Electrochemical and electrocatalytic properties of iron(II) and cobalt(II) phthalocyanine complexes integrated with multi-walled carbon nanotubes

by

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This dissertation is dedicated to my wife Fidelia and two children, Sheni Adrian and Bonoshi Benedicta for their patience and understanding.
DECLARATION

I declare that the thesis hereby submitted to the University of Pretoria for the degree of Doctor of Philosophy has not been previously submitted by me for a degree at any other University, that it is my own work in design and execution, and that all material contained therein has been duly acknowledged.

Solomon Almanto Mamuru...............................
ACKNOWLEDGEMENTS

I wish to express my sincere and profound gratitude to the Almighty father for His guidance, blessing and protection throughout the duration of my study in South Africa. To Prof. Jacob K. Kwaga and the management of Adamawa State University, Mubi for the opportunity given me to study outside the shores of Nigeria, I say thank you. Sincere appreciation to my supervisor, Dr (Prof.) Kenneth I. Ozoemena, who out of his valuable time read through and made necessary corrections, also not forgetting his moral, financial support and harsh criticism; you have made a diamond out of coal. To the staff and members of Chemistry Department, University of Pretoria and the National Research Foundation (NRF) for the prestigious nanoflagship bursary, I am grateful. To my family, especially my mother Catherine Abubakar, my sister Celina Kanmodi, and my brothers Henry and Tunde, for their moral support and encouragement; to all the members of our research group, we had a wonderful time, despite all inconveniences. I am ever grateful to my very good South African friends, Tebogo Mogosoana and Refilwe Mokate; you made my stay in South Africa worthwhile. I will miss you guys. Finally, to all the friends I made while in South Africa, who have in one way or another impacted positively to my stay in South Africa; especially Pius Chin, Esme, Essien, Sello Segoa, and all the staff of the international student division.
ABSTRACT

For the first time, new metallophthalocyanine (MPc) complexes: (i) nanostructured MPc (nanoMPc, where M = iron or cobalt); (ii) octabutylsulphonylphthalocyanine (MOBSPc, where M = iron or cobalt); and (iii) iron (II) tetrakis(diaquaplatinum)octacarboxyphthalocyanine (PtFeOCPc) were synthesized and characterized using advanced microscopic and spectroscopic techniques such as MS, AFM, HRTEM, FESEM, and EDX. Electrochemical techniques such as cyclic voltammetry, square wave voltammetry, chronoamperometry, rotating disk electrode, and electrochemical impedance spectroscopy, were used to explore the redox chemistry, heterogeneous electron transfer kinetics (HET), and electrocatalytic properties of these MPc complexes towards oxygen reduction reaction (ORR), oxidation of formic acid, thiocyanate and nitrite on an edge plane pyrolytic graphite electrode (EPPGE) platform pre-modified with or without acid functionalized multi-walled carbon nanotubes (MWCNTs). The MWCNT-MPc platforms exhibit enhanced electrochemical response in terms of (i) HET towards an outer-sphere redox probe ([Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁺), and (ii) catalytic activities towards the investigated analytes. The MWCNT-nanoMPc electrode exhibits faster HET constant ($k_{app} \approx 30 - 56 \times 10^{-2}$ cm$^{-1}$ s$^{-1}$ compared to their bulk MPc counterparts ($\approx 4 - 25 \times 10^{-2}$ cm$^{-1}$ s$^{-1}$). The MWCNT-nanoMPc exhibited enhanced electrocatalytic properties (in terms of sensitivity and limit of detection, LoD) towards the detection of thiocyanate and nitrite in aqueous solutions. ORR was a 4-
electron process with very low onset potential (-5 mV vs. Ag|AgCl saturated KCl). HET and ORR at MOBSPc complexes supported on MWCNTs showed that the MWCNT–MOBSPc exhibited larger Faradaic current responses than the electrodes without MWCNTs. The rate constant at the MWCNT-MOBSPc electrodes \(k_{\text{app}} \approx (22 - 37) \times 10^{-2} \text{ cm s}^{-1}\) is about a magnitude higher than the electrodes without MWCNT \(k_{\text{app}} \approx (0.2 - 93) \times 10^{-3} \text{ cm s}^{-1}\). The MWCNT–FeOBSPc electrode gave the best ORR activity involving a direct 4-electron mechanism with low onset potential (0.0 mV vs. Ag|AgCl saturated KCl). The onset potential is comparable and even much lower than recent reports. The HET and electrocatalytic properties of PtFeOCPC supported on a MWCNT platform (MWCNT-PtFeOCPC) gave enhanced electrochemical response in terms of (i) HET \(k_{\text{app}} \approx 78 \times 10^{-2} \text{ cm s}^{-1}\), (ii) catalytic rate constant \(k_{\text{cat}} \approx 41 \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}\) and (iii) tolerance towards CO poisoning during formic acid oxidation. The ORR activity is a direct 4-electron transfer process at a rate constant of \(2.78 \times 10^{-2} \text{ cm s}^{-1}\); with a very low onset potential approximately 0.0 mV vs. Ag|AgCl saturated KCl. The electro-oxidation of formic acid at MWCNT-PtFeOCPC follows the preferred ‘direct pathway’. This work clearly proves that the MWCNT-MPCs hybrid exhibit enhanced electrochemical and electrocatalytic activities towards the selected analytes compared to the MPCs alone. Considering the ease of fabrication of these electrodes (drop-dry method), these nanocomposite materials are promising platform for potential application in sensing and cataly
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<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Electrode surface area (cm$^2$)</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver wire pseudo-reference electrode</td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>Silver/silver chloride reference electrode</td>
</tr>
<tr>
<td>CME</td>
<td>Chemically modified electrode</td>
</tr>
<tr>
<td>C.E.</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CTAB</td>
<td>Hexadecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammogram</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient (cm$^2$s$^{-1}$)</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-diazacyclo[5.4.0]undec-7-ene</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EPPGE</td>
<td>Edge plane pyrolytic graphite electrode</td>
</tr>
<tr>
<td>FeOBSPc</td>
<td>Iron(II) octabutylsulphonylphthalocyanine</td>
</tr>
<tr>
<td>Fe(CN)$_6^{4-}$</td>
<td>Hexacyanoferrate(II)</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$</td>
<td>Hexacyanoferrate(III)</td>
</tr>
<tr>
<td>LoD</td>
<td>Limit of detection</td>
</tr>
<tr>
<td>MPC</td>
<td>Metallophthalocyanine</td>
</tr>
<tr>
<td>Pc</td>
<td>Phthalocyanine</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PtFeOCPc</td>
<td>Iron(II) tetrakis(diaquaplatinum)octacarboxy phthalocyanine</td>
</tr>
<tr>
<td>R.E.</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SWV</td>
<td>Square wave voltammetry</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>t</td>
<td>Time(s)</td>
</tr>
<tr>
<td>TBAP</td>
<td>Tetrabutyl ammonium perchlorate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>UV-vis.</td>
<td>Ultra violet visible spectrophotometer</td>
</tr>
<tr>
<td>W.E.</td>
<td>Working electrode</td>
</tr>
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<td>XRD</td>
<td>X-ray diffraction spectroscopy</td>
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<tr>
<td>$\alpha$</td>
<td>Transfer coefficient</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular velocity</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Surface concentration</td>
</tr>
<tr>
<td>$\pi$</td>
<td>Pi bonding</td>
</tr>
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<td>$\lambda$</td>
<td>Wavelength</td>
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<tr>
<td>$\gamma$</td>
<td>Kinematic viscosity</td>
</tr>
<tr>
<td>$c$</td>
<td>Molar concentration of analyte</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>Double-layer capacitance</td>
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<tr>
<td>CPE</td>
<td>Constant phase element</td>
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<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
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<tr>
<td>$E_{pa}$</td>
<td>Anodic peak potential</td>
</tr>
<tr>
<td>$E_{pc}$</td>
<td>Cathodic peak potential</td>
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<td>$E$</td>
<td>Potential</td>
</tr>
<tr>
<td>$E^\circ$</td>
<td>Standard potential</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>Half-wave potential</td>
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<tr>
<td>$\Delta E$</td>
<td>Potential ‘width’</td>
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<td>$\Delta E_p$</td>
<td>Anodic-to-cathodic peak potential separation</td>
</tr>
<tr>
<td>$\Delta E_s$</td>
<td>Step height</td>
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<td>Hertz</td>
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<tr>
<td>$i_{pa}$</td>
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<td>$k_{app}$</td>
<td>Apparent electron transfer rate constant</td>
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<tr>
<td>$k_{cat}$</td>
<td>Catalytic rate constant</td>
</tr>
<tr>
<td>n</td>
<td>Number of electron</td>
</tr>
<tr>
<td>Q</td>
<td>Electrical charge (C)</td>
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<tr>
<td>R</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Charge transfer resistance</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Resistance of electrolyte</td>
</tr>
<tr>
<td>v</td>
<td>Scan rate</td>
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<td>V</td>
<td>Volts</td>
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<td>-Z''</td>
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<td>Real impedance</td>
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<td>$Z_w$</td>
<td>Warburg impedance</td>
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