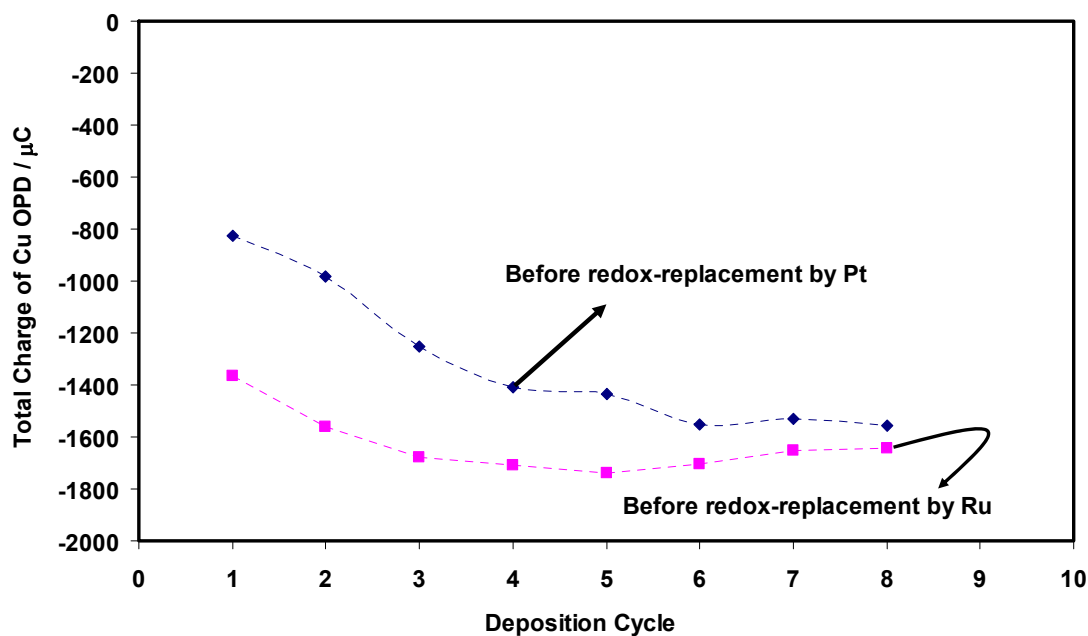


Figure C.2: Variation in total charge developed during Cu deposition stages during sequential deposition to generate $n(\text{Ru} | \text{Pt})_{\text{Cu}}/\text{GC}$.

Table C.1. Expressions of electrochemical impedances found in equivalent circuits used in this work

Circuit A	Circuit B	Circuit C
Total Impedance, Z_T		
$Z_T = Z_{R_s} + \frac{Z_{CPE_{dl}} Z_{R_{ct}}}{Z_{CPE_{dl}} + Z_{R_{ct}}} \quad (C.1)$	$Z_T = Z_{R_s} + \frac{Z_{CPE_{dl}} Z_{R_{ct}}}{Z_{CPE_{dl}} + Z_{R_{ct}}} + \frac{Z_{C_{ads}} Z_{R_{ads}}}{Z_{C_{ads}} + Z_{R_{ads}}} \quad (C.4)$	$Z_T = Z_{R_s} + \frac{Z_{CPE_{dl}} Z_{R_{ct}} Z_{C_{ads}} + Z_{CPE_{dl}} Z_{R_{ct}} Z_{R_{ads}} + Z_{CPE_{dl}} Z_{C_{ads}} Z_{R_{ads}}}{Z_{CPE_{dl}} Z_{C_{ads}} + Z_{CPE_{dl}} Z_{R_{ads}} + Z_{R_{ct}} Z_{C_{ads}} + Z_{C_{ads}} Z_{R_{ads}}} \quad (C.7)$
Real Component of Total Impedance, Z'		
$Z' = R_s + \frac{R_{ct} + R_{ct}^2 Y_o \omega^\alpha \cos(a\pi/2)}{2R_{ct} Y_o \omega^\alpha \cos(a\pi/2) + R_{ct}^2 Y_o^2 \omega^{2\alpha}} \quad (C.2)$	$Z' = R_s + \frac{R_{ct}^2 Q^{-1} \omega^{-\alpha} \cos(a\pi/2) + R_{ct} Q^{-2} \omega^{-2\alpha}}{R_{ct}^2 + 2R_{ct} Q^{-1} \omega^{-\alpha} \cos(a\pi/2) + Q^{-2} \omega^{-2\alpha}} + \frac{R_{ads} C_{ads}^{-2} \omega^{-2}}{R_{ads}^2 + C_{ads}^2 \omega^{-2}} \quad (C.5)$	$Z' = R_s + \frac{\left\{ \begin{aligned} &(R_{ct}^2 + R_{ads}^2) \left(C_{ads}^{-2} Q^{-1} \omega^{-(\alpha+2)} \cos(a\pi/2) \right) \\ &+ (R_{ct} + R_{ads}) \left(C_{ads}^{-2} Q^{-2} \omega^{-(2\alpha+2)} \right) \\ &+ 2R_{ct} R_{ads} C_{ads}^{-2} Q^{-1} \omega^{-(\alpha+2)} \cos(a\pi/2) \\ &+ R_{ct}^2 R_{ads}^2 Q^{-1} \omega^{-1} \cos(a\pi/2) + R_{ct} R_{ads}^2 Q^{-2} \omega^{-2\alpha} \end{aligned} \right\}}{\left\{ \begin{aligned} &R_{ct}^2 R_{ads}^2 + R_{ads}^2 C_{ads}^{-2} \omega^{-2} + 2R_{ct} R_{ads} C_{ads}^{-2} \omega^{-2} + R_{ct}^2 C_{ads}^{-2} \omega^{-2} \\ &+ 2R_{ct} R_{ads}^2 Q^{-1} \omega^{-\alpha} \cos(a\pi/2) + 2R_{ads} C_{ads}^{-2} Q^{-1} \omega^{-(\alpha+2)} \cos(a\pi/2) \\ &+ 2R_{ct} C_{ads}^{-2} Q^{-1} \omega^{-(\alpha+2)} \cos(a\pi/2) + R_{ads}^2 Q^{-2} \omega^{-2\alpha} \\ &+ 2R_{ads}^2 C_{ads}^{-1} Q^{-1} \omega^{-(\alpha+1)} \sin(a\pi/2) + C_{ads}^2 Q^{-2} \omega^{-(2\alpha+2)} \end{aligned} \right\}} \quad (C.8)$
Imaginary Component of Total Impedance, Z''		
$Z'' = \frac{R_{ct}^2 Q \omega^\alpha \sin(a\pi/2)}{2R_{ct} Q \omega^\alpha \cos(a\pi/2) + R_{ct}^2 Q^2 \omega^{2\alpha}} \quad (C.3)$	$Z'' = \frac{R_{ct}^2 Q^{-1} \omega^{-\alpha} \sin(a\pi/2)}{R_{ct}^2 + 2R_{ct} Q^{-1} \omega^{-\alpha} \cos(a\pi/2) + Q^{-2} \omega^{-2\alpha}} + \frac{R_{ads}^2 C_{ads}^{-1} \omega^{-1}}{R_{ads}^2 + C_{ads}^2 \omega^{-2}} \quad (C.6)$	$Z'' = \frac{\left\{ \begin{aligned} &(R_{ct}^2 + R_{ads}^2) \left(C_{ads}^{-2} Q^{-1} \omega^{-(\alpha+2)} \sin(a\pi/2) \right) \\ &+ 2R_{ct} R_{ads} C_{ads}^{-2} Q^{-1} \omega^{-(\alpha+2)} \sin(a\pi/2) \\ &+ R_{ads}^2 C_{ads}^{-2} Q^{-2} \omega^{-(2\alpha+1)} + R_{ct}^2 R_{ads}^2 Q^{-1} \omega^{-\alpha} \sin(a\pi/2) \end{aligned} \right\}}{\left\{ \begin{aligned} &R_{ct}^2 R_{ads}^2 + R_{ads}^2 C_{ads}^{-2} \omega^{-2} + 2R_{ct} R_{ads} C_{ads}^{-2} \omega^{-2} + R_{ct}^2 C_{ads}^{-2} \omega^{-2} \\ &+ 2R_{ct} R_{ads}^2 Q^{-1} \omega^{-\alpha} \cos(a\pi/2) + 2R_{ads} C_{ads}^{-2} Q^{-1} \omega^{-(\alpha+2)} \cos(a\pi/2) \\ &+ 2R_{ct} C_{ads}^{-2} Q^{-1} \omega^{-(\alpha+2)} \cos(a\pi/2) + R_{ads}^2 Q^{-2} \omega^{-2\alpha} \\ &+ 2R_{ads}^2 C_{ads}^{-1} Q^{-1} \omega^{-(\alpha+1)} \sin(a\pi/2) + C_{ads}^2 Q^{-2} \omega^{-(2\alpha+2)} \end{aligned} \right\}} \quad (C.9)$

Table C.1(Continued).

Descriptions of Symbols and Other Relevant Expressions	
–General complex notation of the total impedance, Z_T, at a given frequency ω of the perturbation signal, is given by Equation C10, $Z_T = Z' + iZ'' \quad (C.10)$ where i is the imaginary unit in complex notation defined by $i = \sqrt{-1}$; Z' and Z'' are the real and imaginary components of Z_T, respectively; – $Z_{CPE_{dl}}$ is the impedance of the constant phase element (CPE_{dl}) which is related to the double-layer capacitance (C_{dl}) and accounts for deviations from homogenous electrode-electrolyte interface. $Z_{CPE_{dl}}$ is given by Equation C.11, $Z_{CPE_{dl}} = \frac{1}{Q(i\omega)^\alpha} = \frac{1}{Q\omega^\alpha} (\cos(\alpha\pi/2) - i\sin(\alpha\pi/2)) \quad (C.11)$ where Q is the pre-factor of the CPE_{dl} and α is a unitless parameter such that $0 < \alpha < 1$ (when $\alpha=1$, $Q = C_{dl}$ and deviations of α from 1 correspond to departure from ideal capacitive behavior of an electrode's double-layer); C_{dl} is the double-layer capacitance whose impedance ($Z_{C_{dl}}$) is given by Equation C.12, $Z_{C_{dl}} = -i\omega^{-1}C_{dl}^{-1} \quad (C.12)$ – $Z_{R_{ct}}$ is the impedance of the charge-transfer resistance (R_{ct}), such that $Z_{R_{ct}} = R_{ct} \quad (C.13)$ – Z_{R_s} is the impedance of the solution resistance (R_s), such that $Z_{R_s} = R_s \quad (C.14)$ – $Z_{R_{ads}}$ is the impedance of the resistance due to adsorption processes (R_{ads}), such that $Z_{R_{ads}} = R_{ads} \quad (C.15)$ – $Z_{C_{ads}}$ is the impedance of the pseudo-capacitance related to adsorption processes (C_{ads}), such that $Z_{C_{ads}} = -i\omega^{-1}C_{ads}^{-1} \quad (C.16)$ – Average double-layer capacitance, C_{dl}, from CPE_{dl} parameters for a circuit with R_s in series with CPE_{dl} in parallel with R_{ct}, can be estimated with Equation C.17: $C_{dl} = \frac{Q^{\frac{1}{\alpha}}}{[R_s^{-1} + R_{ct}^{-1}]^{\frac{1-\alpha}{\alpha}}} \quad (C.17)$	

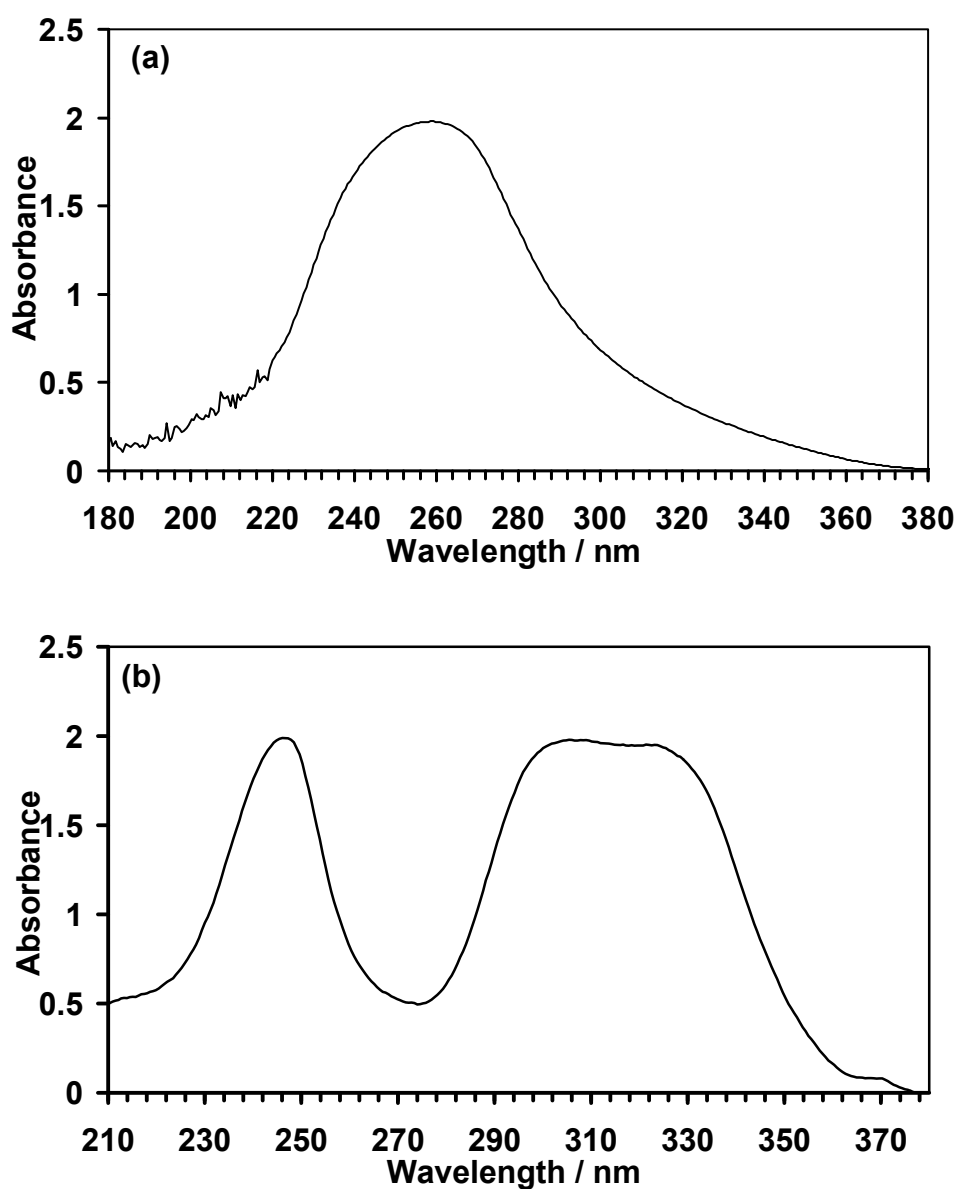


Figure C.3: UV-Visible Spectra of 1 mM solutions of (a) PtCl_6^{2-} and (b) AuCl_4^- in 0.1 M HClO_4 (pH 1), the precursor solutions used in SLRR cycles, showing typical absorption bands of these complexes.

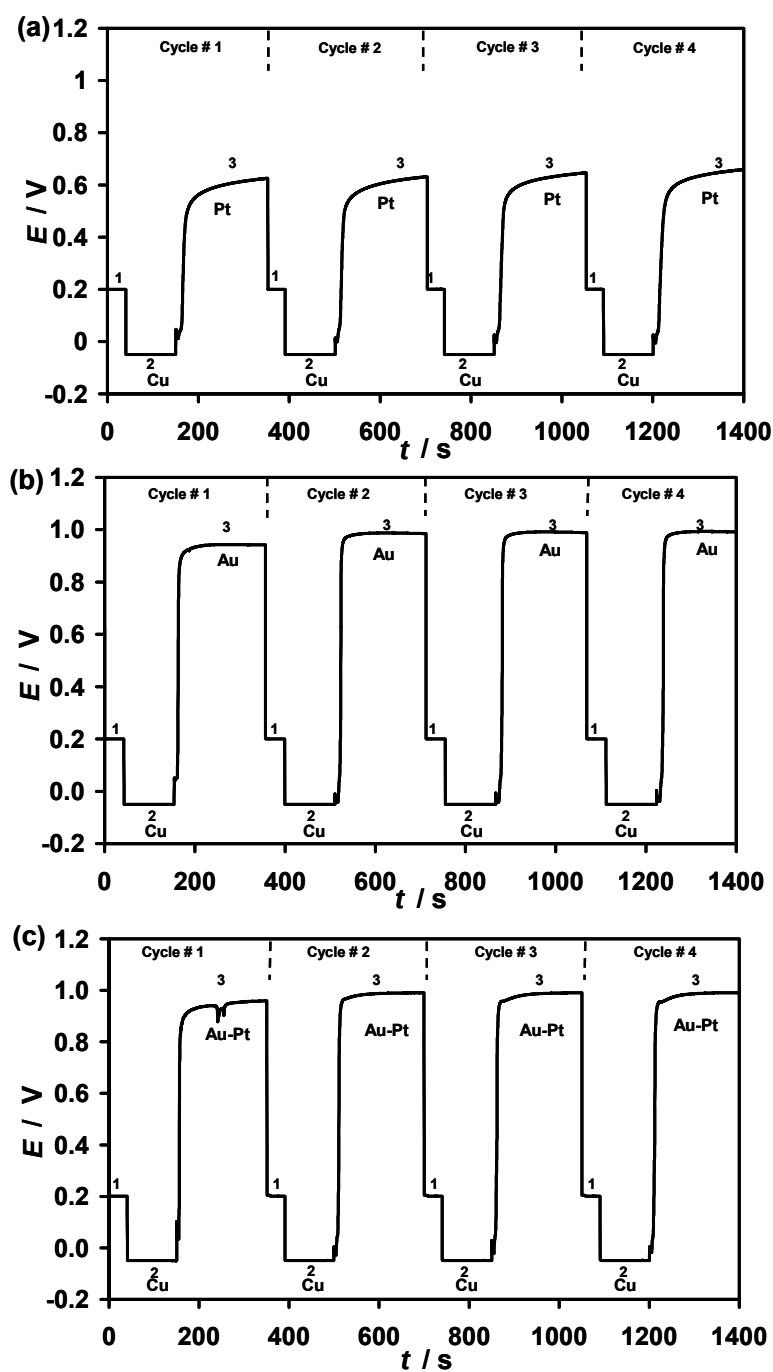


Figure C.4: Potential-time ($E-t$) transients recorded during sequential deposition of monometallic nanoclusters (a) $n(\text{Pt})_{\text{Cu}}/\text{GC}$ and (b) $n(\text{Au})_{\text{Cu}}/\text{GC}$. (c) $E-t$ transients during sequential codeposition of bimetallic nanoclusters (c) $n(\text{Au-Pt})_{\text{Cu}}/\text{GC}$. The deposition cycles involved Cu OPD steps.

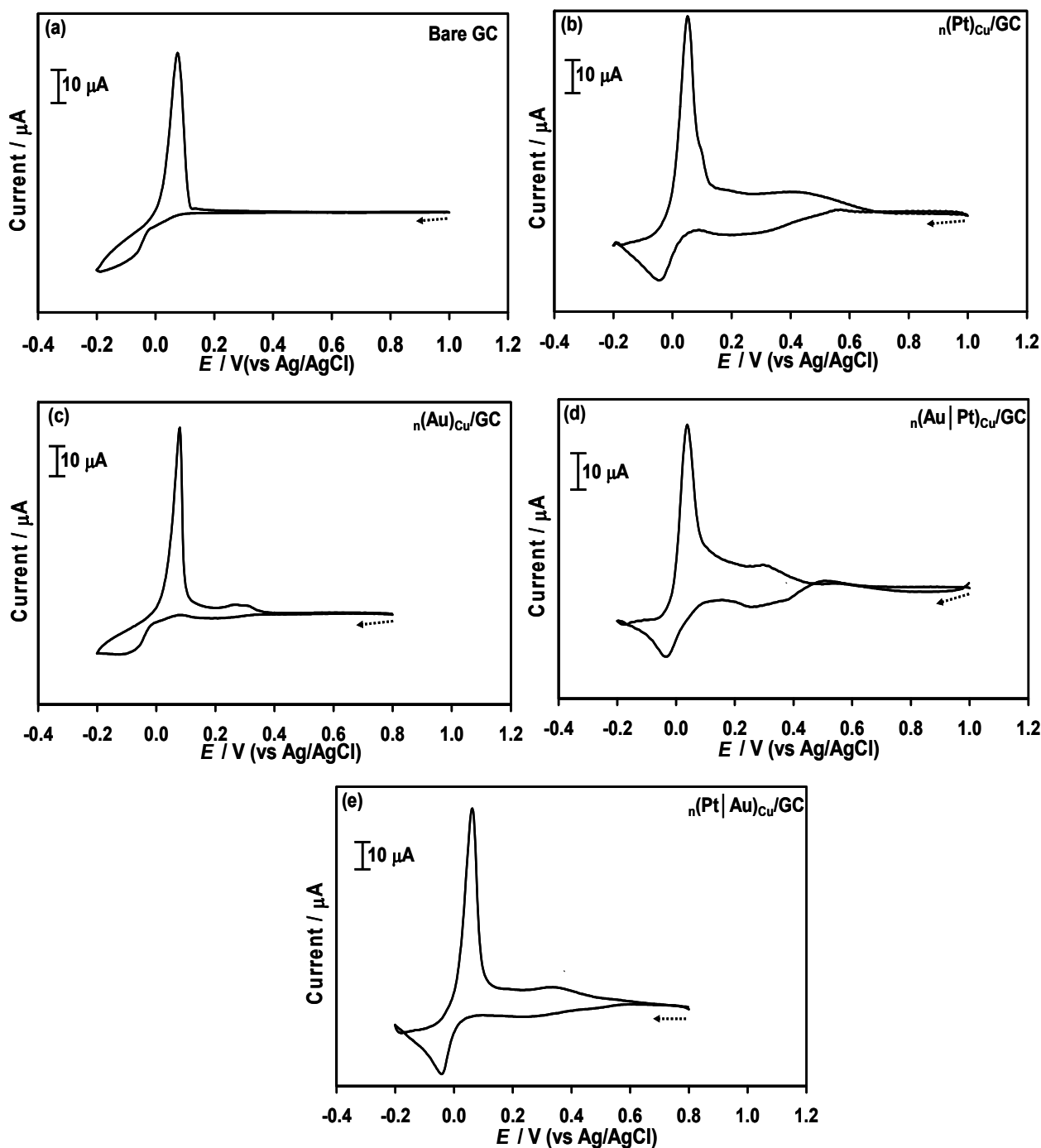


Figure C.5: Cyclic voltammograms recorded in N_2 -saturated 1 mM $CuSO_4$ in 0.1 M $HClO_4$ solution on bare GC electrode and various as-prepared nanoclusters after $n = 8$ deposition cycles via SLRR steps involving Cu OPD at -0.05 V. Scan rate was 5 mV/s. Broken arrows indicate the starting potential and initial scan direction.

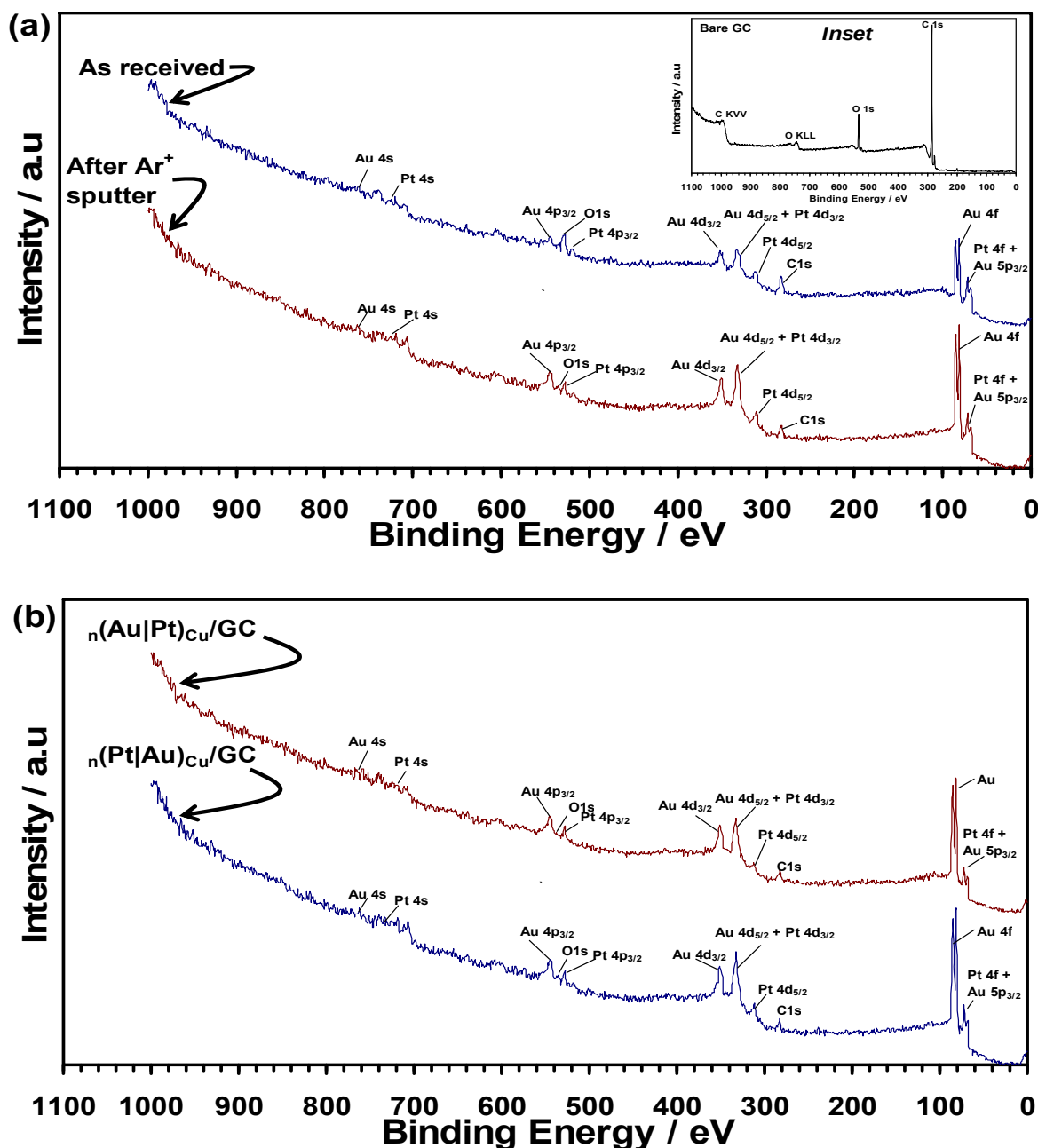


Figure C.6: X-ray photoelectron survey spectra of: (a) As received bare glassy carbon (GC) substrate (Inset) and bimetallic nanocluster electrode $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ before and after Ar^+ ion sputtering procedure; and (b) The two-types of bimetallic nanoclusters investigated in this work after Ar^+ ion sputtering procedure. In all cases, the nanoclusters were obtained after $n = 8$ deposition cycles. Spectrum of the bare GC substrate revealed typical C KVV and O KLL Auger lines originating from carbon and oxygen-containing structures in the GC, respectively, where the Auger transition in KVV was from an initial K shell to final double vacancy in the valence shells; the transitions in KLL were from K shells to final double vacancy in the L shells.

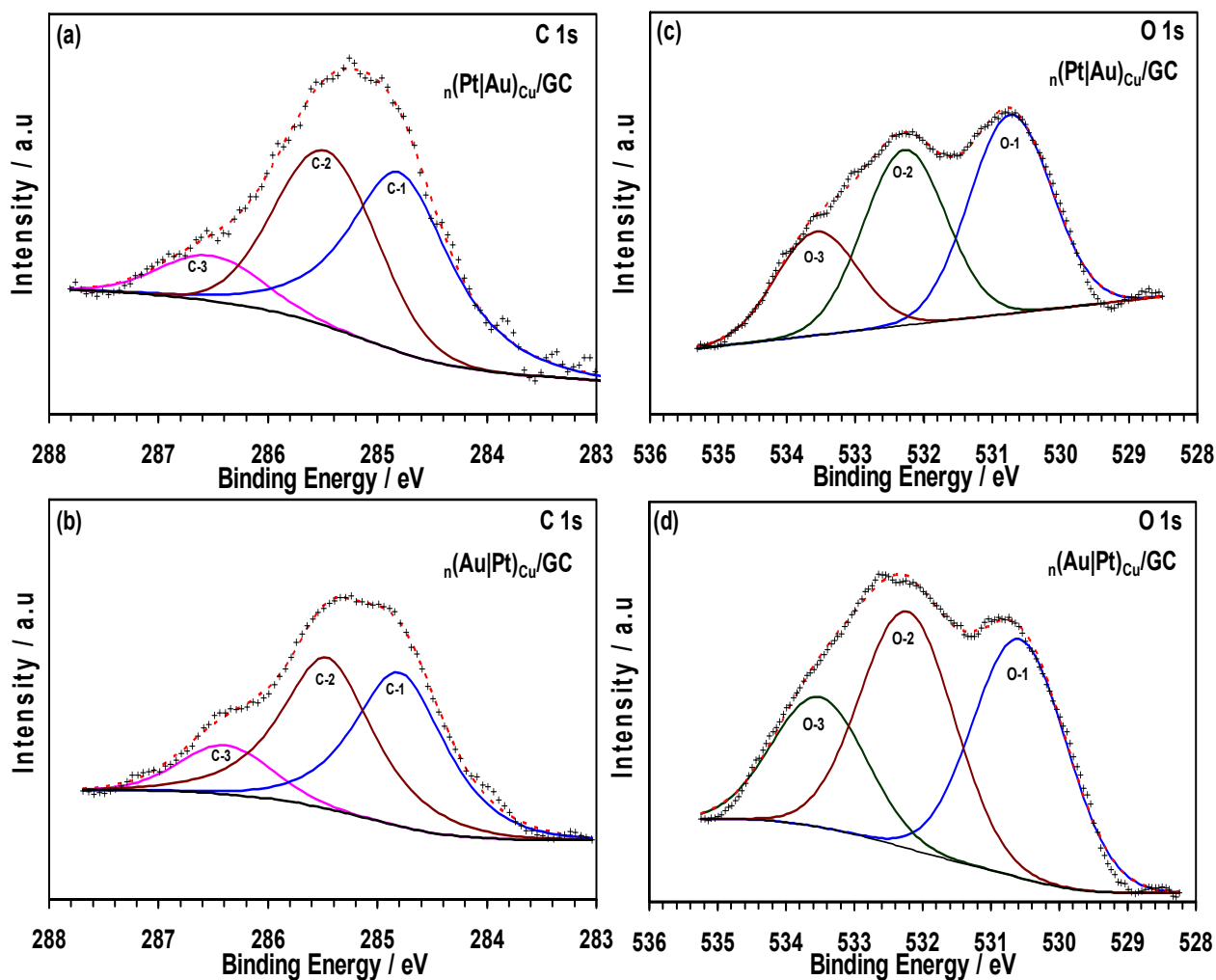


Figure C.7: X-ray photoelectron spectra recorded from as-received samples of the $n(\text{Au}|\text{Pt})_{\text{Cu}}/\text{GC}$ and $n(\text{Pt}|\text{Au})_{\text{Cu}}/\text{GC}$ bimetallic nanoclusters, obtained after $n = 8$ deposition cycles, corresponding to photoelectrons from (a) – (b) C 1s, and (c) – (d) O 1s subatomic levels.

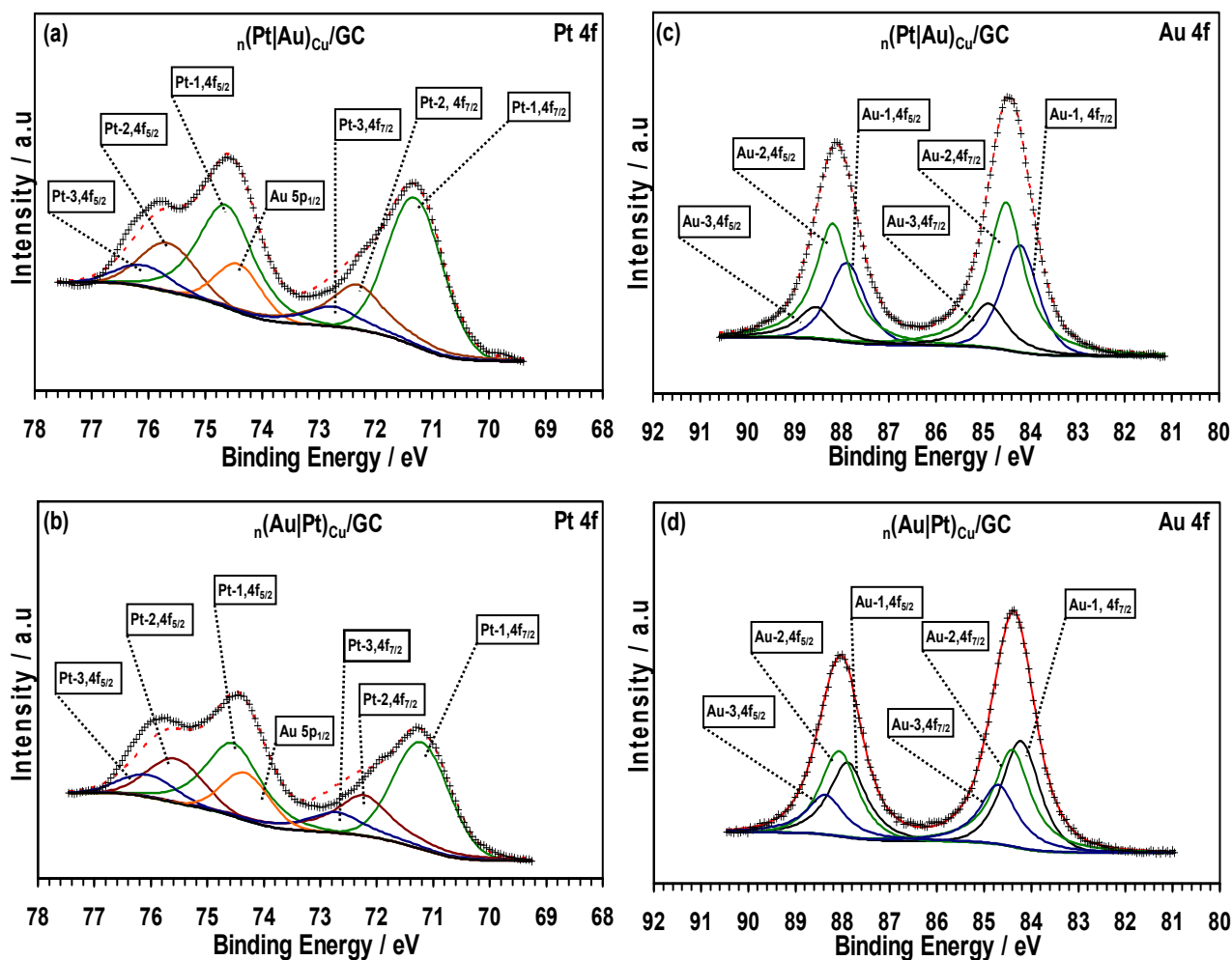


Figure C.8: X-ray photoelectron spectra (with corresponding deconvoluted spectral components) recorded on the bimetallic nanoclusters corresponding to photoelectrons from (a) – (b) Au 4f; and (c) – (d) Pt 4f subatomic levels. Probed samples were sputtered with Argon ions.

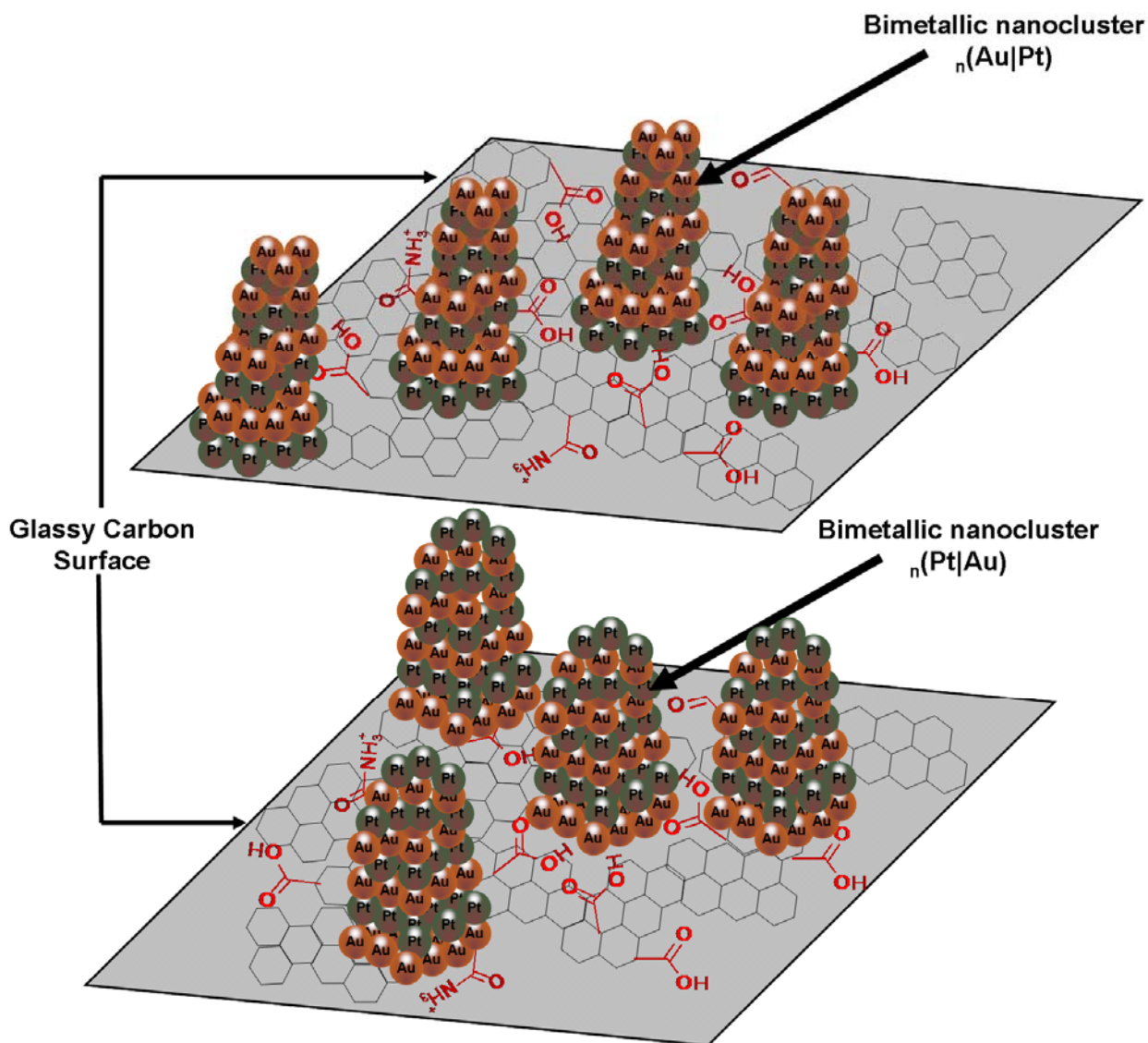


Figure C.9: Schematic drawings of sequentially deposited multilayered bimetallic nanoclusters of platinum and gold with glassy carbon as the substrate.

Table C.2. Representative parameters deduced from electrochemical impedance spectroscopy involving formic acid oxidation reaction* on various nanostructured electrodes

Electrode	Equivalent Circuit	E_{appl}/V (vs Ag/AgCl)	CPE_{dl}							
			R_s/Ω	$R_{\text{ct}}/\text{k}\Omega$	$Q/\Omega^{-1}\cdot\text{s}^\alpha$	α	$C_{\text{dl}}/\mu\text{F}$	$R_{\text{ads}}/\text{k}\Omega$	$C_{\text{ads}}/\mu\text{F}$	X^2
$n(\text{Pt})_{\text{Cu}}/\text{GC}$	A	0.0	4.9	4.52	2.1×10^{-5}	0.836	3.5	–	–	0.26
		0.1	5.0	1.46	2.3×10^{-5}	0.837	3.9	–	–	0.35
	B	0.0	4.4	3.12	1.1×10^{-4}	0.697	4.3	2.12	13.1	0.13
		0.1	4.2	0.87	2.5×10^{-4}	0.632	4.5	0.79	12.5	0.19
	C	0.0	4.9	4.14	1.9×10^{-5}	0.834	3.0	0.71	444	0.25
		0.1	5.0	1.41	2.2×10^{-5}	0.842	4.0	0.16	1881	
$n(\text{Au} \text{Pt})_{\text{Cu}}/\text{GC}$	A	0.0	5.0	3.57	2.3×10^{-5}	0.834	3.7	–	–	0.23
		0.1	7.2	0.95	2.5×10^{-5}	0.796	2.7	–	–	0.24
	B	0.0	4.4	2.17	1.8×10^{-4}	0.657	4.5	1.99	12.5	0.17
		0.1	6.6	0.76	1.4×10^{-4}	0.651	3.3	0.36	11.7	0.16
	C	0.0	3.9	3.35	1.9×10^{-5}	0.849	3.5	0.56	945	0.09
		0.1	7.3	0.88	2.2×10^{-5}	0.810	2.9	0.16	460	0.19

Table C2 (Continued).

Electrode	Equivalent Circuit	E_{appl}/V (vs Ag/AgCl)	CPE_{dl}							
			R_s/Ω	$R_{\text{ct}}/k\Omega$	$Q/\Omega^{-1}.s^{\alpha}$	α	$C_{\text{dl}}/\mu F$	$R_{\text{ads}}/k\Omega$	$C_{\text{ads}}/\mu F$	X^2
$n(\text{Pt} \text{Au})_{\text{Cu}}/\text{GC}$	A	0.0	4.3	2.96	5.4×10^{-5}	0.875	16	—	—	0.26
		0.1	4.3	0.72	6.2×10^{-5}	0.867	17	—	—	0.29
	B	0.0	4.1	2.00	2.5×10^{-4}	0.749	25	1.43	48.7	0.18
		0.1	4.3	0.64	5.8×10^{-5}	0.876	18	0.16	1400	0.29
	C	0.0	4.3	2.82	5.3×10^{-5}	0.880	17	0.31	1567	0.25
		0.1	4.3	0.67	5.7×10^{-5}	0.877	19	0.09	1473	0.28

*Experiments were performed using solutions of 0.5 mol/L formic acid (in 0.1 mol/L HClO_4).