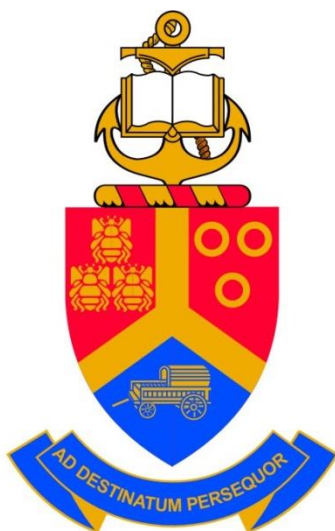


Activated carbon from peanut shell and its molybdenum based nanocomposites for supercapacitor applications

by

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Declaration

I, **Ndeye Fatou Sylla** declare that the thesis entitled “Activated carbon from peanut shell and its molybdenum based nanocomposites for supercapacitor applications”, which I hereby submit for the degree Doctor of Philosophy (Ph.D.), is the result of investigation carried out by me under the supervisor and co-supervision of Prof. N. I. Manyala and Prof. B. D. Ngom, respectively in the Physics Department at the University of Pretoria, South Africa and has not been previously submitted by me for a degree at this or any other tertiary institution.

Signature:.....

Date:.....

Dedication

To my beloved

Dad/El Hadj Adama Sylla and mom Astou Konare

Family and friends

Who have always been my sources of constant support, prayers

Love and motivation to become a better person

Along with my Professor Balla Diop Ngom

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Abstract

Synthesis of activated carbon from biomass waste has recently become the main focus for the majority of the scientific community. In this study, activated carbons derived from peanut shell waste and its molybdenum-based nanocomposites were explored as potential electrode materials for supercapacitor applications. Activated carbons and their composites were synthesized through atmospheric pressure chemical vapour deposition (AP-CVD) and characterized by various techniques such as N₂ adsorption-desorption, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), high-resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS). This study aims on the enhancement of electrochemical performance of the activated carbons derived from peanut shell. To achieve this goal various directions have been adopted.

First, the study is focused on the effect of the potassium-based activating agents (AAs) on the microstructure and electrochemical properties of the activated carbon from peanut shell materials. This approach contributes to the way to design and tune the properties of the porous carbon by selecting the appropriate AAs. The peanut shell waste (PSW) chemically activated carbon (APSW) with potassium hydroxide (KOH) exhibited a good electrochemical energy storage capability owing to their excellent structural and textural properties (2547 m² g⁻¹ specific surface area, and 1.2 cm³ g⁻¹ pore volume).

The second approach consists of enhancing the activated carbon derived from PSW by heteroatom-doping with nitrogen. Post nitrogen-doped activated carbon from PSW was synthesized by KOH activation of the PSW to produce peanut shell waste activated carbon (denoted as PAC) followed by *post-doping* with melamine (NPAC).

The introduction of the nitrogen into the porous carbons enhances PAC physicochemical characteristics, surface chemistry and provides more electrochemical active sites leading to an increase in supercapacitors performances.

The last approach emphasizes on the incorporation of pseudocapacitive materials into PAC by making a composite. The ternary composite of PAC/molybdenum oxide/molybdenum carbide (PAC/MoO₂/Mo₂C) was prepared by one-step pyrolysis process of the PAC and ammonium molybdate precursor. The MoO₂ and Mo₂C nanostructures embedded into the PAC have led to a significant improvement on the performance with a specific capacitance of 253 F g⁻¹ higher than the pristine PAC. This enhancement of the electrochemical performance is attributed to the synergistic effect of the merits of each component (PAC, MoO₂ and Mo₂C) in the ternary offering additional active sites, faster ions diffusion rate, greater electrical conductivity and chemical stability.

The electrochemical performance of the best as-synthesized electrodes materials have been tested in symmetric devices in 2.5 M KNO₃ aqueous electrolyte: APSW-KOH4//APSW-KOH4, NPAC-1//NPAC-1 and PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 in the wide cell potential in the range of 1.8 V to 2 V. In particular the PAC/MoO₂-1/Mo₂C-1 electrode reveals the highest electrochemical performance with a specific energy and power of 51.8 W h kg⁻¹ and 0.9 kW kg⁻¹ at 1 A g⁻¹, respectively as compared to 34.9 W h kg⁻¹ and 1 kW kg⁻¹ for NPAC -1 electrode and 25.2 W h kg⁻¹ and 0.9 kW kg⁻¹ for APSW-KOH4 electrode.

This study highlights a sustainable and eco-friendly one-step pathway of synthesising a ternary composite PAC/MoO₂/Mo₂C as advanced electrode material for high-performance energy storage. Moreover, this work also emphasized an efficient strategy to improve the electrochemical properties towards incorporating Mo-based components into the porous activated carbon materials.

Table of contents

Declaration.....	I
Dedication	II
Acknowledgment.....	III
Abstract.....	V
Table of contents	VII
List of figures.....	XI
List of table	XIII
List of equations	XIV
Chapter 1	1
1.0 Introduction.....	1
1.1 Background and motivation	1
1.2 Research questions	5
1.3 Significance of the study	6
1.4 Aims and objectives of this study	6
1.5 Scope of the thesis.....	7
References	8
Chapter 2	11
2.0 Literature review	11
2.1 Energy storage technologies.....	11
2.2 Supercapacitors: Types and Operation Mechanism	14
2.2.1 Electrical Double Layer Capacitors (EDLC).....	15
2.2.1.1 Mechanism of storage in EDLC	15

2.2.1.2 Electrode materials for EDLC	18
2.2.2 Pseudocapacitors (PCs)	28
2.2.2.1 Mechanism of storage in PCs	28
2.2.2.2 Electrode materials in pseudocapacitors (PCs).....	30
2.2.3 Hybrids capacitors (HCs)	34
2.3 Electrolytes.....	38
2.3.1 Aqueous electrolytes.....	39
2.3.2 Organics electrolytes	40
2.3.3 Ionics liquid electrolytes.....	41
2.4 Electrode material preparation for supercapacitors.....	42
2.5 Electrochemical test of the electrode material	43
2.5.1 Three-electrode set-up	43
2.5.2 Two-electrode set-up	45
2.6 Electrochemical characterization of the electrode material	48
2.6.1 Cyclic voltammetry (CV)	48
2.6.2 Galvanostatic charge - discharge (GCD).....	50
2.6.3 Stability.....	51
2.6.4 Electrochemical impedance spectroscopy (EIS)	52
References	55
Chapter 3	74
3.0 Experimental methods and characterization techniques	74
3.1 Chemical Vapour Deposition	74

3.2 Materials synthesis	76
3.2.1 Synthesis of the activated carbon from peanut shell waste	76
3.2.2 Synthesis of the ex-situ nitrogen doped peanut shell waste activated carbon	77
3.2.3 Synthesis of the peanut shell activated carbon/molybdenum oxide/molybdenum carbide (PAC/MoO ₂ /Mo ₂ C) ternary composite.....	79
3.3 Materials characterization technique.....	80
3.3.1 Gas absorption technique.....	80
3.3.2 Scanning electron microscopy (SEM).....	82
3.3.3 Transmission electron microscopy (TEM)	84
3.3.4 X-ray powder diffraction (XRD).....	85
3.3.5 Raman spectroscopy	88
3.3.6 X-ray photoelectron spectroscopy (XPS)	89
3.3.7 Electrochemical characterization.....	90
References	92
Chapter 4	95
4.0 Results and discussion	95
4.1 Effect of activating agents on the electrochemical performance of high-energy ultra- capacitor electrodes derived from peanut shell waste	95
4.1.1 Introduction	95
4.1.2 Results and discussion	97
4.1.3 Concluding Remarks	113

4. 2 Ex-situ nitrogen-doped porous carbons derived from peanut shell waste as electrode materials for high performance supercapacitor	114
4.2.1 Introduction	114
4.2.2 Results and discussion	116
4.2.3 Concluding Remarks	130
4.3 Enhanced capacitive behaviour of peanut-shell activated carbon/molybdenum oxide/molybdenum carbide ternary composite	131
4.3.1 Introduction	131
4.3.2 Results and discussion	132
4.3.3 Concluding Remarks	133
References	178
Chapter 5	182
5.0 General conclusions and future works.....	182
5.1 Conclusions	182
5.2 Future works.....	186

List of figures

Figure 2.1: Ragone plot showing the relationship between the specific energy and the specific power for various energy storage systems	13
Figure 2.2: Classification of supercapacitors: Electrical Double Layer, Pseudocapacitors and Hybrid capacitors	15
Figure 2.3: Mechanisms for charge storage in EDLC at a positive charge electrode surface (a) Helmholtz model, (b) Gouy-Chapman model, and (c) Stern model	17
Figure 2.4: Types of pores in 3D activated carbon: micropores, mesopores and macropores	20
Figure 2.5: Scheme of two-step route for the synthesis of highly porous willow-derived ACs	22
Figure 2.6: Scheme showing the various nitrogen configurations on the carbon framework	23
Figure 2.7: Schematic diagram of the synthesis of post 3D nitrogen-doped porous carbon .	24
Figure 2.8: Schematic process of the synthesis nanocomposite $\text{CuO}_x@\text{C}$	25
Figure 2.9: Structure diagram of a single layer of 2D graphene	26
Figure 2.10: Structure diagram of (a) SWCNT (b) DWCNT and (c) MWCNT	27
Figure 2.11: (a) Structure diagram of CNO and (b) TEM of CNOs	28
Figure 2.12: Schematic charge storage mechanism of a pseudocapacitive behavior: (a) underpotential deposition, (b) redox pseudocapacitance, and (c) intercalation pseudocapacitance	29
Figure 2.13: Schematic diagram of the synthesis of the binary composite 3DHPC- Mo_2C and asymmetric supercapacitor 3DHPC- $\text{Mo}_2\text{C}//\text{AC}$	35
Figure 2.14: Schematic diagram of sodium ion capacitor (hybrid capacitor) CGH// $\text{MoO}_2@\text{rGO}$	36

Figure 2.15: Schematic of the formation of $\text{MoO}_2/\text{Mo}_2\text{C} / \text{C}$ ternary composite	37
Figure 2.16: Classification of various electrolytes types in supercapacitors	38
Figure 2.17: Different approaches of constructing high-voltage aqueous supercapacitors ...	39
Figure 2.18: Diagram showing supercapacitor electrode preparation	42
Figure 2.19: Schematic representation of (a) half-cell configuration set-up and (b) Swagelok T-cell configuration set-up.....	44
Figure 2.20: Schematic representation of full cell configuration (a) coin-cell set-up and (b) Swagelok cell set-up.	45
Figure 2.21: Cyclic voltammogram characteristics of (a) EDLC and (b) Faradaic systems. .	49
Figure 2.22: Galvanostatic charge-discharge characteristics of (a) EDLC and (b) Faradaic systems.	50
Figure 2.23: Schematic representation of the voltage holding test	52
Figure 2. 24: Schematic representation of Nyquist plot	53
Figure 3.1: Diagram of atmospheric pressure chemical vapour deposition system.	75
Figure 3.2: Schematic synthesis process of the activated carbon from peanut shell.	77
Figure 3.3: Schematic of the synthesis route of the ex-situ nitrogen doping peanut shell activated carbon.	78
Figure 3.4: Schematic of the synthesis process of $\text{PAC}/\text{MoO}_2/\text{Mo}_2\text{C}$ ternary composite.....	79
Figure 3.5: (a) The IUPAC classification of adsorption/desorption isotherms (b) adsorption/desorption hysteresis loop	81
Figure 3.6: High resolution Field Emission Scanning Electron Microscope instrument (Zeiss, Ultra Plus 55 FE-SEM).....	83
Figure 3.7: Transmission Electron Microscopy instrument (HRTEM-JEOL- 2100F).....	85
Figure 3.8: Scheme illustrative of Bragg'law	86
Figure 3. 9: Panalytical X'Pert-Pro X-ray diffractometer system.	87

Figure 3.10: WITec confocal Raman microscope (WITec alpha 300 R, RAS+ , Germany).	89
Figure 3.11: Biologic VMP-300 16-channel potentiostat (Knoxville 37930, USA) controlled by the EC-Lab® V11.33 software.	91
Figure 5.1: Ragone plot of APSW-KOH4// APSW-KOH4, NPAC-1//NPAC-1 and PAC/MoO ₂ /Mo ₂ C-1//PAC/MoO ₂ /Mo ₂ C-1 symmetric devices.	185

List of table

Table 2.1: Characteristic and electrochemical performance of the ACs derived from various biomass sources	21
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List of equations

$E = \frac{1}{2} \times CV^2$ (2.1).....	13
$P_{\max} = \frac{V^2}{4 \times m_T R_S}$ (2.2)	14
$C = \frac{\varepsilon_r \varepsilon_0 A}{d}$ (2.3).....	16
$\frac{1}{C_T} = \frac{1}{C_H} + \frac{1}{C_D}$ (2.4).....	17
$\frac{1}{C_T} = \frac{1}{C_+} + \frac{1}{C_-}$ (2.5)	46
$C_S = 4 \times C_T = \frac{4 \times I \Delta t}{m_T \Delta V}$ (2.6).....	46
$E_D = \frac{1}{2} CV^2 = \frac{1000 \times C_S \times \Delta V^2}{2 \times 4 \times 3600} = \frac{C_S \times \Delta V^2}{28.8}$ (2.7).....	46
$P_D = \frac{3600 \times E_S}{1000 \times \Delta t} = \frac{3.6 \times E_D}{\Delta t}$ (2.8)	46
$Q_+ = Q_-$ (2.9).....	47
$Q = C_S m \Delta V$ (2.10).....	47
$\frac{m_+}{m_-} = \frac{C_{S-} \Delta V_-}{C_{S+} \Delta V_+}$ (2.11)	47
$Q_S = \frac{I \times \Delta t}{3.6 \times m}$ (2.12)	47
$\frac{m_+}{m_-} = \frac{C_{S-} \Delta V_-}{3.6 \times Q_S}$ (2.13).....	47
$E_D = \frac{I}{3.6 \times m_T} \int V(t) dt$ (2.14).....	48
$P_D = 3600 \times \frac{E_D}{\Delta t}$ (2.15)	48

$C_s = \frac{1}{m\nu\Delta V} \int I(V)dV$ (2.16).....	49
$\eta_{CE} = \frac{t_D}{t_C} \times 100$ (2.17).....	51
$\eta_{EE} = \frac{E_D}{E_C} \times 100$ (2.18).....	51
$C(\omega) = C'(\omega) - jC''(\omega)$ (2.19)	53
$C'(\omega) = \frac{-Z''(\omega)}{\omega Z(\omega) ^2}$ (2.20)	54
$C''(\omega) = \frac{Z'(\omega)}{\omega Z(\omega) ^2}$ (2.21).....	54
$C = \frac{1}{2\pi f Z'' }$ (2.22).....	54
$n\lambda = 2d \sin \theta$ (3.1).....	86

1.0 Introduction

1.1 Background and motivation

The increase in energy demand along with population growth is a subject of awareness at the global level in the scientific community. Most of the energy sources used are non-renewable fossil fuels that are being depleted at a fast rate. In addition to these concerns, fossil fuels create deleterious impacts on the environment (climate change, global warming) causing a serious threat in our daily life, safety, human welfare and health. Incidentally, major global interests have considered the development of sustainable energy technologies based on renewable resources that are green, clean and efficient for energy-converting and energy-consuming systems. Renewable energy resources have been deployed at a considerable scale to address the rise in energy demand and mitigate climate change. Most of these sources include solar, wind, hydrothermal and, geothermal that provide energy intermittently making them unreliable for steady energy generation [1]. Therefore, it is paramount to find efficient energy storage systems to not only support continuous energy production and, offset the intermittent energy generation from renewable resources but also to reduce the worldwide energy resources depletion [2]. In this regard, batteries and conventional capacitors are among the predominant energy storage devices. Batteries have been characterized by their high specific energy but their limited specific power hampers their large-scale practical applications while conventional capacitors provide a high specific power but possess low specific energy. Hence, a single energy storage technology that combines such properties concerning high specific energy, high specific power and, low cost among other features is highly desirable.

Supercapacitors (SCs) also referred to as electrochemical capacitors (ECs) or ultracapacitors have recently emerged as an alternative energy storage device. SCs have attracted considerable interest due to their high power density, long life cycle compared to the batteries. They have substantial potential to make pathways into the electricity industry and to minimize the negative effects of energy usage upon human health and the environment [3]. However, they still suffer from low specific energy as compared to batteries which have led to the quest by researchers to resolve this problem. One of the main routes to solving the low specific energy problem is by understanding the basic device storage mechanism which is highly related to the nature of the electrode material. Relying on their energy storage mechanism, SCs constitute of three different types, namely electric double-layer capacitors (EDLCs), pseudocapacitors (PCs) and Hybrid capacitors (HCs).

Carbon-based materials including onion-like carbons (OLCs), carbon nanotubes (CNTs), graphene, carbide-derived carbons (CDCs), and activated carbons (ACs) are common electrode materials for EDLCs in which their charge storage mechanism is based on the accumulation of charges at the electrode/electrolyte interface. ACs are the most popular and commonly utilized electrode materials in commercial supercapacitor owing to their versatile features such as high specific surface area (SSA), tunable porosity, good conductivity and good chemical stability. They can be derived from various types of precursors namely petroleum, coal, synthetic polymers and metal-organic frameworks which are non-renewables, and expensive or often hazardous [4]. Recently, many scientists are thriving in pursuit of ACs from biomass sources due to the environmental benignity, large production, low cost, abundance and availability. There is a variety of biomass carbon sources such as coconut shells, nutshells, banana peels, sunflower shells, and so on [5]. Peanut shells waste (PSW) are one of the biggest agro-industrial waste, hence, they are extremely low-cost raw materials and readily available.

In addition, PSW is a lignocellulosic raw material with high carbon content, different surface functional groups (phenol, hydroxyl, ether etc.) and also has other heteroatoms (sulphur and nitrogen) thus making it a promising precursor for the production of ACs [6][7][8]. Recent reports have demonstrated that ACs derived from PSW provide the merits as a potential electrode material for use in supercapacitors [9][10][11].

ACs can be readily processed either through physical or chemical activation of the carbonaceous precursors materials. The chemical activation leads to the production of porous AC with a large SSA ($\sim 2500 \text{ m}^2 \text{ g}^{-1}$), hierarchical pore structures, and high carbon yield as compared to the physical treatment. In the chemical process, the porous ACs are obtained by impregnating the raw material with the activating agents (AAs) such as zinc chloride (ZnCl_2), potassium hydroxide (KOH) and phosphoric acid (H_3PO_4) among others, followed by carbonization at 450 - 900 °C [12]. Therefore, the effect of the AAs on the physicochemical properties of carbons has been investigated in order to improve the ACs electrode performance. The KOH activation of carbonaceous material is the commonly used chemical process to generate ACs with highly developed micropores and specific surface areas owing to their multiple decomposition steps at high temperature as compared to other AAs [13]. Although ACs have been considered as favourable capacitive electrode material for supercapacitors owing to their above-mentioned properties, their capacitance still needs to be enhanced to meet the growing demand for high energy. To satisfy this demand, researchers have developed a variety of approaches to tailor the electrochemical performance of the AC electrodes. A pre-carbonization approach of the carbonaceous precursors that entails a thermal treatment step prior to the activation process has been reported to improve the electrochemical performance of carbons [14].

The inclusion of this procedure could create additional pores within the carbon network resulting in an increase in specific surface area and the presence of oxygenated functional groups, hence leading to improved charge storage [15][14].

Heteroatoms doping with nitrogen (N), sulphur (S), boron (B), phosphorus (P), and oxygen (O) is another effective strategy for improving the electrochemical storage of the ACs electrode material in supercapacitors. In particular, the introduction of nitrogen into the carbon matrix has led to an improvement of the surface wettability, affinity of the electron donor and electrical conductivity. Moreover, this generates electro-active sites which significantly enhance the capacitive characteristics of the ACs electrode [16]. Various nitrogen-containing agents such as polyaniline, melamine, polypyrrole, urea, and ammonia can be used as precursors to obtain N-doped ACs. The synthesis process N-doped carbon involves *in situ*-doping and *post-doping* procedures. *In-situ doping* involves subjecting both carbonaceous and nitrogen-containing precursors to the carbonization process or a direct carbonization of the precursors containing both carbon and nitrogen elements (polymers, chitosan). Contrarily, the *post-doping* involves the carbonization of the nitrogen-containing precursors onto already synthesized carbons [17]. A recent study [18] on the nanostructure carbon material derived from houttuynia biomass doped with melamine was reported. An improvement on the charge storage performance of the carbon material was obtained due to the nitrogen-doping present which enhanced the wettability inducing a faster electrolyte ions pathway and providing additional electrochemically active sites which could contribute to an increased specific capacitance of the electrodes prepared from ACs [18].

The incorporation of pseudocapacitive materials into the ACs to obtain a composite materials has recently become an attractive approach to enhance the supercapacitive performance [19][20]. Although, these materials are plagued with their low electrical conductivity and poor cycling stability which restrict their applications [21].

Pseudocapacitive materials including transitional metal oxides/hydroxides (TMO/TMOH), transitional metal carbides/nitrides (TMC/TMN), conducting polymers (CP) among others still possess the capability to deliver high specific capacitance as compared to carbon-based materials owing to their reversible faradaic reactions occurring at the electrode/electrolyte interface. Among the pseudocapacitive materials, molybdenum based oxide (MoO_x) and molybdenum carbide (Mo_2C) have been widely exploited as promising electrode materials for supercapacitors owing to various oxidation states (+2 to +6), rich electrochemical activity, relatively low cost [22]. Forming a composite material of activated carbons with MoO_x or Mo_2C combines the merits of both EDLC and pseudocapacitance mechanisms which could improve the electrochemical properties of the supercapacitors. Recent studies of composite materials which include carbon materials with MoO_2 and/or Mo_2C have been reported to enhance the performance metrics of the SCs. This is due to the synergy effect of the characteristics of each component such as the high specific surface area, electrical conductivity, hierarchical pores structure, easy electron and ion transportation, chemical/mechanical stability and electrochemical activity [23][24][25].

1.2 Research questions

This study will be addressing the following questions:

- (i) What would be the effect of potassium-based activating agents on the morphological, structural and electrochemical properties of two-step carbonized activated carbons?
- (ii) How will *post*-nitrogen doping of peanut shell derived carbons influence their surface chemistry and their electrochemical performance in supercapacitors?
- (iii) What would be the effect of incorporating MoO_2 and Mo_2C nanostructures within an activated carbon matrix on the electrochemical performance of ternary composites?

1.3 Significance of the study

This research work will open a new platform on how to tune not only the physicochemical properties of activated carbons and their molybdenum-based nanocomposite but also their surface properties for optimum electrochemical energy storage applications.

1.4 Aims and objectives of this study

The aims and objectives of this research work are as follows:

1. Synthesis and characterization of activated carbons derived peanut shell waste (APSW) through two-step process: Pre-carbonization of the raw material using chemical vapour deposition (CVD) system followed by chemical activation via CVD system:
 - The effect of various potassium-based activating agents (K-based AAs) such as potassium hydroxide (KOH), potassium carbonate (K_2CO_3) and potassium hydrogen carbonate ($KHCO_3$) on the electrochemical properties of the PSW.
 - Investigation of the role of the various mass concentrations of the K-based AAs on the textural and electrochemical properties of the PSW.
2. Synthesis and characterization of *in-situ* and *post N-doped* ACs using the optimized AA with different mass concentrations via CVD system:
 - To investigate the influence of the *in-situ N-doping* on the structural, chemical and electronic properties of the PSW.
 - To determine the impact of varying the mass ratio of the optimized AA on the properties of *post N-doped* activated carbons and their application in supercapacitors.

3. Synthesis and characterization of a ternary composite material based on MoO_2 , Mo_2C and ACs and their use in hybrid supercapacitors:

- To study how mass loading of the molybdenum salt precursor influence the composition and properties of a ternary composite obtained through a one-step pyrolysis process.
- Investigation of the effect of incorporating metal oxide and metal carbide (MoO_2 and Mo_2C) into the ACs and their electrochemical properties in supercapacitors.

1.5 Scope of the thesis

The thesis is divided into five chapters as follows:

Chapter 1 presents the background and motivation, aims and objectives, research questions, significance of the study and the scope of the thesis.

Chapter 2 presents a literature review on supercapacitors.

Chapter 3 presents the synthesis procedures and characterization techniques used in this work.

Chapter 4 describes the discussion of the results obtained on:

4.1 Effect of porosity enhancing agents on the electrochemical performance of high-energy ultracapacitor electrodes derived from peanut shells waste

4.2 Ex-situ nitrogen-doped porous carbons as electrode materials for high performance supercapacitor

4.3 Enhanced capacitive behaviour of peanut-shells activated carbon/molybdenum oxide/molybdenum carbide ternary composite.

Chapter 5 provides the general conclusions obtained from this study and future research work.

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2.0 Literature review

2.1 Energy storage technologies

Energy storage systems are composed of devices that can store electrical energy in various forms (mechanical, chemical, electrical, electrochemical, etc.) which are then generated as required [1]. These storage systems play an important role in ensuring the continuity of energy supply and to enhance their reliability for useful applications [2]. Fuel cells, batteries (Lithium-ion battery, Nickel-metal hydride battery, lead-acid battery.) and supercapacitors (SCs) can be categorized into electrochemical energy storage devices [3][4]. These storage technologies have similar design architectures consisting of two electrodes separated by a membrane with electrolyte in between and the separator only allows ionic conduction from electrolytes. Batteries and SCs have stimulated wide attention, mainly due to their key performing factors in term of specific energy, specific power, lifetime and cycling rate [5]. Batteries convert chemical energy to electrical energy based on the oxidation-reduction reaction mechanism in the bulk electrode materials [6]. Among the various types of batteries, Lithium-ion batteries (LiBs) are one of the most promising and advanced form of electrical energy storage devices used in many devices due to their high specific energy efficiency. For good performance rechargeable batteries, LiBs has been widely adopted in portable electronic devices (mobile phones, laptops, tablets), hybrid or plug-in electric vehicles [7][8]. However, they can't deliver a high specific power due to the low charge-discharge rate coupled with a poor cycle life.

Supercapacitors (SCs) also referred to as electrochemical capacitors (ECs) or ultracapacitors can provide high specific power, good charge/discharge ability, excellent cycling stability, long lifespan and high efficiency with low maintenance cost as compared to batteries [9][3].

This high power supplied by the SCs can be delivered in a very short time (in few seconds) which is suited for applications such as stop-start systems and regenerative braking systems in cars (electric/hybrid electric vehicles), consumer electronics (laptops, smart phones, smart toys, wearable devices, etc.), back-up power systems (uninterruptible power supply, engine generators, solid state drives) and emergency exit doors (in electric buses, planes) [10][11][12]. Furthermore, SCs also serve as storage systems which can solve the issue of intermittent power supply into the grid from the renewable energy systems (wind, solar, tide) [13]. However, even with all advantages mentioned above, SCs are still lacking due to their low specific energy values when compared to batteries.

The performance of SCs compared to other energy storage systems is shown in figure 2.1. This figure represents the Ragone plot, which highlights the relationship between the specific energy and the corresponding specific power for different energy storage devices. Herein, SCs can be considered to fill the energy/power gap between batteries and conventional capacitors [3][14]. SCs store much specific energy than conventional capacitors, which rely on the electrostatic charge separation across a dielectric medium between the two electrodes. On the other hand, batteries and fuels cell can store great amount of energy relative to SCs owing to the nature of storage through redox chemical processes [15][16]. Thus, researchers are focusing on enhancing the specific energy of the SCs while still retaining their high specific power. Typically, the electrode material and electrolyte are among the main factors which determine the performance of the SCs.

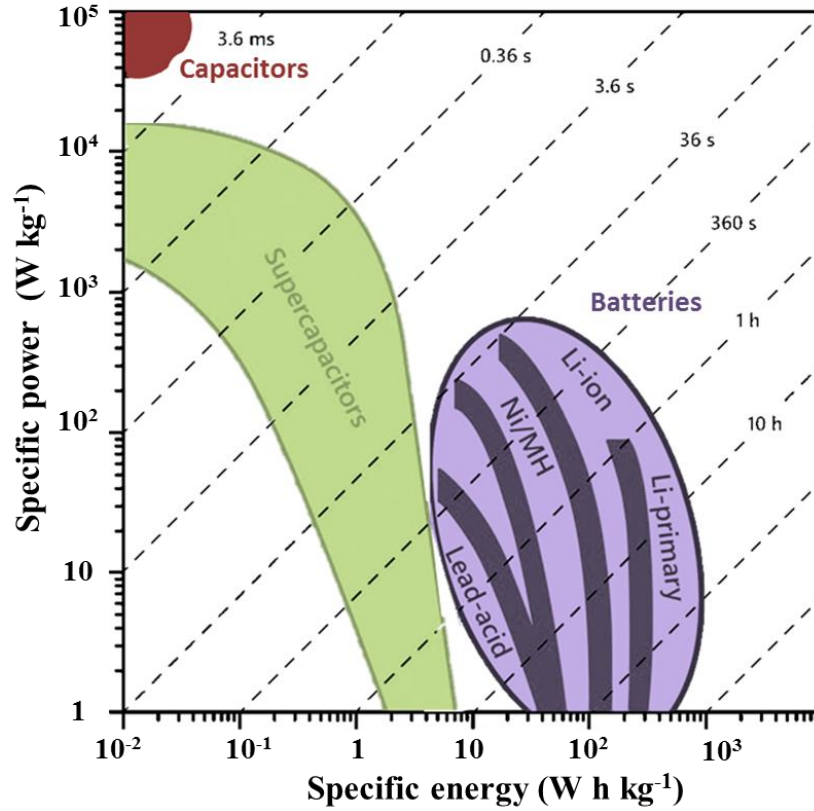


Figure 2.1: Ragone plot showing the relationship between the specific energy and the specific power for various energy storage systems [17].

Therefore, it is important to develop electrode material with desirable properties such as high specific surface area, good porosity, and high electrical conductivity in order to increase their performance. There are various approaches for evaluating the performance metrics of the SCs, including the specific energy, specific power, cell capacitance, operating voltage, and the equivalent series resistance [18][19]. The specific energy stored (E) and maximum power (P) delivered by the SCs are determined by using equations (2.1) and (2.2) respectively.

$$E = \frac{1}{2} \times CV^2 \quad (2.1)$$

$$P_{\max} = \frac{V^2}{4 \times m_T R_S} \quad (2.2)$$

where C (F g^{-1}) is the specific capacitance of the cell, V represents the cell voltage (V), m_T is the total mass of the two electrodes and R_S (Ω) is the equivalent series resistance (*ESR*).

As a result, research to obtain high performance (mainly specific energy and power) necessitates an improvement of the specific capacitance, to extend operating voltage and to reduce the value of R_S [20].

2.2 Supercapacitors: Types and Operation Mechanism

Electrochemical capacitor, first commercialized in 1971 by Nippon Electric Company (NEC) under the name “Supercapacitor”, has similar design to a conventional capacitor [21]. The structure consists of two electrodes oppositely charged which are immersed in an electrolyte and separated with an ionic permeable membrane. They are grouped into two categories based on their charge storage process: (i) electrical double layer capacitors (EDLCs) which store energy electrostatically by adsorption/desorption of ions on the interfacial electrode/electrolyte and (ii) pseudocapacitors (PCs) or Faradaic capacitors (FCs) which accumulate charges by swift redox reaction occurring at the electrode/electrolyte interface. Therefore the combination of both mechanisms defined the new class of SCs named Hybrids capacitors [22]. A flowchart of the three different classes of SCs is shown in figure 2.2 and their mechanism will be explained in detail in the section 2.2.1 and 2.2.2.

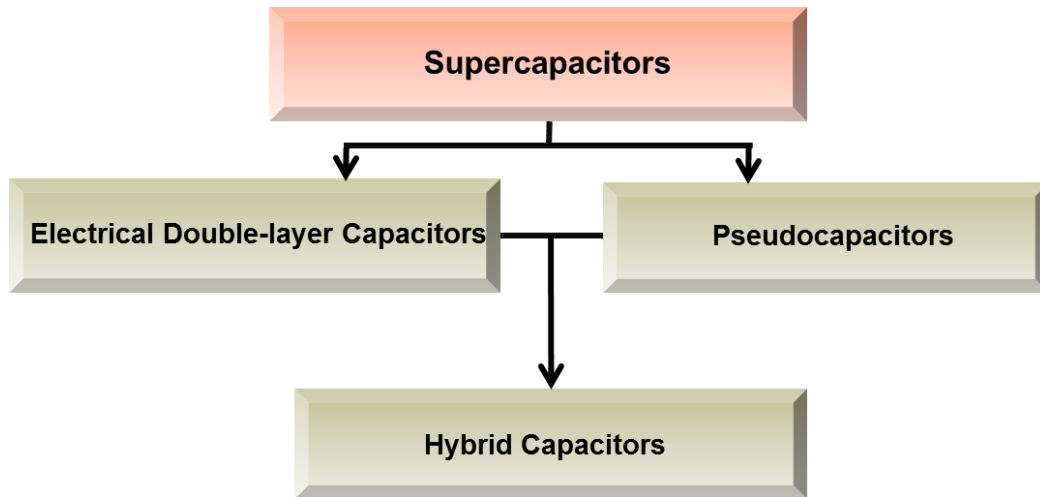


Figure 2.2: Classification of supercapacitors: Electrical Double Layer, Pseudocapacitors and Hybrid capacitors [23].

2.2.1 Electrical Double Layer Capacitors (EDLC)

2.2.1.1 Mechanism of storage in EDLC

EDLC storage is typically based on a separation of charges at the surface of conductive electrodes (both negative and positive) and the adjacent electrolyte under an applied potential. This process leads to a formation of electrical double layer (EDL) whereby no transfer of charges is involved on the interface of the conductive electrode. In similar terms, pure electrostatic interactions occur between the electrolyte ions and the polarized surface electrode where the charges are accumulated [24].

The principle of EDL was initially introduced and modelled by Hermann von Helmholtz in the 19th century and was called the “Helmholtz double layer” model. His model consisted of the formation of two distinct layers of opposite charges at the electrode/electrolyte interface as shown in figure 2.3(a) [25]. The distance between the two layers is in the order of atomic dimensions which is smaller than the distance of the two plates in conventional capacitors.

The capacitance C (in F) represented the electric charge stored in the EDLC can be expressed by equation (2.3) [26]:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (2.3)$$

where ϵ_r is the electrolyte dielectric constant, ϵ_0 is the dielectric constant of the vacuum, A (in m²) is the surface area of the active material, and d (in m) is the distance of the charge separation or thickness of the double-layer.

Helmholtz double layer model neglected on the explanation of other phenomena occurring at the surface of the active electrode, for instance the absence of the ionic interactions [27]. Later, this model was modified by Gouy and Chapman who considered the presence of a diffuse layer and the interaction of the ions in the EDL region whereas continuous distribution of ions in the electrolyte is controlled by thermal motion. Gouy-Chapman model also named “Gouy-Chapman diffuse layer” is exhibited in figure 2.3(b) [28]. Stern further modified the Gouy-Chapman diffusion layer due to the overestimation of EDL capacitance [29]. The new concept of Stern consisted on the combination of both previous theories Helmholtz double layer and the Gouy-Chapman diffuse layer as presented in figure 2.3(c). In his model, he developed two ionic distribution regions which are defined as a compact layer or Stern layer formed by adsorbed ions and diffuse layer described by Gouy-Chapman theory. In the compact layer, there are two planes including the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) [27][30].

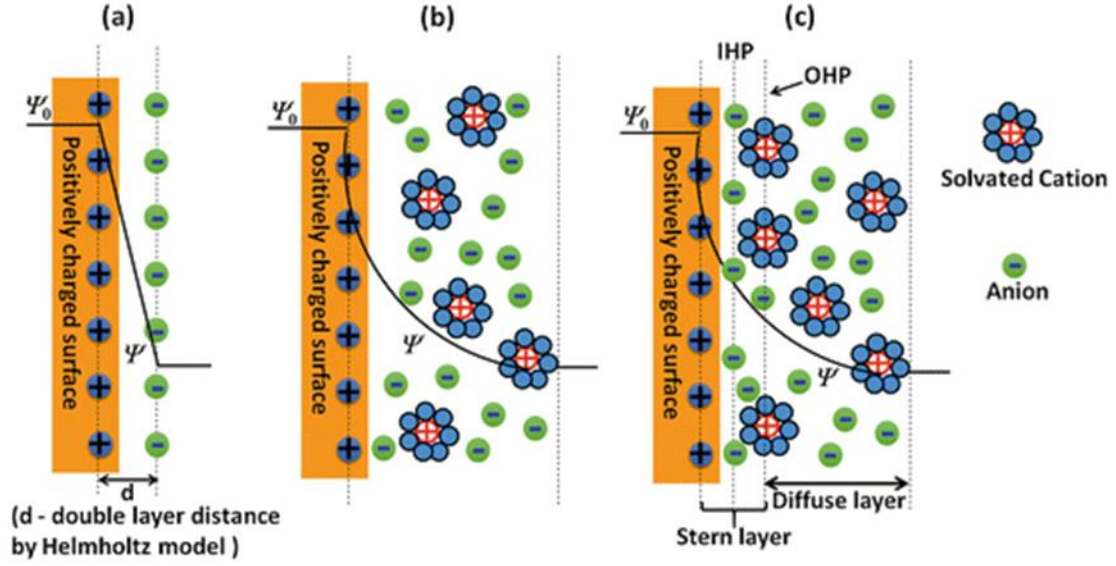


Figure 2.3: Mechanisms for charge storage in EDLC at a positive charge electrode surface (a) Helmholtz model, (b) Gouy-Chapman model, and (c) Stern model [29].

The total capacitance of the EDLC (C_T) corresponds to the equivalent of the capacitances obtained from the compact double layer (C_H) and the diffuse layer (C_D) shown in equation (2.4) [29][31]:

$$\frac{1}{C_T} = \frac{1}{C_H} + \frac{1}{C_D} \quad (2.4)$$

The charge storage of the EDLC is controlled by the surface area of the electrode in contact with the electrolyte, the thickness of the double layer as well as a chemical attraction toward the adsorbed ions to the electrode surfaces [29]. Carbon-based materials have been considered as ideal electrode materials for EDLC due to their remarkable features which will be discussed shortly in the following section.

2.2.1.2 Electrode materials for EDLC

As mentioned above, the capacitance of EDLCs is highly influenced by the type of electrode material and the electrolyte used. Thus, carbon-based materials in their various forms have met the efficiency criteria of EDLC electrodes. These include: (i) High specific surface area associated with an interconnected pore structure allowing an easy access of the electrolyte ions into the inner sections of the electrode surface, (ii) good electrical conductivity reducing the internal resistance and (iii) great surface wettability and chemical stability [31][3].

In addition, carbon-based materials have been commonly employed for supercapacitors in different applications (industrial, automotive, electronics, etc.) owing to their relative low cost, commercially accessible, easily scalable processing, wide operating temperature [32]. Various carbon materials namely activated carbon, graphene, carbon nanotubes (CNTs), nano-onions (CNOs), and so on have been extensively studied as electrodes in EDLCs [33].

- **Activated carbons (ACs)** are the most popular electrode materials utilized in commercial electrical double layer supercapacitor. ACs owing to their versatile properties such as high accessibility surface area, well-defined porous structures, surface functional group and physical/chemical stability have strongly attracted researchers to use them in different applications (hydrogen storage, electrochemical capacitors, water purification, and so on) and in fundamental research [34][35]. A variety of precursors including coal, petroleum, oil coke, wood, biomass, and so on have been used to produce three-dimensional (3D) ACs [36][37]. Recently, agriculture waste such as peanut shell, walnut shell, and banana peel/stem have been widely exploited in the preparation of ACs due to the fact that they are environmentally friendly, abundant, sustainable, renewable in nature, and competitive in cost [38][39][40].

ACs can be prepared by either physical (thermal) activation, chemical activation, or a combination of both physical and chemical processes. Physical activation considers the treatment of the raw material in the presence of oxidizing gases such as steam, carbon dioxide (CO_2), oxygen (O_2), air or their mixtures as activators at high temperature (700-1200 °C) [35][37][41]. In chemical activation, the process is performed in the temperature range of 400 - 900 °C and involves the impregnation of the raw material with chemical activating agents like sodium hydroxide (NaOH) [42], potassium hydroxide (KOH) [43], phosphoric acid (H_3PO_4) [44], sulphuric acid (H_2SO_4) [45], zinc chloride (ZnCl_2) [46] and iron chloride (FeCl_3) [47]. In particular, the chemical procedure can offer the formation of larger porous carbon network leading to a high specific surface area ($>2500 \text{ m}^2 \text{ g}^{-1}$), higher product yield, lower required temperature and lesser time for activation as compared to physical activation [35].

Therefore, the obtained ACs rely on the condition of the activation process, the type of carbon precursors and the activating agent used as shown in table 2.1. The pores in the ACs are categorized in a wide range of sizes: Micropores (less than 2 nm), mesopores (2 - 50 nm) and macropores (larger than 50 nm) as shown in figure 2.4. Micropores contribute the most important part in storing and adsorbing the charges or ions, while the mesopores and macropores serve as a channel of charge transportation and buffer reservoir of ions from electrolyte respectively [48][49]. Theoretically, the capacitance of the supercapacitor is correlated to the high specific surface area of the active material (equation 2.3) which is favourable for storing large amount of energy. Research studies have shown that the high specific surface area can lead to a high specific capacitance and hence specific energy and power [50][51][52].

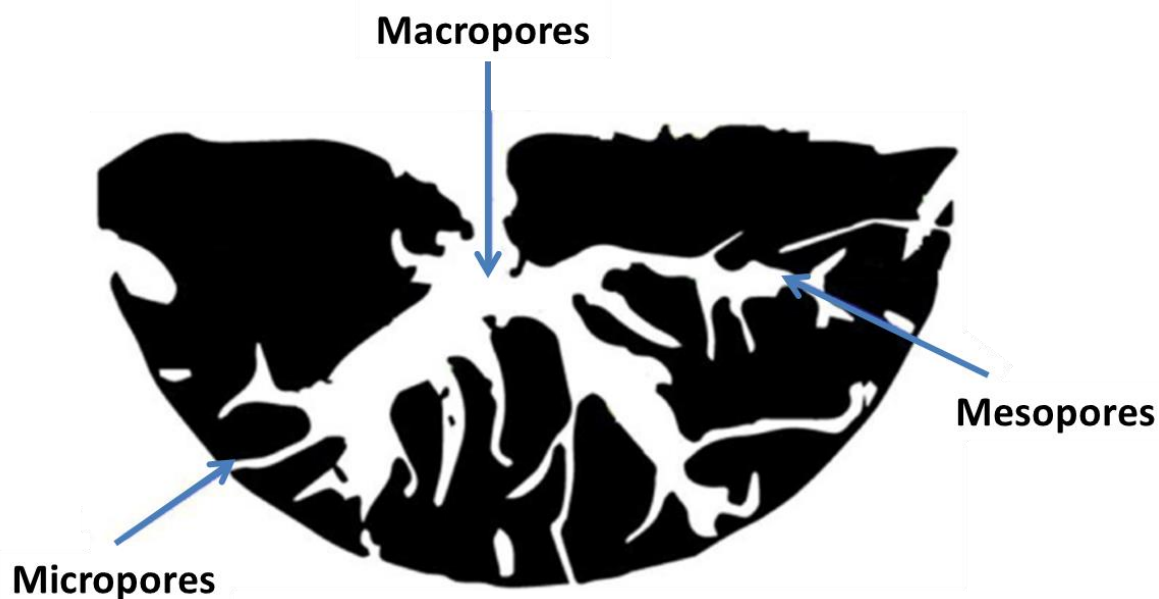


Figure 2.4: Types of pores in 3D activated carbon: micropores, mesopores and macropores [53].

For example, Teo *et al.*[54] have prepared ACs by KOH activation of rice husk at 850 °C. The ACs exhibited a large specific surface area of 2696 m² g⁻¹ and delivered a specific capacitance of 147 F g⁻¹ associated with specific energy of 5.11 W h kg⁻¹ in 6 M KOH aqueous electrolyte. This good specific capacitance is correlated to the high specific surface area contributing to fast ions transport at electrode/electrolyte interface [54]. However, it has been found in the literature that a wide range of AC materials are not following this trend [55][56]. In Conway's report [57], it was found that an ACs with a high SSA value of 3000 m² g⁻¹ provided only a capacitance around 10 μF cm⁻² as compared to the theoretical capacitance of EDLCs in the range of 15 - 25 μF cm⁻². The recorded smaller capacitance value could be linked to the inaccessibility of the electrolyte ions into all micropores which implied that not only large surface areas contribute to the specific capacitance [58].

Table 2.1: Characteristic and electrochemical performance of the ACs derived from various biomass sources

Raw Materials	Activating agent	Activation conditions	BET-SSA ($\text{m}^2 \text{g}^{-1}$)	Electrolyte	Specific current or scan rate	Capacitance (F g^{-1})	Ref.
Ground soybean	H ₂ O steam	Hydrothermal carbonization/physical activation (800 °C 0.3 cm ³)	1222	1 M Na ₂ SO ₄	1 A g ⁻¹	151.5	[59]
Loftus seed shell	NaOH 1:2	Carbonization (450 °C @1h)/ N ₂ activation (650 °C @2h)	3188	6 M KOH	0.5 A g ⁻¹	286	[42]
Cherimoya tree	KOH 1:1	N ₂ Carbonization(300 °C @1h)/ N ₂ activation (800 °C@2h)	1480	1 M H ₂ SO ₄	0.125 A g ⁻¹	237	[43]
Olive tree	H ₃ PO ₄ 1:1	N ₂ Carbonization (500 °C@2h)	1116	1 M H ₂ SO ₄	0.125 A g ⁻¹	257	[43]
Sakura petals	KOH 1:4	N ₂ Carbonization (600 °C@2h)/ N ₂ activation (750 °C@1h)	1433.8	6 M KOH	0.2 A g ⁻¹	265.8	[52]
Green stem cassava	ZnCl ₂ 0.3 M/CO ₂	N ₂ Carbonization (600 °C@ 1h 44mn)/physical activation (900 °C@2h 30mn)	329	1 M H ₂ SO ₄	1 mV s ⁻¹	164	[60]
Rice husk	FeCl ₃	Hydrothermal pretreatment/N ₂ activation (600 °C@1h)	454.6	6 M KOH	0.5	130.3	[61]
White sugar	KOH 1:2	H ₂ SO ₄ pre-treatment/ Ar activation (400 °C@2h)	713.1	1 M Na ₂ SO ₄	1	242.67	[62]
Peanut shell	ZnCl ₂ 1:2	N ₂ activation (700 °C@1h30mn)	889.97	1 M Na ₂ SO ₄	0.5	239.88	[63]

Other parameters of the AC electrodes including the pore size distribution, pore structure, pore shape, electrical conductivity, surface functionalities, could also determine the electrochemical performance of the supercapacitors. Many studies on the AC materials have been reported to tailor better EDLCs performance. For instance, an additional step prior to the activation process has been found to be a promising approach which influences the porous structure (micro, meso, macropores) with a large specific surface area, accessibility of pores and number of oxygenated surface functional groups. This will lead to a contribution on the capacitive performance of the ACs as compared to the one-step activation [64][65]. Phiri *et al* [65] synthesized an activated carbon derived from willow wood by a two-step process which consisted initially of carbonization at 600 °C followed by a chemical activation using KOH at 800 °C as shown in figure 2.5. Their work demonstrated that the highly porous willow carbon obtained exhibited a high SSA of 2793 m² g⁻¹ with an associated pore volume of 1.45 cm³ g⁻¹ resulting to a high specific capacitance of 395 F g⁻¹ in aqueous electrolyte [65].

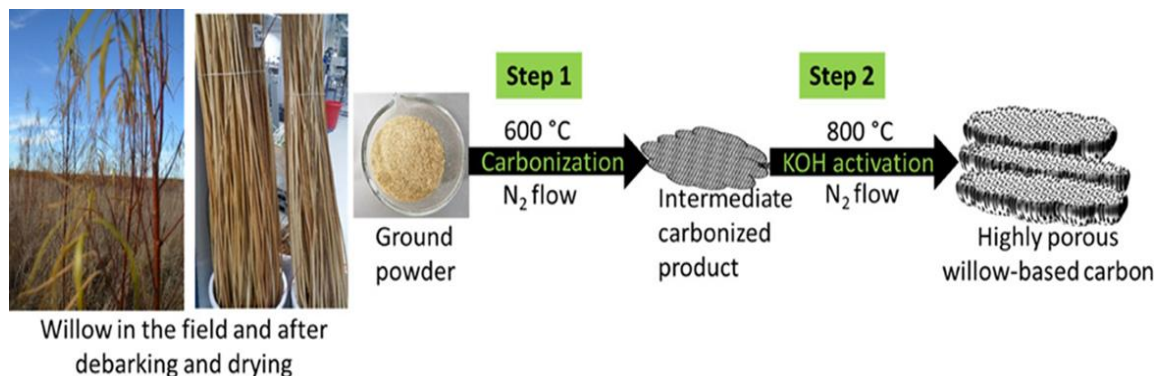


Figure 2.5: Scheme of two-step route for the synthesis of highly porous willow-derived ACs [65].

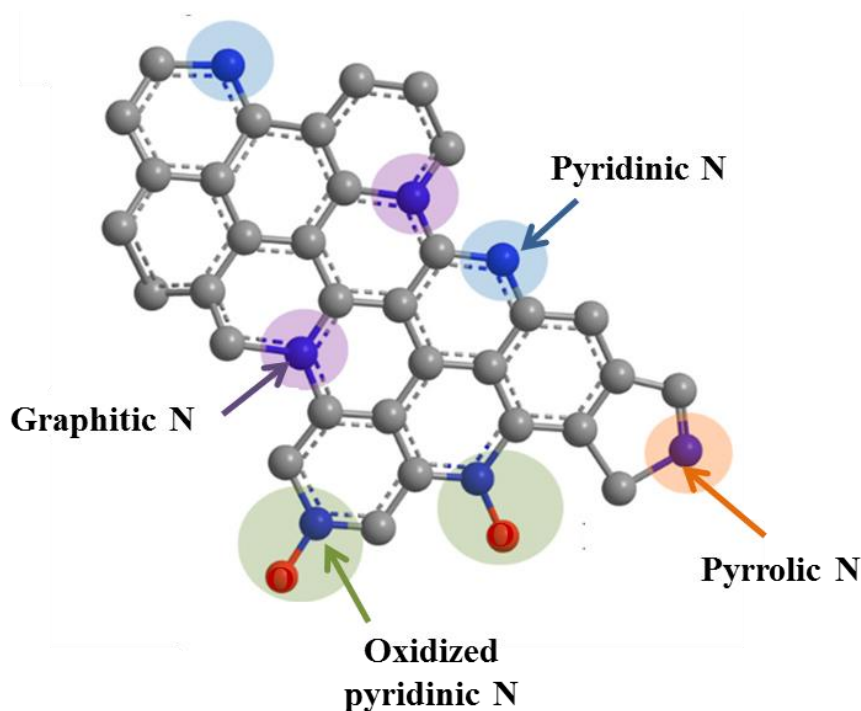


Figure 2.6: Scheme showing the various nitrogen configurations on the carbon framework [66].

Another strategy for improving the electrochemical performance is the modification of the ACs surface chemistry by introducing oxygen-containing compounds (phenol, lactone, ether, quinone, carboxylic acid, etc.) or heteroatoms doping such as nitrogen (N), sulphur (S), phosphorous (P) and boron (B). These surface functional groups lead to an enhancement of the electron acceptor/donor features, the surface wettability at the interfacial electrode/electrolyte and, the electrical conductivity which have significant impact on the EDLCs performance [67][44][68]. In particular, nitrogen-doping of porous carbon skeleton enhances their physicochemical characteristics and offers numerous, electrochemically active sites leading to the formation of multiple forms of functional nitrogen groups, i.e. pyridinic N, pyrrolic N, graphitic N/quaternary N and oxygenated pyridinic nitrogen (NO_x) as illustrated in figure 2.6 [69][70][66].

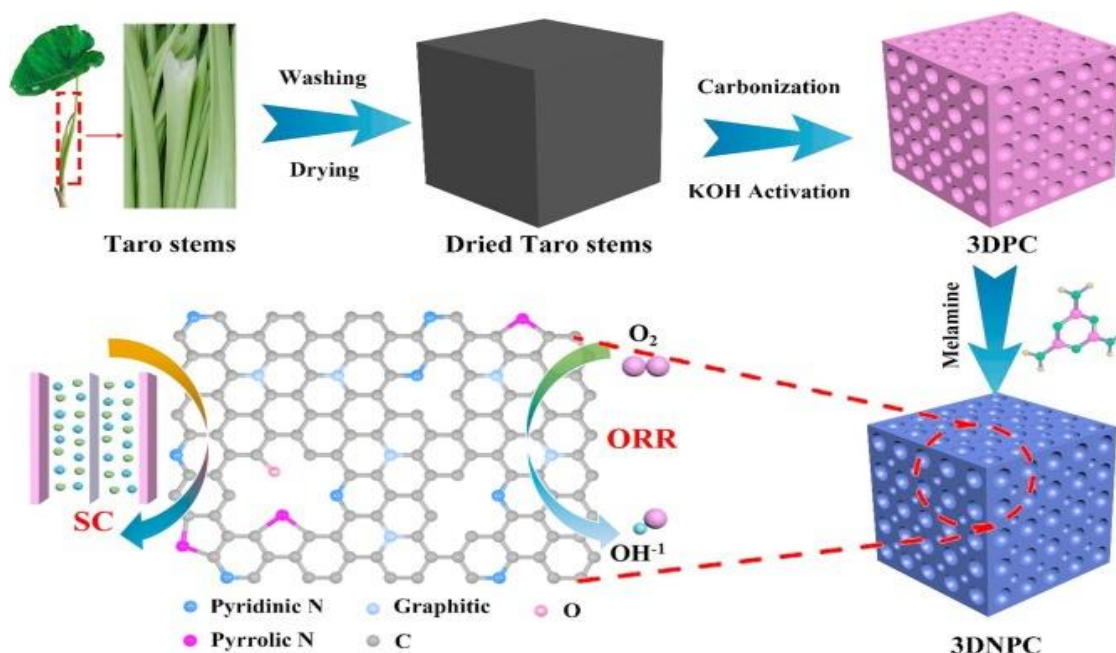


Figure 2.7: Schematic diagram of the synthesis of post 3D nitrogen-doped porous carbon [71].

Nitrogen containing precursors including urea [72], melamine [71], ammonia [73], and so on have been employed as precursors for the nitrogen-doped activated carbon. There are two main ways of doping carbon with nitrogen:

- (i) *In-situ doping* which consists on direct carbonization of the nitrogen-rich compounds such as polymers, ionic liquid, metal-organic frameworks, chitosan or carbonization of carbonaceous material with a nitrogen containing source [74][69][64].
- (ii) *Post-doping* which entails the incorporation of the nitrogen source into the porous carbon network in the carbonization procedure [69][75][68].

He and co-workers [71] have prepared a post 3D nitrogen-doped of porous carbon derived from taro stems (3DNPC) as represented in figure 2.7. The 3DNPC was obtained by first activating the raw material with KOH then doped using melamine. Their work emphasized that the N-doped endows to attain the great capacitive performance of the 3DNPC electrode (specific capacitance of 236.4 F g^{-1} with a specific energy and power of 5.56 W h kg^{-1} and 5 kW kg^{-1} respectively in 6 M KOH aqueous electrolyte) [71].

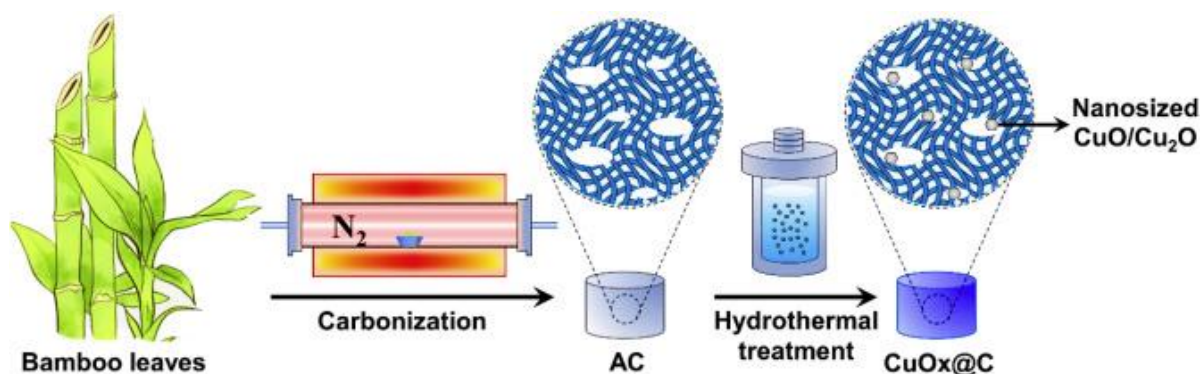


Figure 2.8: Schematic process of the synthesis nanocomposite $\text{CuO}_x\text{@C}$ [76].

Apart from the above mentioned approaches, incorporating foreign electrochemically-active components (metal oxides, metal carbides, metal hydroxides and conducting polymers) into the porous ACs framework have been considered as an efficient method for enhancing the electrochemical performance of EDLCs. This introduces redox reaction and hence an additional pseudocapacitive effect on the ACs surface network [77][78][79]. Wang *et al* [76] have prepared nanocomposite of metal oxide/carbon by first carbonizing the bamboo leaves followed by a hydrothermal process mixing the ACs and the copper precursor ($\text{Cu}(\text{OAc})_2$) as shown in figure 2.8. Their study showed that the $\text{CuO}_x\text{@C}$ provided better electrochemical efficiency than the ACs (specific capacitance improved from 72.6 to 147 F g^{-1}) [76].

- **Graphene**, a large family of two dimensional (2D) carbon structure is adorned with unique distinctive features like high electrical conductivity, large theoretical surface area (estimated at $2630 \text{ m}^2 \text{ g}^{-1}$), excellent mechanical, thermal and chemical properties that are appropriate for electrochemical energy storage [81][82]. Graphene is constituted by one atomic thick sheet of sp^2 hybridized carbon into a honeycomb framework (figure 2.9).

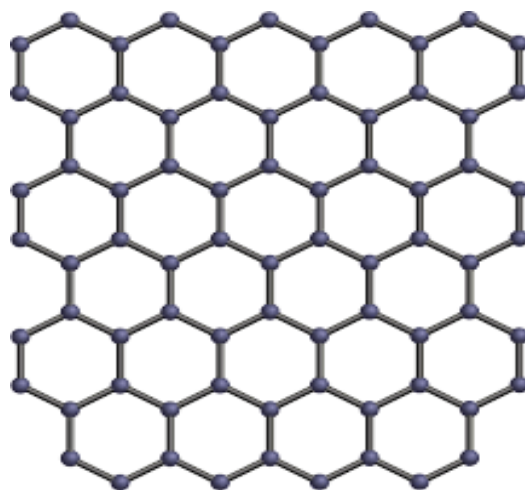


Figure 2.9: Structure diagram of a single layer of 2D graphene [80].

Several methods including thermal exfoliation of graphite oxide, Hummer's method, chemical vapour deposition, mechanical and electrochemical exfoliation of graphite have been used to produce graphene [80][83]. Despite these excellent properties, researchers have been working on the restacking problem of graphene layers which results in lowering its surface area and hence a decrease of the capacitance value. Incorporating metal oxide/conducting polymer into the graphene layers, functionalization of the graphene surface by heteroatom are some methods that not only aid in mitigating this restacking issue but also improving their electrochemical performance [82][84].

- **Carbon nanotubes (CNTs)** are another allotropic type of carbon in cylindrical shapes which belong to one-dimensional tubular structure (1D) that is mostly synthesized by catalytic chemical vapour deposition (CCVD), laser ablation or electrical arc discharge [86][87][88]. There are different types of CNTs depending on the number of concentric walls including single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT) and multi-walled carbon nanotubes (MWCNT) (see figure 2.10) [85].

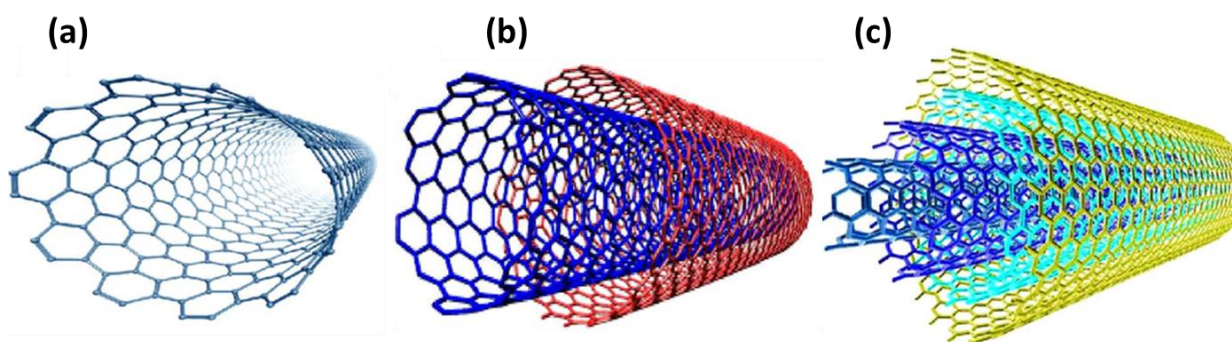


Figure 2.10: Structure diagram of (a) (SWCNT (b) DWCNT and (c) MWCNT [85].

CNTs have been recognized as attractive electrode for EDLC supercapacitor due to the high electronic conductivity, electrochemical stability, large mechanical strength [89][90]. In particular, the open structure of the CNTs materials allows the accessibility of the electrolyte into the inner of the electrode surface area leading to a good electrochemical performance [89]. The specific surface area values of $120 - 500 \text{ m}^2 \text{ g}^{-1}$ and specific capacitance values ranging between 2 to 200 F g^{-1} (lower than activated carbon) have been reported for pure CNTs [91][92]. These characteristics can be enhanced by several methods studied such as the formation of composites with other materials and the activation of the CNTs [89][93][94].

- **Carbon nano-onions (CNOs)** considered as zero-dimensional nanostructure (0D) are spherical in form with concentric multi-layered fullerenes (see figure 2.11) [95]. CNOs also known as onions like carbon (OLCs) can be obtained by thermal annealing of nanodiamond particles at elevated temperature ($> 1200 \text{ }^\circ\text{C}$) in an inert atmosphere under a high vacuum [96]. CNOs with a moderate specific surface area ($400 - 600 \text{ m}^2 \text{ g}^{-1}$) and high electrical conductivity provide a great specific power owing to their fast charging and discharging rate [97][98]. However, they suffer from low capacitance and specific energy which need to be improved either by adding electro actives material or by introducing porosity on the outer shell [99][96].

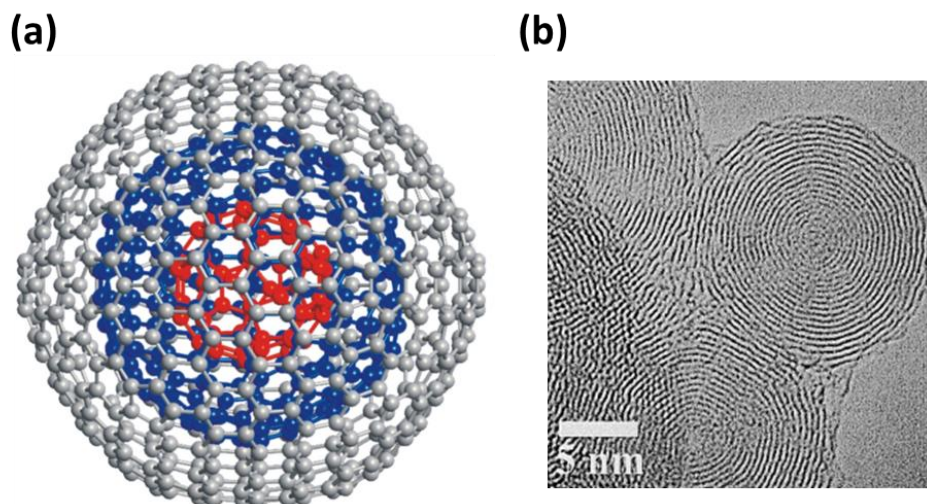


Figure 2.11: (a) Structure diagram of CNO and (b) TEM of CNOs [95].

2.2.2 Pseudocapacitors (PCs)

2.2.2.1 Mechanism of storage in PCs

The charge storage of pseudocapacitors (PCs) or Faradaic capacitors (FCs) relies on a fast-reversible oxidation-reduction process also called faradaic process at or near the surface of the electrode material. This faradaic process implies a charge transfer between the electrode and electrolyte through the double layer under an applied potential, unlike EDLCs whereby the process is electrostatic [1]. Based on Conway's report [57], three faradaic mechanisms occur at the PCs electrodes as illustrated in figure 2.12: (i) underpotential deposition, (ii) redox pseudocapacitance, and (iii) intercalation pseudocapacitance.

Underpotential deposition (UPD) consists of an absorbed monolayer formation of metal ions onto a surface of a dissimilar metal substrate (Au, Pt, Ag, etc.) at a potential higher than the redox potential. This leads to a partial charge transfer between the deposited metal monolayer and metal substrate. For example, a UPD occurs when Pb is deposited onto an Au substrate surface [101].

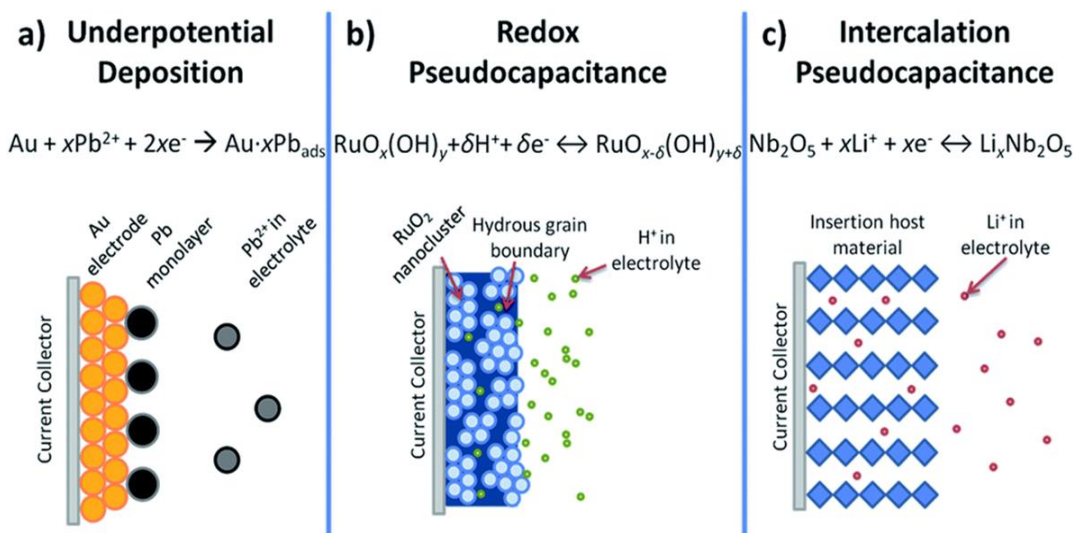


Figure 2.12: Schematic charge storage mechanism of a pseudocapacitive behavior: (a) underpotential deposition, (b) redox pseudocapacitance, and (c) intercalation pseudocapacitance [100].

Redox pseudocapacitance corresponds to electrochemical adsorption of ions onto the surface or near-surface of the electrode material (RuO_2 , MnO_2 , polypyrrole, polyaniline etc.) resulting in a faradaic charge transfer. A typical example of the electro-adsorption of protons at the surface of RuO_2 electrode [102].

Intercalation pseudocapacitance relates to the insertion of ions into the layers or tunnels of faradaic electrode material accompanied by a redox charge transfer without crystallographic phase change. An example of the intercalation of the Li^+ ions into the layers of Nb_2O_5 [103].

As described above, all three pseudocapacitive processes occur owing to their physical mechanisms and their various types of electrode materials. Therefore, the electrochemical features show similarities which depend on the relationship between the electrode potential (V) and the extent of faradaic charge/discharge (Q) [104]. The faradaic charge transfer process happening in the surface electrode may offer the pseudocapacitors to deliver greater specific capacitance and hence specific energy as compared to EDLCs. However, they suffer from low specific power, cycling stability, and electrical conductivity as a result of the redox reactions [100]. Transition metal carbides, nitrides, oxides/hydroxides, conducting polymers are among the most popular pseudocapacitive electrode materials [105][106].

2.2.2.2 Electrode materials in pseudocapacitors (PCs)

Typically, pseudocapacitive electrode materials provide promising electrochemical performance with their high capacitance, specific energy and rate capability. These have led to a significant interest in exploring these materials for energy storage devices.

Transitional metal compounds such as oxides, hydroxides, carbides, nitrides, phosphides, sulphides and conducting polymers have been commonly used as electrode for pseudocapacitors [107][105][106]. In addition to these materials, transitional 2D metal carbides/nitrides (MXenes), metal-organic frameworks (MOFs), and layered double hydroxides (LDHs) have been recently investigated as potential electrode materials for pseudocapacitive behaviour [108][107][105][109][110].

- **Transition metal oxides (TMOs)**

Transitional metal oxides (TMOs) such as RuO_2 , MnO_2 , Fe_3O_4 , Co_3O_4 , MoO_2 , and so on are conventional pseudocapacitive electrode materials which have been extensively studied. They store their charges by reversible surface redox reactions, and offer several oxidations states which make them suitable electrode material for faradaic capacitors. As reported in 1971 [111], ruthenium oxide (RuO_2) was the first electrode material discovered that demonstrated pseudocapacitive behaviour. RuO_2 has shown superior characteristics for pseudocapacitors electrode such as high theoretical specific capacitance $\sim 1400 \text{ F g}^{-1}$, three stable oxidations states, great reversibility, long life cycle and, high rate capability [100][112]. The extreme cost of RuO_2 limits its availability and applications which have motivated researchers to investigate on others TMOs that could display similar behavior [100]. Some of such oxides are molybdenum oxides such as MoO_2 and MoO_3 which are among TMOs considerably studied as efficient candidates in supercapacitors owing to their several oxidations states (Mo^{2+} , Mo^{4+} , Mo^{5+} , and Mo^{6+}), great electrochemical activity, affordable cost, and non-toxic.

MoO₂ has a high theoretical capacity of 838 mA h g⁻¹ with a good chemical stability and low electrical resistivity ($8.8 \times 10^{-5} \Omega \text{ cm}$ at 300 K). This is beneficial for rapid charge storage [113][114]. Though, the main drawback of MoO₂ is their limited cycling stability and low rate capability [115].

Diverse nanostructures of MoO₂ have been synthesized using different methods including direct oxidation of molybdenum [116], hydrothermal [117], thermal decomposition [118], chemical vapour reduction [114], and template assisted approach [113], and so on. For instance, Li *et al.* [113] have synthesized ordered mesoporous MoO₂ (*m*-MoO₂) as negative electrode material by carbonization of ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O and silica KIT-6 as hard template. Their report indicated that *m*-MoO₂ showed a good supercapacitive performance with a specific capacitance of 146 F g⁻¹ at 5 mV s⁻¹ scan rate and 10% capacitance loss over 1000 cycles in 1 M LiOH aqueous electrolyte [113]. In the study of Wu and co-workers [115], presented the synthesis of hierarchical mesoporous MoO₂ spheres via in situ hydrothermal process. MoO₂ spheres exhibited a great performance specific capacitance of 381 F g⁻¹ at 0.3 A g⁻¹ and a capacitance retention of 83.5 % after 1000 cycles in 1 M LiOH [115]. On the other hand, Zhu *et al* [114] prepared a two-dimensional (2D) MoO₂ through one-step chemical vapour reduction using commercial MoO₃ powder. In their synthesis, they added graphene oxide (GO) in order to enhance their electrochemical performance of the 2D MoO₂ sheet. An excellent pseudocapacitive behaviour was achieved for the 2D MoO₂/GO with a specific capacity of 1097 C g⁻¹, energy density of 259 W h L⁻¹, power density of 934 W L⁻¹ at 2 mV s⁻¹ and 80% capacitance retention up to 10,000 cycles in LiClO₄ organic electrolyte [114].

- **Transition metal carbides (TMCs)**

In recent years, transitional metal carbides (TMCs) which refer to interstitial alloys family , have received as interesting advanced materials due to their distinctive features including an excellent electrical/thermal conductivity, high melting point, strong corrosion resistance as well as good mechanical/chemical stability. The combination of these characteristics has prompted researchers to explore TMCs for different applications particularly as potential electrode materials for energy storage. A series of TMCs have been investigated such as titanium carbide (TiC), vanadium carbide (VC), molybdenum carbide (Mo₂C), tungsten carbide (W₂C), etc. [119][107][120][121]. Many studies have reported different methods for designing nanostructures TMCs with various dimensionalities such as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three dimensional structures (3D) [107][120][122]. For example Chen *et al* [122] have produced multilayered TiC nanoflakes through a biotemplate strategy where they used a cotton towel as a carbon source and a biotemplate. In their study, TiC nanoflakes, as electrode materials for supercapacitors exhibited good electrochemical performance [122].

Among the TMCs, Mo₂C is one of the most interesting carbides owing to their high specific conductance ($1.02 \times 10^2 \text{ S cm}^{-1}$), good capacity (600-1000 mA h g⁻¹), electrochemical efficiency, good chemical stability and large specific surface area [123][124]. Moreover, these superior proprieties can offer additional active sites, facilitate electron and ion transportation, and a reduction of the charge resistance which make them desirable electrode material for electrochemical capacitors [123][125][124][121]. Several approaches have been developed for the synthesis of Mo₂C nanostructures.

Temperature-programmed reaction (TPR) and carbothermal reduction process are typical methods of producing Mo_2C [126][127][128]. For example, Yang *et al* [128] produced a porous $\beta\text{-Mo}_2\text{C}$ catalyst supported on carbon network ($\text{Mo}_2\text{C}@\text{C}$) for hydrogen evolution reaction. In their study, $\text{Mo}_2\text{C}@\text{C}$ was obtained by calcination of the activated carbon from walnut shell and ammonium heptamolybdate at 1173 K in Ar atmosphere [128]. Xu and co-workers [129] developed Mo_2C nanoflakes by annealing the mixture of ammonium molybdate and 4-Cl-o-phenylenediamine at 850 °C under N_2 gas. Mo_2C nanoflakes as negative electrode provided good specific capacitance value of 88 F g⁻¹ at 0.5 A g⁻¹ in 2 M EMIMAc/AN ionic electrolyte and the assembled asymmetric device $\text{Mo}_2\text{C}//\text{AC}$ achieved specific energy of 44.1 W h kg⁻¹ with 95.6% capacitance retention over 1200 cycles [129]. Additionally, the performance Mo_2C can further be enhanced by forming a composite or adding a carbon based materials. For instance, Hussain *et al* [121] have synthesized Mo_2C nanosheets decorated with carbon nanotubes (CNTs) by a chemical reduction approach followed by carbonization. In their report, the composite $\text{Mo}_2\text{C}@\text{CNT}$ revealed a symmetric capacitance of 367 F g⁻¹ at 1 A g⁻¹ with specific energy of 50.9 W h kg⁻¹ at a specific power of 500 W kg⁻¹, along with an good cycling stability with ~ 97% capacity retention after 5000 cycles in KOH electrolyte [121].

2.2.3 Hybrids capacitors (HCs)

Research efforts have been recently made on developing hybrids capacitors (HCs) to tailor the energy storage performance. HCs rely on the combination of two kinds of electrodes materials with dissimilar charge storage process: Capacitive-type and faradaic-type electrode materials, respectively. Therefore, HCs can efficiently access the benefits of both EDLCs and faradaic electrodes owing to synergistic effect arising from the individual material electrode that makes up the device. Capacitive electrodes provide large surface area, good stability, and high electrical conductivity while faradaic electrodes offer high specific capacitance/capacity due to great electrochemical activity and rich redox reactions. Thus, producing a device that provides appreciable power and energy capabilities [130][131]. In order to achieve this enhanced electrochemical performance, there is also a need to consider an optimization of the individual electrode materials which constitutes the HCs (asymmetric or composite -like) depending on their configuration [132].

Composite materials consisting of carbon based material (activated carbon, carbon nanotubes, graphene, etc.) with pseudocapacitive material (metal oxide/carbide, conducting polymer, etc.) have been introduced as a fascinating alternative to promote the energy storage capability. They combine the advantages and mitigate the limitations of both EDLCs and pseudocapacitors electrode materials leading to an enhanced electrochemical performance. This combination can offer such potentialities which embody large surface area, hierarchical porous structure, good cyclic stability properties, reduction of the charge transfer resistance, easy electron and ion transportation, additional electrochemically active sites and extended potential windows [133][132][78]. Mostly, composite materials are common electrodes that flourish hybrids capacitors. For instance, Lu *et al* [134] synthesised a binary composite of molybdenum carbide nanoparticles with three dimensional hierarchical porous carbon (3DHPC-Mo₂C) as illustrated in figure 2.13.

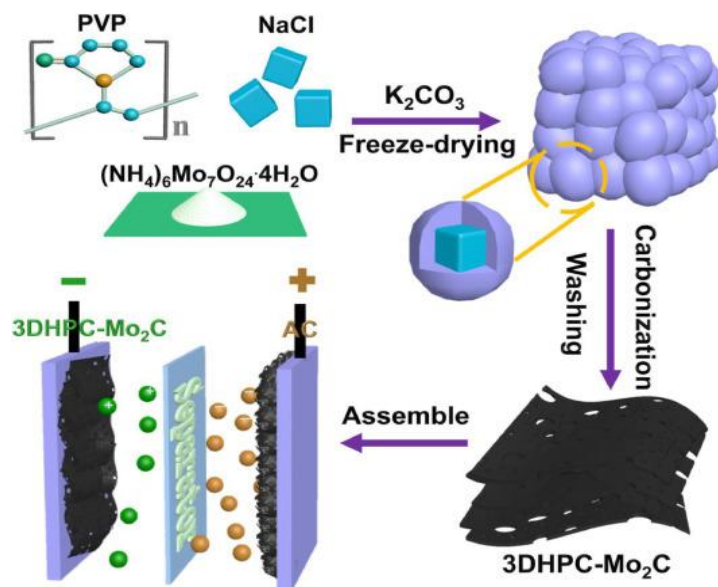


Figure 2.13: Schematic diagram of the synthesis of the binary composite 3DHPC-Mo₂C and asymmetric supercapacitor 3DHPC-Mo₂C//AC [134].

Their study indicated that the porous carbons prevented the agglomeration of the ultrafine Mo₂C nanoparticles and also facilitated ions transportation, while the Mo₂C provided a high conductivity and additional active sites. This led to excellent electrochemical features with a specific capacitance of 206 F g⁻¹ at 0.5 A g⁻¹ and a 96.6% capacitance retention over 7000 cycles in 6 M KOH aqueous electrolyte. Furthermore, the 3DHPC-Mo₂C binary composite was used as a negative electrode with AC as the positive electrode to assemble an asymmetric device (AC//3DHPC-Mo₂C). The AC//3DHPC-Mo₂C delivered a great supercapacitive performance (specific energy and power of 20 W h kg⁻¹ and 224 W kg⁻¹ respectively) in EMIMAC/AN ionic liquid electrolyte. This is due to their combined benefits of the capacitive electrode (AC) and the pseudocapacitive electrode (3DHPC-Mo₂C) [134]. Similarly, Ramakrishnan *et al* [135] proposed sodium-ion capacitors (NICs) where they associated: (i) Nanocomposite material of molybdenum dioxide and reduced graphene oxide (MoO₂@rGO) as negative electrode and (ii) Activated carbon derived from goat hair (CGH) as a positive electrode (shown in figure 2.14).

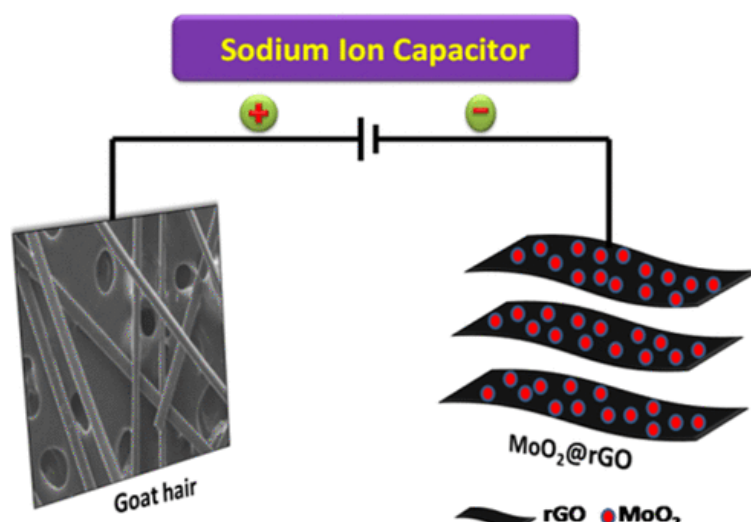


Figure 2.14: Schematic diagram of sodium ion capacitor (hybrid capacitor) CGH//MoO₂@rGO [135].

The binary composite MoO₂@rGO delivered a good capacitance of 298 F g⁻¹ owing to synergistic effect of the nanosized MoO₂ particles onto the conductive surface of the rGO. The obtained hybrid supercapacitor CGH//MoO₂@rGO recorded a specific energy of 79 W h kg⁻¹ and a 95 W kg⁻¹ specific power at 0.04 A g⁻¹ in 0.75 M NaPF₆ [in ethylene carbonate (EC) and diethyl carbonate (DEC) {1:1 (v/v)}]. This great electrochemical performance could be correlated to the combination of the merits for both CGH and MoO₂@rGO electrode materials. On the other hand, the electrochemical performance of the binary composite can be further enhanced by introducing another component to form a ternary composite. For instance, the formation of ternary composite which combine a carbon nanostructure with MoO₂ and Mo₂C have been proven to enhance the electrochemical performance in the energy storage.

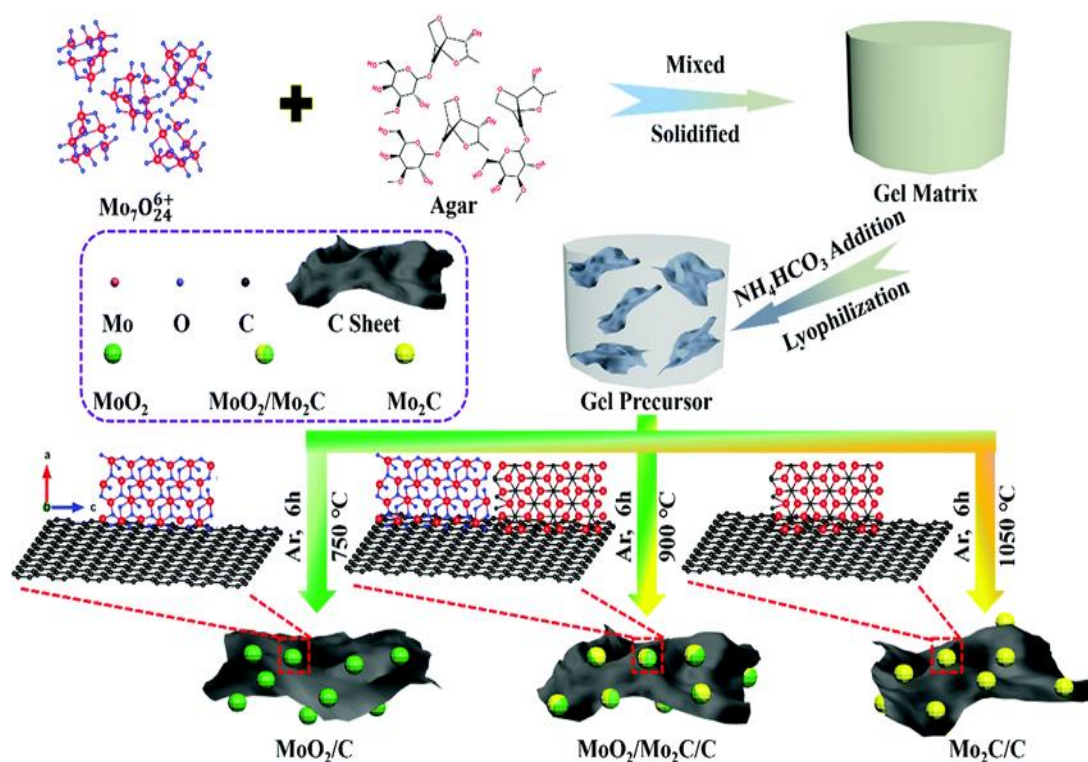


Figure 2.15: Schematic of the formation of $\text{MoO}_2/\text{Mo}_2\text{C}/\text{C}$ ternary composite [124].

Hou et al [124] have synthesized a $\text{MoO}_2/\text{Mo}_2\text{C}/\text{C}$ ternary composite by optimized annealing of the bio-inspired ammonium molybdate tetrahydrate and agar gel as shown in figure 2.15. $\text{MoO}_2/\text{Mo}_2\text{C}/\text{C}$ as an anode has demonstrated enhanced electrochemical features owing their synergistic effect of the heterostructures MoO_2 and Mo_2C anchored on 3D holey carbon nanostructure. These results are comparable to the binary composites MoO_2/C and $\text{Mo}_2\text{C}/\text{C}$ which are lower than the $\text{MoO}_2/\text{Mo}_2\text{C}/\text{C}$ [124].

2.3 Electrolytes

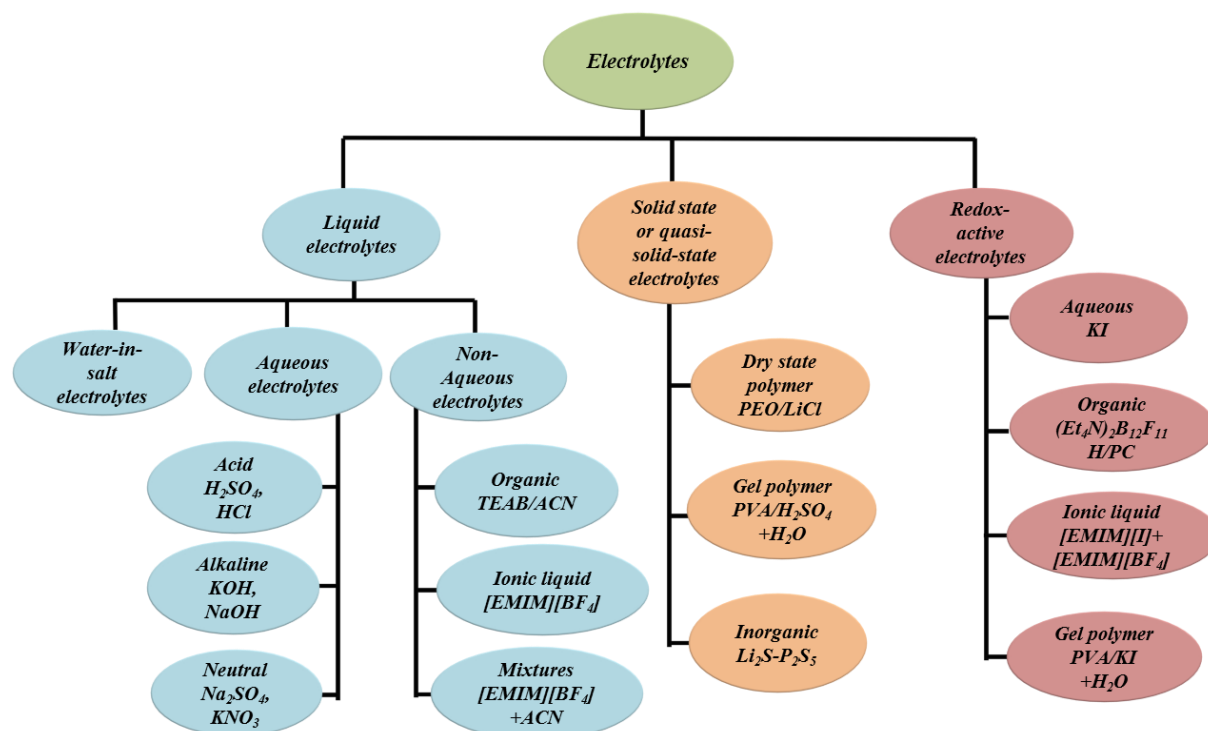


Figure 2.16: Classification of various electrolytes types in supercapacitors [136].

Electrolytes constitute one of the main components that have a significant influence on the electrochemical performance of supercapacitors. They supply ionic conduction necessary for the charge storage and transportation as well as determine the electrochemical stability potential window (ESPW). The ion concentration, size, type and its interaction with the electrode material are major factors for any electrolyte [137]. In addition, others requirements for the choice of electrolytes in supercapacitors include wide potential window, temperature range, good electrochemical stability, high ionic conductivity, environmentally benignity and low cost [136][138]. To date, a wide number of electrolytes have been developed for SCs applications which are regrouped into different types include liquid electrolytes, solid or semi-solid state electrolytes and redox electrolytes as illustrated in figure 2.16.

2.3.1 Aqueous electrolytes

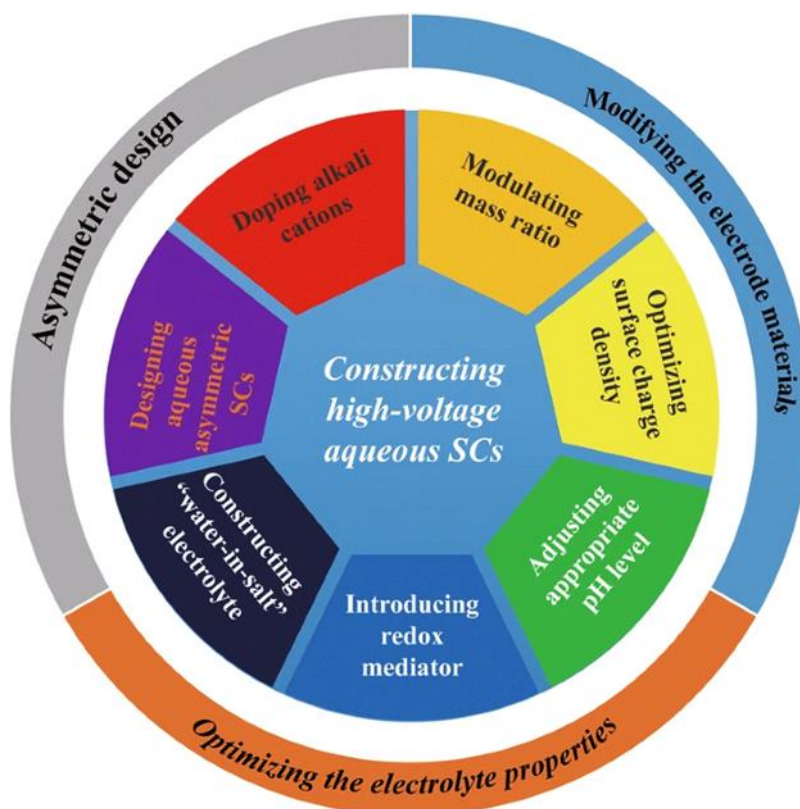


Figure 2.17: Different approaches of constructing high-voltage aqueous supercapacitors [139].

Among these, aqueous electrolytes, organic electrolytes and ionic liquid electrolytes are the most commonly reported in the literature [132][136].

Aqueous electrolyte containing alkaline (KOH, NaOH), acidic (H_2SO_4 , HNO_3) and neutral (Na_2SO_4 , KNO_3) based electrolytes are the most popularly used electrolytes in supercapacitors owing to their excellent conductivity (up to $\sim 1 \text{ S cm}^{-1}$), low equivalent series resistance (ESR), safety to operate, availability, and relative cost effectiveness. But, the operating potential of aqueous electrolyte is limited by the thermodynamic stable potential of water which is 1.23 V. Aqueous electrolytes offer a higher capacitance compared to organics electrolytes or ionic electrolytes but their relatively narrow cell potential ($\sim 1 \text{ V}$) limits their achievable specific energy when used in supercapacitors [138][139]. This limited cell potential has hampered aqueous SCs to be employed in practical long-term applications.

Several efforts have been devoted to boost the cell potential of aqueous electrolytes which could significantly enhance the energy density for use in SCs. These methods include the modification of the nature of the electrolyte features, modifying the electrode materials and building an asymmetric device as summarized in figure 2.17. For example, the pH value plays a vital role in controlling the EPSW of aqueous electrolyte [140]. To be specific, neutral electrolytes can achieve a larger cell potential (1.8 V and above) for carbon-based supercapacitor as compared to acidic or alkaline aqueous electrolytes which is limited by the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [140][138][139].

2.3.2 Organics electrolytes

Organic electrolytes possess a wide operating potential window in the range of 2.6 - 2.9 V which make them predominantly used in commercial applications as compared to aqueous electrolytes [136]. However, the high flammability and production cost are part of their demerits. In addition they suffer from low ionic conductivity ($\sim 100 \text{ mS cm}^{-1}$) owing to their high ESR which inhibits the ability to achieve a high specific power. The most popular solvents successfully used in organic electrolytes contain propylene carbonate (PC) and acetonitrile (ACN) [141]. Common organic electrolytes are prepared using tetraethylammonium tetrafluoroborate (TEABF_4), tetraethylphosphonium tetrafluoroborate (TEPBF_4), ethylmethylpyrrolidinium (EMP) and triethylmethyammonium tetrafluoroborate (TEMABF_4) as salts dissolved in PC, ACN or other different solvents like ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and so on [142]. ACN-based electrolytes offer higher conductivity and lower viscosity and the ability to dissolve in different solvents but they are posed with their high toxicity and environmental instability as compared PC-based electrolytes.

The PC-based electrolytes provide higher flash points, lower toxicity, larger EPSW and wider range of working temperatures and can be used as an alternative to replace ACN-based electrolytes [137][141].

2.3.3 Ionics liquid electrolytes

Ionic liquid electrolytes (ILs) are free solvent electrolytes that can overcome the narrow operating voltage of aqueous electrolytes as well as resolve the volatility, and flammability concerns associated with organic electrolytes [143]. ILs are room temperature molten salts with a melting point below 100 °C. They have attracted great interest as alternative electrolytes in SCs due to their unique structure and excellent physical and chemical features such as wide operating potential window (up to 4.5 V) leading to a high energy density, high thermal, chemical and electrochemical stability, relatively non-toxic, non-flammable and low vapour pressure [136][144]. Typical examples of ILs studied in SCs contain imidazolium (Im), ammonium, and pyrrolidinium (PYR) as cations, while some common anions include tetrafluoroborate (BF₄), bis (trifluoromethanesulfonyl)imide (TFSI), bis(fluorosulfonyl)imide (FSI), and hexafluorophosphate (PF₆) etc. [137][144]. ILs are limited by their insufficient ionic conductivity and high viscosity at low temperature which lead to possible ion inaccessibility to the electrode surface and poor contact at the electrode/electrolyte interface. However, tremendous efforts have been made to enhance the properties of ILs such as a mixture of ILs with organic solvent (PC or ACN) [145], or an eutectic IL mixture [146] among others.

2.4 Electrode material preparation for supercapacitors

The electrochemical features are determined by the electrode material. Hence the preparation method of the electrode constitutes a crucial step to achieve an optimum electrochemical performance. Typically, the electrode materials in SCs have been fabricated by a mechanical process by mixing active material with/without conductive additives (e.g. acetylene carbon black (ACB) or carbon) to enhance the conductivity, a binder (e.g. polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF)) and a few drops of solvent (e.g. N-methyl-2-pyrrolidone (NMP), ethanol) which are added to create a homogeneous slurry. This slurry is coated on a current collector or made a free standing electrode then dried with an appropriate temperature. The current collectors used for the electrode material are nickel foam, carbon cloth or paper, platinum, aluminium, copper foils which have high electronic conductivity, chemical stability and a good corrosion resistance. The as-obtained electrode material is referred to working electrode.

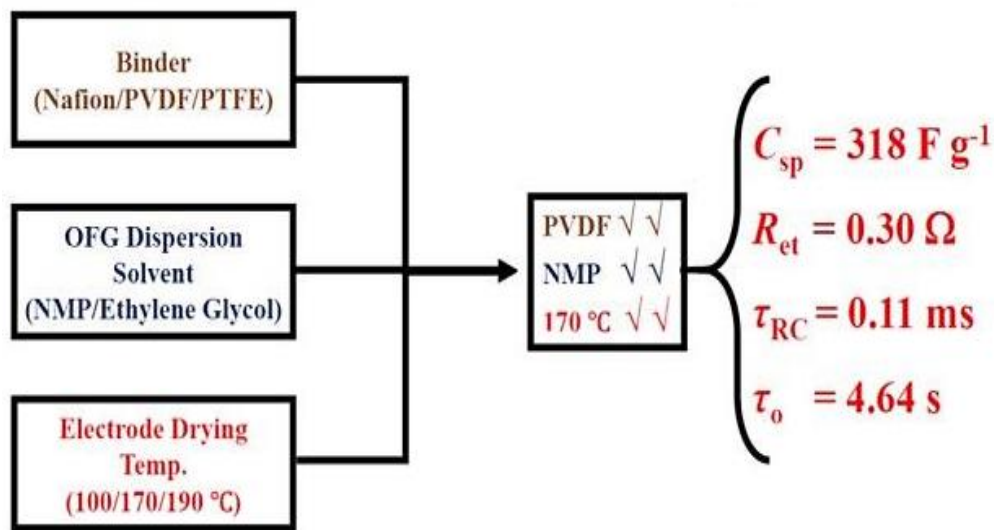


Figure 2.18: Diagram showing supercapacitor electrode preparation [147].

A study on the importance of the SCs electrode preparation has been reported by Arunumar and co-workers [147]. In their work, they used oxygen-functionalized few-layer graphene (OFG) as an active material mixed with different binders (PVDF, PTFE, and nafion) and solvent (ethylene glycol and NMP) and applied on platinum foils current collector then dried at different temperatures (100, 170, and 190 °C) as shown in figure 2.18. They found that the electrode material made with PVDF and NMP exhibited the highest electrochemical performance. This can be associated to the good solubility of the PVDF binder and the low viscosity of the NMP solvent [147].

2.5 Electrochemical test of the electrode material

Electrochemical measurement of the electrode is usually first performed on three-electrode set-up or half-cell configuration before being performed on a two-electrode set-up or full-cell configuration.

2.5.1 Three-electrode set-up

Three-electrode configuration is used to investigate primarily the electrochemical characteristics of the single electrode including potential windows, specific capacitance/capacity, cycling stability, etc. The set-up of the tree electrode test is shown in figure 2.19 which is composed of a working electrode (active material), a counter electrode, reference electrode and electrolyte.

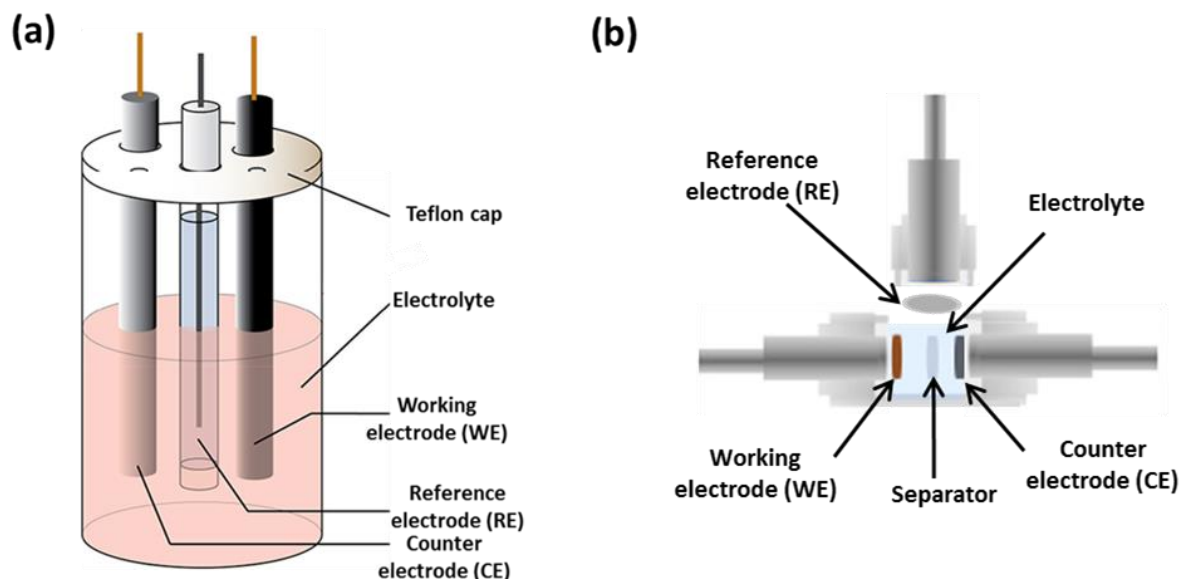


Figure 2.19: Schematic representation of (a) half-cell configuration set-up [148] and (b) Swagelok T-cell configuration set-up.

- The working electrode (WE) consists of the as prepared electrode as described in the above section 2.5.
- Reference electrode (RE) measures and controls the potential of the working electrode with no current passing through it. Common reference electrodes have been used in the half-cell configuration such as silver/silver chloride ($Ag/AgCl$), mercury/mercury oxide (Hg/HgO) and saturated calomel electrode (SCE). However their choice on the electrochemical test mainly depends on the nature of the electrolyte. For instance, SCE are used for acidic while $Ag/AgCl$ is better for neutral aqueous electrolytes.
- Counter electrode (CE) facilitates the current passing through the working electrode by the alteration of its potential within the electrolyte. Counter electrode requires conductive materials that will not interact with the electrolyte. Glassy carbon and platinum are the commonly employed CEs.

2.5.2 Two-electrode set-up

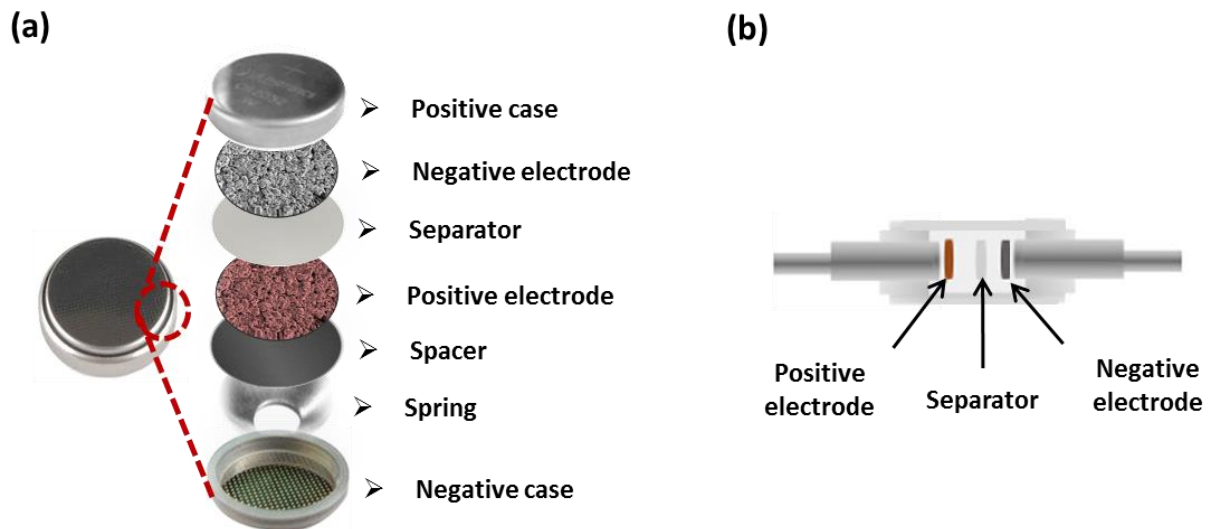


Figure 2.20: Schematic representation of full cell configuration (a) coin-cell set-up and (b) Swagelok cell set-up.

The two-electrode configuration evaluates the electrochemical features of the full cell (device). Their configuration consists of a positive electrode and negative electrode which are separated with an ionic permeable membrane and soaked in an electrolyte and as illustrated in figure 2.20. The configuration of the full device can be symmetric (both electrodes similar) or asymmetric (both electrodes dissimilar). The electrochemical characteristics of the full cell such as energy density, power density, and cycling stability, and so on can be evaluated using two-electrode configuration. Additionally, this configuration is controlled by the potential windows of both positive and negative electrodes.

- **Symmetric device**

A symmetric device combines similar electrode materials as positive and negative electrodes. In the case of EDLC device, the full cell capacitance C_T is given by the equation below [105]:

$$\frac{1}{C_T} = \frac{1}{C_+} + \frac{1}{C_-} \quad (2.5)$$

where C_+ and C_- are the capacitance of the positive electrode and negative electrode respectively. Since $C_+ = C_-$, the total capacitance is equal to half of the single electrode capacitance ($C_T = C_+/2$). The specific capacitance of the symmetric device is associated to the specific capacitance of single electrode C_s ($F\ g^{-1}$) that can be described by equation (2.6):

$$C_s = 4 \times C_T = \frac{4 \times I \Delta t}{m_T \Delta V} \quad (2.6)$$

Based on the specific capacitance of the single electrode and the operating potential voltage of the full cell, the specific energy E_D ($W\ h\ kg^{-1}$) is evaluated by equation (2.7) [149]:

$$E_D = \frac{1}{2} C V^2 = \frac{1000 \times C_s \times \Delta V^2}{2 \times 4 \times 3600} = \frac{C_s \times \Delta V^2}{28.8} \quad (2.7)$$

Additionally, the specific power of the full symmetric device P_D ($W\ kg^{-1}$) is given by equation (2.8) [149]:

$$P_D = \frac{3600 \times E_s}{1000 \times \Delta t} = \frac{3.6 \times E_D}{\Delta t} \quad (2.8)$$

where I represents the current (A), Δt is the time (s) of the discharge slop from GCD, ΔV is the operating potential (V) and m_T is the total mass loading (g) of both positive (m_+) and negative (m_-) electrodes, which are the same $m_+ = m_-$.

- Asymmetric device

Asymmetric device is made by two dissimilar electrodes as positive and negative electrodes. The capacitance of the individual electrode is not the same ($C_+ \neq C_-$). Therefore, the charge stored on each electrode should be balanced in asymmetric device by using the following equation [105]:

$$Q_+ = Q_- \quad (2.9)$$

Where Q_+ and Q_- represent the charge stored in the positive and negative electrode respectively.

In EDLC electrodes material Q is given by equation (2.10) [105]:

$$Q = C_s m \Delta V \quad (2.10)$$

where C_s is the specific capacitance of the electrode ($F\ g^{-1}$), ΔV is the working potential (V) and m is the mass (g) of the active material.

Then the mass balance between the two electrodes will be obtained according to the equation below [105]:

$$\frac{m_+}{m_-} = \frac{C_{s-} \Delta V_-}{C_{s+} \Delta V_+} \quad (2.11)$$

In the case of faradaic electrode materials, the specific capacity is the proper term because the charge will not be constant within the potential window. The specific capacity Q_s ($mA\ h\ g^{-1}$) is determined using the following equation [150]:

$$Q_s = \frac{I \times \Delta t}{3.6 \times m} \quad (2.12)$$

where I is the current (A), Δt is the time (s) of the discharge slop from GCD and m (g) is the mass of the active electrode.

Then the mass balance between the negative electrode and positive electrode is calculated using equation below:

$$\frac{m_+}{m_-} = \frac{C_{s-} \Delta V_-}{3.6 \times Q_s} \quad (2.13)$$

The specific energy E_D (W h kg⁻¹) and the specific power P_D (W kg⁻¹) of the device are expressed by applying the equations (2.14) and (2.15) [151][152]:

$$E_D = \frac{I}{3.6 \times m_T} \int V(t) dt \quad (2.14)$$

$$P_D = 3600 \times \frac{E_D}{\Delta t} \quad (2.15)$$

where I is the current (A), m_T (g) is the total mass of the positive and negative electrodes, $\int V(t) dt$ is area under the discharge curve and Δt is the time (s) of the discharge slop from GCD.

2.6 Electrochemical characterization of the electrode material

The electrochemical performance of the electrode material is evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), stability test and electrochemical impedance spectroscopy (EIS).

2.6.1 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) technique is commonly used to evaluate the electrochemical behaviour of the electrode material in three-electrode and two-electrode systems. This technique not only offers an insight on the charge storage mechanism, stable operating potential window and the resistivity but also enables the calculation of the capacitance and rate performance of the electrode material. CV test is evaluated by cycling the voltage window of the electrode material at a steady sweep rate (scan rate), thus generating a current response. This current response is relied on the potential scan as well as the interaction of electrode/electrolyte.

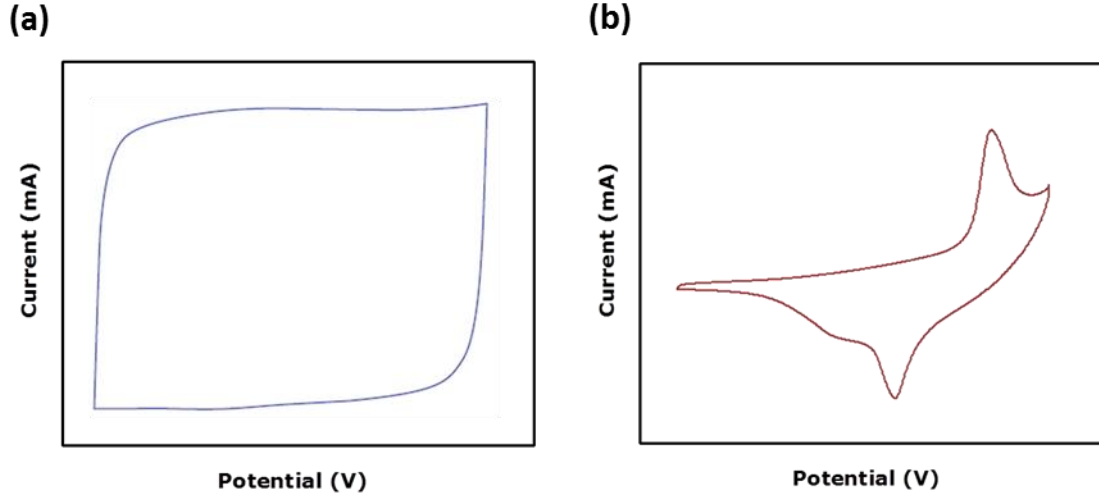


Figure 2.21: Cyclic voltammogram characteristics of (a) EDLC and (b) Faradaic systems.

Therefore the plot of the current passing through the electrode against the applied voltage corresponds to “cyclic voltammogram” [153] as representing in figure 2.21. In figure 2.21(a), the CV profile exhibits a typical rectangular characteristic indicating a reversible capacitive behaviour of the EDLC electrode. While in figure 2.21(b), the CV curve reveals the presence of redox peaks suggesting reversible redox process relative to pseudocapacitive electrode material [154].

In a faradaic behaviour, the specific capacitance C_s ($F\ g^{-1}$) of the electrode material can be calculated from the CV curve using the equation below [104]:

$$C_s = \frac{1}{m \nu \Delta V} \int I(V) dV \quad (2.16)$$

where $\int I(V) dV$ is the integrated area under the CV curve, $m(g)$ is the total mass of the active material, ν is the scan rate ($V\ s^{-1}$) and $\Delta V (V)$ represents the width of the potential windows.

2.6.2 Galvanostatic charge - discharge (GCD)

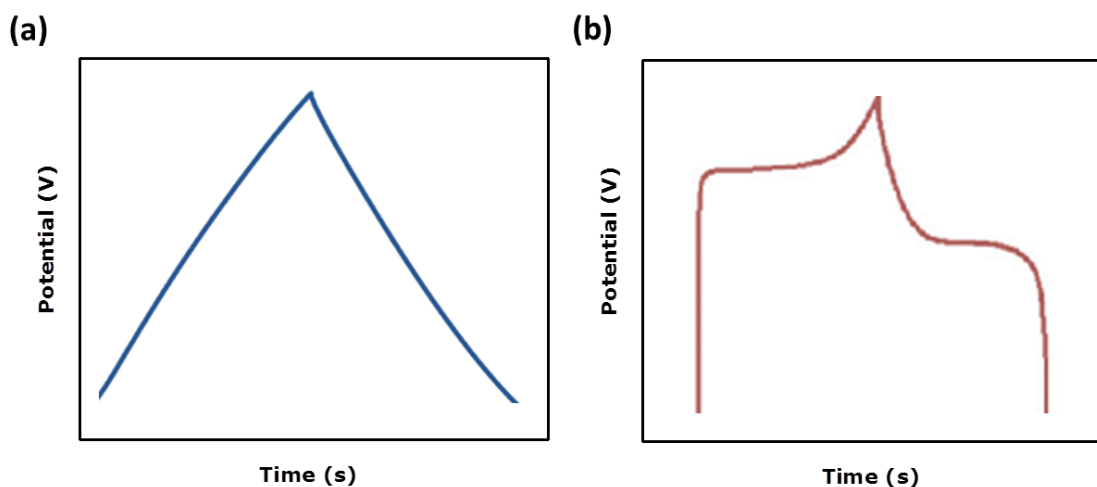


Figure 2.22: Galvanostatic charge-discharge characteristics of (a) EDLC and (b) Faradaic systems.

Galvanostatic charge - discharge (GCD) or constant current charge discharge (CCCD) is the most commonly employed technique for the investigation of the electrochemical performance of SCs. GCD also referred to chronopotentiometry (CP) is performed by subjecting a constant current (I) to the active material, thus the resulting potential (V) is recorded as a function of time [19]. A characteristic GCD plot is displayed in figure 2.22, in which the electrode potential is depicted as time-dependent. As shown in figure 2.22(a), the GCD profile reveals a linear triangular shape with an ohmic potential drop (IR drop) suggesting a typical EDLC behaviour of the electrode material. However a non-linear GCD curve is observed in figure 2.22(b) indicating the Faradaic nature of the electrode material [154]. The GCD test helps to determine the specific capacitance/capacity, specific energy, and specific power of the active material as above-described in the section 2.5.2. In addition, rate capability and cycling stability of the electrode material can be obtained through the GCD test.

2.6.3 Stability

- **Cycle life**

The life cycle test is a significant characterization for evaluating the stability of the electrochemical energy storage device. Galvanostatic charge discharge test is commonly used to perform the cycling stability which is determined by continuously repeating several charge-discharge cycles at a constant specific current. Coulumbic efficiency (η_{CE}) energy efficiency (η_{EE}) and specific capacitance/capacity retention are essential factors given information about cycling life. Therefore, (η_{CE}), and (η_{EE}) can be expressed by using the equations (2.17) and (2.18) [155]:

$$\eta_{CE} = \frac{t_D}{t_C} \times 100 \quad (2.17)$$

where t_D and t_C are the discharge and charge time, respectively.

$$\eta_{EE} = \frac{E_D}{E_C} \times 100 \quad (2.18)$$

where E_D and E_C represent the discharging and charging energies, respectively.

- **Voltage Holding**

The voltage or floating test is an alternative and reliable characteristic which was recently developed to further assess the stability of the supercapacitor electrode. The floating test implies a potentiostatic conditions which is performed by holding a constant cell potential as function of the aging time as sketched in figure 2.23 [156]. Thus, the specific capacitance/capacity and the equivalent series resistance from the IR voltage drop are evaluated from the occasional charge/discharge cycles for the entire period. In addition, the current leakage can also be determined [156][158].

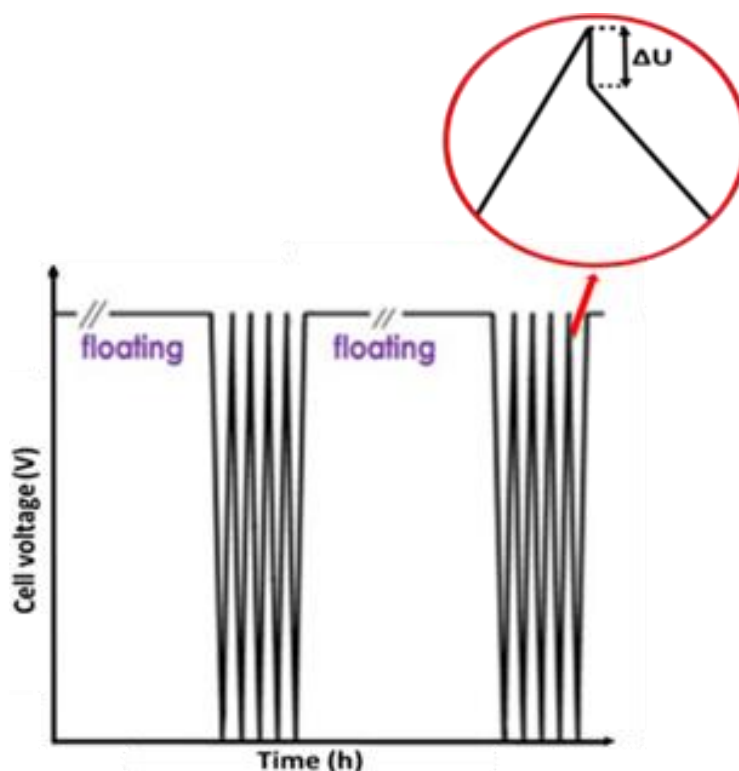


Figure 2.23: Schematic representation of the voltage holding test [157].

The floating test possesses the merit of proving information on the possible degradation phenomena of the SCs devices that could happen during the electrochemical process at the maximum operating potential.

2.6.4 Electrochemical impedance spectroscopy (EIS)

EIS test is a crucial electrochemical technique which relies on alternating potential over a wide range of frequencies (generally from MHz to mHz) at an open circuit potential or constant alternating current. Typical EIS data represented by Nyquist plot consists on the plot of the real impedance (Z' axis) against the imaginary impedance ($-Z''$ axis) as illustrated on figure 2.24.

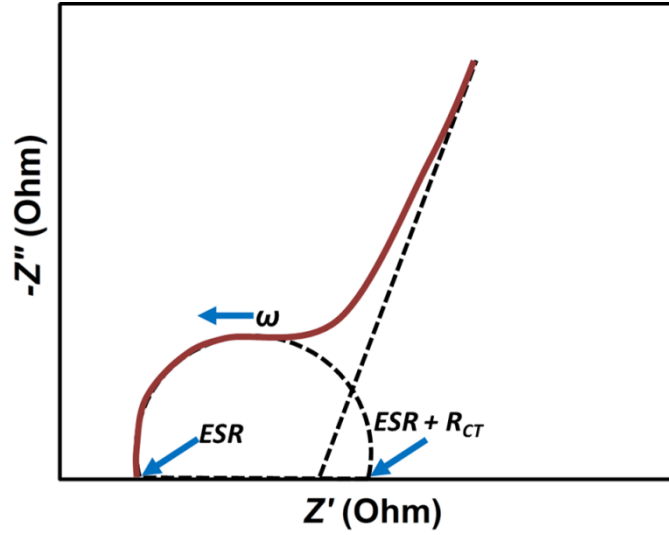


Figure 2.24: Schematic representation of Nyquist plot [159]

At high frequency region ($>10^4$ Hz), the semi-circle is assigned to charge transfer resistance (R_{CT}) which is relative to the electronic conductivity. The intersection with the real Z' axis at high frequency consists of the equivalent series resistance (ESR) corresponding to the sum of resistance within the electrolyte, interfacial resistance electrolyte/electrode and resistance between electrode and current collector. ESR provides a mean of calculating the maximum power density (P_{max}) as expressed above in equation (2.2). At the low frequency region (<1 Hz), a vertical line is observed indicates the nature of the diffusion of the ions [104][30]. This line must be straight and parallel to the imaginary axis characteristic of a pure capacitive behaviour. However, the deviated vertical line at an angle of 45° in mid-frequency region represents the ionic diffusion mechanism (Warburg resistance) [159].

At low frequency level, the capacitance $C(\omega)$ as function of the frequency is determined by the sum of the real $C'(\omega)$ and the imaginary $C''(\omega)$ parts of the capacitance by using the equations (2.19), (2.20) and (2.21) [160][161].

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (2.19)$$

$$C'(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} \quad (2.20)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \quad (2.21)$$

where $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary parts of the impedance $Z(\omega)$ respectively given by $Z(\omega) = Z'(\omega) - jZ''(\omega)$, ω is the angular frequency ($\omega = 2\pi f$)

$C'(\omega)$ is attributed to the capacitance of the cell measured via constant-current discharge. However, $C''(\omega)$ is associated to the energy dissipation during irreversible Faradaic process [162][163].

Bode plot is also another important representation of the *EIS* test that is defined by the plot of the phase angle against the frequency. For instance, the phase angle of a capacitive electrode material is close to a value of -90° [164]. Therefore, the capacitance C (F) of the active can be found from the Bode curve as expressed in the equation below:

$$C = \frac{1}{2\pi f|Z''|} \quad (2.22)$$

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3.0 Experimental methods and characterization techniques

This chapter presents the synthesis and the characterization of materials, which has huge interests in basic research and device applications. In this thesis, the activated carbon and its molybdenum based nanocomposites have been mainly synthesized using a chemical vapor deposition (CVD) system and characterized using several techniques such as gas adsorption analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy. In order to verify their viability as supercapacitors electrode materials, in-depth electrochemical analysis were investigated to probe their performance.

3.1 Chemical Vapour Deposition

Chemical vapour deposition (CVD) technique is a chemical process used for the production of high-purity materials in bulk, thin-film and powder forms [1]. The CVD process utilizes a dynamic flow system whereby gaseous precursors react chemically in the deposition chamber under a heat zone [2]. The CVD method involves deposition on a substrate surface in which the chemical reaction occurring in the gaseous phase, producing one or more condensed phases [2][3]. It is a common synthesis technique employed due to the simple set-up architecture, uniform deposition layer of thin-film materials and high purity of the product [4]. The entire process is controlled by factors such as the surface chemical reaction, chemical kinetics, reactant transport, growth temperature and pressure variation [5][6].

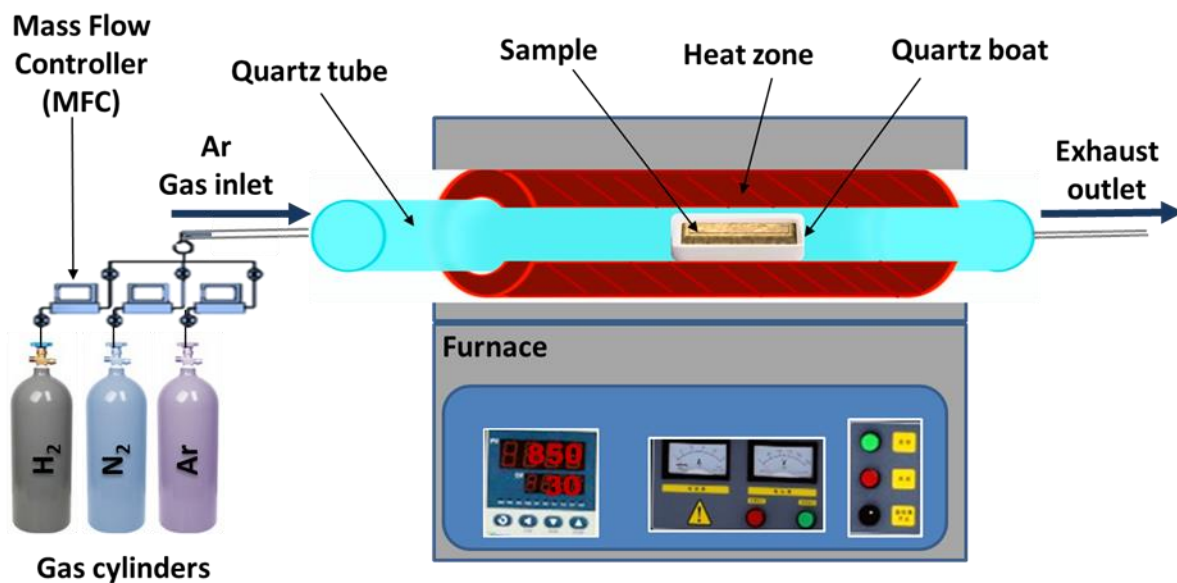


Figure 3.1: Diagram of atmospheric pressure chemical vapour deposition system.

There are various types of CVD processes such as atmospheric pressure chemical vapor deposition (APCVD), low-pressure chemical vapor deposition (LPCVD), metal-organic chemical vapour deposition (MOCVD), laser-enhanced chemical vapour deposition (LECVD), plasma-enhanced chemical vapour deposition (PECVD) [7].

In this work, the CVD system used is the APCVD due to the low cost, the potential for large scale production and the fast/facile operation [5][8]. The APCVD system is an effective method for the synthesis of various carbon-based materials and their composites. Figure 3.1 represents a schematic diagram of the APCVD process used in this study for the production of the activated carbon and its molybdenum based nanocomposites. Thus, the synthesis mechanism involves the breaking down of the volatile carbon precursors in the furnace to produce the materials.

The APCVD system is composed of a reaction chamber (2-inch diameter quartz tube) enshrouded by a furnace that is attached to the mass flow controllers (MFCs) which are connected to various gaseous precursors like Argon (Ar), Hydrogen (H_2), Nitrogen (N_2).

The nature and flow rates of these gaseous precursors passing into the reactor zone play an important role in the deposition and growth of materials. Argon is the carrier gas utilized in this study, which delivers the reactants into the reaction chamber and maintains an inert environment.

3.2 Materials synthesis

3.2.1 Synthesis of the activated carbon from peanut shell waste

The peanut shell waste (PSW) used in this study as raw material was collected from Senegal in the downtown district of Saint-Louis. The obtained PSW was first washed using deionized water (DI), dried over 12 h under direct sunlight and then ground into a fine powder. Figure 3.2 illustrates the schematic for the entire synthesis process for obtaining the activated carbon from PSW using a two-step carbonization and chemical activation route at high temperatures.

In the first step, 5 g of the fine PSW powder was mixed together with 1 g of NaCl and 0.5 g of urea as nitrogen source. Some drops of DI water were added to the mixture to make a sludge which was then put it in a quartz crucible to be dried in an oven at 80 °C overnight. The dried compact mixture was placed into the APCVD system to be carbonized at 600 °C for 2 h at a heating rate of 5 °C min⁻¹ under Argon gas flow (250 sccm). The obtained product labelled as carbonized PSW (CPSW) was washed several times with DI water and dried at 80 °C. For the second step, a weighed amount of CPSW was mixed with potassium-based activating agents (AA) namely, KHCO₃, K₂CO₃ and KOH, at different impregnation weight ratios of 1:1, 1:2, 1:4 and 1:6 for the CPSW:AA, respectively. The mixture of CPSW:AA at different ratios in a form of compact mould was chemically activated at 850 °C with a heating time of 5 °C min⁻¹ for 1 h under 250 sccm Argon flow.

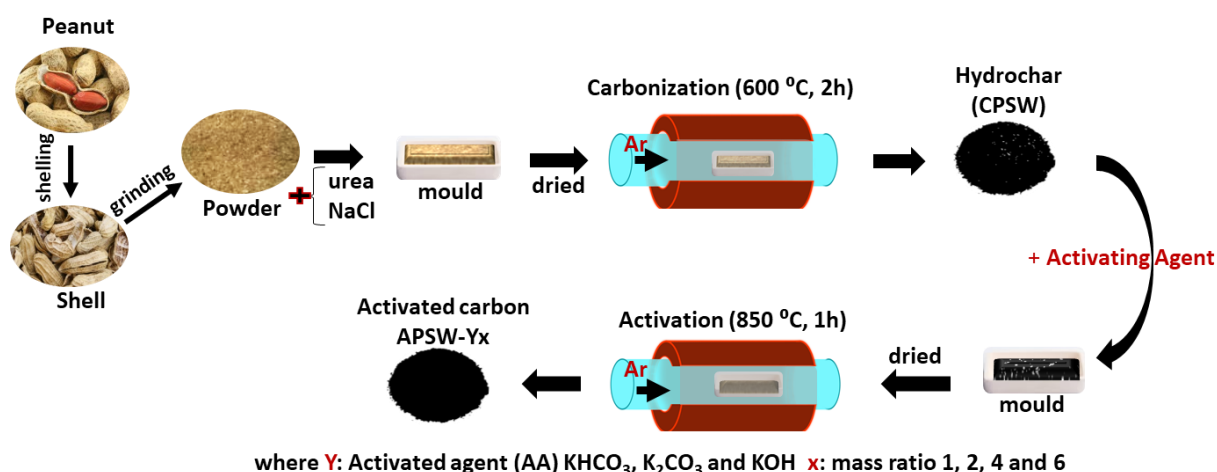


Figure 3.2: Schematic synthesis process of the activated carbon from peanut shell.

The obtained black powder was immersed in 3 M HCl and kept in the sonicator for 8 h to remove the excess unreacted AA. Afterward the sample was rinsed with DI repeatedly until a neutral pH was reached then dried for 12 h at 80 °C. The as-synthesized activated carbons from peanut shells are denoted as APSW-Yx where Y represents the AA and x the mass ratio of AA.

3.2.2 Synthesis of the ex-situ nitrogen doped peanut shell waste activated carbon

The *ex-situ* nitrogen-doped activated carbon from peanut shell waste was synthesized using a two-step route involving a chemical activation of the peanut shell raw material followed by nitrogen-doping of the activated carbon material as shown in figure 3.3.

Firstly, the as-obtained peanut shell (PS) waste was washed with deionized water (DI) and dried in an oven at 60 °C, then grinded into a powder. A weighed amount of the PS powder was added in a agate mortar with potassium hydroxide (KOH) activating agent (AA) in different weight ratios of 1:0.5, 1:1 and 1:2 (PS:KOH).

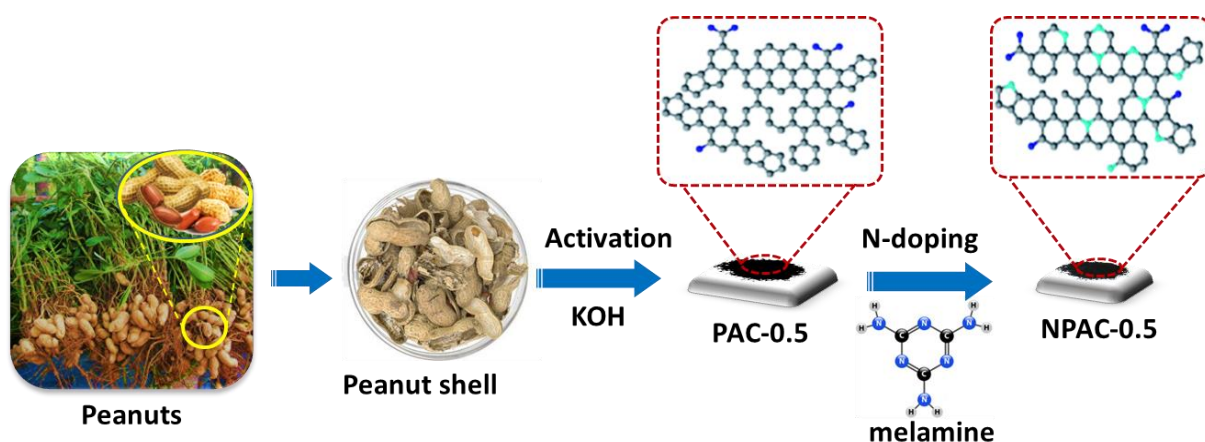


Figure 3.3: Schematic of the synthesis route of the ex-situ nitrogen doping peanut shell activated carbon.

The formed solid mixture was transferred into a tube furnace and followed by the chemical activation process, which involved heating up to 850 °C at a ramp rate of 5 °C min⁻¹ under a continuous argon flow and maintained for 1 h. The resulting material was treated in 3 M HCl to remove the excess unreacted AA, sonicated for 12 h, washed with abundant DI water until the pH became 7 and finally dried at 80 °C in an oven. The obtained peanut shell activated carbon materials were denoted as PAC-0.5, PAC-1 and PAC-2 for PS:KOH in a weight ratio of 1:0.5, 1:1 and 1:2, respectively. Subsequently, in the second step, the ex-situ-nitrogen-doped peanut shell activated carbon (NPAC) was prepared by using melamine (C₃H₆N₆) as the nitrogen source. To produce the NPAC, 1 g of the as-synthesized PAC-0.5 material was mixed with 5 g of melamine in an optimized mass ratio. The mixture was further pyrolyzed in the CVD furnace at 850 °C at a heating rate of 5 °C min⁻¹ and held for 1 h under an inert atmosphere. Afterwards, the reactor chamber was cooled down to room temperature and the final product obtained was denoted as NPAC-0.5. A similar procedure was used to synthesize the NPAC-1 and NPAC-2 samples from the pre-activated PAC-1 and PAC-2 samples respectively.

3.2.3 Synthesis of the peanut shell activated carbon/molybdenum oxide/molybdenum carbide (PAC/MoO₂/Mo₂C) ternary composite

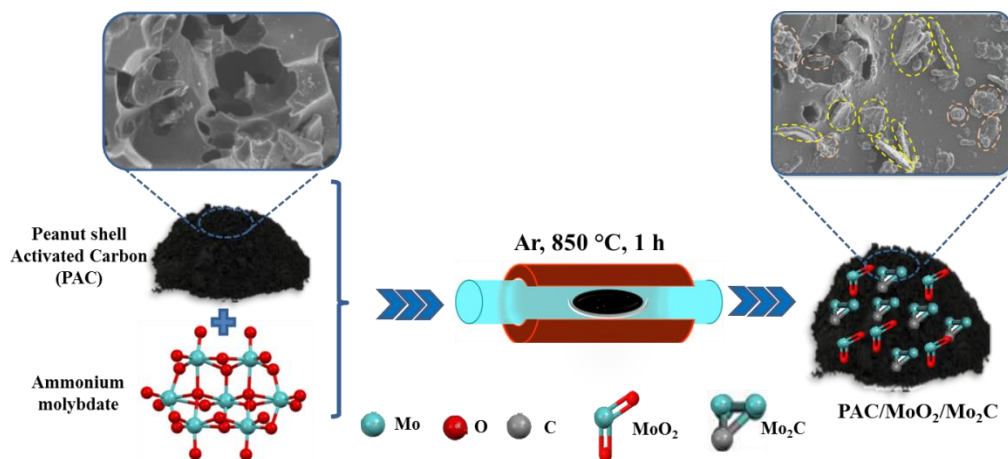


Figure 3.4: Schematic of the synthesis process of PAC/MoO₂/Mo₂C ternary composite.

The ternary composite formed by peanut shell activated carbon with molybdenum oxide and molybdenum carbide (PAC/MoO₂/Mo₂C) was obtained by a one-step pyrolysis of PAC and various mass ratio of molybdenum precursor as illustrated in figure 3.4.

Peanut shell waste activated carbon (PAC) was prepared by a KOH activation following a reported procedure from the previous section 3.2.2. The as-synthesized PAC sample was mixed with ammonium molybdate tetrahydrate in mass ratios of 1:0.5, 1:1 and 1:2 for the PAC to the inorganic salt in an agate mortar. Few drops of deionized water were added to the as-prepared mixture to ensure thorough mixing of both materials which was then loaded onto a porcelain boat and air dried at 80 °C for 12 h in an electric oven. The porcelain boat was transferred into a horizontal tube furnace and heated to 850 °C at a ramping rate of 5 °C min⁻¹. The furnace was kept constant at this temperature for 1 h under 250 sccm of argon gas flow. After cooling down to room temperature, the ternary composite was obtained and labelled PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2 corresponding to the mass ratio of 1:0.5, 1:1 and 1:2 respectively.

3.3 Materials characterization technique

3.3.1 Gas absorption technique

Gas adsorption/desorption analysis is a crucial textural method for the porosity measurement of powder porous materials. This technique is used to determine the specific surface area (SSA), the pore volume, pore size distribution (PSD) and general porosity in materials [9].

In this study, the textural features of the carbon materials were investigated using a Micrometrics TriStar II 3020 (version 2.00) pore analyser with a Brunauer, Emmett and Teller (BET) technique. The BET method is the most common measurement model used to evaluate the SSA obtained from the nitrogen (N_2) adsorption/desorption isotherms in a relative pressure range (P/P_0) of 0.01-1.0. The PSD is obtained by adopting a Barrett-Joyner-Halenda (BJH) method with the associated isotherm.

For the measurement process, N_2 adsorption/desorption isotherms of the materials were obtained by initially weighing the sample, then outgassing the sample to eliminate all the contaminants (water, adsorbed gas, and moisture) at elevated temperature (180 °C) for 24 h using a VacPrep Degasser machine. Thereafter, the degassed samples were reweighed before being placed into a sealed quartz tube chamber where the analysis was run by measuring the volume of N_2 gas adsorbed to the surface at the boiling point of nitrogen (-196 °C). The amount of gas dosed over the sample minus that evacuated was to obtain the quantity of gas adsorbed by the sample. The nature of the adsorption/desorption isotherm obtained provides information on the pore size of the material.

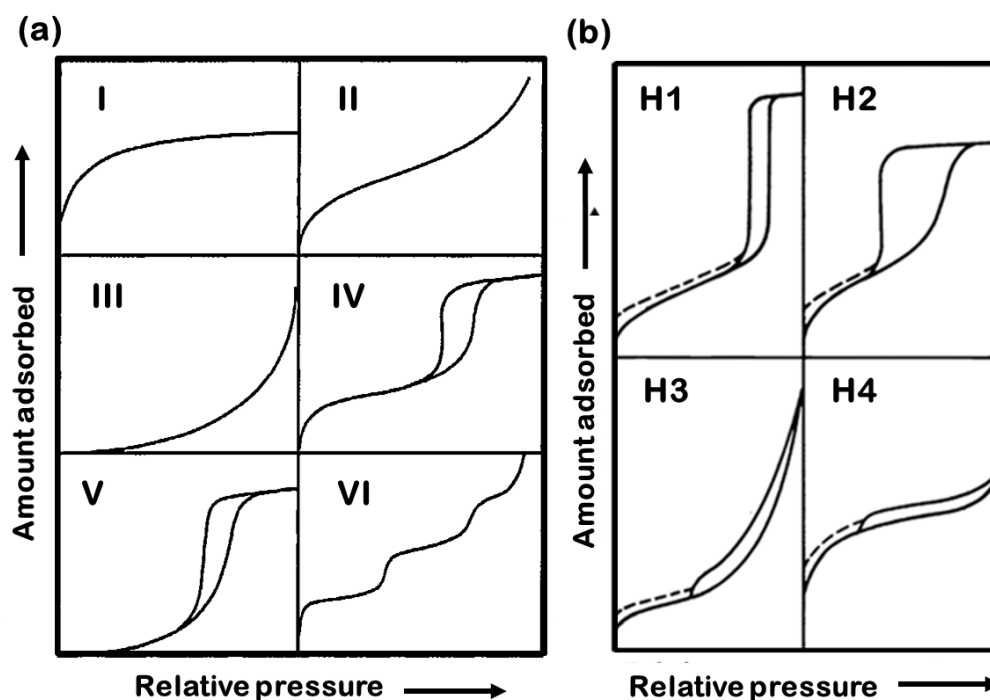


Figure 3.5: (a) The IUPAC classification of adsorption/desorption isotherms (b) adsorption/desorption hysteresis loop [11].

The characteristics of the adsorption isotherm were initially introduced by Brunauer and co-workers in 1940 where they reported five isotherm types [10]. Afterwards, in 1985, the International Union of Pure and Applied Chemistry (IUPAC) [11] published six classes of adsorption isotherm and also classified the pore size according to internal pore width. A material is said to contain micropores if the size of its pores is < 2 nm, mesopores, if pore size range from 2-50 nm and macropores for pore sizes > 50 nm. The types of adsorption/desorption isotherm and loop hysteresis are shown in figure 3.5. Figure 3.5 (a) illustrates the IUPAC classification of the various types of adsorption/desorption isotherms. Type I also named Langmuir type is related to the adsorption of microporous adsorbents, which the amount adsorbed toward, is limited to the completion of only one layer. Types II and III are given by the adsorption of non-porous adsorbents with a strong and weak interaction between the adsorbate and adsorbent respectively.

Type IV and V correspond to mesoporous adsorbents with a hysteresis loop. Type VI reflects a stepwise multilayer adsorption where each step represents the formation of one layer on a non-porous surface [12][11].

Figure 3.5 (b) exhibits the classification of hysteresis loops into types H1, H2, H3, and H4. H1 is attributed to the porous materials with a narrow size distribution of uniform pores. H2 possess more complex pore structure with a wide pore size distribution and ill-defined shape. H3 is associated to the aggregates of plate-like particles. H4 contains a complex materials with micropores, mesopores and or macropores network [11][13][14].

3.3.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is one of the useful electron microscopy techniques for high-resolution surface imaging in the fields of nanomaterials science.

SEM is performed with a focused electron beam that is generated from a Schottky field emission source, which requires a high-applied field under ultra-high vacuum. When the incident electron beam hits the specimen surface, it interacts with the atoms of the specimen to produce a variety of signals at the surface of the solid samples. The varieties of signal produced can be used to examine the specimen characteristics such as the topography, morphology, chemical composition and crystallography as well as the orientation. Typical signals detected include the secondary electrons (SE), backscattered electrons (BSE), Auger electrons, cathodoluminescence (CL) characteristic X-rays, Bremsstrahlung X-rays and transmitted electrons [15].



Figure 3.6: High resolution Field Emission Scanning Electron Microscope instrument (Zeiss, Ultra Plus 55 FE-SEM).

The signal generated by the secondary electrons is used for imaging and provides good morphological information of the sample topography. The SEM having a SE detector offers high-resolution images of the sample surface in the order of 1 nm and large depth of field producing images in three-dimensional appearance. Backscattered electrons (BSE) are mostly used with the spectra made from the characteristic X-rays and give information on the elemental composition of the sample. The signal from the BSE is highly dependent on the atomic number (Z) of the sample.

The Energy dispersive X-ray spectroscopy (EDX or EDS) is a microanalysis technique where the X-rays are emitted by exciting the inner shell electron of the specimen. The X-rays detected are spectrally resolved with an appropriate energy dispersive detector and integrated into the SEM instrument. EDX method is used to determine the chemical composition and the elemental distribution of the sample [16][17].

In this thesis, the surface morphology of all samples was investigated by field emission scanning electron microscope (FE-SEM) using a high resolution Zeiss Ultra Plus 55 (shown in figure 3.6) operated at 1.0 kV. This was coupled with an energy dispersive X-ray (EDX) spectrometer, which was operated at 20 kV to carry out elemental analysis. The samples used for surface morphology studies were prepared by placing the sample of interest onto conductive carbon tape attached to an aluminum substrate holder. For the EDS analysis, samples were prepared using a non-conductive epoxy resin. The powder samples were immersed in epoxy resin, dried in an oven then polished until the surface of the sample was exposed.

3.3.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) technique is also a surface morphology method used to study materials but at a greater resolution than SEM. TEM is considered as a useful and versatile technique for the microstructural characterization of materials. TEM is based on the transmission of electron beams through a very thin specimen. The image is generated when the high-energy electron beam is illuminated through thin area of the sample [18]. The obtained image goes through several magnifications lenses to achieve high magnification and is recorded by a fluorescent viewing screen, CCD (charge-coupled device) camera or photographic plate.

The penetrating electrons in the sample provides detailed information about the surface features, crystallite structure, shape and size, as well as chemical composition of the sample. TEM offers high resolution capability of imaging the lattice patterns in a crystalline sample [18][19].



Figure 3.7: Transmission Electron Microscopy instrument (HRTEM-JEOL- 2100F).

In this study, a high-resolution transmission electron microscopy (HR-TEM) JEOL 2100F (shown in figure 3.7) equipped with LaB6 filament, a Gatan U1000 camera of 2028 x 2028 pixels and operated at 200 kV was used to analyze the electron micrographs for all samples. For the sample preparation, the material under study was dispersed in ethanol using an ultrasonic bath and the homogeneous mixture was drop-cast onto carbon-coated copper grids.

3.3.4 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) is a reliable analytical technique for structure determination of crystalline materials including inorganic, organic and pharmaceutical compounds, minerals, catalysts, metals and ceramics.

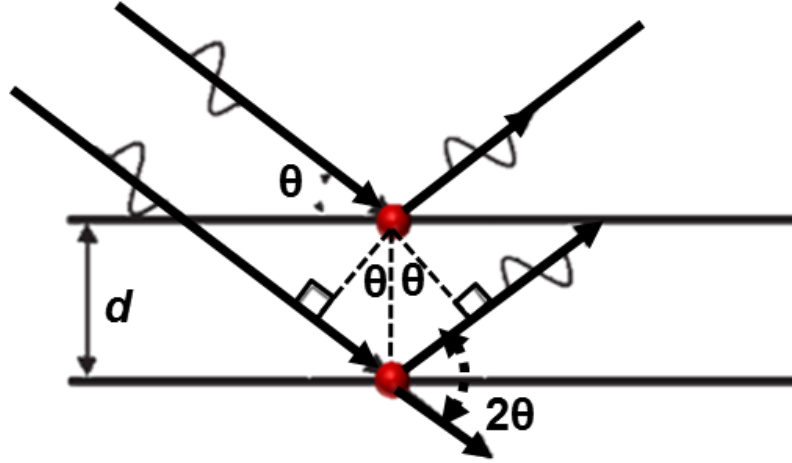


Figure 3.8: Scheme illustrative of Bragg's law [21].

The XRD is recognized as a non-destructive and resourceful tool used in identifying the lattice parameters, crystalline phase, crystallite size, and phase composition of materials [20]. An XRD system is composed of three main components: the X-ray tube, the sample holder and the X-ray detector. Therefore, the diffraction patterns are obtained from the scattering of monochromatic-X-rays (generated from a cathode ray tube) on a crystalline sample.

The interaction of the incident X-rays with the crystal planes of the sample (as shown in figure 2.8) generates constructive interference when Bragg's law [21] is satisfied which is given by;

$$n\lambda = 2d \sin \theta \quad (3.1)$$

where n is an integer value (1, 2, 3...), signifying order of reflection, λ is the wavelength of the monochromatic X-rays, d is the distance between the planes in the atomic lattice-spacing and θ is the Bragg angle representing the angle between the incident X-ray and sample surface. The angle between the projection of the X-ray source and the X-ray detector is 2θ .

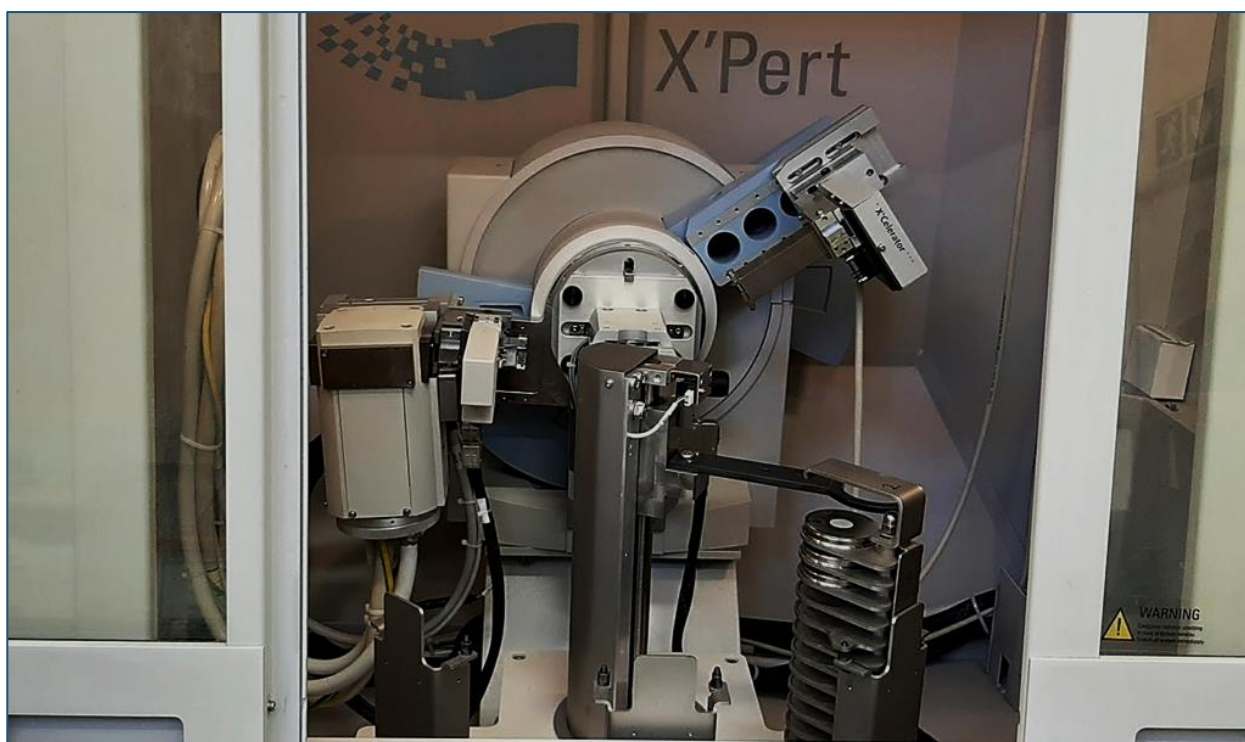


Figure 3. 9: Panalytical X'Pert-Pro X-ray diffractometer system.

The diffracted X-rays are recorded by an X-ray detector, which moves in a circle around the specimen and show up as diffracted intensities at a range of 2θ angle [22].

In this thesis, the XRD patterns of all samples were obtained using an X'Pert-Pro diffractometer (Panalytical BV, Netherlands) in 2θ geometry with a cobalt $K\alpha$ radiation of $1.789 \text{ \AA}$ and the cobalt tube was operated at 35 kV and 50 mA. Figure 3.9 shows the X'Pert-Pro X-ray diffractometer instrument.

3.3.5 Raman spectroscopy

Raman spectroscopy is one most important laser spectroscopic technique used for the study of vibrational, rotational and crystal structure in a molecular system. This non-destructive method relies on the non-elastic scattering process from the incident monochromatic light which is emitted generally from a laser near infrared, visible or near ultraviolet region [23].

The interaction of the photons from the laser source with molecular vibrations in a sample produces scattered photons, which results in frequency/energy change compared to the incident photon. When an incident photon from laser interacts with a molecule, the photon scattering can be elastic or non-elastic. Most of the scattered photons are elastic and referred to as *Rayleigh scattering*, i.e. the emitted photons have the same frequency as the incident one. Therefore the inelastic scattering known as Raman scattering are very weak due to molecular vibrations in which the photon may gain or lose energy meaning the frequency of the scattered photon can be higher (anti-Stokes Raman scattering) or lower (Stokes Raman scattering) than the incident photon [24]. In a Raman spectrum, Stokes scattering with higher intensity are usually used for measurement. Thus the Raman spectrum consists of the plot of the intensity of the scattered photon versus the energy difference between incident and scattered photon (Raman shift). Raman spectroscopy can be employed for the analysis of materials in solid, powder or liquid form for various applications [25].

In this work, the Raman spectra analysis was carried out using a WITec confocal Raman microscope (WITec alpha 300 R, RAS+, Germany) as represented in figure 3.10. This system is operated with a 532 nm laser set at a 5 mW emitting power to minimize heating effects.

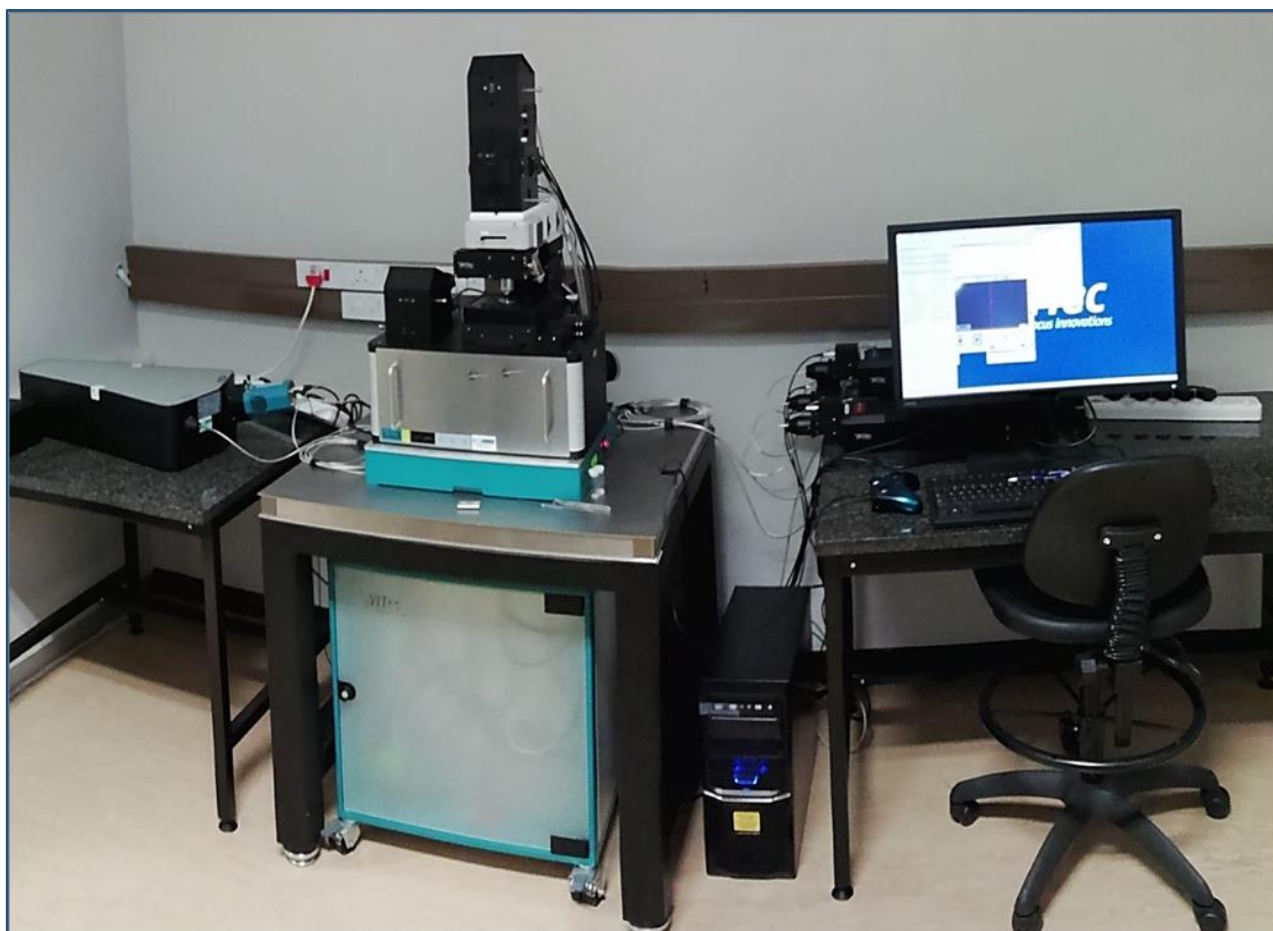


Figure 3.10: WITec confocal Raman microscope (WITec alpha 300 R, RAS+ , Germany).

3.3.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a powerful analytical technique for surface analysis. XPS also known as Electron Spectroscopy for Chemical Analysis, is widely used to determine the surface elemental composition, elemental identification, chemical state and electronic structure of the element. This sensitive surface method probes to a depth of 10 nm of the material and can detect all of the elements except hydrogen and helium [26][27]. XPS analysis has to be done usually under ultrahigh vacuum (UHV) conditions at around 10^{-9} millibar within the measurement chamber. XPS spectra are typically produced by irradiating a material surface using X-rays source (Al $K\alpha$ or Mg $K\alpha$) that is accompanied by the emission of an X-ray photon (photoelectrons).

These photoelectrons are elastically scattered from the sample with a certain kinetic energy. The kinetic energy of the emitted electrons can be measured using an electron energy analyzer. Thus the plot of the number of electrons detected relative to the binding energy represents the photoelectron spectrum [28]. In the XPS spectrum, each peak corresponds to atoms emitted with a particular characteristic binding energy that determines the elemental identity, chemical state of every element present in or on the surface of the specimen. In addition, the intensity of the peak of the identified element is proportional to the amount of that element in the sample.

X-ray photoelectron spectroscopy (XPS) was used to determine the surface chemistry of all materials in this work. The measurements were performed using a Physical Electronics VersaProbe 5000 spectrometer operating with a 100 μm monochromatic Al-K α exciting source and a 180° hemispherical electron energy analyzer to collect photoelectrons. The samples were analyzed at a 45° angle between the sample surface and the path to the analyzer. Survey spectra were taken at pass energy of 117.5 eV, with a step size of 0.1 eV.

3.3.7 Electrochemical characterization

The electrochemical analysis of all electrode materials used in this work was performed at standard laboratory conditions with a Biologic VMP-300 16-channel potentiostat (Knoxville 37930, USA) as shown in figure 3.11. The potentiostat is an electronic instrument that monitors the potential difference of working electrode (WE) with a current passing through and a reference electrode (RE) with no current passing through while measuring the current applied through the counter electrode (CE). This instrument is controlled by the EC-Lab® V11.33 software and provides a variety of analysis tools such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) in both three-electrode (half-cell) and two-electrode (full-cell) testing configurations.

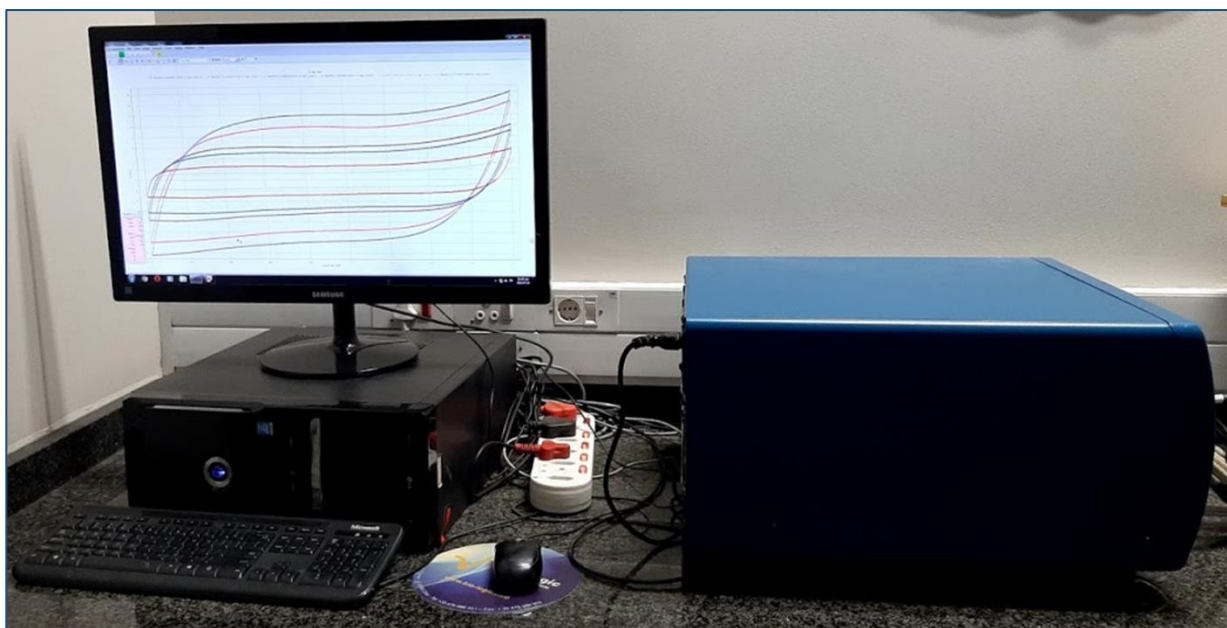


Figure 3.11: Biologic VMP-300 16-channel potentiostat (Knoxville 37930, USA) controlled by the EC-Lab® V11.33 software.

The preparation of all electrode materials was done by using a mixing recipe which involves adding 80 wt% active materials with a 10 wt% carbon acetylene black (CAB) as conducting agent and 10 wt% polyvinylidene difluoride (PVDF) as binder. Subsequently, a few drops of N-methylpyrrolidone (NMP) solvent are added to the mixture to make a slurry. This is coated onto nickel foam-graphene and bare nickel foam current collectors and dried in an electric oven for 12 h at 60 °C to ensure complete evaporation of the NMP.

The electrochemical tests were carried out using a three-electrode set-up which consists of the as-prepared electrode serving as working electrode, a glassy carbon plate or disc serving as counter electrode and a Ag/AgCl (in saturated KCl) serving as the reference electrode. In the two-electrode configuration, a Swagelok testing cell with a glass microfiber filter paper to separate the electrodes was used. A variety of aqueous electrolytes were employed to evaluate the electrochemical performance of the electrodes materials reported in this thesis.

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4.0 Results and discussion

This chapter outlines the results and discussion of all as-synthesized samples after characterization and electrochemical analysis presented in the preceding chapter.

4.1 Effect of activating agents on the electrochemical performance of high-energy ultra-capacitor electrodes derived from peanut shell waste

4.1.1 Introduction

Carbon-based materials have been considered as promising electrode materials for supercapacitors, also named ultra-capacitors or electrochemical capacitors. Carbon materials including activated carbons (ACs), carbon nanotubes (CNTs), onion-like carbons (OLCs), carbon aerogels, graphene and carbide-derived carbons have attracted considerable attention due to their good conductivity, high specific surface area and tunable pore size distribution [1][2]. Compared to other carbons, the ACs, especially those derived from biomass waste sources are outstanding due to their cost-effectiveness, environmentally friendliness, easy abundance and easy availability. These carbonaceous materials can be made from various biomass waste sources such as tea waste, pecan nutshells, peanut shells, banana stems, cucumis melo fruit peels, baobab fruit shells among others [3][4]. Basically, two different processes have been used to prepare activated carbon through chemical and physical activation. Chemical activation involves the presence of chemical activating agents impregnated into the raw carbon source with subsequent pyrolysis.

The activating agents have a direct influence on the properties of the activating carbon materials such as the creation of a porous network, surface area and charge storage capability [5][6]. Many researchers have reported on alkali (KOH, NaOH), acids (H_3PO_4 , HNO_3) and metal salts (ZnCl_2 , FeCl_3) as activating agents to produce porous carbon materials from biomass waste. For example, Asim et al. [7] have reported the synthesis of hierarchical porous activated carbon from baobab fruit shell via H_3PO_4 and KOH activation process and obtained a specific surface area (SSA) of $911.7 \text{ m}^2 \text{ g}^{-1}$ and $1059.3 \text{ m}^2 \text{ g}^{-1}$, respectively [7]. Sun and co-workers [8] have used ZnCl_2 and KOH as activating agents to produce porous activated carbon derived from *Pteroceltis tatarinowii* Maxim (PTM) bark waste. Their study reported a higher SSA of $1721 \text{ m}^2 \text{ g}^{-1}$ for KOH activated carbon than the one activated with ZnCl_2 with $1210 \text{ m}^2 \text{ g}^{-1}$ [8]. Typically, potassium-based salts mostly used as chemical agents are more effective activators for the generation of high SSA and hierarchically porous network which can significantly contribute to the high specific capacities [9][6][10].

As one of the leading agricultural waste, peanut shells have been widely used as a precursor for the production activated carbon because of low ash content, low apparent density, porous structure as well as richness in lignin, cellulose and hemicellulose. In addition, peanut has a great potential as one of the major oil-bearing crops in the world for human consumption [11][12][13]. Several kinds of activating agents such as ZnCl_2 , FeCl_3 , H_3PO_4 , KOH have been conducted to produce peanut shell derived ACs in different applications [14][15][11][12].

Herein, we focus on the synthesis of hierarchically porous carbon derived from peanut shells waste (PSW) through two steps: Carbonization followed by a chemical activation processes. The activated carbon peanut shell waste (APSW) was obtained using potassium-based salt as activating agents such as KHCO_3 , K_2CO_3 and KOH by varying the mass impregnations.

The main aim of this study is to investigate the effect of the potassium-based salts on the morphological, structural and electrochemical properties of the APSW materials.

4.1.2 Results and discussion

The study of the as-synthesized activated carbon from peanut shell waste is presented in this section. The details of the experimental procedures, characterization and electrochemical results have been presented in the publication below:

OPEN

Effect of porosity enhancing agents on the electrochemical performance of high-energy ultracapacitor electrodes derived from peanut shell waste

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In this study, the synthesis of porous activated carbon nanostructures from peanut (Arachis hypogaea) shell waste (PSW) was described using different porosity enhancing agents (PEA) at various mass concentrations via a two-step process. The textural properties obtained were depicted with relatively high specific surface area values of $1457 \text{ m}^2 \text{ g}^{-1}$, $1625 \text{ m}^2 \text{ g}^{-1}$ and $2547 \text{ m}^2 \text{ g}^{-1}$ for KHCO_3 , K_2CO_3 and KOH respectively at a mass concentration of 1 to 4 which were complemented by the presence of a blend of micropores, mesopores and macropores. The structural analyses confirmed the successful transformation of the carbon-containing waste into an amorphous and disordered carbonaceous material. The electrochemical performance of the material electrodes was tested in a 2.5 M KNO_3 aqueous electrolyte depicted its ability to operate reversibly in both negative and positive potential ranges of 0.90 V . The activated carbon obtained from the carbonized CPSW:PEA with a mass ratio of 1:4 yielded the best electrode performance for all featured PEAs. The porous carbons obtained using KOH activation displayed a higher specific capacitance and the lower equivalent series resistance as compared to others. The remarkable performance further corroborated the findings linked to the textural and structural properties of the material. The assembled device operated in a neutral electrolyte (2.5 M KNO_3) at a cell potential of 1.80 V , yielded a ca. 224.3 F g^{-1} specific capacitance at a specific current of 1 A g^{-1} with a corresponding specific energy of 25.2 Wh kg^{-1} and 0.9 kW kg^{-1} of specific power. This device energy was retained at 17.7 Wh kg^{-1} when the specific current was quadrupled signifying an excellent supercapacitive retention with a corresponding specific power of 3.6 kW kg^{-1} . These results suggested that peanut shell waste derived activated carbons are promising candidates for high-performance supercapacitors.

The global demand for energy increases exponentially due to the new development and skyrocketing consumption of electronic gadgets such as mobile phones, laptops, and hybrid electric vehicles¹. Furthermore, most of the energy generation sources used are fossil fuel-based (non-renewable) which creates enormous environmental damage. Thus, there is a need to design and fabricate efficient and also environmentally friendly energy storage systems to meet the continuous energy demand. Energy storage technology plays a key role in continuous energy production systems and has a potential to offset the intermittent problem related to some renewable energy sources (solar, wind, wave, etc.)². Actually, batteries and supercapacitors are the most common devices for electrical energy storage³. Batteries are currently the primary energy storage system, despite their limitation in safety and operating in high specific power applications. Supercapacitors (SCs), sometimes referred to as ultra-capacitors (or electrochemical capacitors (ECs)) possess high power delivery capability but are plagued

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with a lower specific energy as compared to batteries⁴. SCs have attracted significant attention due to their long cycle life, stability, low maintenance and efficiency^{5,6}. According to their charge storage mechanism, two types of SCs can be classified namely electrical double layer capacitors (EDLCs) and faradic capacitors (FCs). EDLCs store charges electrostatically with the charged ion located at the surface of the electrode material. However, the charge storage of FCs (or pseudocapacitors) involves a fast redox reaction at the electrode-electrolyte interface^{7,8}.

Carbon-based materials such as carbon nanotubes (CNTs), activated carbon (AC), carbon aerogels, graphene etc. have been mostly used as the electrodes materials for EDLC due to their high specific surface area, good electrical conductivity and large pore size distribution (micro, meso and macropores)^{9,10}.

More importantly, the ACs obtained from biomass sources have attracted considerable attention due to their high abundance, relatively low-cost synthesis route and environmentally safe trait. A variety of biomass materials such as oil palm kernel shell¹¹, cumin waste¹², chitosan¹³, cattail¹⁴, banana peels¹⁵, orange peels¹⁶, rice husk¹⁷ etc., have been used as precursors for producing highly porous AC materials via chemical and physical activation processes. Chemical activation involves the impregnation of carbonaceous raw materials with chemical activating reagents such as potassium hydroxide (KOH), zinc chloride (ZnCl₂), phosphoric acid (H₃PO₄) with subsequent pyrolysis^{18,19}. The porosity enhancing agents (PEAs) play an important role in the activation process by creating a porous network, which aids the development of a high specific surface area (SSA). This can contribute to the charge storing ability and also facilitate easy access of the electrolytes ions into the pores of the AC electrode materials.

In the literature, different porosity enhancing agents (PEAs) have been used to produce hierarchically porous carbon materials derived from biomass precursors. For example, M. Sivachidambaram *et al.*²⁰ prepared activated carbon from Tamarindus indica fruit shell using H₃PO₄ activating agent and obtained an 846 m² g⁻¹ SSA with a total pore volume of 0.60 m³ g⁻¹. Similarly, Z. Sun *et al.*²¹ activated raw Pteroceltis tatarinowii bark with ZnCl₂ and KOH. In their report, the KOH-activated raw material showed a higher SSA of 1721 m² g⁻¹ and total pore volume of 0.90 m³ g⁻¹ as compared to the one activated with ZnCl₂ (1210 m² g⁻¹ and 0.57 m³ g⁻¹, respectively).

Recently, J. Han *et al.*²² synthesized giant miscanthus, corn stalk, and wheat stalk-derived activated carbons with KOH and recorded specific surface area values of 2212, 2434 and 2327 m² g⁻¹ with a pore volume 0.99, 1.22, 1.10 m³ g⁻¹ respectively. Generally, most chemical activation studies which reported high porosity proposed potassium-based salts to be more effective in pore creation and activation of carbonaceous materials as compared to other PEAs (H₃PO₄, ZnCl₂, NaOH...)^{19,23–25}.

Peanut shell waste is of great interest as it is a common agricultural waste that is cheap, readily available, and can be made useful as a renewable energy source²⁶. Recently, activated carbon from peanut shell waste has been generated using ZnCl₂, FeCl₃ and H₃PO₄ and applied in supercapacitors, Lithium and Sodium batteries and as well as in wastewater treatment^{27–30}. These results on peanut shell waste derived activated carbons suggested an improvement in the pore creation during carbonization/activation process due to the multiple composition of the peanut shell such as lignin, cellulose and hemicellulose³¹. However, a study of the effect of potassium based porosity enhancing agents on the morphological, structural and electrochemical properties of peanut shell waste derived carbons to our knowledge has not been explored.

In this work, we therefore focus our study on the synthesis of hierarchically porous activated carbon from peanut (Arachis hypogea) shell waste (PSW) via two steps (carbonization/activation) using different potassium-containing PEAs namely KHCO₃, K₂CO₃ and KOH with varying mass concentrations. In addition, the effect of the various mass concentrations on the textural and electrochemical properties of the activated carbon-based material electrodes for supercapacitor devices was explored. The PSW activated with KOH at a ratio of 1:4 (APSW-KOH4) exhibited the best initial electrochemical performance in half-cell configuration in 2.5 M KNO₃. The choice of this neutral electrolyte was based on the pH value which controls the ability to operate in a wider potential window due to the electrolyte stable potential windows (ESPWs) as compared to acidic or alkaline aqueous electrolytes which is limited by the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)^{32–34}.

Additionally the size of the ions in the KNO₃ (K⁺, NO₃⁻) ions are suitable to be transported within the pores of the as-synthesized APSW sample. The best charge transport dynamics was recorded in the APSW-KOH4 sample which gives the ideal pore sizes for efficient ion transport and charge storage. KNO₃ aqueous electrolyte also has a high conductivity, is environmentally friendly, non-corrosive and cheap to synthesize^{35,36}. Thus, symmetric cells composed of APSW-KOH4//APSW-KOH4 electrodes material were assembled and tested. The full device displayed a high specific energy of 25.2 Wh kg⁻¹ with a corresponding high specific power of 0.9 kW kg⁻¹. A good device stability was demonstrated with an 83% capacitance retention up to 15,000 cycles. Amazingly, the device further showed an enhancement in the performance after being subjected to voltage holding (floating) tests for more than 6 days (150 h) floating time.

Experimental Method

Material synthesis. The porous activated carbon nanostructures were obtained via a two-step pyrolysis technique of peanut shell waste (PSW) material at elevated temperatures. The collected PSW was initially washed with deionized water (DI) thoroughly and dried over 12 h under direct sunlight. Then, the dried PSW was ground into fine powder. Thereafter, 5 g of PSW powder was mixed with 0.5 g of urea, 1 g of NaCl and a few drops of deionized water (DI) to make a sludge. A compact rectangular block (B-1) from the sludge mixture was placed in an oven at 80 °C to dry overnight.

The dried compact block mixture was transferred into a horizontal tube furnace set at 600 °C (ramp rate of 5 °C min⁻¹) for a period of 2 h in 250 sccm flow of Argon gas. The black product obtained (referred to as carbonised peanut shell waste (CPSW)) was washed severally with DI and dried at 80 °C.

For the activation process at elevated temperature, a weighed amount of CPSW was mixed with three different porosity enhancing agents (PEAs) namely, KHCO_3 , K_2CO_3 and KOH , at different mass loading ratios of 1:1, 1:2, 1:4 and 1:6 for the CPSW:PEA, respectively. The moulded mixtures in form of blocks of CPSW:PEA at different ratios were also prepared to ensure an efficient contact between the PEA and the material surface. The moulded blocks (B-2) were subjected to pyrolysis at 850°C using a 5°C min^{-1} ramp rate for a 1 h period using 250 sccm of Argon gas flow. The resulting products were soaked in 3 M HCl and sonicated for 8 h to get rid of the excess unreacted PEA. Finally, the filtered solids materials were rinsed with DI until a neutral pH before drying at 80°C for 12 h. The activated carbon nanostructures from peanut shell waste are indicated as APSW-Yx where Y denotes the PEA and x the mass ratio of PEA.

Materials characterization. The material textural features were determined by using the Brunauer-Emmett-Teller (BET) technique measured from a Micrometrics TriStar II 3020 (version 2.00) system at -196°C . Furthermore, porosity properties i.e. the pore size distribution (PSD) was analysed with the Barrett-Joyner-Halenda (BJH) and density functional theory (DFT) plots. The Raman spectra of the APSW material was performed using a WITec confocal Raman microscope (WITec alpha300 RAS+) operating with a 532 nm laser set at a 5 mW emitting power to minimize heating effects.

X-ray photoelectron spectroscopy (XPS) analysis of the synthesized material was done using a Thermo Fisher photoelectron spectrometer fitted with a monochromatic Al $\text{K}\alpha$ radiation X-ray source. A Zeiss Ultra-plus 55 field emission scanning electron microscope (FE-SEM), operated at 1.0 kV was used to characterize the surface morphologies of the samples. TEM measurements were obtained using a cold field-emission JEOL F200 TEM operating at 200 kV.

Electrochemical characterization. The electrochemical measurement in the three and two electrodes was performed using a Biologic VMP-300 16-channel potentiostat (Knoxville, USA). The preparation of the electrode was done by mixing 80% of the active material (APSW-Yx), 10% polyvinylidene difluoride (PVDF) and 10% carbon acetylene black (CB). Thereafter, few drops of N-methylpyrrolidone (NMP) were added to the mixture to make a slurry in an agate mortar. This mixture was pasted onto nickel foam-graphene (NFG) current collector and then dried in an electric oven for 12 h at 60°C to ensure complete evaporation of the NMP. The three-electrode analysis (half-cell test) was done using a glassy carbon counter electrode (CE) and Ag/AgCl (in saturated KCl) reference electrode (RE). The symmetric device was assembled in a Swagelok system with a glass microfiber filter paper to separate the two electrodes (full-cell). The mass per area of the single electrode in the cell was approximately 3 mg cm^{-2} .

All electrochemical test such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and stability tests were carried out with the APSW-Yx materials operated in a 2.5 M KNO_3 aqueous electrolyte.

Results and Discussion

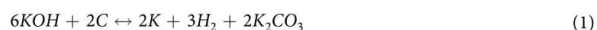
Textural, structural and morphological characterization. The N_2 -adsorption/desorption analysis was used to determine the textural properties of the APSW with different PEA as shown in Fig. 1.

Figure 1(a–c) displays isotherms with indicated BET SSA for the APSW for each PEA (KHCO_3 , K_2CO_3 and KOH) with different mass ratios (1:1, 1:2, 1:4 and 1:6). The adsorption isotherms for all the APSW-Yx exhibit a hybrid of type I and IV isotherms with a H4 hysteresis loop according to the IUPAC. At low relative pressure ($P/P_0 < 0.01$) the adsorption isotherm shows a steep uptake of N_2 which is associated to a well-developed micropores. An hysteresis loop between the adsorption and desorption branches indicates the presence of mesoporous at a medium pressure, while a little adsorption increase was observed relating to the existence of macropores at high pressure ($P/P_0 > 0.9$)^{37,38}. In the samples, APSW- KHCO_3 4, APSW- K_2CO_3 4 and APSW-KOH4 exhibited rises of isotherm at P/P_0 of 0.43, and a small hysteresis loop occurs at P/P_0 of 0.43–0.70. The appearance of the hysteresis loops indicate the existence of a bit bigger pore³⁹. It can be seen that the APSW-Yx reveal a hierarchically porous texture with a coexistence of micro, meso and macropores which provide fast interfacial ion-transport kinetics and efficient ion accessible surface area for charge storage^{40,41}.

Figure 1(d–f) shows the Barrett-Joyner-Halenda (BJH), which determined the pore size distribution (PSD) analysis of the APSW-Yx samples. The PSD observed peaks confirm the presence of micropores and mesopores. However, the presence of macropores is not seen in the PSD plots due to limitation in the pore width range displayed. The SSA and the total pore volume of the APSW-Yx are summarized in Fig. S1(a,b). The SSA and the total pore volume kept increasing as the amount of PEA added was increasing up to a threshold (1:4) then experienced a decrease with further increase in PEA (1:6).

The same trend was observed for all porosity enhancing agents used in this study.

The surface areas of all prepared materials are shown in Table S1 therefore APSW- KHCO_3 4, APSW- K_2CO_3 4 and APSW-KOH4 exhibit the higher SSA $1457 \text{ m}^2 \text{ g}^{-1}$, $1625 \text{ m}^2 \text{ g}^{-1}$ and $2547 \text{ m}^2 \text{ g}^{-1}$, respectively as compared to the others carbon materials. In addition, the sample activated with KOH in a mass ratio of 1:4 displayed the highest SSA of $2547 \text{ m}^2 \text{ g}^{-1}$ and largest total pore volume of $1.2 \text{ cm}^3 \text{ g}^{-1}$. The highest SSA and the total pore volume could be attributed to the multiple decomposition steps for the KOH as compared to other PEAs. In the course of the activation with the different PEAs at elevated temperature, the decomposition reaction taking place results in the improvement of the porosity via gasification from the generated carbon dioxide (CO_2) and carbon monoxide (CO) gas²⁵. In addition, the H_2 gas produced during KOH decomposition could etch the carbon atoms creating more pores⁴². The process of activation with the PEAs (KOH , K_2CO_3 and KHCO_3) within the sample can be described by the following reactions^{25,43,44}:



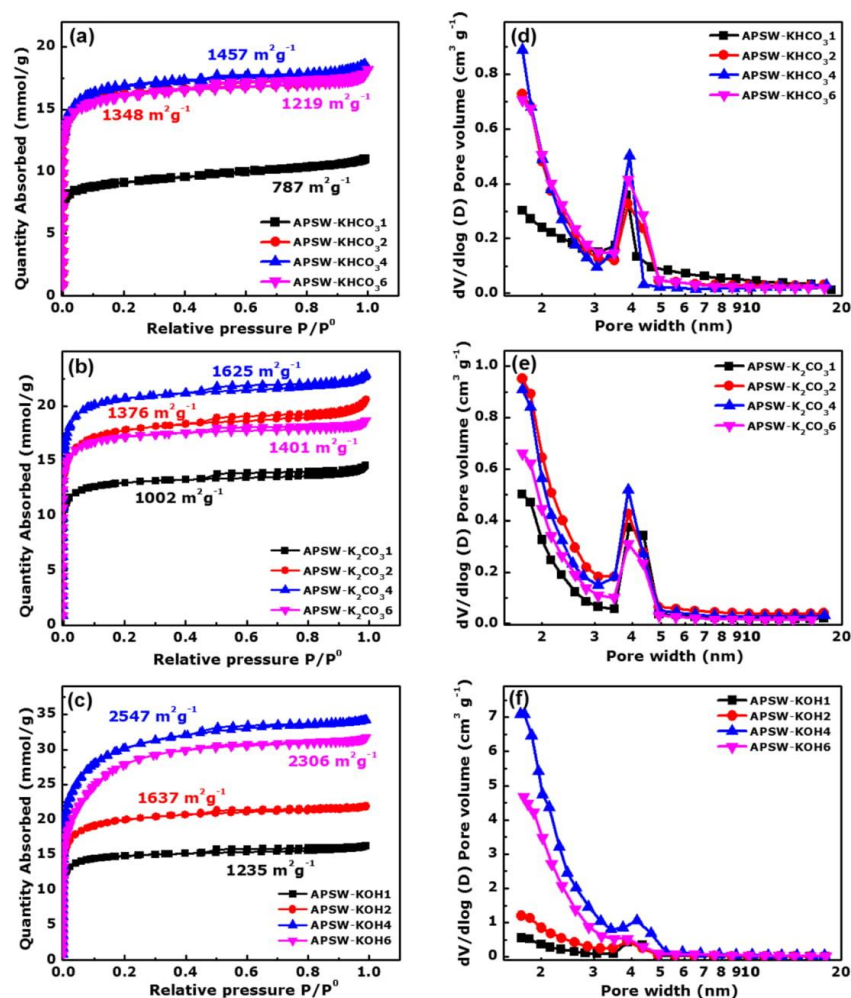
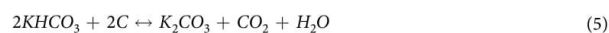


Figure 1. (a–c) N₂ absorption-desorption isotherms; (d–f) pore size distribution data of the activated carbon from peanut shell waste for varying porosity enhancement agents KHCO₃, K₂CO₃ and KOH contents respectively.



During this process, the KOH reacts with the carbon (C) to generate K₂CO₃ and metallic potassium as shown in Eq. (1) at 400 °C. At higher temperatures (>700 °C), the K₂CO₃ decomposes to give potassium oxide (K₂O) and CO₂ (Eq. 2). Additionally, the K₂CO₃ could react with the C to yield K₂O and CO thus, creating pores within the carbon matrix (Eq. 3). Finally, the generated K₂O undergoes further reaction with C to give K and CO. The K intercalates into the carbon matrix and be readily removed by washing the final products resulting in the creation

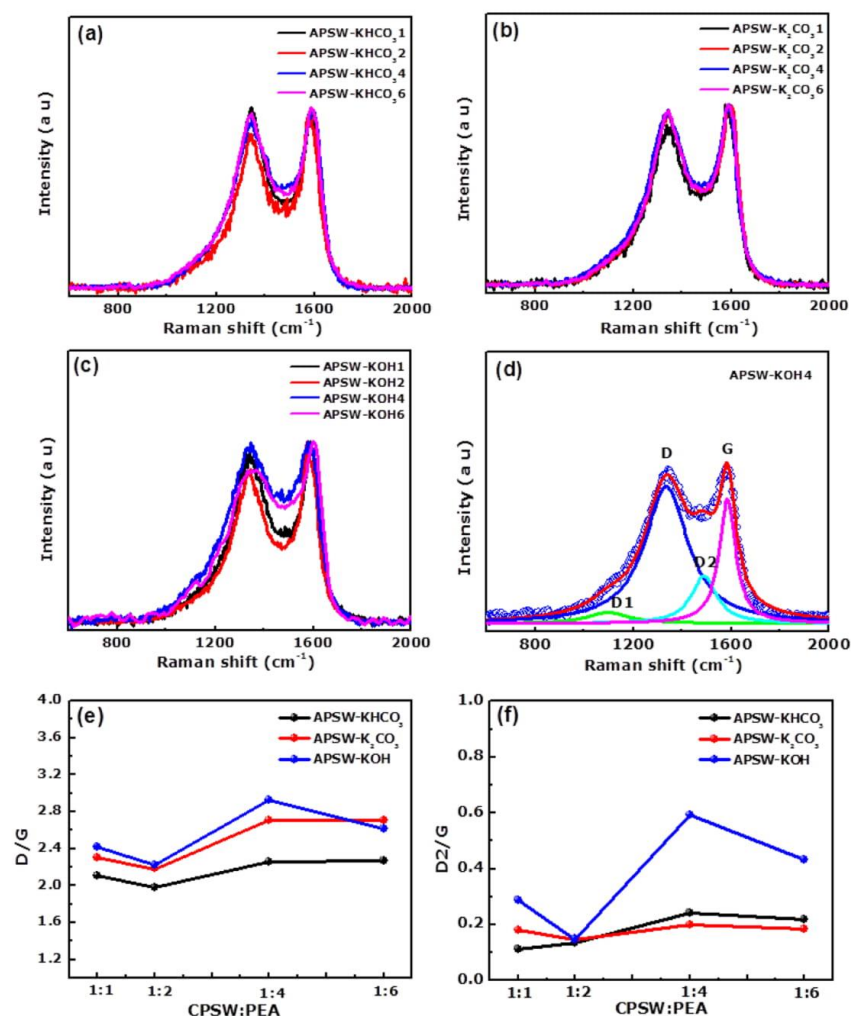


Figure 2. Raman spectra of the APSW samples at different mass ratio with: (a) KHCO_3 , (b) K_2CO_3 and (c) KOH PEA respectively, (d) deconvolution of the Raman spectrum for APSW-KOH4 sample, (e) D/G and (f) D2/G ratios as function of APSW- KHCO_3 , APSW- K_2CO_3 and APSW-KOH at different mass ratios.

of irregular channels and pores within the APSW (Eq. 4). Similarly, the KHCO_3 undergoes initial decomposition to give K_2CO_3 as shown in Eq. 5²⁵. Consequently, the K_2CO_3 further reacts with carbon or decomposes to give CO and CO_2 emission as shown previously in Eqs 2–4.

The variation of activating agents was done in order to select the best sample for the electrochemical investigation of electrode device. For example, the high specific surface area and larger of porous carbon material could give better electrochemical capacitance^{39,45}.

The Raman spectra of the activated peanut shell waste samples were used to investigate the combined effect of the carbonization and activation at elevated temperature processes on the structure of the samples. Figure 2 shows the Raman spectra of the samples for three different PEAs (KHCO_3 , K_2CO_3 and KOH). In all Figures, the Raman spectra depict the characteristic D ($\sim 1340\text{ cm}^{-1}$) and G ($\sim 1583\text{ cm}^{-1}$) bands attributed to carbonaceous materials with A_{1g} and E_{2g} symmetry. The D band arises due to defects or disorder in the graphitic structure of the carbon material and the G band is a characteristic feature of the graphitic material and corresponds to the tangential vibration of the sp^2 carbon atoms⁴⁶.

In Fig. 2(a–c), the Raman spectra for the APSW- KHCO_3 , APSW- K_2CO_3 and APSW-KOH samples at different ratios in the range of 1 to 6 are displayed respectively.

The Raman spectra of the samples were deconvoluted using a Lorentzian function (see Fig. S2 in the supporting information) to obtain the integral areas of the D and G peaks which were used to calculate the D/G ratio of the disordered carbon (D) relative to the graphitic carbon (G). Figure 2(d) shows an example of the deconvoluted Raman spectrum for the APSW-KOH4 sample. In Fig. 2(d), the D1 and D2 bands correspond to the vibration of the sp^2 - sp^3 bonds and amorphous carbon at interstitial sites of the disordered graphitic structure of the carbon material, respectively⁴⁶.

Figure 2(e) displays a plot of (D/G) ratio of the APSW-Yx at different ratios (1 to 6) which reveals a higher ratio of disordered carbon relative to the graphitic carbon for an activating ratio of 1:4 for all PEAs.

The sample APSW-KOH4 (2.9) is slightly higher compared to APSW-KHCO₃4 (2.3) and APSW-K₂CO₃4 (2.7). Similarly, Fig. 2(f) shows the plot of the D2/G ratio as a function of mass concentration for the various PEAs. It was observed that a higher ratio (or concentration) of amorphous carbon (D2) relative to the graphitic carbon (G) is recorded for the activating ratio of 1:4 for all PEAs, showing the values of APSW-KOH4, APSW-KHCO₃4 and APSW-K₂CO₃4 as 0.60, 0.20, 0.18 respectively. Moreover, the effective crystallite size, L_a , was calculated using the Knight formula^{47,48}:

$$L_a = \frac{C(\lambda)}{D/G} \quad (6)$$

where the D/G represents the ratio of the integrated area of D to G band, and $C(\lambda) = 4.96 \text{ nm}$. $C(\lambda)$ is the wavelength-dependent pre-factor estimated as $C(\lambda) \approx C_0 + \lambda C_1$ (for $400 < \lambda < 700 \text{ nm}$ range in which $\lambda = 532 \text{ nm}$ for our current study). C_0 and C_1 are estimated to be -12.6 nm and 0.033 nm , respectively, from a plot of $C(\lambda)$ as function of frequency (see ref.⁴⁷). APSW-KOH4 sample displays a smaller effective crystallite size compared to other APSW-Yx (see Fig. S3 and Table S2).

Briefly, a higher ratio of disordered carbon relative to the graphitic carbon and the smaller effective crystallite size observed for APSW-KOH4 sample compared to APSW-KHCO₃4, and APSW-K₂CO₃4 samples could be a reason for high SSA and the total pore volume observed for KOH as compared to other PEAs which could be attributed to the multiple decomposition steps of KOH (Eqs 1–5) during activation at elevated temperature.

Figure 3 shows the scanning electron micrographs of the peanut shell waste samples at low and high magnifications before and after subsection the activation at elevated temperatures. The micrographs of the carbonized sample presented in Fig. 3(a,b) display a sheet-like morphology with a relatively mutilated surface at higher magnification as compared to the raw material (PSW) which shows agglomerated nanoparticles (see Fig. S4).

However, the effect of the activating agents KHCO₃, K₂CO₃, and KOH with a mass ratio of 1:4 leads to the creation of irregular connected microcavities like morphology for all the samples as observed on the morphology on the samples displayed in Fig. 3(c–h). It is noteworthy to state that the micropores and mesopores are not visible from the microscopy analysis. Figures (c), (e) and (f) show the presence of the isolated nanocavities in the samples (illustrated with arrows). It is clear that the morphology of the APSW-KOH4 sample presents larger cavities with a dense distribution of relatively smaller-sized nanocavities on the surface (see high magnification SEM image in Fig. 3(h)) due to the reactivity of KOH³⁷. Figure S5 displays the high resolution transmission electron microscopy (HRTEM) micrographs of the carbon materials before and after being activating with a mass ratio of 1 to 4. The HRTEM images confirm the SEM of the as prepared carbon materials. The insets Fig. S5 reveal same morphology as of the activated materials which confirm the SEM analysis. Such channels (microcavities and nanocavities) allow good accessibility of electrolytes into the material allowing good wettability and thereby a better material pores/electrolyte ions interaction⁴⁹.

The XPS spectra showing the chemical state of the APSW-Y4 samples as displayed in Fig. 4. To determine the elemental composition (at.%), XPS analysis of all the APSW samples obtained with a mass ratio of 1:4 was performed (Fig. 4). All the samples showed a high carbon content (>85 at.%), an oxygen content of 11–14 at.% and 0.6–1.2 at.% N (see Table S3). The low nitrogen content is proposed to be due to the evolution of nitrogenous volatile products during the carbonization process⁵⁰. The APSW-KHCO₃4 gave the highest oxygen content agreeing with earlier reports in literature²⁵. However, the use of K₂CO₃ as a porosity-enhancing agent allowed the retention of a higher nitrogen content within the activated carbon matrix as compared to the other PEAs.

As expected, the APSW-KOH4 with the highest surface porosity gave a low nitrogen content indicating the loss of a higher number of nitrogenous groups during the activation process. Although the nitrogen content for the APSW-KOH4 was low, slightly higher carbon content was present as compared to the APSW-KHCO₃4 and APSW-K₂CO₃4. This suggests that the carbon matrix of the APSW-KOH4 was comprised of more defective carbons in the form of sp^2/sp^3 carbon domains and/or sp^3 bonded nitrogen, which corroborated with the high D/G ratios observed in the Raman measurements.

Figure 4 displays the deconvolution of the high resolution XPS signals of C1s, N1s and O1s in APSW-KHCO₃4, APSW-K₂CO₃4 and APSW-KOH4 materials. Figure 4(a,d,g) show the XPS core level spectra of C 1s of the APSW-Y4 samples which were deconvoluted into 5 peaks linked to carbon components namely, C = C (sp^2 carbon, 284.7 eV), C–C (sp^3 carbon, 285.3 eV), C–OH/C–N (286.5 eV), C–O–C (287.6 eV) and C = O (288.9 eV), respectively^{46,47}. The XPS core level spectra of N 1s of the APSW-Y4 samples (Fig. 4(b,e,h)), reveals three different nitrogen configurations; pyridinic-N (398.0 eV), pyrrolic-N (399.6 eV), and quaternary-N (401.0 eV) which are typically found in N-containing carbon materials⁵¹. Hence, the prepared and pristine (raw) materials exhibits the same carbon, nitrogen and oxygen components.

In aqueous electrolyte-based systems, the pyrrolic-N and pyridinic-N provide hydrophilic polar sites for better charge accumulation on the activated sample surface while the quaternary-N influences carbon conductivity^{52,53}.

The O 1s spectra of the APSW-Y4 samples (Fig. 4(c,f,i)) displayed binding energies at 532.7 and 530.9 eV corresponding to the C–OH/C–O–C and C = O, respectively⁵⁴. The presence of oxygen and nitrogen functional groups could aid in electrode wettability and impact on the electrochemical performance^{25,55}.

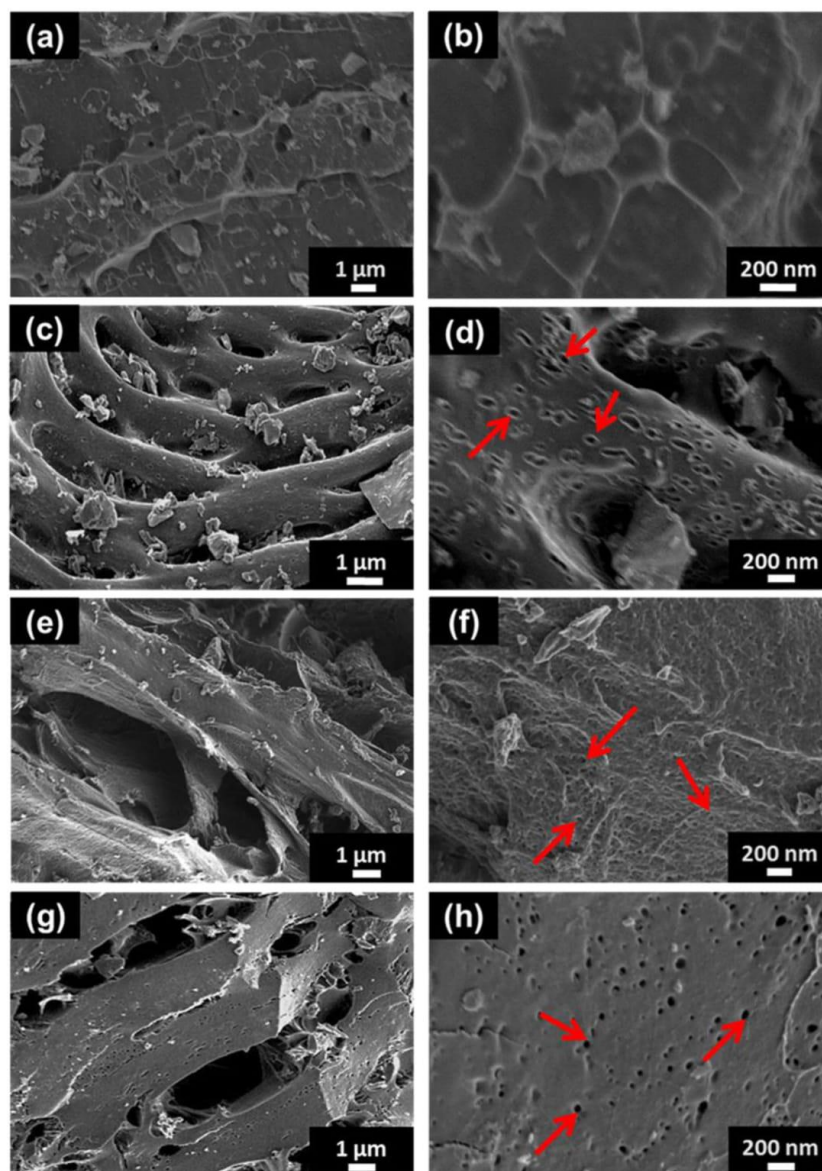


Figure 3. SEM images at low and high magnification of (a,b) CPSW; (c,d) APSW-KHCO₃; (e,f) APSW-K₂CO₃ and (g,h) APSW-KOH.

Electrochemical characterization. The electrochemical performance of the activated peanut shell waste sample was analysed firstly in three-electrode measurement using 2.5 M KNO₃ aqueous electrolyte as shown in Figs S4–S6.

From all the electrochemical results presented, it is clear that the materials synthesized with a CPSW:PEA mass ratio of 1:4 gave the highest electrochemical performance. Figure 5(a) displays the cyclic voltammogram (CV) curves at a scan rate of 20 mV s^{−1} of the samples activated with KHCO₃, K₂CO₃ and KOH at mass ratio 1:4.

All the CV plots demonstrated a typical EDLC behaviour with its characteristic rectangular outline in both negative (−0.9–0.0 V) and positive (0.0–0.9 V) potential window ranges. Furthermore, it is seen that

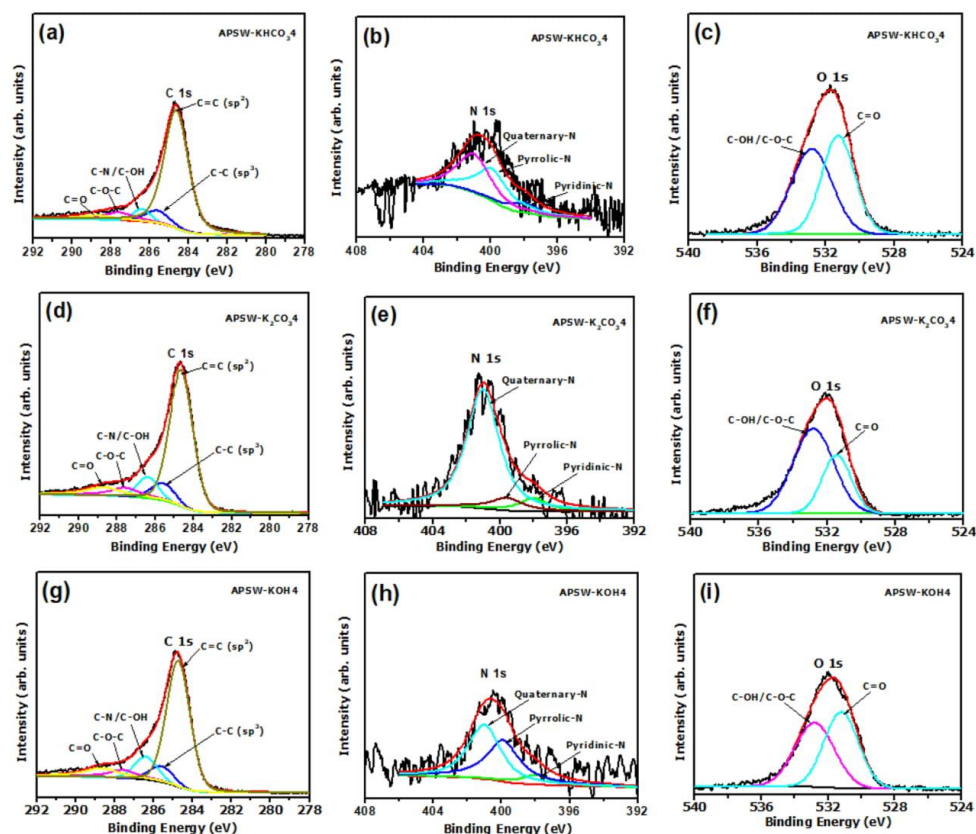


Figure 4. Deconvoluted core levels XPS spectra (C 1s, N 1s and O 1s) of (a–c) APSW-KHCO_{3.4}; (d–f) APSW-K₂CO_{3.4} and (g–i) APSW-KOH₄.

the APSW-KOH₄ sample exhibits a higher current response in both potentials compared to other APSW-Y₄. Figure 5(b,c) present the galvanostatic charge-discharge (GCD) profiles at a specific current of 1 A g⁻¹ operating in the same potential window in both negative and positive ranges (0.0–0.9 V and –0.9–0.0 V) as reported for the cyclic voltammetry tests. The GCD curves display a triangular shape with a linear discharge profile indicating a typical capacitive nature. However, activated sample APSW-KOH₄ displayed a longer discharge time as compared to the APSW-KHCO_{3.4} and APSW-K₂CO_{3.4}. The specific capacitance (C_s in F g⁻¹) of the sample electrodes as a function of the CPSW:PEA is illustrated in Fig. 5(d,e) in the positive et negative potential windows evaluated using Eq. 7 below⁵⁶:

$$C_s = \frac{I_s \Delta t}{\Delta V} \quad (7)$$

where I_s (A g⁻¹) represents the specific current, Δt (s) is the discharge time from the slope of the discharge part of the GCD plot, and ΔV (V) is the potential window.

The specific capacitance values for all the sample electrodes were calculated at a specific current of 1 A g⁻¹. All APSW-Y₄ sample electrodes demonstrated the best electrochemical performance in terms of the calculated C_s compared to other ratios (1:1, 1:2 and 1:6). The APSW-KOH₄ electrodes exhibited the highest specific capacitance of 242.3 F g⁻¹, which is in agreement with the high current response from the CV plots.

This is linked to the high SSA and pore volume with a wider pore sizes distribution reported from the textural analysis in which the KOH-activated sample had over an order of magnitude higher amount of pores as compared to the other PEAs (see Fig. 1(d–f)).

In addition, the D/G and D2/G ratio in relation to the smaller effective crystallite size from the Raman analysis also contributes to the enhanced electrochemical performance.

Electrochemical impedance spectroscopy (EIS) study further investigates the capacitive behaviour of the as-fabricated sample electrodes and determines the nature of the electrode in relation to the electrolyte and

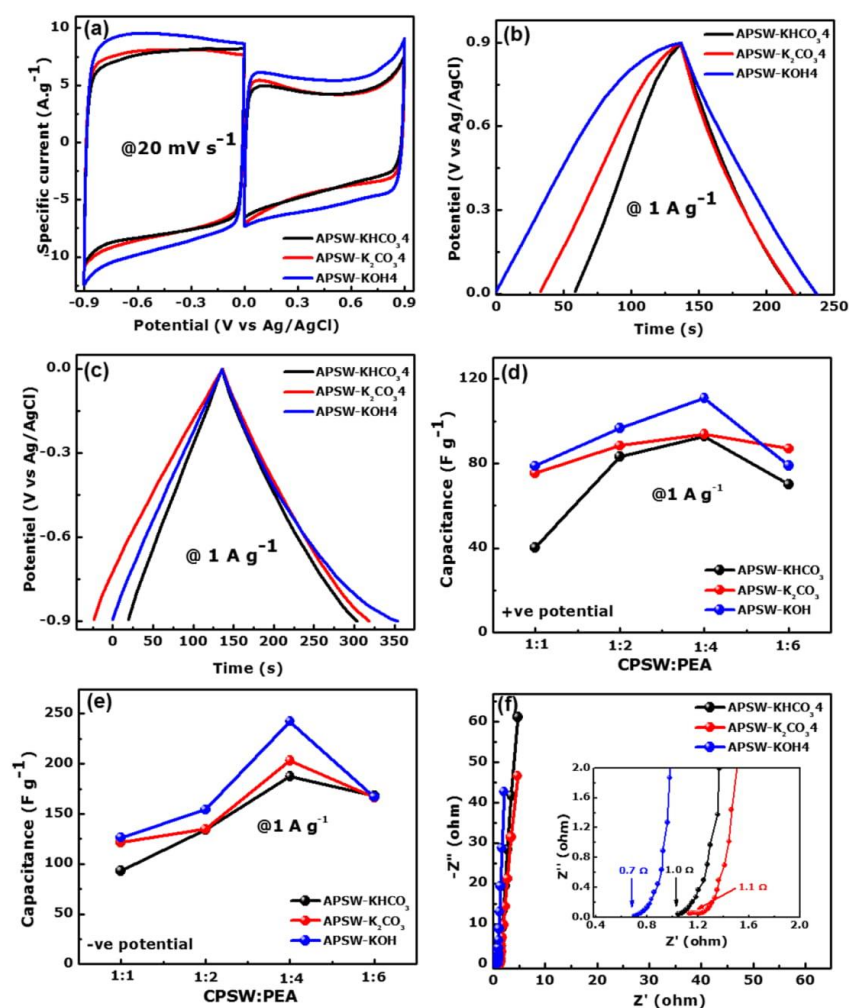


Figure 5. (a) CV curves at 20 mV s⁻¹ scan rates in positive and negative potential windows, (b,c) GCD plots at 1 A g⁻¹ in positive and negative potential windows, respectively of the APSW-Y4 electrodes, (d,e) specific capacitance as a function of the ratio CPSW:PEA in positive and negative potential windows, (f) Nyquist plot of the APSW-Y4 samples.

electrode/electrolyte interface. Figure 5(f) displays the Nyquist plot for the APSW-Y4 sample electrodes with a quasi-vertical line parallel to imaginary Z'' -axis in the low frequency region. This is a clear indication that all the samples exhibit mainly a capacitive form of energy storage. The deviation from the complete vertical line in an ideal capacitor is related to the presence of a little ionic resistance even with the dominant capacitive response. The overall length of the Nyquist plot is linked to the nature of the ion diffusion length within the electrode material.

The real Z' -axis intercept in the high frequency region describes the equivalent series resistance (ESR) values for the different sample electrodes and is shown in the inset to Fig. 5(f). This resistance is composed of the resistance of the electrolyte ions, internal resistance of the activated carbon electrode material and the interfacial contact resistance between the current collector and active material. The APSW-KOH4 sample electrodes exhibited the lowest ESR and the shortest diffusion path length in addition to a much more ideal response with respect to its vertical profile parallel to the $-Z''$ -axis. This shows a good electrode–electrolyte interaction and fast ion diffusion occurring at the electrode–electrolyte interface, resulting in low impedance values. The surface interaction at the electrode–electrolyte interface is greatly influenced by the surface chemistry of the electrode material.

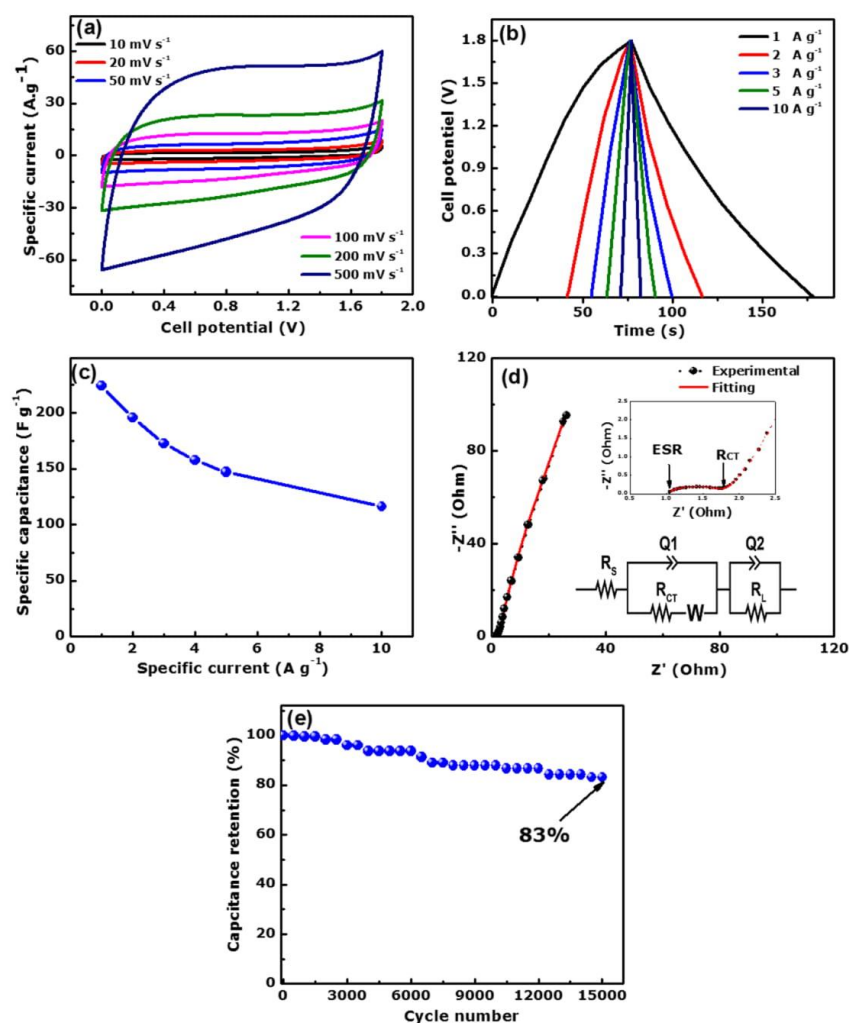


Figure 6. Electrochemical measurement of the APSW-KOH4//APSW-KOH4 symmetric cell displaying. (a) CV curves at different scan rates. (b) GCD plots at different specific currents, (c) specific capacitance as a function of specific current, (d) Nyquist plot and (e) capacitance retention against cycle number at 5 A g⁻¹.

The presence of a higher D/G defect ratio and the larger amount of amorphous carbon domains in APSW-KOH4 caused higher affinity for aqueous KNO₃ electrolyte ions resulting in surface hydrophilicity and good carbon surface wettability. Secondly, the large pore volume and increased specific surface area of the APSW-KOH4 allowed for easier accessibility of the electrolyte ions to the electrode surface. Overall, the good textural properties and the distinct interfacial surface features of APSW-KOH4 contributed to low impedance values. It is evident that the APSW-KOH4 electrode displayed the best storage performance due to the high SSA coupled with the combination of a wide distribution of pore sizes, which provides adequate electrochemically active sites and easy diffusion path for the electrolyte ions.

Based on the most promising material and electrochemical characteristics exhibited by the APSW-KOH4 sample electrode, a symmetric device (full cell) with APSW-KOH4//APSW-KOH4 material electrodes was assembled accordingly.

Figure 6(a) presents the CV profiles of the APSW-KOH4//APSW-KOH4 symmetric cell in a similar 2.5 M KNO₃ neutral electrolyte.

An extended operating cell potential of 1.8 V was obtainable at different scan rates ranging from 10 to 500 mV s⁻¹. A typical rectangular shape was retained up to 0.5 V s⁻¹ demonstrating its high rate capability and the fast ionic diffusion within the material electrode.

The galvanostatic charge-discharge plots at different specific current (1–10 A g⁻¹) is shown in Fig. 6(b). The GCD curves exhibited a symmetric and quasi-linear charge-discharge profile coupled with a small IR drop indicating an impressive electric double layer capacitive feature.

In order to determine the specific capacitance per single electrode C_{el} for the full device, the Eq. 8 below is used⁵⁷;

$$C_{el} = 4 \frac{I \Delta t}{\Delta V} \quad (8)$$

where I (A g⁻¹) is the constant specific current, Δt (s) is the discharge time from the slop of GCD, and ΔV (V) is the full cell potential.

The calculated specific capacitance values (from the GCD curves) as a function of the specific current is shown in Fig. 6(c). A high specific capacitance per electrode of 224.3 F g⁻¹ was recorded at 1 A g⁻¹ specific current for the symmetric device. This is comparable to the values obtained in the literature on similar activated carbon from other biomass resources^{36,58,59}.

The symmetric cell exhibited an equivalent series resistance (ESR) and charge transfer resistance (R_{CT}) of 1.0 Ω and 0.8 Ω respectively (Fig. 6(d)). The skewed vertical line at the low-frequency region is attributed to some resistance to fast ion-diffusion, which results in its deviation from the ideal capacitive trend.

The equivalent circuit modelled using the data from the Nyquist plot with a ZFIT fitting tool from the EC-Lab software is shown in inset to the Fig. 6(d).

In the circuit, the ESR component is connected in series with the R_{CT} and the Warburg impedance (W) which are linked in parallel with the constant phase element (Q1).

The constant phase element, CPE (denoted as Q) is related to the capacitive behaviour and roughness of the porous activated carbon electrode. This is expressed as:

$$Q = \frac{1}{T(j\omega)^n} \quad (9)$$

where T represent the frequency independent constant with dimensions of (F cm⁻²) ^{n} and ω is the angular frequency. The values for n range from -1 to 1. When $n = 0$, the CPE element is an ideal resistor; when $n = 0.5$, the CPE transforms to a Warburg element; for $n = 1$, a pure capacitance is depicted; when $n = -1$, the CPE functions as an inductor^{60,61}. A Warburg element is observed at the high to low frequency transition and can be determined by:

$$W = \frac{A}{\omega^{0.5}} \quad (10)$$

where A represents the Warburg coefficient, ω is the angular frequency and $n = 0.5$ ^{60,62}.

The skewed vertical line at the low-frequency region from the ideal capacitive trend could be attributed to the leakage resistance (denoted R_l) which is in parallel with the leakage capacitance (Q_2). The summarized values of the fitting parameters are shown in the Table S4.

Figure 6(e) exhibits the capacity retention of the APSW-KOH4//APSW-KOH4 symmetric device as a function of the cycle number at a specific current 5 A g⁻¹. A satisfactory electrochemical stability (83% capacity retention) for the device was recorded even up to 15,000 constant galvanostatic charge-discharge cycles.

The Ragone plot presents the variation of the specific energy (E_d) with the specific power (P_d) as shown in Fig. 7(a). The energy E_d (Wh kg⁻¹) and the specific power (W kg⁻¹) for the symmetric cell were evaluated using Eqs 11 and 12 below respectively⁵⁷:

$$E_d = \frac{C_{el}(\Delta V)^2}{28.8} \quad (11)$$

$$P_d = 3600 \frac{E_d}{\Delta t} \quad (12)$$

where C_{el} (F g⁻¹), ΔV (V) and Δt are as described in Eq. (8).

A specific energy of the symmetric cell of 25.2 Wh kg⁻¹ was obtained with a corresponding specific power of 0.9 kW kg⁻¹ at a specific current 1 A g⁻¹.

More importantly, the specific energy was still maintained at 13.0 Wh kg⁻¹ with a specific power of 9 kW kg⁻¹ even with the specific current being increased to 10 times its original value (10 A g⁻¹).

The reported values are much higher as compared to other carbonaceous raw peanut shell activated with K₂CO₃ and KHCO₃ as shown in Fig. S7 of the supporting information.

A comparison of the results from this study with other similar selected reports in the literature on activated carbon from biomass waste materials is presented in Fig. 7(a) and Table 1.

The specific energy and specific power reported in this work for APSW-KOH4 in 2.5 M KNO₃ was relatively higher and in some cases, comparable with those related reports on symmetric supercapacitors based on biomass-derived carbons operated in neutral aqueous electrolytes.

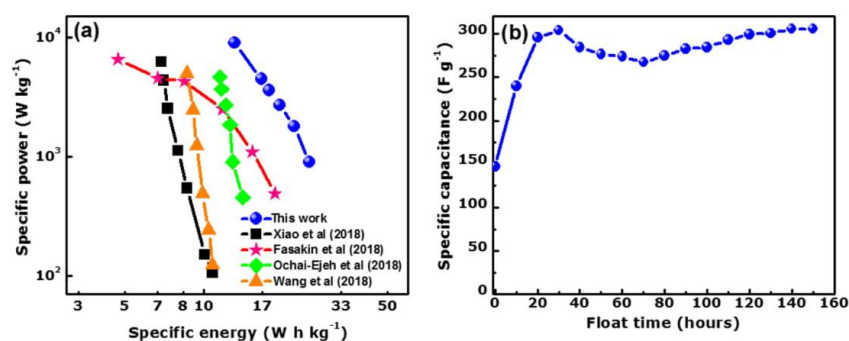


Figure 7. (a) Ragone plot of the APSW-KOH4//APSW-KOH4 device and (b) specific capacitance against voltage holding time for a period of 150 h at 5 A g⁻¹.

Materials	PEA	Electrolyte	Specific current (A g ⁻¹)	Specific energy (Wh kg ⁻¹)	Specific power (W kg ⁻¹)	Ref
Peanut shell	ZnCl ₂	1 M H ₂ SO ₄	0.5	10.8	106.9	²⁷
Banana peels	KOH	1 M NaNO ₃	0.5	18.6	485	³⁶
Soybean Pods	KOH	1 M Na ₂ SO ₄	0.5	22.28	450	⁶³
Quercus Suber	KHCO ₃	3 M KNO ₃	0.5	14	450	³⁵
Quercus Suber	KOH	1 M Na ₂ SO ₄	0.5	18.6	449.4	⁶⁴
Pueraria	K ₂ CO ₃	6 M KOH	0.5	8.46	123	⁶⁵
Fresh clover stems	KOH	1 M H ₂ SO ₄	0.5	10.7	125	⁶⁶
Coconut shell	KOH	PVA-KOH-CB gel electrolyte	0.5	11	325	⁶⁷
Sawdust	KOH	6 M KOH	0.5	8.4	250	⁶⁸
Waste bagasse	KOH	1 M Na ₂ SO ₄	0.5	22.3	220.9	⁵⁸
White Sugar	KOH	1 M Na ₂ SO ₄	1	19	750	⁶⁹
Peanut shell waste	KOH	2.5 M KNO ₃	1	25.2	900	This work

Table 1. Comparison of electrochemical results of activated carbon from various biomass.

For example, F. O. Ochai-Ejeh *et al.*⁴⁹ reported the synthesis of porous carbon from Quercus Suber using KHCO₃. The full symmetric device was done using the similar aqueous electrolyte 3 M KNO₃ and obtained a specific energy of 14 Wh kg⁻¹ with a specific power of 450 W kg⁻¹ at 0.5 A g⁻¹ specific current.

Recently, Z. Xiao and co-workers²⁷ produced porous carbon using the same biomass peanut shells activated with ZnCl₂. In their report, the electrochemical measurement of the symmetric cell was tested in 1 M H₂SO₄ aqueous electrolyte. The values of the specific energy and specific power were 10.8 Wh kg⁻¹ and 106.9 W kg⁻¹ respectively at 0.5 A g⁻¹.

The high specific energy and power acquired in our work can be related to the high SSA with a large pore volume and the significant degree of amorphous carbon present in the APSW-KOH4 sample contributing to enhancing the electrochemical results.

To further evaluate the stability of the obtained symmetric device, a voltage holding was carried out at an operating cell potential of 1.8 V for a period of 150 h (more than 6 days).

Figure 7(b) displays the specific capacitance as function of the floating time for each 10 h interval. It is worthy to note that the recorded C_s increase remarkably for the first 30 h following a small drop between the 40 to 80 h periods. Thereafter, another increase in charge storage capability was observed up to the 90 h mark before stabilising for higher floating times. An overall increase in the specific capacitance values was observed from 147 to 307 F g⁻¹.

The improvement in the recorded C_s can be attributed to the accessibility of the ions to initially inaccessible pore sites through increased wettability and a large diffusion of ions between the electrolyte/electrode during the long floating time. A higher specific energy of 34.5 Wh kg⁻¹ at 5 A g⁻¹ was obtained after 150 h floating time as compared to the initially recorded specific energy of 16.5 Wh kg⁻¹ before floating test at the same specific current value.

It is obvious that the increase of C_s after being subjected to floating tests also generates a simultaneous increase in the device specific energy (twice compared to the initial value).

Conclusion

The activated carbon from peanut shell waste was successfully synthesized via a two-step carbonization and activation process at elevated temperature using different porosity enhancing agents KHCO_3 , K_2CO_3 and KOH with varying mass ratios (CPSW:PEA). Among the PEAs, the carbonisation/activation process with KOH resulted in a porous carbon material with the best textural properties.

The APSW-KOH4 exhibited the largest specific surface area of $2547 \text{ m}^2 \text{ g}^{-1}$, and pore volume of $1.2 \text{ cm}^3 \text{ g}^{-1}$. The complex pore framework composed of cavities facilitated efficient ionic transport within the material. The Raman spectra clearly illustrated the degree of amorphous carbon present in the lattice structure. XPS analysis of the APSW-KOH4 confirmed the presence of a high concentration of carbon with a little amount of nitrogen and oxygen.

The electrochemical measurement performed on material electrodes in half-cell set-ups demonstrated a reversible operating capability in both the positive (0.0–0.9 V) and the negative (−0.9–0.0 V) potential windows. The assembled symmetric device using the best materials from the textural, structural and initial electrochemical tests (APSW-KOH4//APSW-KOH4) displayed a specific capacitance of 224.3 F g^{-1} , a high specific energy of 25.2 Wh kg^{-1} corresponding to power density of 0.9 kW kg^{-1} at 1 A g^{-1} in a cell potential of 1.8 V.

In addition, a good device stability was demonstrated with 83% capacity retention after 15000 cycles and an improvement in electrochemical energy storage capability over a 150 hours floating time (more than 6 days).

The obtained results validate the potential adoption of the porous activated carbon from peanut shell waste as a suitable electrode material for enhanced energy storage.

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Author Contributions

N.F.S., N.M.N., B.D.N. and D.M. conceived and designed the study. N.F.S. performed all the experiments as well as the material and electrochemical characterization. M.J.M. and B.K.M. assisted with the Raman and XPS analysis. All authors contributed to the interpretation of results and discussion. N.M. and B.D.N. supervised the experiments and revised the paper.

Additional Information

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4.1.3 Concluding Remarks

Peanut shell waste derived activated carbon has been successfully prepared through two steps carbonization and chemical activation using KHCO_3 , K_2CO_3 and KOH as activating agents in different mass ratios. The obtained results demonstrate that the activated carbon from peanut shell (APSW) sample synthesized with KOH at a mass ratio of 1 to 4 (APSW-KOH4) presented the best structural, textural and electrochemical properties as compared to the other samples. The APSW-KOH4 exhibits a high specific surface area of up to $2547 \text{ m}^2 \text{ g}^{-1}$ with a coexistence of micro, meso and macropores.

The as-fabricated symmetric device (APSW-KOH4//APSW-KOH4) delivered a good charge storage capacity with a specific capacitance of 224.3 F g^{-1} , a specific energy of 25.2 W h kg^{-1} with a corresponding specific power of 0.9 kW kg^{-1} at a specific current of 1 A g^{-1} in 2.5 M KNO_3 aqueous electrolyte. Furthermore, a good cycling stability was recorded with a capacitance retention of 83% after 15000 cycles as well as an enhancement of the electrochemical performance after floating time of 150 hours at 1.8 V cell potential. These results promote the use of peanut shell waste to produce a sustainable electrode material for energy storage device.

4. 2 Ex-situ nitrogen-doped porous carbons derived from peanut shell waste as electrode materials for high performance supercapacitor

4.2.1 Introduction

Recently, researchers have devoted great interest to improve the electrochemical performance of the electrode materials in energy storage fields, including supercapacitors and batteries. Porous carbons have been demonstrated as promising electrode materials for supercapacitors, especially for an electrical double-layer capacitor (EDLC) due to their versatile properties such as: Chemical stability, excellent electrical conductivity, high active surface area, well-defined pore structure [1][2]. Various techniques such as physical/chemical activation method, microwave irradiation, hard/soft template method and so on have been adopted to produce porous carbon derived from zeolites, metals framework, biomass, polymers etc. [16]. Among them, porous carbon derived from biomass source has gained more attention due to their low cost, renewable nature, sustainable and abundance [17].

Electric double-layer capacitance originating from the electrostatic adsorption of the ions between electrolyte/electrode interface can be enhanced using different approaches [18][19][20]. Heteroatom-doping of carbons using sulfur (S), nitrogen (N) or boron (B) is one of the most effective approaches for improving the electrochemical properties of porous carbon materials [21][22][23]. Of these, nitrogen atom doping has been proved suitable to enhance the electron/donor characteristics, the electrical conductivity, the surface chemistry which all facilitate the electrochemical activity of porous carbons resulting in improved EDLC performance [24][25]. The heteroatom doping of porous carbons can be achieved through two main approaches namely *in-situ* and *ex-situ (post) doping* route using various nitrogen sources melamine, polyaniline, urea, ammonia, polypyrrole, etc. [26][27][28].

For instance, Han and co-workers [27] have used Pueraria as a carbonaceous material precursor to synthesize nitrogen-doped porous activated carbon (NPC) using two-step methods. Their study indicated that nitrogen-doping contributed to the enhancement of the specific capacitance from 44 F g^{-1} for un-doped electrode sample to 250 F g^{-1} for NPC electrode at a specific current of 0.5 A g^{-1} in 6 M KOH .

Another report by Gou et al. [28] revealed an improvement of specific capacitance for porous nitrogen-doped carbon derived orange peels (PN-OPC) from 138 F g^{-1} to 255 F g^{-1} at a specific current of 0.5 A g^{-1} using 6 M KOH upon treatment with a nitrogen-containing precursor.

In the previous study (section 4.1), APSW had a low nitrogen doping which we refer to as an *in-situ N-doped* coming from two-step processes. Initially, the raw peanut shell waste (PSW) was mixed with urea (which acted as a source of nitrogen) and pyrolyzed at 600°C . Afterwards, the pyrolysis sample was chemically activated at 850°C and resulted in N-doped activated carbon material with a low nitrogen-content ($0.6 \text{ at\%}$) [29]. To overcome this drawback due to volatilization of the nitrogen during activation route, we suggest the synthesis of post-N-doped of porous carbon. The *ex-situ doping (post-doping)* of the carbons is superior to the in-situ doping approach as it allows for minimal loss of heteroatoms even at higher temperatures. In this work, the *post-N-doped* peanut shell activated carbon that we denote it as NPAC instead of APSW even though the source of carbon was from PSW, was prepared via a two-step approach, namely, chemical activation with KOH of PSW to produce activated carbon denoted as PAC, followed by a *post-doping* step using melamine to produce nitrogen doped activated carbon (NPAC). The *post-N-doping* of the ACs significantly influenced the surface chemistry as well as the physicochemical properties of the NPACs.

Moreover, this study focused also on the effect of the mass ratio of peanut shell waste (PSW) to varied activating agent, KOH (1:0.5, 1:1 and 1:2) on both PAC and NPAC materials and their application in supercapacitors.

4.2.2 Results and discussion

The results obtained from the study of the *ex-situ* nitrogen-doped activated carbon are described in details in the publication below:



Ex-situ nitrogen-doped porous carbons as electrode materials for high performance supercapacitor



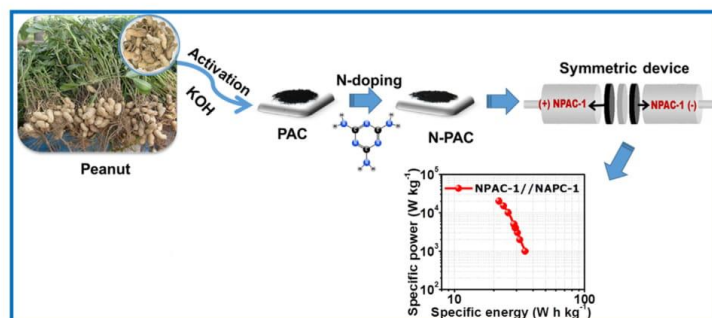
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ABSTRACT

Nitrogen (N) doping of porous carbon materials is an effective strategy for enhancing the electrochemical performance of electrode materials. Herein, we report on *ex-situ* (post) nitrogen-doped porous carbons prepared using a biomass waste, peanut shell (PS) as a carbon source and melamine as the nitrogen source. The synthesis method involved a two-step mechanism, initial chemical activation of the PS using KOH and *post* N-doping of the activated carbon. The effect of the activating agent/precursor ratio and the *ex-situ* N-doping on the structural, textural, electrochemical properties of the porous carbons was studied. The *ex-situ* N-doped porous carbon with an optimum amount of KOH to PS exhibited the best capacitance performance with a specific surface area (SSA) of $1442 \text{ m}^2 \text{ g}^{-1}$ and an enriched nitrogen content (3.2 at %). The fabricated symmetric device exhibited a 251.2 F g^{-1} specific capacitance per electrode at a gravimetric current of 1 A g^{-1} in aqueous electrolyte (2.5 M KNO_3) at a wide cell voltage of 2.0 V . A specific energy of 35 Wh kg^{-1} with a corresponding specific power of 1 kW kg^{-1} at 1 A g^{-1} was delivered with the device still retaining up to 22 Wh kg^{-1} and a 20 kW kg^{-1} specific power even at 20 A g^{-1} . Moreover, long term device stability was exhibited with an 83.2% capacity retention over 20 000 charge/discharge cycles and also a good rate capability after 180 h of floating at 5 A g^{-1} . This great performance

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of the symmetric supercapacitor can be correlated to the surface porosity and *post* nitrogen-doping effect which increased the electrochemically-active sites resulting in a remarkable charge storage capability.
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1. Introduction

Porous carbons have received considerable attention in the scientific community over recent years. They have been applied in various energy-related systems such as sensors, hydrogen storage, supercapacitors and batteries [1]. This is due to their high electrical conductivity, chemical and thermal stability, ease of processability and ability to tune their textural surface properties [2,3]. More importantly, these properties are advantageous in the fabrication of electrode materials for electrical double-layer capacitors (EDLCs). In principle, EDLCs energy storage mechanism entails an electrostatic interaction between the electrode/electrolyte interface. Therefore, the performance of the EDLCs depends on the reversible ion adsorption in the porous carbon electrode materials [4,5]. As such, the development of suitable porous materials with improved electrochemical performance has received immense efforts. These porous carbons can be derived from biomass [6,7], polymers [8,9], metal-organic frameworks [10,11] and zeolites [12,13], using a wide range of synthesis techniques such as physical and chemical activation [14], templating method [15], template-free method [16] and microwave irradiation [17] among others. During the synthesis of porous carbons, it is possible to tune their physicochemical properties and surface features and consequently impact on their electrochemical performance.

Typically, the electrochemical performance of porous carbons is dependent on the surface area, electrical conductivity and the surface interaction between the electrode and the electrolyte interface [1]. Thus, several strategies have been developed to enhance the electrochemical performance of porous carbon-based electrode materials. One of the approaches involves the modification of the carbon surface chemistry by use of surface functionalization process [18–20]. For instance, Wu et al. [20] synthesized porous carbons using rod-like hydroxyapatite (as a template) and sucrose (carbon source) followed by an oxidation process using nitric acid (HNO₃).

The authors suggested that the modification of the surface chemistry of the porous carbons contributed to the improvement of the specific capacitance from 110 F g⁻¹ in the non-modified carbons to 128 F g⁻¹ in the modified counterparts. They correlated it to the increase in the oxygen content and the creation of new functional groups after acid treatment [20]. The surface functional groups play an important role in the enhancement of the surface wettability at the electrode/electrolyte interface and consequently improve the electrochemical performance of the electrode materials.

A second approach for improving the electrochemical performance of porous carbons is the two-step activation process that allows for the creation of a porous carbon network [21–23]. For example, Cheng et al. [21] used a two-step activation process to synthesize a porous activated carbon with hierarchical pore network and improved surface features. The first step involved the activation of shiitake mushroom with H₃PO₄ at 500 °C which exhibited a specific surface area (SSA) of 1341 m²g⁻¹ and a capacitance of 196 F g⁻¹. The second step was done by further activation of the carbon with KOH at 800 °C which yielded an improvement of SSA and specific capacitance of 2988 m²g⁻¹ and 306 F g⁻¹, respectively. The two-step process aided in increasing the number of oxygenated functional groups on the carbon surface as well as the surface area as compared to the one-step activation.

Lastly, heteroatom doping of porous carbons with nitrogen (N), boron (B), oxygen (O), sulfur (S), and phosphorous (P) atoms has proved to enhance the electrochemical performance in supercapacitors [24–27]. It is well known that the incorporation of heteroatoms in the carbon matrix changes the electron-donating or accepting character and conductivity of carbons and thus, influencing their capacitance and electrochemical properties [28]. Compared to other heteroatoms, nitrogen is of great interest as its atomic size is comparable to that of carbon (65 pm vs 70 pm).

Therefore, different nitrogen-containing precursors such as melamine, urea, ammonia, polyaniline and polypyrrole have been used to synthesis N-doped porous carbons [29–32]. Two main approaches are employed for nitrogen doping of carbons; *in-situ* and *ex-situ* doping process [33]. *In-situ* doping treatment can be done either by direct pyrolysis of nitrogen-containing precursors for example organics polymers [34], biomass [35], ionic liquids [36] or by the growth of carbon nanomaterials in the presence of a nitrogen precursor [37]. In this regard, *in-situ* nitrogen-doping of activated carbons can be carried out by direct activation of nitrogen-containing biomass or by the activation of carbonaceous sources in the presence of a nitrogen-containing precursor. The main drawback of this process is that most of the oxygenated nitrogen groups are lost at higher temperatures (during activation) resulting in a lower nitrogen content being incorporated within the carbon matrix.

In our previous work, we synthesized an *in situ* N-doped porous carbon by the direct pyrolysis of a mixture of peanut shell waste biomass (carbon source) and urea (as a nitrogen source) at 600 °C followed by activation at high temperature (850 °C) [38]. We obtained a low nitrogen (0.6 at%) content and this was attributed to the volatilization of the nitrogen-containing groups during the activation step. To circumvent this problem, we propose the *ex-situ* N-doping of porous carbons as it will allow the incorporation of larger nitrogen content within the carbon matrix. Typically, the *ex-situ* N-doping process requires the introduction of nitrogen source into the matrix of an already activated porous carbon nanomaterial via thermal treatment [39]. While the amount of nitrogen content incorporated in porous carbons can be controlled by the precursor used, ammonia gas is the commonly used source of nitrogen which not only limits the N-content but is also not environmentally friendly [40]. Moreover, most of the studies on N-doped porous carbons emphasize the effect of the mass ratio of carbon to nitrogen (C/N) precursor as well as the doping temperature effects [39,41]. To this end, very few reports exist on the effects of the mass ratio of activating agents on *ex-situ* N-doped activated carbons and their application in supercapacitors.

In the present study, the properties of the *ex-situ* nitrogen-doped porous carbons obtained from peanut shell are investigated. The synthesis method involved two steps mechanism: (1) Chemical activation of the peanut shell using KOH, and (2) nitrogen doping of the porous peanut activated carbon. Their electrochemical performances were evaluated in a three and two-electrode configuration using an aqueous electrolyte (2.5 M KNO₃). The effect of the activating agent/precursor ratio (KOH/PS) and the *ex-situ* N-doping on the electrochemical behaviour was studied. Despite the many reports on biomass-derived porous carbon materials in the literature, to the best of our knowledge, studies on the strong influence of the chemical activation ratio and *ex-situ* N-doping on the electrochemical performance of these materials have been

rarely reported. Thus, this study will not only provide a procedure for retaining the relatively high *N*-doping concentration but also elucidate the vital role of textural and structural parameters for optimum electrochemical properties of *N*-doped porous carbons in supercapacitors.

2. Experimental section

2.1. Precursor materials

The peanut shell waste used in this study was collected from a marketplace in downtown Saint Louis, Senegal. Argon gas, Ar (99%) was purchased from Afrox, South Africa. Potassium hydroxide, KOH (99%), melamine, $C_3H_6N_6$ (99%), hydrochloric acid, HCl (37%), potassium nitrate, KNO_3 (99.99%), carbon acetylene black (99.95%), polyvinylidene fluoride, PVDF (99%) and *N*-methyl-2-pyrrolidone, NMP (99%), were all purchased from Merck (Pty) Ltd, South Africa. Polycrystalline nickel foam with an areal density of 420 g m^{-2} and 1.6 mm thickness and microfiber filter paper (0.18 mm thickness) were procured from Alantum Munich, Germany, and ACE chemicals, South Africa, respectively.

2.2. Preparation of pristine and ex-situ *N*-doped activated carbons

The peanut shell (PS) waste serving as a raw material (RM) was thoroughly washed with deionized water (DI) and dried in an oven pre-set at 60°C . The RM was ground and mixed with potassium hydroxide activating agent (AA) in different mass ratios of 1:0.5, 1:1 and 1:2 (PS:AA). The mixture was transferred into a tubular furnace and heated-up to 850°C at a heating rate of 5°C min^{-1} under argon gas and held at the final temperature for 1 h. The obtained product was impregnated with aqueous 3 M HCl to remove all traces of unreacted AA, sonicated for 12 h and then washed with DI until a neutral pH was achieved. Thereafter, the solid peanut shell activated carbon sample was filtered and labelled as PAC-0.5, PAC-1 and PAC-2 for PS:AA mass ratios of 1:0.5, 1:1 and 1:2, respectively. These samples were dried for further characterization.

An *ex-situ*-doping route was used to prepare the nitrogen-doped peanut shell activated carbon (NPAC). Firstly, 5 g of melamine used as a nitrogen source was added to 1 g of the as-synthesized PAC-0.5 sample in an optimized mass ratio. Pyrolysis of the sample at 850°C was carried out for 1 h under a stream of inert argon gas to produce NPAC-0.5. A similar *ex-situ*-doping procedure was undertaken for the PAC-1 and PAC-2 samples to yield NPAC-1 and NPAC-2, respectively. To further emphasize this unique *ex-situ*-doping concept applied in this study, melamine was introduced prior to activation for a good comparison. The nitrogen content in NPAC-samples was compared from characterization carried out.

2.3. Material characterization

The N_2 sorption isotherms of the samples were measured at 77 K from 0.01 to 1.0 relative pressure (P/P_0) using a Micrometrics TriStar II 3020 pore analyzer. The active surface area was determined using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method was used to describe the pore size distribution. A 532 nm laser-powered WITec alpha300 RAS + confocal Raman microscope (WITec, Germany) was used for the detailed Raman analysis. A PANalytical X'Pert Pro powder diffractometer with Co-K α radiation ($\lambda = 1.789 \text{ \AA}$) was used to collate the X-ray diffraction (XRD) patterns. The surface morphology of the PAC and NPAC samples were characterized on a Zeiss Ultra-plus 55 field emission scanning electron microscope (FE-

SEM) operated at 1.0 kV. The chemical composition of the NPAC samples was analyzed by X-ray photoelectron spectroscopy (XPS, VG Escalab 220i-XL) coupled with a monochromatic aluminium K α source of radiation.

2.4. Electrochemical characterization

The working electrodes used for electrochemical analysis were fabricated with 80 wt% active materials, 10 wt% carbon acetylene black and 10 wt% polyvinylidene difluoride (PVDF) in an agate mortar with the final addition of few drops of *N*-methylpyrrolidone (NMP) to form a slurry. The slurry was coated on clean Nickel foam (NF) grids followed by subsequent vacuum drying of the electrodes for 12 h at 80°C .

The electrode materials' electrochemical performances in half- and full-cell configurations were evaluated in 2.5 M KNO_3 aqueous electrolyte using a Bio-Logic VMP-300 16-channel potentiostat (Knoxville, USA) at room temperature. The three-electrode (half-cell) measurements were performed using a Swagelok T-cell composed of silver (Ag)-disc reference electrode, carbon disc counter electrode and a microfiber filter paper separator.

The symmetric devices were assembled in the Swagelok testing cell using similar materials present on both electrodes with the charge/mass balancing taken into consideration. The cyclic voltammetry (CV) profiles were evaluated at different scan rates (in mV s^{-1}) and the galvanostatic charge-discharge (GCD) plots were obtained by varying the specific current (in A g^{-1}). The electrochemical impedance spectroscopy (EIS) measurements were done on an open circuit voltage, V_{OC} at 100 kHz to 10 mHz frequency range.

The specific capacitance for the half cell C_s (in F g^{-1}) and the single electrode for the symmetric device C_{el} (in F g^{-1}) was determined from the discharge slope of the GCD plots using the Eqs. (1) and (2), respectively [42,43]:

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (1)$$

$$C_{el} = 4 \frac{I\Delta t}{m\Delta V} \quad (2)$$

where I (in A) is the current, m (in g) represent the total mass of the electrode Δt (in seconds) is the discharge time from the slop of GCD, and ΔV (in V) is the operating voltage.

The specific energy E_d (Wh kg^{-1}) and the specific power P_d (W kg^{-1}) for the symmetric device were evaluated according to the Eqs. (3) and (4) [44]:

$$E_d = \frac{C_{el}(\Delta V)^2}{28.8} \quad (3)$$

$$P_d = 3600 \frac{E_d}{\Delta t} \quad (4)$$

3. Results and discussion

3.1. Morphological, textural and structural characterization

Fig. 1 shows the SEM images of the pristine and the *N*-doped PAC samples at low and high magnification (see insets to images). All the synthesized carbon materials displayed an interconnected porous structure with irregular-shaped pores. It can be seen that the activation of the peanut shell with potassium hydroxide leads to the creation of a porous framework on the structure of the carbons. This is expected to occur due to the release of carbon monoxide (CO) and carbon dioxide (CO_2) gases upon the reaction of KOH and carbon [45]. The decomposition of the KOH generates potas-

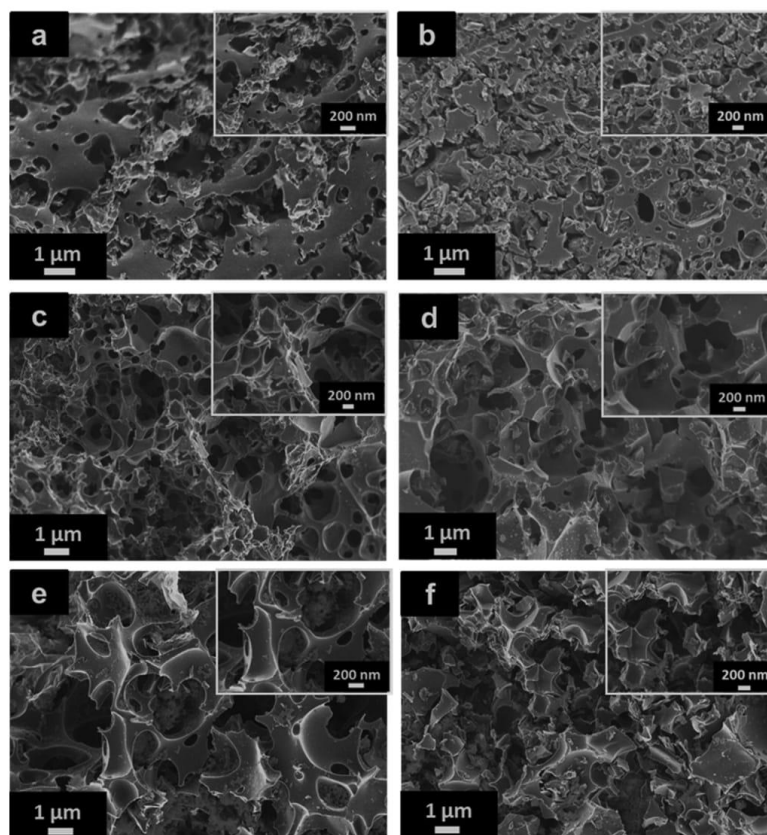


Fig. 1. SEM images of the pristine (a) PAC-0.5, (c) PAC-1, (e) PAC-2 and N-doped (b) NAP-0.5, (d) NPAC-1 and (f) NPAC-2 samples at low magnification (insets showing the high magnification).

sium bicarbonate, metallic potassium and hydrogen gas. At elevated temperatures ($>700\text{ }^{\circ}\text{C}$) the decomposition of the potassium bicarbonate produces CO_2 and CO gases which promotes further pore activation through carbon gasification [46,47]. The as-prepared PACs display a tunable morphology and porous structure as shown in Fig. 1(a), (c) and (e).

In addition, the increase of the mass ratio of KOH from 0.5 to 1 resulted in a more evident porous morphology (PAC-1 in Fig. 1(c)). However, upon a mass ratio increase of KOH to 2, a highly distorted interconnected porous structure in the PAC-2 was observed (Fig. 1(e)). After nitrogen doping, the morphology of the NPACs materials exhibited a less porous structure as compared to their pristine counterparts (Fig. 1(b), (d) and (f)). This could be ascribed to the carbon and nitrogen (C/N) patches emanating from melamine decomposition that can block the already existing pores on the carbon matrix during the *ex-situ* nitrogen doping step [18,48].

The electron dispersive spectroscopy (EDS) elemental mapping was carried out to determine the elemental composition of the N-PAC samples with an example of N-PAC-1 shown in Fig. S1. This EDS mapping reveals a uniform distribution of the C, O and N elements which similar to all N-PAC samples.

The textural properties of the PAC and NPAC samples were investigated by nitrogen sorption isotherms and the pore size dis-

tribution analysis. Fig. 2(a,b) revealed the N_2 adsorption-desorption isotherms of the PACs and NPACs samples with different mass ratios of (PS:AA) 1:0.5, 1:1 and 1:2.

The isotherm curves of all the samples showed a hybrid type I and IV characteristics with a H4 hysteresis loop suggesting the presence of micropores and mesopores [49]. At a low relative pressure range, the isotherms of the obtained PACs and NPACs showed steep N_2 adsorption exhibiting an abundant presence of micropores besides the hysteresis loop reflecting the presence of mesopores. The pore size distribution plots illustrated in Fig. 2(c,d) confirm the existence of both the micropores and mesopores in the pristine (undoped) and N-doped carbon derived from peanut shell.

Table 1. summarizes the textural properties of the PAC and NPAC samples. It is evident that the BET specific surface area (SSA) increases with increasing mass ratio of KOH from 0.5 to 1 and decreases with a further increase to 2. A similar trend is noticed for the total pore volume and the micropore volume of the carbon materials. The PAC-1 and NPAC-1 samples exhibit the highest surface areas of $1557\text{ m}^2\text{ g}^{-1}$ and $1442\text{ m}^2\text{ g}^{-1}$ as well as the highest pore volumes of $0.76\text{ cm}^3\text{ g}^{-1}$ and $0.69\text{ cm}^3\text{ g}^{-1}$, respectively. These results demonstrate the creation of stable pores that contribute to the SSA improvement with activation using a moder-

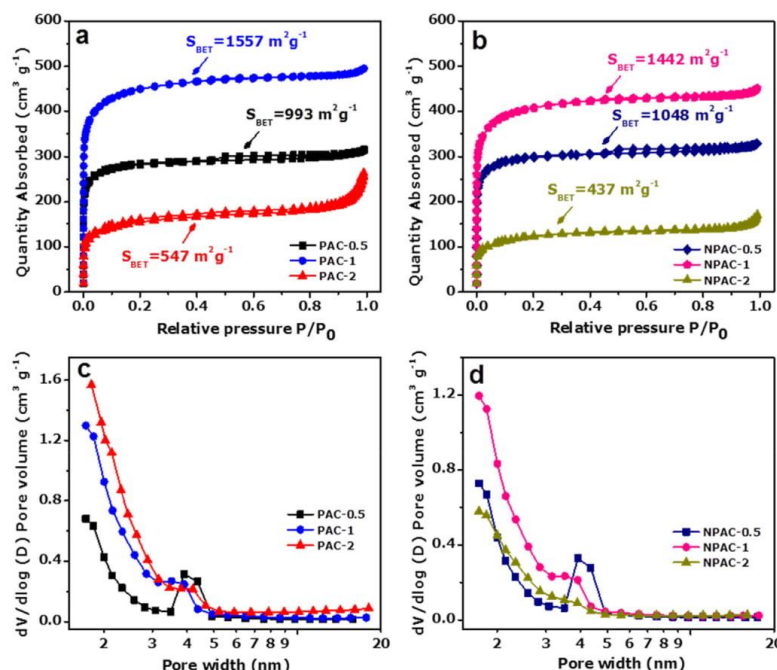


Fig. 2. (a–b) N_2 absorption-desorption isotherms; (c–d) pore size distribution of the pristine and N -doped samples obtained at different mass ratios of KOH.

Table 1

Textural properties and Raman data of the pristine and N -doped samples.

Samples		Textural properties			Raman data		
		S_{BET} ($m^2 g^{-1}$)	V_{total} ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	D-band (cm^{-1})	G-band (cm^{-1})	I_D/I_G ratio
Pristine	PAC-0.5	993	0.48	0.42	1339	1589	0.95
	PAC-1	1557	0.76	0.63	1341	1590	0.96
	PAC-2	548	0.38	0.19	1348	1591	0.98
N -doped	NPAC-0.5	1048	0.50	0.43	1342	1590	1.02
	NPAC-1	1442	0.69	0.59	1340	1591	1.03
	NPAC-2	437	0.25	0.15	1344	1590	1.21

ate KOH content. However, the lowest SSA assigned to the PAC-2 and NPAC-2 materials ($548 m^2 g^{-1}$ and $437 m^2 g^{-1}$) could be attributed to the excess amount of KOH as well as less extent of activation as further affirmed by the decrease in the total pore volume and the micropore volume as depicted in Table 1. The excessive amount of KOH may have resulted in saturation of the reaction sites with unreacted KOH that inhibited the creation of extra pores after a particular point during the process of pores creation. This leads to the inhibition of pore creation and also the collapse of the interconnected carbon [50]. The SSA of the NPAC-1 and NPAC-2 materials was found to be slightly lower than that of the PAC-1 and PAC-2. As proposed earlier from the morphology results, this can be ascribed to the decomposition of melamine into patches of nitrogen-containing functionalities (carbon/nitrogen deposits) which can cover some of the pre-existing pores in the PAC [19].

In addition, the *ex-situ* N -doping of the carbons with melamine can cause the destruction of the pore walls and the blockage of some of the pores by the functional groups [18]. Consequently,

NPAC-1 and NPAC-2 displayed lower pore volumes as compared to PAC-1 and PAC-2, respectively. This decrease in surface area and pore volume upon *ex-situ* N -doping of PAC materials has been observed elsewhere and is in agreement with those studies on N -doped carbons [48,51,52].

The structure of the as-prepared carbon samples was further investigated by Raman spectroscopy and XRD. Fig. 3(a,b) display the Raman spectra of the pristine and the N -doped carbon materials at different mass ratios of potassium hydroxide. The spectra of all samples show the D peak ($1339–1348 cm^{-1}$) and G peak ($1589–1591 cm^{-1}$) bands attributed to the disorder (defect) in the graphitic structure and the tangential vibration of the sp^2 carbon atoms, respectively [53]. The ratio of the relative intensity of the D and G peaks (I_D/I_G) is used to determine the graphitization degree of the carbon materials [54]. The I_D/I_G values of PACs and NPACs (as shown in Table 1) indicate that increasing the mass ratio of the KOH led to a higher degree of disorder (higher I_D/I_G ratios) in the carbon matrix. These results suggest that the KOH activation could generate more active sites in the carbon structure corresponding to

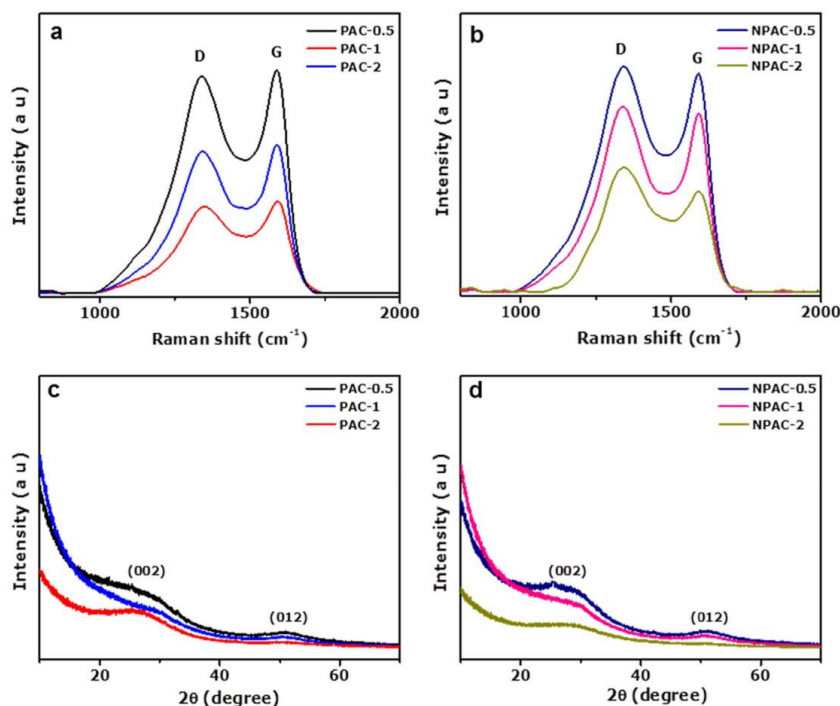


Fig. 3. (a–b) Raman spectra and (c–d) XRD pattern of the pristine and the N-doped samples.

other previous reports on activated carbons [55,56]. Fascinatingly, the NPAC samples revealed even higher I_D/I_G values as compared to the pristine carbons (PAC). This can be ascribed to the introduction of nitrogen in the carbon structure creating more structural distortions which affect the intensity of the D band [57]. The presence of even more defective sites on the graphitic lattice could aid electrochemical surface reactions.

Fig. 3(c,d) show the XRD patterns of the as-prepared carbon samples. The PACs and NPACs samples display two diffraction peaks at 2θ values of 26 and 51° which correspond to the (0 0 2) and (0 1 2) planes in the graphite structure, respectively. These peaks were broad indicating that all the carbon materials are amorphous carbon confirming the low degree of graphitic crystalline structure [58]. However, the diffraction peaks of N-doped carbon samples are slightly shifted to higher 2θ values compared those of undoped samples, which are due to the incorporation of nitrogen in the carbon [59].

3.2. XPS analysis

The XPS analysis was performed to determine the chemical composition and surface chemistry after the N-doping process of the pristine activated carbon materials. Fig. 4(a) displays the XPS survey spectra of the NPAC-0.5, NPAC-1 and NPAC-2 samples which indicated the presence of three peaks C1s (285 eV), N1s (399 eV) and O1s (533 eV) confirming the successful incorporation of the nitrogen atoms into the carbon matrix. The atomic percentages (% at) of each component calculated from the integral peak area of the XPS data is shown in Table 2. It can be seen that as the KOH activation mass ratio increases, the nitrogen content

decreases from 6.4 at.% for NPAC-0.5 to 3.2 at.% for the NPAC-1 then increases to 8.9 wt% for the NPAC-2.

The NPAC-1 showed the lowest N and O content owing to the creation of more pores on the surface at the optimum activation ratio. NPAC-1 displayed the highest carbon content and the lowest oxygen content suggesting that most of the nitrogen atoms were attached to the carbon atoms in the form of pyrrolic-N, pyridinic-N and graphitic-N. The lowest oxygen content in NPAC-1 is associated with the initial oxygen content in the undoped PAC-1 as recorded in the supporting information (Table S1.). Similarly, the high N content for NPAC-2 could be ascribed to the formation of carbon and nitrogen deposit over the collapsed carbon structure thus increasing the amount of nitrogen and oxygen functionalities [18]. This is in agreement with the lower surface area and pore volume values reported for the NPAC material. Moreover, the high N and O content in NPAC-2 sample confirms the presence of a high number of structural defects (high I_D/I_G) as observed from the Raman data.

The different chemical environments of the carbon, nitrogen and oxygen atoms in the NPAC samples were determined by deconvolution of the high-resolution XPS spectra of the C1s, N1s and O1s peaks (Fig. 4(b–d) and S2). In addition, the XPS data of the undoped PAC-1 sample is given in the supplementary information (Fig. S4) as an example of all the PAC samples. It is clear that for the pristine PAC samples, there is no nitrogen which confirms the presence of the nitrogen in N-PAC samples is due to the melamine. The high resolution of the core level C1s spectra (Fig. S2(a–c)) were deconvoluted into three component peaks. The main peak 284.4 eV is ascribed to the sp^2 hybridized carbon (C=C), while the two other peaks at 285.5 eV and 287.0 eV are associated to the sp^3

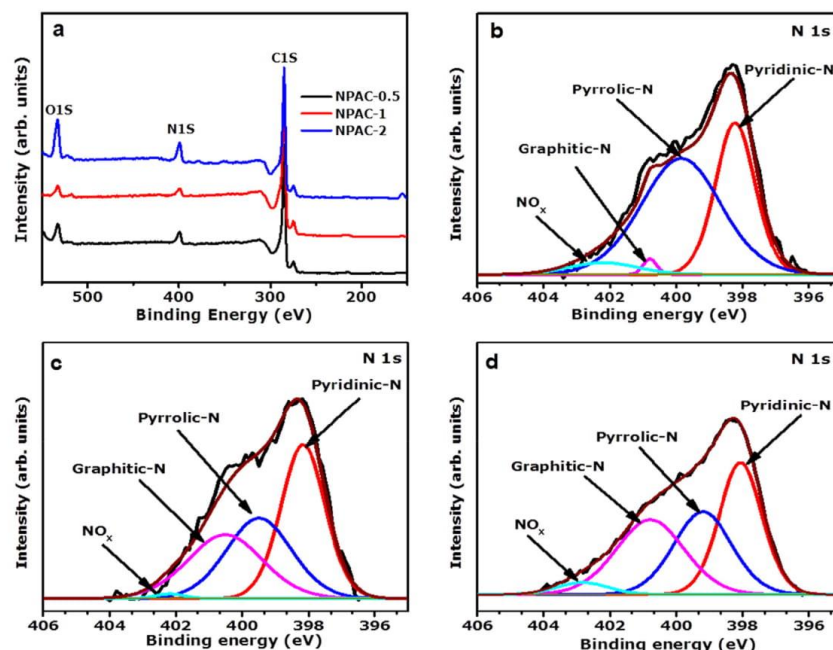


Fig. 4. (a) XPS survey spectra of the N doped samples and XPS spectra of deconvoluted N1s peaks, (b) NPAC-0.5, (c) NPAC-1 and (d) NPAC-2 materials.

Table 2
Elemental composition of the NPAC materials.

Samples	Elemental Composition (at.%)		
	C	O	N
NPAC-0.5	87.9	5.8	6.3
NPAC-1	94.0	2.8	3.2
NPAC-2	80.5	10.6	8.9

hybridized carbon (C–C) or C–N and O–C=O, respectively [60,61]. Fig. 4(b–d) reveals the high resolution of the N1s spectra deconvoluted into four peaks 398.2, 399.8, 400.8 and 402.2 eV corresponding to pyridinic-N, pyrrolic-N, graphitic-N and oxygenated pyridinic nitrogen (NO_x) [62–64].

The average % concentration of the different N-configuration in N1s is summarized in Supplementary Table S2.

The NPAC-0.5 was comprised of 37% pyridinic-N, 56.7% pyrrolic-N and 1.3% graphitic-N and 5% NO_x while NPAC-1 had of 40% pyridinic-N, 31% pyrrolic-N and 28% graphitic-N and 1% NO_x. The high percentage of pyridinic-N and pyrrolic-N indicates that the nitrogen atoms are bonded to the edges of carbon and sp³ hybridized carbon. The NPAC-0.5 material possessed the lowest graphitic N and highest NO_x among all N doped samples meaning that most of the nitrogen atoms reside on the edges as oxygenated nitrogen groups. However, the NPAC-1 sample displayed the lowest NO_x suggesting that the majority of the nitrogen atoms were incorporated inside the carbon matrix and not on the edges. In contrast, the NPAC-2 sample had the highest graphitic-N content (31.5%) and a relatively higher NO_x content (3.8%) as compared to the NPAC-1. The high percentage of graphitic-N can be ascribed to the replacement of the carbon by nitrogen atoms within the carbon lattice during the *ex-situ* doping process. The deconvolution of

the O1s core level spectra (Fig. S2(d–f)) show three peaks at 530.5, 531.7 and 533.0 eV which can be assigned to C–O or, C=O/N–O and O–C=O bonds, respectively [65,66].

The XPS analysis clearly shows that the atomic composition of the NPAC samples is greatly influenced by the mass ratio of PS: KOH. The surface chemistry of the NPAC materials plays a major role in determining their physical, structural and electrochemical properties. Specifically, the various nitrogen configurations in the N-doped carbons are known to play a vital role in improving the material's electrochemical performance [33]. The pyridinic and pyrrolic nitrogen aid in increasing the overall amount of charge stored due to the enhanced charge accumulation on the electrolyte/electrode interface and surface wettability of the electrodes [67]. Meanwhile, the graphitic N and the oxidized pyridinic-N can enhance the electron transport which improves the electrode materials' electrical conductivity [33,64].

3.3. Electrochemical analysis

To evaluate the electrochemical performance of the PACs and NPACs, the electrodes materials were firstly performed in half-cell configuration as shown in Fig. 5. Fig. 5(a,b) show the cyclic voltammetry (CV) plots at a scan rate of 40 mV s^{−1} for the PACs and NPACs, respectively with different KOH mass ratios in both positive and negative potential window. All the CV curves exhibited a quasi-rectangular shape revealing an electric double layer (EDL) capacitive behaviour in both positive (0.0–0.9 V) and negative (−1.0 to 0.0 V) operating potential windows. A slight difference was noticed in the CV curve in positive potential for PAC-1 compared to the other samples. The observed abnormality in the sample's CV curve suggests some difficulties in charge propagation resulting in the somewhat resistive behavior of its voltammogram [68]. Nevertheless, the PAC-1 still preserved the highest value of

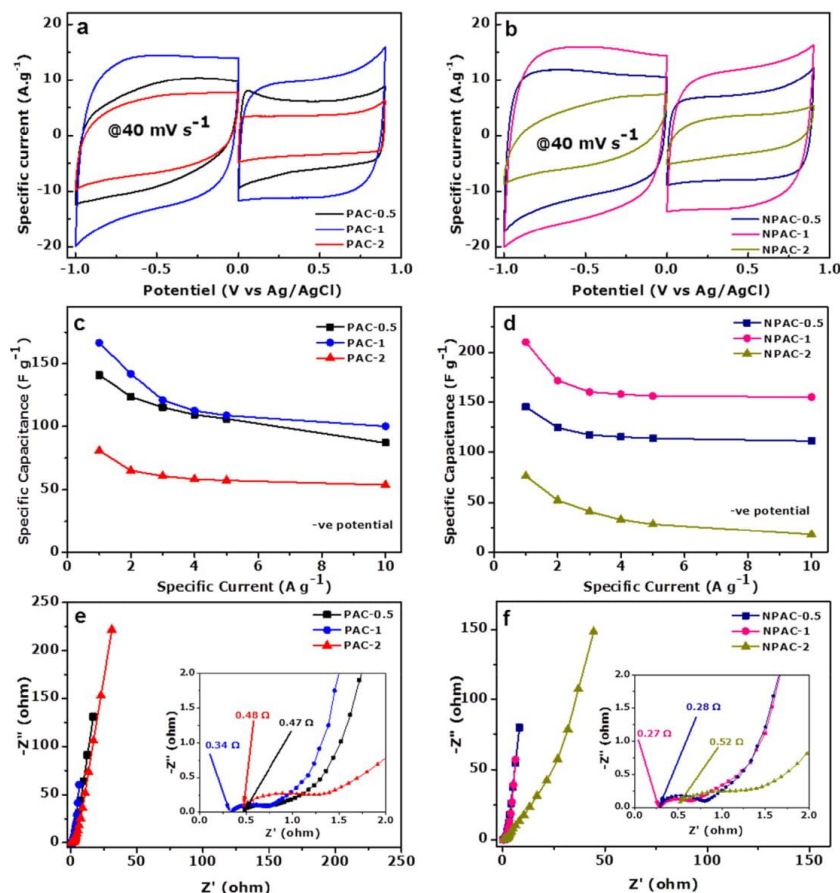


Fig. 5. Electrochemical performance of the pristine and *N*-doped PACs in a three-electrode configuration: (a and b) Cyclic voltammetry at scan rate of 40 mV s⁻¹, (c and d) specific capacitance at various gravimetric current values and (e and f) Nyquist plots.

current response, being remarkably higher than for PAC-0.5 and PAC-2. The PAC-1 and NPAC-1 electrodes displayed a quasi-rectangular CV profile with a higher current response in both operating potentials as compared to the PAC and NPAC at other KOH mass concentrations. This higher current response could be attributed to the enhanced porous network, reactive carbon material surface and the presence of nitrogen atom from *ex-situ* doping which aids in charge accumulation and ions transport at the electrode/electrolyte interface.

The galvanostatic charge discharge (GCD) profiles for all the working material electrodes displayed a symmetrical triangular characteristic with a small IR drop at 1 A g⁻¹ specific current within a potential range of -1.0 to 0.0 V and 0.0–0.9 V as seen in Fig. S4(a,d). This triangular behaviour confirms the typical double layer capacitive nature of the carbon materials as seen from the CV curves. The storage mechanism in this study exhibits a clear EDLC signature with a rectangular-like CV and quasi-symmetric GCD curve with respect to potential as a function of discharge time. The quasi-behavior is linked to some pseudocapacitance contribution from the functional groups on the carbon surface. The specific capacitance (C_s) as-calculated from the slope of the discharge

section of the GCD profiles using Eq. (1) in the positive and negative operating potential windows is presented in Fig. 5 and S4(e,f). Fig. 5(c,d) depicted the C_s of the PAC and NPAC electrodes materials in the negative potential window of -1.0–0.0 V while Fig. S4(e,f) displayed the C_s in the positive potential ranging from 0.0 to 0.9 V as function of the specific current ranging from 1 to 10 A g⁻¹. As clearly observed in these figures, the PAC-1 and NPAC-1 exhibited higher C_s values of 167 F g⁻¹ and 216 F g⁻¹, respectively at 1 A g⁻¹. These values demonstrate that after nitrogen doping the specific capacitance of the PAC-1 electrode was improved appreciably by 30% of the pristine value which agrees with the higher current response recorded in the CV profiles. In addition, the low C_s of the PAC-2 and NPAC-2 electrodes (80.77 F g⁻¹ and 76.4 F g⁻¹, respectively) could be attributed to the low specific surface area (~500 m² g⁻¹) resulting from the free carbon and nitrogen atoms that covered the pores which limits the ion diffusion into the porous carbon.

Electrochemical impedance spectroscopy (EIS) was tested to further investigate ion diffusion and transport kinetics of the pristine and *N*-doped PAC electrodes. Fig. 5(e,f) shows the Nyquist plot of the pristine and *N* doped PACs material electrodes.

All the electrode materials displayed a vertical line slightly deviated from the $-Z''$ axis (imaginary impedance axis) at low frequency demonstrating an ideal capacitive behaviour. At high frequency, the intersection with the real Z' axis represents the equivalent series resistance (ESR) which consists of the intrinsic resistance within the electrolyte, resistance at electrolyte/electrode interface and contact resistance between electrode and current collector [69]. The presence of the semi-circle at the high to mid frequency reveals the charge transfer resistance (R_{ct}) due to the presence of the functional groups on the surface of the carbon material [70]. From Fig. 5(e and f), it is clearly observed that the presence of nitrogen in the carbon matrix reduce the ESR and R_{ct} values of the PAC-0.5 and PAC-1 (inset to the Fig. 5(e–f)) which indicating a fast ions transport into the electrode-electrolyte interface and less resistance between the electrode and current collector. The ESR of the PAC-2 increased after the incorporation of the nitrogen into the carbon network from 0.48Ω to 0.52Ω due to the oxygen and nitrogen containing groups which increase the resistance of the electrode materials. For all the electrodes materials, PAC-1 and NPAC-1 electrodes displayed the low internal resistance values which can be ascribed to the presence of fewer oxygen containing groups and an abundant porous network

enabling better accessibility of the pores to the electrolyte ions as compared to the other PAC and NPAC electrodes. A similar trend was observed by Hulicova-Jurcakova et al. where carbons with less oxygenated functional groups gave lower internal resistance than carbons with higher oxygen-containing [6]. Moreover, the NPAC-1 electrode showed a shorter diffusion length and smaller R_{ct} among the other electrodes as observed from the Nyquist plot. This smaller R_{ct} and the shorter diffusion length are associated with the good surface wettability from the electrode-electrolyte interactions and the ion kinetic into the electrode pores, respectively.

In general, the NPAC-1 electrode exhibited a relatively better electrochemical performance as compared to the other doped and pristine material electrodes. Incorporating the nitrogen atom (via *ex-situ*-doping) into the carbon matrix with a moderate quantity of KOH delivered abundant electrochemically-active sites on the material electrode surface, which could create a good interfacial contact between the electrode and electrolyte for ion dynamics. The electrochemical performance of the NPAC-1 electrode is linked to their high degree of disorder (I_D/I_G ratio), resulting in their high degree of amorphous carbon state which provided good surface hydrophilicity and surface wettability. Additionally, the high specific surface area and the large pore size distribution of

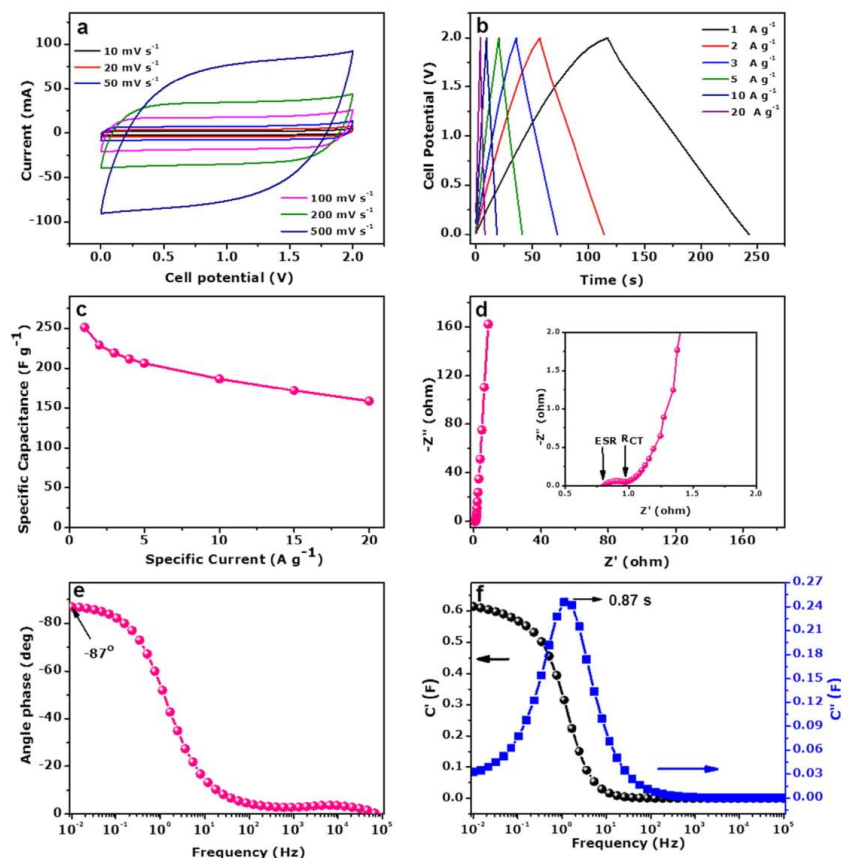


Fig. 6. Electrochemical performance of the NPAC-1//NPAC-1 symmetric device: (a) Cyclic voltammetry at different scan rates, (b) galvanostatic charge-discharge plots at various specific current, (c) specific capacitance as a function of specific current, (d) Nyquist plots, (e) Bode plot and (f) capacitance C' and C'' variation as a function of frequency.

the material are favourable for easy ion diffusion to the active electrode surface.

Subsequently, a symmetric device was assembled using the NPAC-1 samples as both positive and negative electrodes using the same electrolyte 2.5 M KNO₃.

Fig. 6(a) displays the cyclic voltammetry (CV) curves of the NPAC-1//NPAC-1 device in a two-electrode cell fixture at different scan rates from 10 to 500 mV s⁻¹.

The CV curves show a rectangular-like shape which indicates an ideal capacitive behaviour in an extended voltage window of up to 2.0 V. The rectangular-like behaviour is still maintained even at high scan rate of 0.5 V s⁻¹ which reveals a good rate capability and also rapid ion diffusion [71]. The galvanostatic charge discharge (GCD) profiles at various specific current values (1–20 A g⁻¹) for the NPAC-1//NPAC-1 device are shown in Fig. 6(b). All the GCD profiles exhibit a quasi-symmetric triangular pattern with a small IR drop suggesting an excellent charge-discharge reversibility and good double layer capacitive charge storage in the assembled symmetric supercapacitor. Fig. 6(c) represents the specific capacitance of the device at different specific currents calculated from the GCD profiles using equation (2). It has been seen that the *ex-situ*-doped NPAC-1//NPAC-1 possesses a relatively high specific capacitance per electrode (C_{el}) of 251.2 F g⁻¹ at 1 A g⁻¹. A C_{el} value of 158.4 F g⁻¹ was still retained even at a high specific current of 20 A g⁻¹ demonstrating a good electrode rate capability. Such C_{el} value is comparable with those results reported in the literature on nitrogen doped carbon materials from biomass [72–75].

The electrochemical impedance spectroscopy (EIS) was also carried out on the as-fabricated NPAC-1//NPAC-1 symmetric device. Fig. 6(d) presents the Nyquist plot of the symmetric cell which exhibited an almost linear vertical line in low frequency. This confirms the ideal EDLC behaviour as seen from the CV and GCD curves. The inset of Fig. 6(d) showed the ESR and R_{ct} of 0.79 Ω and 0.17 Ω, respectively. These small values are an indication of

fast ion transport and good charge transfer process within the electrodes. Fig. 6(e) exhibited the Bode curve of the symmetric device which displayed the plot of the phase angle against the frequency. It can be seen that at low frequency region, the phase angle of the cell is -87° close to an ideal capacitor of -90°. This result of the cell device suggested a low ion diffusion resistivity [76]. In Fig. 6(f), the complex capacitance ($C(\omega)$) of the as-prepared device was plotted as a function of the frequency.

The complex capacitance $C(\omega)$ represents the real part and the imaginary part of the complex capacitance and was determined by using the Eqs. below [77,78].

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (5)$$

$$C'(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} \quad (6)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \quad (7)$$

where $Z'(\omega)$ and $Z''(\omega)$ represent the real and imaginary part of the complex impedance $Z(\omega)$ respectively given by $Z(\omega) = Z'(\omega) - jZ''(\omega)$, ω is the angular frequency ($\omega = 2\pi f$).

At low frequency, the real part of the complex capacitance $C'(\omega)$ corresponds to the capacitance delivered of the cell measured via constant-current discharge. While the imaginary part of the capacitance, $C''(\omega)$ is related to the energy loss by dissipation during irreversible process at electrode/electrolyte interface [79,80]. From Fig. 6(f), the $C'(\omega)$ decreases gradually when the frequency increases. On the other hand, the $C''(\omega)$ versus frequency exhibit a maximum peak at a frequency f_0 of 1.1 Hz corresponding to the relaxation time τ_0 of the device. τ_0 is defined by $1/2\pi f_0$ which represented the minimum time required to charge the symmetric cell [81]. The device shows a small constant time of 0.87 s which

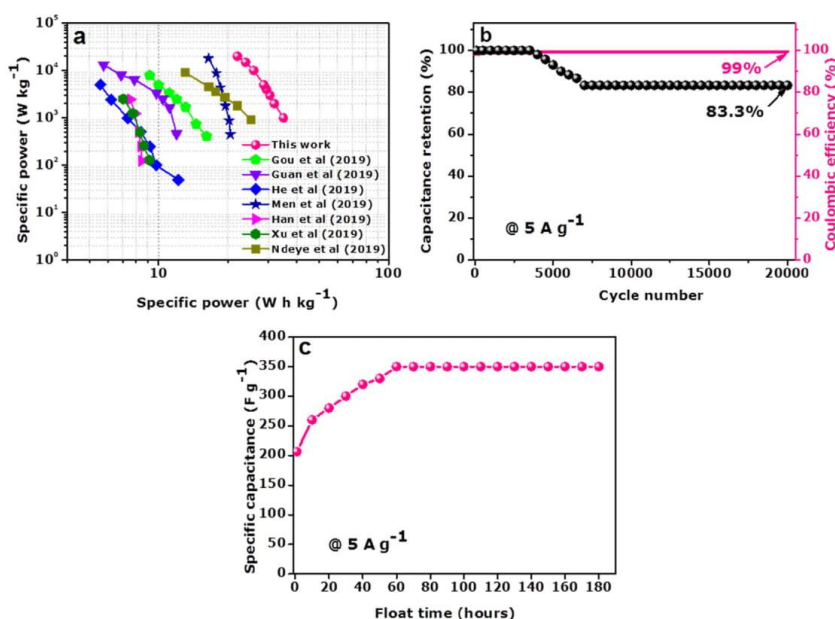


Fig. 7. (a) Ragone plot for the NPAC-1//NPAC-1 device, (b) Coulombic efficiency and specific capacitance retention vs. cycle number and (c) specific capacitance as function of voltage holding time for a period of 180 h.

Table 3
Comparison of the electrochemical performance of nitrogen doped activated carbon from biomass.

Raw Materials	Precursors	Electrolyte	Operating Potential windows	Specific current ($A\ g^{-1}$)	Specific energy ($Wh\ kg^{-1}$)	Specific power (Wkg^{-1})	Ref
<i>In-situ doping</i>							
Pomelo mesocarps	CaCl ₂ / urea	0.5 M Na ₂ SO ₄	1.8 V	0.25	14.7	90	[83]
Orange peel	FeCl ₃ /urea	0.5 M Li ₂ SO ₄	1.6 V	0.5	16	400	[84]
Pine Nut shell	KOH/melamine	1 M Na ₂ SO ₄	1.8 V	1	11.9	463.6	[72]
Dumpling flour	KOH/urea	6 M KOH	1.2 V	0.5	15.92	358.28	[87]
Cauliflower	KOH/imidazole dinone	1 M Na ₂ SO ₄	1.8 V	0.5	20.5	448.8	[88]
Pueraria	K ₂ CO ₃ /melamine	6 M KOH	1 V	0.5	8.46	123	[75]
Cellulose	NaOH/urea	1 M Na ₂ SO ₄	1.8 V	0.5	17.24	452	[89]
Cycas leaves	KOH/urea	6 M KOH	1 V	0.5	9.13	125	[90]
Peanut shell	KOH/urea	2.5 M KNO ₃	1.8 V	1	25.2	900	[38]
<i>Ex-situ doping</i>							
Taro stems	KOH/melamine	PVA/KOH	1 V	10	5.56	5000	[41]
Ginkgo leaves	KOH + K ₂ CO ₃ /ureophil	6 M KOH	1 V	0.5	7.8	241.1	[91]
Peanut shell	KOH/melamine	2.5 M KNO₃	2 V	1	34.9	1000	This work
				10	25.9	10,000	

indicated the symmetric cell can be fully charged within a relatively short period of time. This small value of the relaxation time suggests also a good electrical conductivity as well as a higher pores accessibility for fast ions transport into the electrode/electrolyte interface [82]. These results could be attributed to the synergistic effect of the nitrogen doping and improved surface porosity of the porous carbon matrix.

Fig. 7(a) displays the Ragone plot of the NPAC-1//NPAC-1 symmetric supercapacitor. The fabricated device delivers a specific energy of 35 $Wh\ kg^{-1}$ corresponding to a specific power of 1 $kW\ kg^{-1}$ at specific current of 1 $A\ g^{-1}$.

Moreover, the specific energy was still maintained at 22 $Wh\ kg^{-1}$ with a specific power of 20 $kW\ kg^{-1}$ even at high specific current of 20 $A\ g^{-1}$. These values of the specific energy and specific power for the NPAC-1//NPAC-1 device are higher than most recently reported values in the literature on nitrogen doped activated carbon derived from biomass as shown in Table 3, and Fig. 7(a). Until now, limited reports exist in the literature on biomass-based nitrogen doped activated carbon from using KNO₃ electrolyte. Hui and co-workers [83] reported the nitrogen-doped porous carbon nanosheets from pomelo mesocarps (N-PMNC). The preparation of the N-PMNC was done by an *in-situ doping* procedure by mixing the pomelo mesocarps with CaCl₂ and urea. The symmetric device fabricated possesses a specific energy of 14.7 $kWh\ kg^{-1}$ with specific power of 90 $W\ kg^{-1}$ in 0.5 M Na₂SO₄ at 0.25 $A\ g^{-1}$ specific current. Recently, Hao *et al.* [84] synthesized a porous nitrogen-doped orange peel (PN-OPNC) by an *in situ-doping* method using FeCl₃ and urea as activating agent and nitrogen source, respectively. The PN-OPNC//PN-OPNC symmetric device was tested in a potential window of 1.6 V using 0.5 M Li₂SO₄ electrolyte. The device exhibited a specific energy of 16 $kWh\ kg^{-1}$ with specific power of 400 $W\ kg^{-1}$ at specific current of 0.5 $A\ g^{-1}$. Donglin and co-authors [41] prepared a 3D nitrogen-doped porous carbon (3DNPC) via two steps by pyrolyzing the mixture taro stems with KOH followed by an *post doping* with melamine. The specific energy of the symmetric cell was 5.56 $Wh\ kg^{-1}$ with a specific power of 5 000 $W\ kg^{-1}$ in polyvinyl alcohol (PVA)/KOH as electrolyte at 10 $A\ g^{-1}$. The good electrochemical performance of the NPAC-1//NPAC-1 could be ascribed to the good surface chemistry of the porous carbon material with a moderate mass ratio of the KOH followed by the incorporation of the nitrogen atom in the carbon matrix. The cycling stability of the symmetric device was evaluated after continuous charging and discharging of the device over several cycles (~20 000) at specific current of 5 $A\ g^{-1}$. As observed in Fig. 7(b), the symmetric cell exhibits a coulombic efficiency of 99% and a capacitance retention of 83.3% after 20 000 constant galvanostatic cycles.

The observed sharp drop in capacitance at around 4000 cycles of cycling test is due to the electrochemical degradation of the electrode material as a result of the wide operating potential (2.0 V) and high specific current applied to the device [85]. Nonetheless, the device was observed to become stable after about 7000 cycles and could maintain this stable condition even for a very large cycle number of over 20 000 cycles. Fig. S5(a-b) in supporting information reveals the comparison of the CV curves and Nyquist plot of the device before and after the cycling of over 20,000 cycles. The CV curves of the cell at a scan rate 40 $mV\ s^{-1}$ (Fig. S5(a)) show a similar behaviour with no significant level of degradation. These could be due to consumption of some of the active sites in the electrode material that results in some subsequent capacitance loss [86]. An increase of the ESR and R_{ct} values of 1.07 Ω and 0.21 Ω from the initials values has been observed in Fig. S5(b). These small increases and the shorter diffusion length demonstrated that NPAC-1 electrode did not deteriorate significantly after the cycling stability.

The notable stability of the cell can be confirmed after investigating the specific capacitance for each floating test (voltage holding) as shown in Fig. 7(c). The floating test analysis showed the specific capacitance for each 10 h period of holding at a maximum operating cell voltage (2.0 V) for 180 h. Fig. 7(c) shows a specific capacitance increase for the first 60 h of floating after which the specific capacitance was retained constant value for the next 120 h.

The increased specific capacitance value for the device can be ascribed to the opening of small pores, surface wettability and enhanced surface interaction of the electrode ions with the carbon electrode upon voltage holding. The large micropore of the NPAC-1 play a role in the charging of the double layer capacitor and the mesopores volume provide charge propagation pathways during process. The surface functionalities on the NPAC-1 influence the surface chemistry and interactions of the electrolyte ions with the carbon electrode leading to lower electrolyte ion resistance and improved charge storage capability during the voltage holding process. In addition, the excellent capacitance retention portrayed by the NPAC-1 electrode material reveals a stable electrolyte ion interaction with the carbon surface. Thus the voltage holding test is beneficial for pore opening and faster ion transport and charge storage.

The specific capacitance of the symmetric device was enhanced to 350 $F\ g^{-1}$ by 69.5% from the initial value of 206.4 $F\ g^{-1}$ up to 180 h (1 week and 12 h) holding time at 5 $A\ g^{-1}$. This improvement is also emphasized with an increase in the device specific energy value from 28.7 to 48.6 $Wh\ kg^{-1}$ after the floating test. Noteworthy, the specific energy of the cell obtained after holding test at

5 A g⁻¹ is higher than that of the cell at 1 A g⁻¹ (35 W h kg⁻¹) before the holding test. Thus, this device demonstrated an excellent electrochemical stability over a long period of time (~7 + days) in 2.5 M KNO₃ aqueous electrolyte.

4. Conclusion

Ex-situ nitrogen-doped porous carbons have been successfully prepared through two steps process: chemical activation of the peanut shell with different mass ratios of KOH as an activating agent followed by nitrogen-doping with melamine. The experimental results obtained show the effect of the mass loading of activating agents on the properties of *ex-situ* N-doped activated carbon. The nitrogen-doped carbon yielded with the optimum mass ratio of 1:1 (PS:KOH) was found to be the best electrode material which displayed a high specific surface area of 1442 m² g⁻¹ and varying nitrogen configurations (40% pyridinic-N, 31% pyrrolic-N, 28% graphitic-N and 1% NO_x). The assembled supercapacitor (NPAC-1//NPAC-1) based on the *ex-situ* nitrogen-doped peanut shell activated carbon electrode showed an excellent specific energy and power of 34.9 Wh kg⁻¹ and 1 kW kg⁻¹, respectively in a wide potential range of 2.0 V with a capacitance retention of 83.2% up to 20 000 cycles. NPAC-1//NPAC-1 also presented good stability through voltage holding analysis up to 180 h displaying a high specific capacitance and specific energy which demonstrated that the cell device performed better after the voltage holding test. This study revealed that the *ex-situ* nitrogen-doped porous carbon process is a promising and sustainable route for the synthesis of relatively high nitrogen content N-doped AC for outstanding energy storing capability.

Credit author statement

N.F.Sylla, N.M.Ndiaye, B.K.Mutuma and D. Momodu conceived the idea and designed the work. N.Manyala and B.D.Ngom refined the idea and supervised the work. N.F.Sylla performed all the experiments as well as the material and electrochemical characterization. M.Chaker assisted with and XPS analysis. All authors contributed to the interpretation of results and discussion.

Declaration of Competing Interest

The authors declare no competing interests.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2020.02.061>.

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4.2.3 Concluding Remarks

In summary, we have synthesized porous activated carbon derived from peanut shell waste (PAC) via a chemical activation followed by a nitrogen-doping treatment to get nitrogen doped activated carbon (NPAC). It was found that the mass ratios of PSW to KOH (1:0.5, 1:1 and 1:2) impact on the surface chemistry and porosity of both pristine and post-nitrogen-doped activated carbon samples respectively. Therefore, the samples obtained with an equal amount of PSW to KOH (PAC-1 and NPAC-1) presented the best SSA and electrochemical performances as compared to their respective samples. NPAC-1 electrode exhibited a specific capacitance of 216 F g^{-1} which is higher to PAC electrode (167 F g^{-1}). The symmetric supercapacitor NPAC-1//NPAC-1 was assembled within a cell potential of 2.0 V using 2.5 M KNO_3 aqueous electrolyte. This NPAC-1//NPAC-1 device provided a high specific energy 34.9 W h kg^{-1} with an associated specific power of 1 kW kg^{-1} as well as a good stability with 83.3% capacitance retention after 20,000 cycles. The present study features an immense potential to develop a sustainable and low-cost approach of synthesizing post-nitrogen-doped porous carbon for high-performance supercapacitor.

4.3 Enhanced capacitive behaviour of peanut-shell activated carbon/molybdenum oxide/molybdenum carbide ternary composite

4.3.1 Introduction

In the previous section 4.2, porous peanut shell activated carbon (PAC) was synthesized through KOH activation of PSW at 850 °C before introduction of melamine to produce NPAC samples. The PAC sample has shown large ion-accessible surface area, tunable pore structure, chemical stability and relative good electrical conductivity. However, the specific capacitance of PAC electrode is still not satisfactory and in the section 4.2 the improvement was achieved through nitrogen doping. In this present study, we have introduced pseudocapacitive (PC) materials into the PAC material by a one-step pyrolysis of various ammonium molybdate precursor to PAC at 850 °C. The thermal decomposition of the molybdenum precursor onto the PAC has led to the formation of PAC/ MoO₂/Mo₂C ternary composites. MoO₂ and Mo₂C are among PCs materials that have demonstrated favourable electrochemical activities due to their high specific capacity, multiple oxidation states, reversible redox reactions, and electrochemical active sites [30]. Therefore, the supercapacitive performance of the PAC can be enhanced by the synergistic effect of the ternary composite whereby it will combine the merits of each component: (i) High surface area associated with porous structure of PAC, (ii) rich electrochemical activity from the faradaic reactions of MoO₂ and (iii) good electrical conductivity and chemical stability of Mo₂C. For instance, recent reports have demonstrated that carbon/molybdenum oxide/molybdenum carbide (C/MoO₂/Mo₂C) electrode has shown good electrochemical performance in Li-ions batteries[31][30]. To the best of our knowledge, no studies have been reported on the electrochemical properties of C/MoO₂/Mo₂C heterostructure for supercapacitors applications.

4.3.2 Results and discussion

The results obtained from the study on the enhanced capacitive behaviour of peanut-shell activated carbon/molybdenum oxide/molybdenum carbide ternary composite are described in details in the publication below, which is still under review:

Enhanced capacitive behaviour of peanut-shell activated carbon/molybdenum oxide/molybdenum carbide ternary composites

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Abstract

Biomass-waste activated carbon/molybdenum oxide/molybdenum carbide ternary composites are prepared using a facile in-situ pyrolysis process in argon ambient with varying mass ratios of ammonium molybdate tetrahydrate to porous peanut shell activated carbon (PAC). The formation of MoO₂ and Mo₂C nanostructures embedded in the porous carbon framework is confirmed by extensive structural characterization and elemental mapping analysis. The best composite when used as electrodes in a symmetric supercapacitor (PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1) exhibited a good cell capacitance of 115 F g⁻¹ with an associated high specific energy of 51.8 W h kg⁻¹ as well as a specific power of 0.9 kW kg⁻¹ at a cell voltage of 1.8 V at 1 A g⁻¹. Increasing the specific current to 20 A g⁻¹, still showed a device capable of delivering up to 30 W h kg⁻¹ specific energy and 18 kW kg⁻¹ of specific power. Additionally, with a great cycling stability, a 99.8% coulombic efficiency and capacitance retention of ~ 83% were recorded for over 25000 galvanostatic charge-discharge cycles at 10 A g⁻¹.

The voltage holding test after a 160-h floating time resulted in increase of the specific capacitance from 74.7 to 90 F g⁻¹ at 10 A g⁻¹ for this storage device. The remarkable electrochemical performance is based on the synergistic effect of metal oxide/metal carbide (MoO₂/Mo₂C) with the interconnected porous carbon. The PAC/MoO₂/Mo₂C ternary composites highlight promising Mo-based electrode materials suitable for high-performance energy storage. Explicitly, this work also demonstrates a simple and sustainable approach to enhance the electrochemical performance of porous carbon materials.

Keywords: porous carbon, ternary composite, molybdenum oxide, molybdenum carbide, energy storage.

1. Introduction

The high demand for energy in conjunction with the rapid depletion of fossil fuels has made it essential to develop alternative energy sources. Various researchers have shown an increased interest in the development of clean, sustainable and renewable energy sources such as solar, wind and geothermal [1][2]. However, there are still challenges linked to the production and continuous supply of energy in large quantities from these renewable energy systems [3]. Therefore, in order to supply energy needs on a long-term basis, in addition to it being affordable, sustainable and environmentally friendly, it is important to find diverse, efficient, safe and flexible methods for its simultaneous generation and storage [4][5]. Batteries and supercapacitors are the most renowned energy storage devices with supercapacitors being given gross attention by energy researchers globally due to their high performance features such as high specific power, long life cycle, and quick charge-discharge dynamics [6][7].

Supercapacitors are typically categorized into electrical double layer-capacitor (EDLC) and pseudocapacitors. The former operates on a charge storage process that relies on an electrostatic charge accumulation formed at the interfacial region of electrode/electrolyte while the latter depends on reversible faradic-type redox reactions at the electrode surface material [8][9].

Porous carbon such as carbon nanotube, graphene, activated carbon (AC), and carbon onions owing to their large surface area, good electrical conductivity, and great stability are mainly investigated as electrode materials for EDLC [10][11][12][13]. Porous AC materials obtained from biomass waste (peanut shell, walnut shell, pinecone, and so on) have gained interest due to their distinctive features of well-developed surface area with hierarchically pore structure, abundant availability of precursors sources, environmentally friendly and low cost [14][15][16][17][18][19]. In addition, surface functional groups obtained from the AC can favour an easy ion adsorption/desorption at the electrode/electrolyte interface leading to an optimum electrochemical performance [20][21]. However, there is still a need to improve their performance to meet the high energy demand.

To date, various methods have been reported to enhance the electrochemical performance of the porous ACs. For instance, the introduction of oxygen functional groups (ketone, ether, carboxylic acid, quinone, and so on) by oxidizing the porous carbon surface could promote the hydrophilicity and also surface reactivity of the carbon material [22][23][24]. Moreover, the presence of the surface oxygen-containing species not only provides some pseudocapacitance effect but also enriches the surface wetting capability which contributes a significant improvement in the capacitance and the overall specific energy/power of the carbon electrode material [25][26][24].

Song *et al.* [24] prepared O/S dual-modified nanoporous carbon (OSC) by a hydrothermal oxidation method using H_2O_2 (O) and H_2SO_4 (S) as oxidants. Their study revealed that the OSC electrode delivered a specific capacitance of 168 F g^{-1} , 3.5 times higher than the pristine nanoporous carbon in 6 M KOH aqueous electrolyte due to the introduction of the oxygen functional groups on the surface of nanoporous carbon [24]. Another promising method is the heteroatom-doping (nitrogen, sulphur, phosphorous, boron and so on) of porous AC matrix which enhances the capability to store charge in the material. Therefore, heteroatom doping into the porous carbon framework results in the modification of the electronic structure, which can remarkably improve the electrical conductivity, the surface wettability, properties of the electrons donor and hence the electrochemical features of the porous carbon materials [27][28][29][30]. For instance, we reported previously in our study on the synthesis of nitrogen-doped peanut shell activated carbon (NPAC) by chemical activation and nitrogen-post-doping processes with KOH and melamine respectively. The NPAC showed a considerable increase in the specific capacitance value (167 F g^{-1} to 216 F g^{-1}) for the non-doped PAC and NPAC electrodes in a 2.5 M KNO_3 aqueous electrolyte [31].

Incorporating transition metal oxides/hydroxides or conducting polymer into the porous carbon network is as well an effective strategy that can improve the electrochemical properties of these carbon materials. The integration of porous carbon with transition metal oxides (MnO_2 , NiO , Fe_3O_4 , MoO_2 , etc.) forming composites synergistically combines the advantages and mitigates the limitations of both materials [32][33][34][35][36]. MoO_2 is one of the most promising pseudocapacitive transition metal oxides which possesses several oxidation states (+2 to +6), high theoretical specific capacitance, excellent redox reaction capability, low electrical resistivity, good electrochemical activity, and low cost [37][38][39].

Thus, the MoO₂ incorporated into the porous carbon may provide more electrochemical active sites which could influence additional surface pseudocapacitive effect endowing enhanced electrochemical performance of the composite [40][41][42][43][44]. Lina *et al.* [40] synthesized MoO₂ nanoparticles decorated into 3D porous graphene (MoO₂-rGO) using a hydrothermal route. Their work indicated that the MoO₂-rGO composite enhanced specific capacitance to 356 F g⁻¹ as compared to the 3D porous graphene (244 F g⁻¹) in 6 M KOH aqueous electrolyte [40].

Others studies have also shown the incorporation of transition metal carbide (Mo₂C, W₂C, TiC, etc.) in the carbon framework could improve the performance metrics of the electrochemical capacitors [45][46][47]. Among the transition metal carbides, Mo₂C has recently attracted great interest due to the high specific conductance (1.02 x10² S cm⁻¹), great conductivity (electrical and thermal), and good chemical stability [48][49][50]. Furthermore, these remarkable proprieties can offer additional actives sites, facilitate electron and ion transportation, good cyclic stability properties and a reduction of the charge resistance which could produce a relatively high electrochemical performance [50][51]. Hussain and co-workers [52] have prepared carbon nanotubes (CNTs) decorated with molybdenum carbide nanosheets (Mo₂C@CNT) by a chemical reduction approach followed by carbonization. In their report, the hybrid composite Mo₂C@CNT exhibited a specific capacitance value of 365 F g⁻¹ which is 3.5 times higher than the CNTs (103 F g⁻¹) in KOH electrolyte owing to the synergy between the Mo₂C and CNTs [52].

Forming a ternary composite of metal oxide (MoO₂), metal carbide (Mo₂C) and porous carbon material result in a combination of the advantages of each component that could considerably enhance the electrochemical features of the energy storage device [53][54][50]. For instance, Ihsan *et al.* [48] have prepared a MoO₂/Mo₂C/C spheres by a two-step, hydrothermal process followed by a calcination procedure.

Yang *et al.* [54] have also synthesized MoO₂/Mo₂C/C hybrid microspheres by a template-free method. Both studies showed a great rate capability, cycling stability, good capacity as anode materials for Li-ion batteries. However, to the best of our knowledge no reports exist on the application of these Mo-based materials/porous carbon (MoO₂/Mo₂C/C) ternary composites as supercapacitor electrodes.

In this study, we have established a facile and low-cost approach of synthesizing a ternary composites (PAC/MoO₂/Mo₂C) as electrode material for supercapacitor by one-step pyrolysis route through varying mass ratios of ammonium molybdate tetrahydrate to porous peanut shell activated carbon (PAC) (1:0.5; 1:1; 1:2). The in-situ formation of MoO₂ and Mo₂C nanostructures incorporated into the PAC network were confirmed by the XRD, Raman, HRTEM, SAED, SEM, EDX mapping as well as the XPS analysis. The obtained ternary composites portrayed interesting merits based on the existing incorporated nanostructures of the MoO₂-Mo₂C within the nanoporous PAC-based material including: (i) High specific surface area with hierarchically porous structure of the PAC, (ii) pseudocapacitive effect by the redox reaction of MoO₂ and (iii) superior electrical conductivity and stability of the Mo₂C. The best ternary composite (PAC/MoO₂/Mo₂C-1) exhibited superior capacitive performance in both half and full-cell test owing to the synergistic effect of the MoO₂ and Mo₂C nanostructures embedded into the PAC matrix. Moreover, our study demonstrates a simple and sustainable approach to enhance the electrochemical performance of porous carbon materials.

2. Experimental

2.1. Materials

In this study, all chemical reagents were used as-obtained without any further purification. Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 99.98%), potassium nitrate, (KNO_3 , 99.99%), potassium hydroxide (KOH , 99 %), polyvinylidene fluoride (PVDF, 99%), carbon acetylene black (CAB, 99.95%), hydrochloric acid (HCl , 37%) and N-methyl-2-pyrrolidone (NMP, 99%) were supplied from Merck (South Africa). Argon gas (Ar , 99.99%) was purchased from Afrox (South Africa) and polycrystalline nickel foam mesh (with 1.6 mm thickness, 420 g m^{-2} areal density) was obtained from Alantum (Munich, Germany).

2.2. Synthesis of the peanut shell waste derived activated carbon (PAC)

Peanut shell waste derived activated carbon (PAC) was prepared by a one-step chemical activation following a reported procedure from our previous study [31]. Briefly, the peanut shell waste raw material was mixed with KOH pellets in an optimized ratio by mass and then subjected to chemical activation at an elevated 850°C temperature for 1 h to obtain the final product.

2.3. Synthesis of the peanut shell derived activated carbon/molybdenum oxide/molybdenum carbide (PAC/ MoO_2 / Mo_2C) ternary composites

The synthesized PAC sample was mixed with ammonium molybdate tetrahydrate in mass ratios of 1:0.5, 1:1 and 1:2 for the PAC to the inorganic salt in an agate mortar. Few drops of deionized water were added to the as-prepared mixture to ensure thorough mixing of both materials which was then loaded onto a porcelain boat and air dried at 80°C for 12 h in an electric oven.

The porcelain boat was transferred into a horizontal tube furnace and heated to 850 °C at a ramping rate of 5 °C min⁻¹. The furnace was kept constant at this temperature for 1 h under 250 sccm of argon gas flow. After cooling down to room temperature, the ternary composites were obtained and labelled PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2 corresponding to the mass ratio of 1:0.5, 1:1 and 1:2, of PAC to the inorganic salt respectively. The schematic procedure for preparing the PAC/MoO₂/Mo₂C ternary composites is illustrated in figure 1.

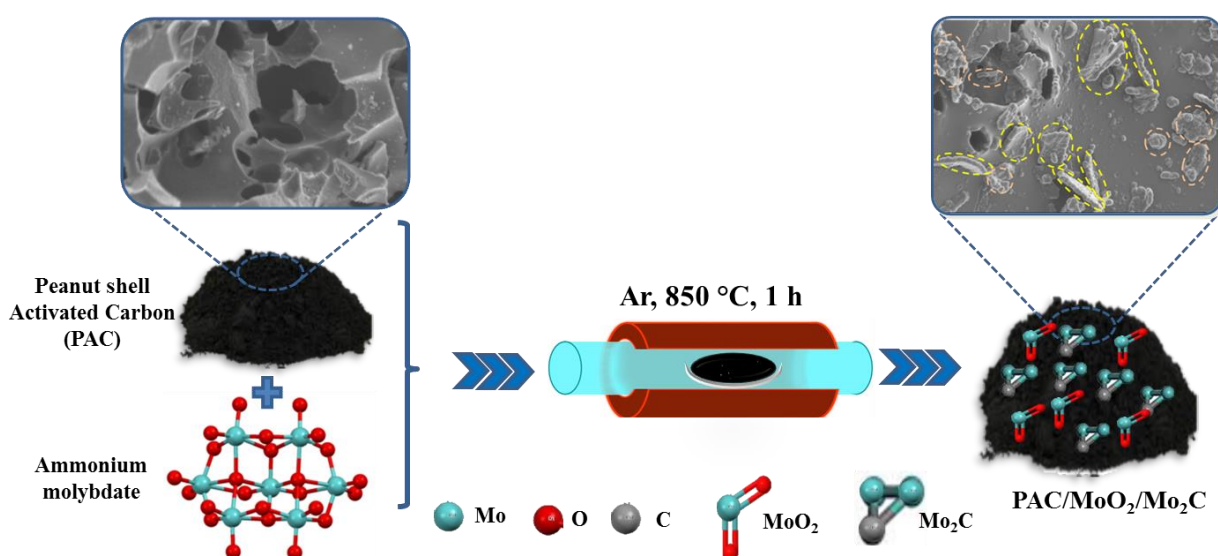


Figure 1: Schematic illustration for the synthesis method of the PAC/MoO₂/Mo₂C ternary composites

2.4. Physical characterization

Powder X-ray diffraction (XRD) analysis of the PAC/MoO₂/Mo₂C samples was determined using a Bruker D8 Advance diffractometer using Cu K α ($\lambda = 1.5406$ Å) radiation operating in the 2θ range of 10 - 80°. Raman spectra of the ternary composite materials were characterized on WITec alpha300 RAS+ confocal Raman microscope (WITec, Germany) using a 532 nm excitation laser at a power of 5 mW.

High-resolution transmission electron microscope (HRTEM) micrographs and selected area electron diffraction (SAED) patterns were obtained using a JEOL JEM-2100F field emission gun transmission electron microscope (FEG-TEM) operating at 200 kV. Scanning electron microscope (SEM) micrographs and energy dispersive X-ray (EDX) mapping were carried out using a Zeiss Ultra-plus 55 field emission scanning electron microscope (FE-SEM). The SEM images and EDX mapping images were operated at 1.0 and 10 kV accelerating voltage respectively. The surface area distribution was performed by Brunauer-Emmett-Teller (BET) and porosity pore size by Barrett-Joyner-Halenda (BJH) methods on the Micrometrics TriStar II 3020 (version 2.00) system in a relative pressure (P/P_0) range of 0.01 - 1.0 at 77 K. X-ray photoelectron spectroscopy (XPS) of the samples was obtained by a VG Escalab 220i-XL instrument equipped with a monochromatic Al - $K\alpha$ (1486.6 eV) source of radiation.

2.5. Electrochemical characterization

The PAC/MoO₂/Mo₂C electrodes were prepared by mixing the active material, carbon acetylene black (CAB) as conductive additive and polyvinylidene difluoride (PVDF) as binder in a weight ratio of 8:1:1, respectively in an agate mortar. Few drops of N-methylpyrrolidone (NMP) as solvent was added to the mixture to obtain slurry which was uniformly coated on nickel foam (NF) as current collector followed by drying at 80 °C for a period of 12 h in an electric oven.

The cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were investigated using VMP-300 16-channel potentiostat (Bio-Logic, Knoxville, USA) associated with EC-Lab[®] (V11.33) software. The three electrode (half-cell) test was performed using the as-prepared electrode as working electrode, the glassy carbon as counter electrode (CE) and Ag/AgCl (in saturated 3M KCl) as reference electrode (RE).

For the two-electrode measurement (full-cell), a Swagelok cell and a microfiber filter paper (separator) were used to assemble the symmetric device. All electrochemical tests were performed in 2.5 M KNO₃ aqueous electrolyte at room temperature.

The specific capacitance C_s (F g⁻¹) of the half-cell was obtained from the GCD profiles using the following equation [55]:

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where I represents the current (mA), Δt is the time (s) of the discharge slop from GCD, m is the mass (mg) of the active electrode, and ΔV is the operating potential (V).

The specific capacitance C_s (F g⁻¹), specific energy E (W h kg⁻¹) and the specific power P (W kg⁻¹) for the symmetric device were calculated using the mass total m_T (mg) of the positive and negative electrode from the equations (2), (3), and (4) [56][57]:

$$C_s = \frac{I\Delta t}{m_T\Delta V} \quad (2)$$

$$E = \frac{C_s\Delta V^2}{7.2} \quad (3)$$

$$P = 3600 \frac{E_d}{\Delta t} \quad (4)$$

3. Results and discussion

3.1. Structural, morphological and textural characterization

XRD patterns of the as-prepared PAC/MoO₂/Mo₂C ternary composites are displayed in figure 2(a).

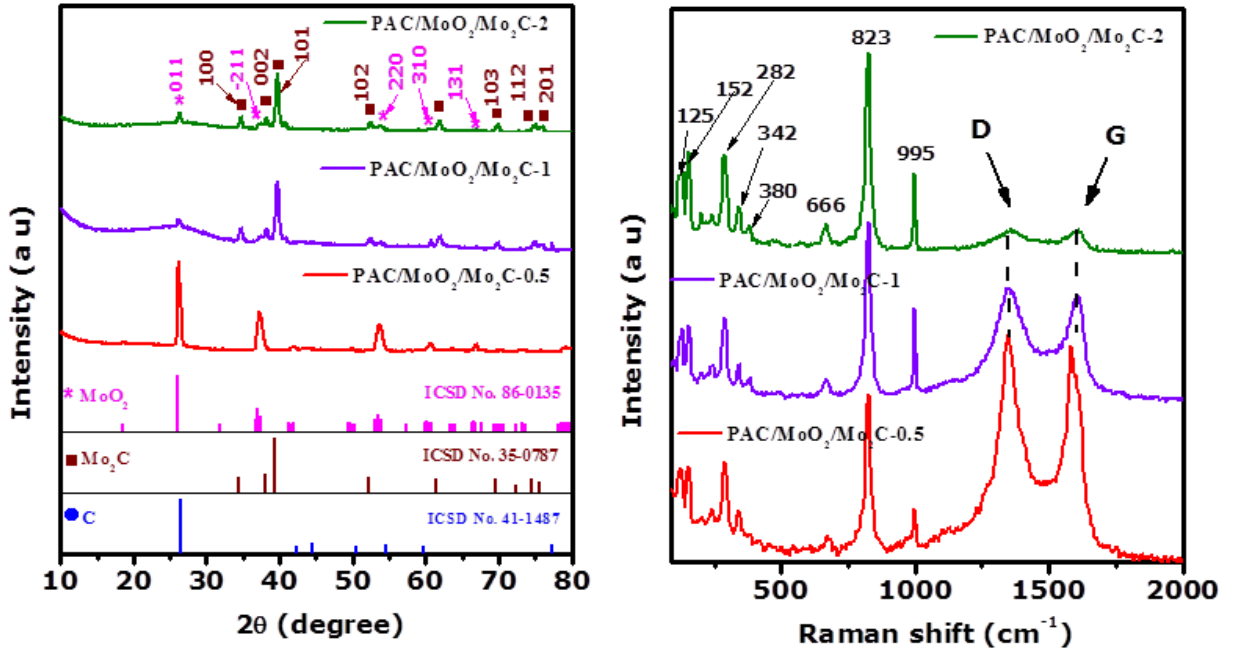


Figure 2: (a) XRD patterns and (b) Raman spectra of the PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2.

These XRD spectra reveal diffraction peaks matching with the monoclinic MoO₂ (ICSD card No. 86-0135, space group: P21/c, cell parameters: $a=5.6096$ Å, $b=4.8570$ Å, $c=5.6259$ Å) and the hexagonal Mo₂C (ICSD card No. 35-0787, space group: P63/mmc, with cell parameters: $a=3.0124$ Å, $b=3.0124$ Å, $c=4.7352$ Å) in PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2 samples. All diffraction peaks located with approximate 2θ values of 26.1° , 37.1° , 53.7° , 60.7° and 66.9° corresponding to (011), (211), (220), (310) and (131) crystallographic planes, respectively can be assigned to the monoclinic MoO₂ [58][59]. Therefore, the other featured peaks located at 2θ of 34.3° , 37.9° , 39.4° , 52.1° , 61.5° , 69.5° , 74.6° and 75.5° can be ascribed to the (100), (002), (101), (102), (110), (103), (112) and (201) crystallographic planes from the hexagonal Mo₂C, respectively [60][61]. Additionally, the broad peak around 2θ of 26.5° corresponding to (002) diffraction of graphite (ICSD card No. 41-1487) could be attributed to the presence of the amorphous carbon domains of the PAC which overlaps with MoO₂ peak at 26.1° [58][61].

The Raman spectra of the as-prepared PAC/MoO₂/Mo₂C porous ternary composites are shown in figure 2(b). The characteristic peaks at around 125, 152, 200, 342, 381 and 666 cm⁻¹ bands could be attributed to the vibration modes of the monoclinic MoO₂. The Raman active modes at 285, 825 and 998 cm⁻¹ bands could be assigned to vibrational features of the Mo₂C [62][63][64][65][66]. Two other characteristics peaks are also observed at (1341 - 1360 cm⁻¹) and (1583 - 1609 cm⁻¹) which correspond to the D and G bands, respectively (as shown in table 1). The D band is associated to the disordered graphitic structure in carbon matrix while the G is due to the sp²-hybridized graphitic carbon [67][68]. The intensity ratio of D and G bands (I_D/I_G ratio) recorded in table 1 reveals the graphitization degree of the as-synthesized ternary composites [69]. The I_D/I_G ratio values decreased from 1.03 to 0.97 with increasing mass ratio of the molybdenum precursor to the porous carbon. This indicates a balanced amorphous carbon to the graphitic carbon in the PAC/MoO₂/Mo₂C composites resulting from the MoO₂ and Mo₂C nanoparticles embedded into the porous carbon network [70][71].

Table 1: Raman data of the PAC/MoO₂/Mo₂C ternary composites

Samples	D-band (cm ⁻¹)	G-band (cm ⁻¹)	I _D /I _G ratio
PAC/MoO ₂ /Mo ₂ C-0.5	1349	1583	1.03
PAC/MoO ₂ /Mo ₂ C-1	1341	1607	1.01
PAC/MoO ₂ /Mo ₂ C-2	1360	1610	0.97

High resolution transmission electron microscopic (HRTEM) micrographs and selected area electron diffraction (SAED) patterns were further performed to provide more crystal structural information of the PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2 ternary composites as shown in figure 3. Figure 3(a-c) revealed the HRTEM micrographs of the ternary composites in which the lattice fringes are highlighted in yellow arrow and the layer of amorphous PAC in orange arrow.

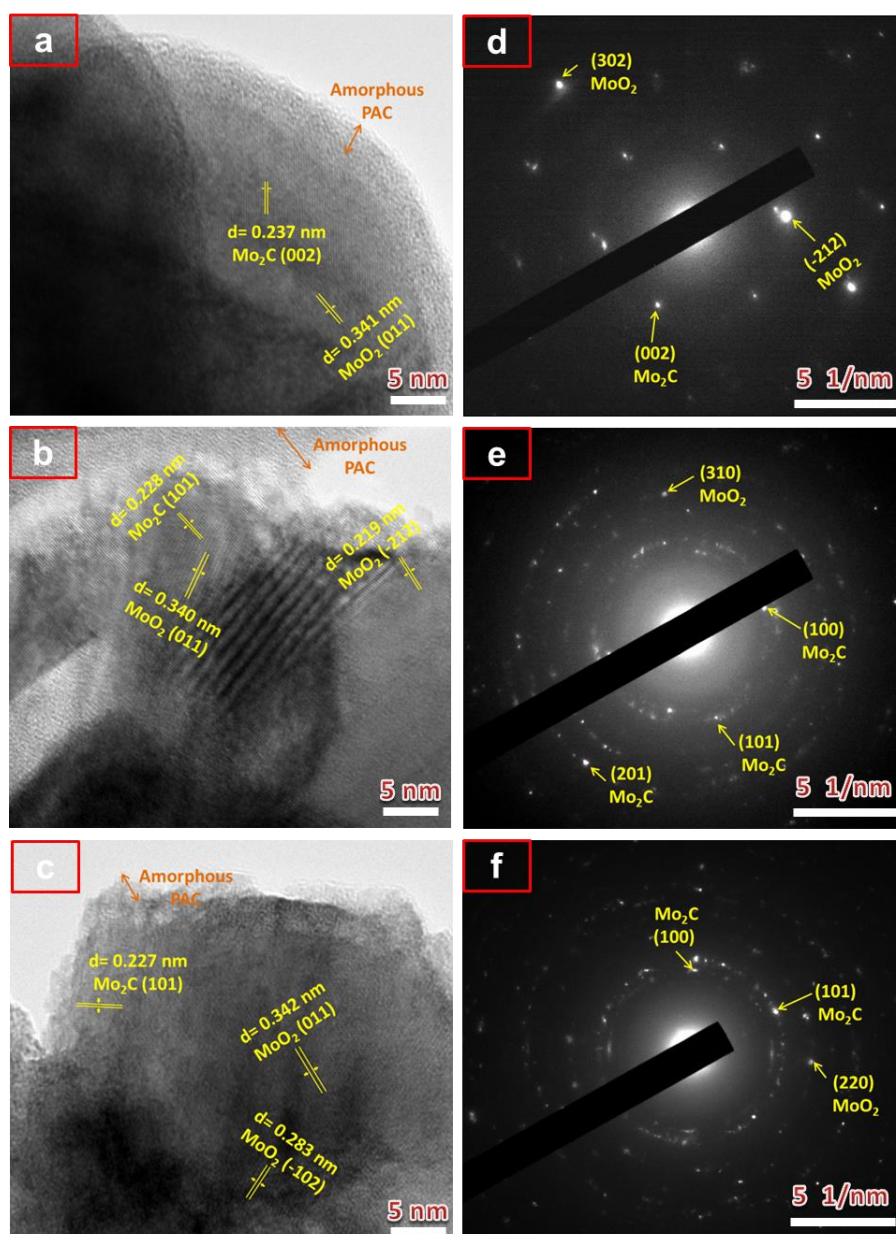


Figure 3: HRTEM micrographs and SAED patterns of (a, d) PAC/MoO₂/Mo₂C-0.5, (b, e) PAC/MoO₂/Mo₂C-1 and (c, f) PAC/MoO₂/Mo₂C-2 ternary composites, respectively.

The lattice fringes with an inter-planar spacing (d) approximate values of 0.340 nm, 0.219 nm and 0.283 nm are corresponding to the crystallographic planes (011), (-212) and (-102) of the monoclinic MoO₂ (ICSD card No. 86-0135) respectively. The other d-spacing values of 0.237 nm and 0.227 nm are assigned to the crystallographic planes (002) and (101) of the hexagonal Mo₂C (ICSD card No. 35-0787) respectively.

The as-obtained SAED patterns of the PAC/MoO₂/Mo₂C ternary composites are exhibited in figure 3(d-f). The SAED patterns show the bright diffraction rings which are attributed to (302), (310) and (220) planes of MoO₂ and those (002), (100), (101) and (201) planes to Mo₂C.

These results imply a successful incorporation of the MoO₂ and Mo₂C heterostructures into the amorphous PAC matrix through a pyrolysis process which are consistent with the XRD analysis in figure 2(a).

The SEM micrographs of PAC/MoO₂/Mo₂C ternary composites prepared at different mass ratios of molybdenum precursor to PAC are displayed in figure 4. The morphology of the ternary composites reveals the formation of a mixture of agglomerated nanoparticles and nanoplates embedded into the interconnected porous structure of the PAC at low magnification (figure 4(a, c and e)).

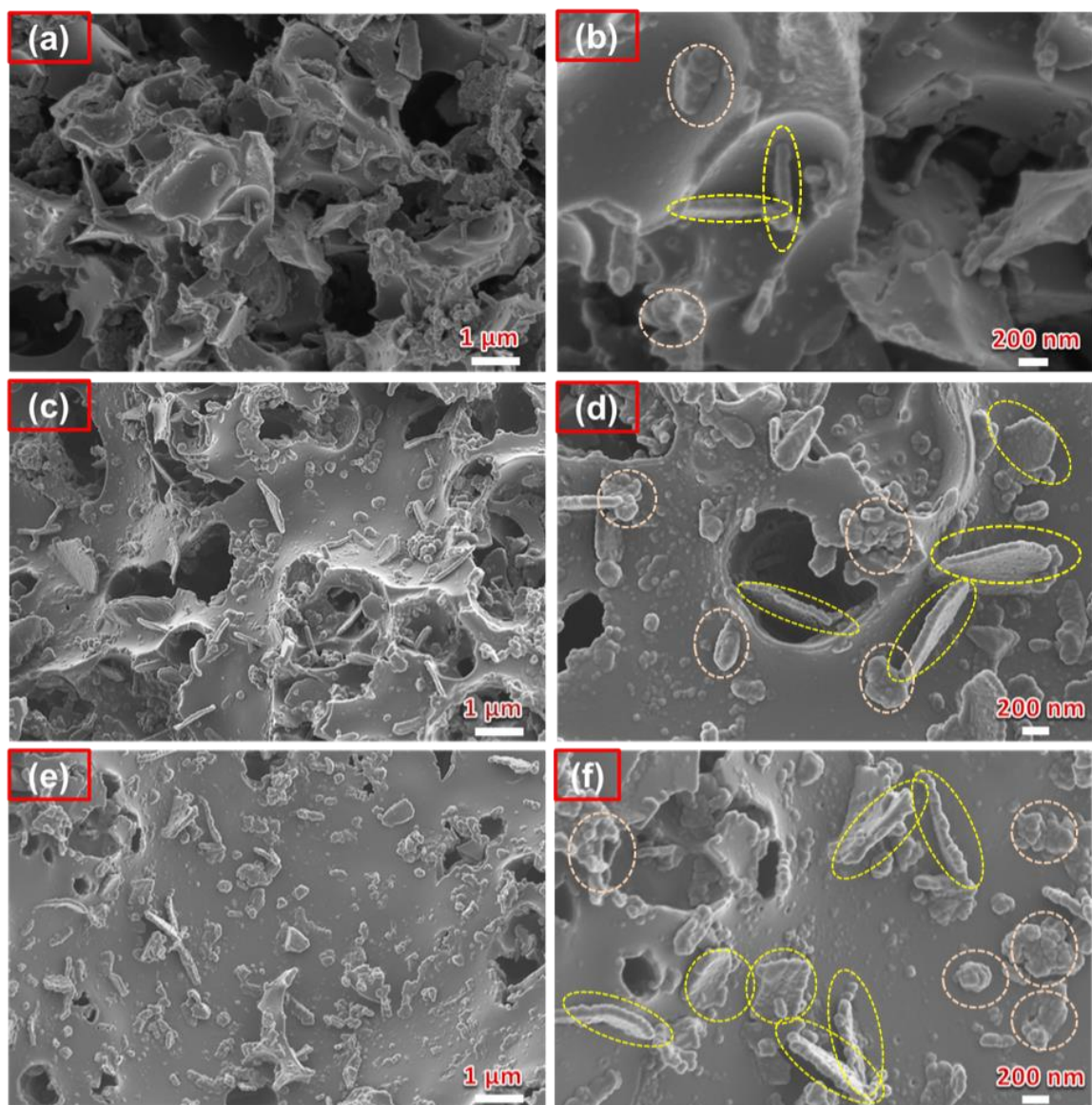


Fig. 4. SEM micrographs at low and high magnification of (a, b) PAC/MoO₂/Mo₂C-0.5, (c, d) PAC/MoO₂/Mo₂C-1 and (e, f) PAC/MoO₂/Mo₂C-2 ternary composites.

An increase of molybdenum content reveals an increased tendency of both agglomerated nanoparticles and nanoplates morphologies as highlighted in circles in figure (4b, d and f) (high magnification). These two different morphologies are perhaps due to the presence MoO₂ and Mo₂C in the composites, but it is not easy to tell identify which of these belongs to a specific morphology.

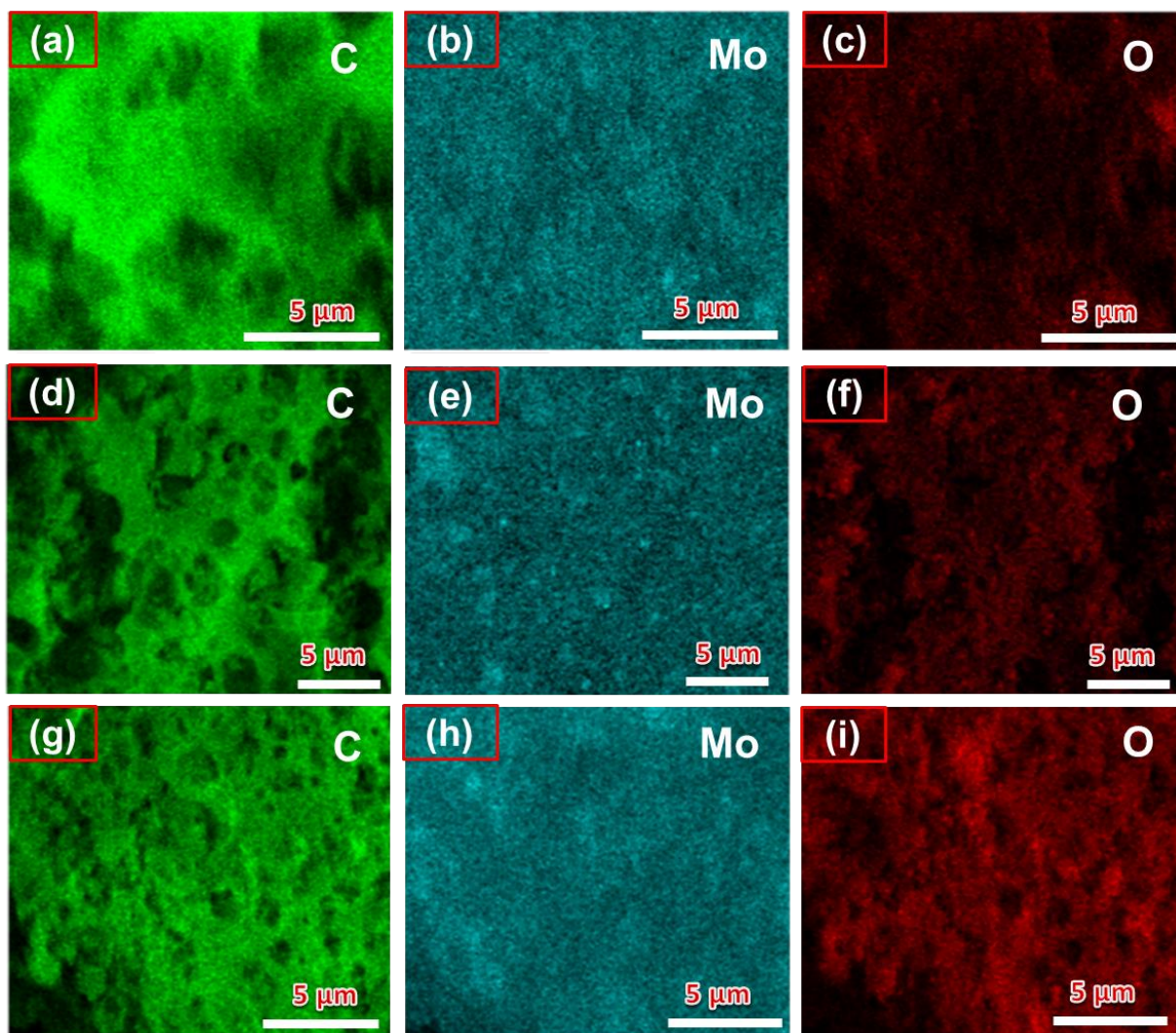


Fig. 5. EDX mapping images showing the distribution of C, Mo and O individual elements in: (a - c) PAC/MoO₂/Mo₂C-0.5, (d - f) PAC/MoO₂/Mo₂C-1 and (g - i) PAC/MoO₂/Mo₂C-2 ternary composites.

EDX mapping was also applied to determine the elemental distribution of the PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2 ternary composites as seen in figure 5(a-i). It is observed that the Mo, O and C elements are uniformly distributed throughout the interconnected porous carbon structure. This suggests that the agglomerated nanoparticles and nanoplates were composed of MoO₂ and Mo₂C embedded into the carbon matrix.

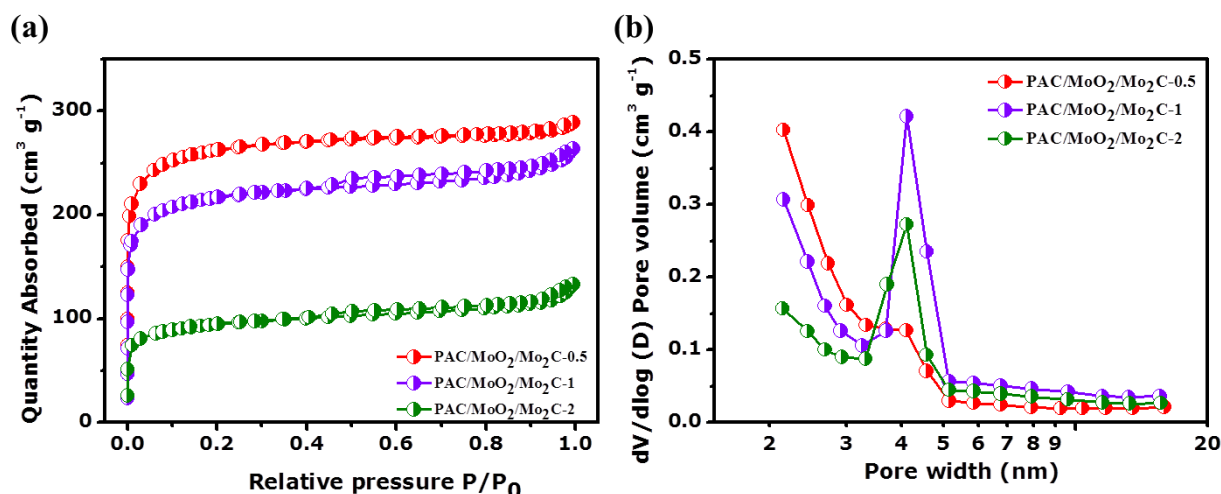


Figure 6: (a) N₂ absorption-desorption isotherms, (b) pore size distribution of the PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2.

N₂ adsorption/desorption experiment was conducted to investigate the textural properties of the PAC/MoO₂/Mo₂C ternary composites as shown in figure 6 and table 2. Figure 6(a-b) presents the sorption isotherms and the pore size distribution curves, respectively of the ternary composites. All isotherms depicted a type IV features associated with a H4 hysteresis loop which indicates the coexistence of the micropores and mesopores structures in the ternary composites [72][73]. The BET specific surface area (SSA) values of PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2 samples are 804, 711 and 301 m² g⁻¹, respectively. A decrease in SSA was observed upon increasing the ammonium molybdate precursor loading from 0.5 to 2. For the total pore volume (table 2), the same trend is also identified for all samples from with the decrease from 0.44 to 0.20 cm³ g⁻¹.

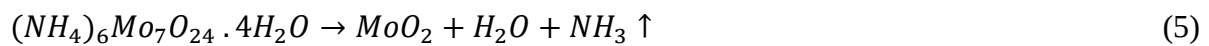
The decrease in the SSA and total pore volume could be ascribed to the embedding of the MoO₂ and Mo₂C nanoparticles into the porous PAC during the pyrolysis process which can block some pores [74].

Table 2: Textural properties of the PAC/MoO₂/Mo₂C ternary composites

Samples	BET SSA	Total pore	Micropore
	(m ² g ⁻¹)	volume (cm ³ g ⁻¹)	volume (cm ³ g ⁻¹)
PAC/MoO ₂ /Mo ₂ C-0.5	804	0.44	0.23
PAC/MoO ₂ /Mo ₂ C-1	711	0.40	0.19
PAC/MoO ₂ /Mo ₂ C-2	301	0.20	0.07

However, the SSA of the as-synthesized samples are much higher than that reported for similar materials such as MoO₂/Mo₂C/C composite prepared via ion-exchange method (73.4 m² g⁻¹) [75], MoO₂/Mo₂C/C spheres by hydrothermal and calcination processes (159.6 m² g⁻¹) [48] and MoO₂/Mo₂C/C microspheres obtained by a mild polymer regulation procedure followed by calcination treatment (57.6 m² g⁻¹) [76].

The formation of the nanoparticles MoO₂ and Mo₂C in the ternary composite emanates from the interaction between the ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) and the porous PAC (denoted as C) at elevated temperature (≥ 800 °C) under argon atmosphere. It is good to mention that typically activated carbon (PAC) comprises of OH and COOH groups on the surface which makes it acidic, this favours a thermal reduction of the ammonium molybdate precursor to MoO₂ instead of MoO₃. The MoO₂ could react with carbon at high temperature and under inert atmosphere (Ar) to give Mo₂C. This process can be described with the following equations [54][77].



During the pyrolysis, the ammonium molybdenum precursor decomposes to form MoO₂, H₂O and ammonia gas (NH₃) being released at high temperature. In addition, the generated MoO₂ nanoparticles could react with the porous carbon (PAC) leading to the formation of Mo₂C.

The formation of a ternary composite comprising of PAC, MoO₂ and Mo₂C could possibly enhance ion intercalation as well as create an interconnected porous network. This might promote an easy diffusion of the electrolyte's ions through the electrode materials and further enhance the fast transport of the ions which are beneficial for the electrochemical analysis.

3.2. XPS analysis

The surface chemistry property and the elemental composition of the as-synthesized ternary composites were determined using X-ray photoelectron spectroscopy (XPS). The wide survey scan spectrum depicted the distinctive peaks of the carbon (C 1s), molybdenum (Mo 3p_{1/2}, Mo 3p_{3/2} and Mo 3d) and oxygen (O 1s) elements in PAC/MoO₂/Mo₂C-0.5, PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2 composites as illustrated in figure 7(a).

Table 3 presents the atomic percentage (at.%) of C, Mo and O elements in the as-synthesized ternary composites. From these samples, it can be seen that the carbon content decreases from 73.9 to 54.9 at.% as the yield of the molybdenum increases. However, the molybdenum and oxygen contents were found to increase from 8.6 to 20.2 at.% and 17.5 to 24.9 at.%, respectively. Notably, the PAC/MoO₂/Mo₂C-2 material exhibited the smallest carbon content and highest molybdenum and oxygen contents. This could be due to the formation of MoO₂ and Mo₂C nanoparticles during the pyrolysis process. On the other hand, the elemental composition in the ternary composites is significantly influenced by the mass loading of molybdenum precursor into the PAC.

Table 3: Elemental composite of the PAC/MoO₂/Mo₂C ternary composites

Samples	Elemental Composition (at.%)		
	C 1s	O 1s	Mo 3d
PAC/MoO ₂ /Mo ₂ C-0.5	73.9	17.5	8.6
PAC/MoO ₂ /Mo ₂ C-1	62.4	22.6	15.0
PAC/MoO ₂ /Mo ₂ C-2	54.9	24.9	20.2

The high-resolution XPS spectra of the Mo 3d split into $3d_{5/2}$ and $3d_{3/2}$ spin-orbit components in the binding energy range of 226 - 241 eV as presented in figure 7(b-d). In figure 7(b), the deconvolution of the core level Mo 3d spectrum exhibits six sets of peaks which indicate the presence of four oxidation states Mo^{2+} , Mo^{4+} , Mo^{5+} and Mo^{6+} in PAC/MoO₂/Mo₂C-0.5 ternary composite. The peak located at 228.8 eV ($\text{Mo}^{2+} 3d_{5/2}$) is associated to Mo-C bond in Mo₂C while the pair of peaks located at 229.6 and 232.9 eV ($\text{Mo}^{4+} 3d_{5/2}/3d_{3/2}$) are attributed to the formation of MoO₂ [54][78][79][80]. The pair of peaks at binding energies of 231.0 and 234.4 eV ($\text{Mo}^{5+} 3d_{5/2}/3d_{3/2}$) and that located at 232.5 and 235.9 eV ($\text{Mo}^{6+} 3d_{5/2}/3d_{3/2}$) are the characteristics of the MoO₃ which could be assigned to the surface oxidation and sample oxidation in air of the metastable phase of the MoO₂ [81][82][83][84]. Figure 7(c-d) presents the fitting of the core level Mo3d in PAC/MoO₂/Mo₂C-1 and PAC/MoO₂/Mo₂C-2 ternary composites. In comparison with PAC/MoO₂/Mo₂C-0.5 ternary composite, there are no changes in the number of peaks deconvoluted which means that all the composites have similar oxidation states (Mo^{2+} , Mo^{4+} , Mo^{5+} and Mo^{6+}). Table S1 presents the atomic percentage (at.%) of all deconvoluted peaks of the ternary composites. What is noticeable is that PAC/MoO₂/Mo₂C-1 has high at.% of Mo₂C and MoO₂ as compared to the other composites. This could be beneficial in the electrochemical measurements of these composites because these two materials are expected to improve the electrochemical properties of PAC where MoO₂ is expected to contribute pseudocapacitive behaviour, while Mo₂C will contribute stability and conductivity.

The high-resolution C 1s and O 1s core levels of the ternary composites are shown in figure S1. The fitting of the C 1s spectrum (figure S1(a-c)) shows the characteristic peak of Mo-C bond in Mo₂C at 283.3 ± 0.2 eV [85][86].

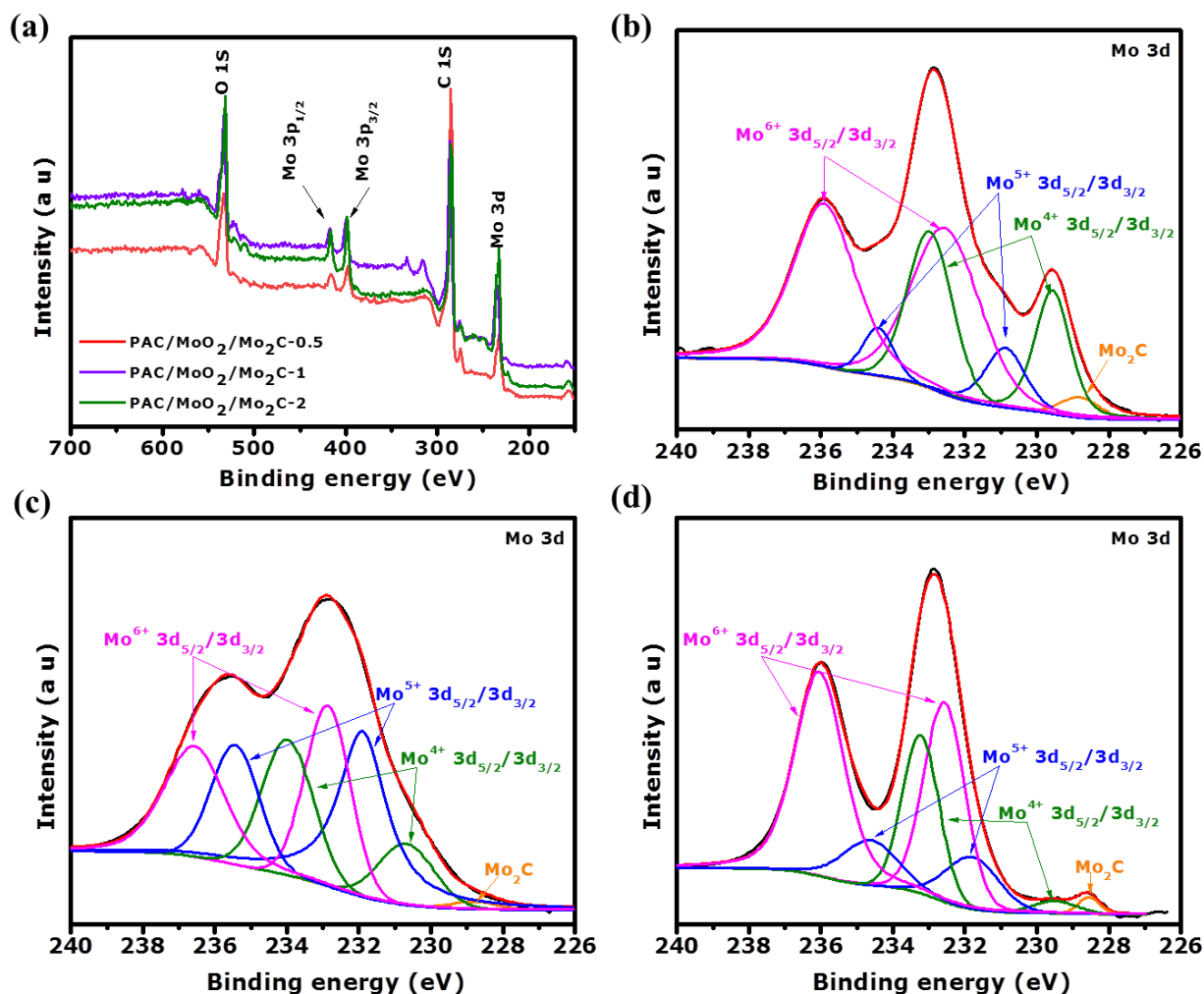


Figure 7: (a) XPS survey spectra of the as-synthesized ternary composites and high resolution of Mo 3d, (b) PAC/MoO₂/Mo₂C-0.5, (c) PAC/MoO₂/Mo₂C-1 and (d) PAC/MoO₂/Mo₂C-2 ternary composites.

The other four peaks are attributed to the C=C (sp^2 hybridized), C-C (sp^3 hybridized), C-OH and O-C=O bonds corresponding to the binding energies at 284.4 ± 0.3 eV, 285.2 ± 0.2 eV, 287.5 ± 0.6 and 290.7 ± 0.3 eV, respectively [87][88][89]. The deconvolution of the O 1s feature (figure S1(d-f)) exhibits a peak located at 530.6 ± 0.2 eV linked to Mo-O bond, the two other peaks at 533.3 ± 0.2 eV and 536.4 ± 0.2 eV are associated to C-O and O-C=O bonds, respectively [90][91][92]. The results of the XPS analysis confirm the formation of the MoO₂ and Mo₂C nanoparticles in all ternary composites which are consistent with the XRD, Raman, HRTEM and SAED results.

3.3. Electrochemical characterization

All measurements of the ternary composite electrodes with different molybdenum precursor content were done first in a three-electrode configuration using 2.5 M KNO_3 aqueous electrolyte. Figure 8(a-b) displays the comparative cyclic voltammetry (CV) profiles of the PAC/ MoO_2 / Mo_2C -0.5, PAC/ MoO_2 / Mo_2C -1 and PAC/ MoO_2 / Mo_2C -2 electrodes at a constant scan rate of 50 mV s^{-1} in both negative and positive potential windows of -0.9 - 0 V and 0 - 0.9 V vs. Ag/AgCl, respectively. A quasi-rectangular characteristic was observed for all CV profiles indicating an electrical double layer capacitor (EDLC) behaviour for these samples [93]. It can be seen that the CV profile of PAC/ MoO_2 / Mo_2C -1 electrode displays a higher current response than other electrode materials. This superior current response could be assigned to the moderate loading of molybdenum precursor into the porous carbon network which provided more active sites enhancing the fast ion diffusion and good interaction between the interface of electrode/ KNO_3 electrolyte.

Figure S2(a) and b display the galvanostatic charge-discharge (GCD) comparison curves of the PAC/ MoO_2 / Mo_2C ternary composites. The GCD curves of all electrodes are performed within both negative (-0.9 - 0.0 V vs. Ag/AgCl) and positive (0.0 - 0.9 V vs. Ag/AgCl) operating potential windows, respectively at a constant specific current of 1 A g^{-1} . The GCD curves depicted a symmetrical triangular profile that confirms the electrical double layer capacitor nature of the ternary composites electrodes supported by the CV curves [94]. It is also observed that the GCD curve of the PAC/ MoO_2 / Mo_2C -1 electrode has a longer discharge time as compared to PAC/ MoO_2 / Mo_2C -0.5 and PAC/ MoO_2 / Mo_2C -2 electrodes agreeing with the CV results. Furthermore, the details of the CV curves at different scan rates from 10 to 100 mV s^{-1} and GCD profiles at specific currents ranging from 1 to 10 A g^{-1} of the PAC/ MoO_2 / Mo_2C -1 ternary composite because of showing superior electrochemical properties, are shown in figure S3(a-b) and figure S3(c-d), respectively.

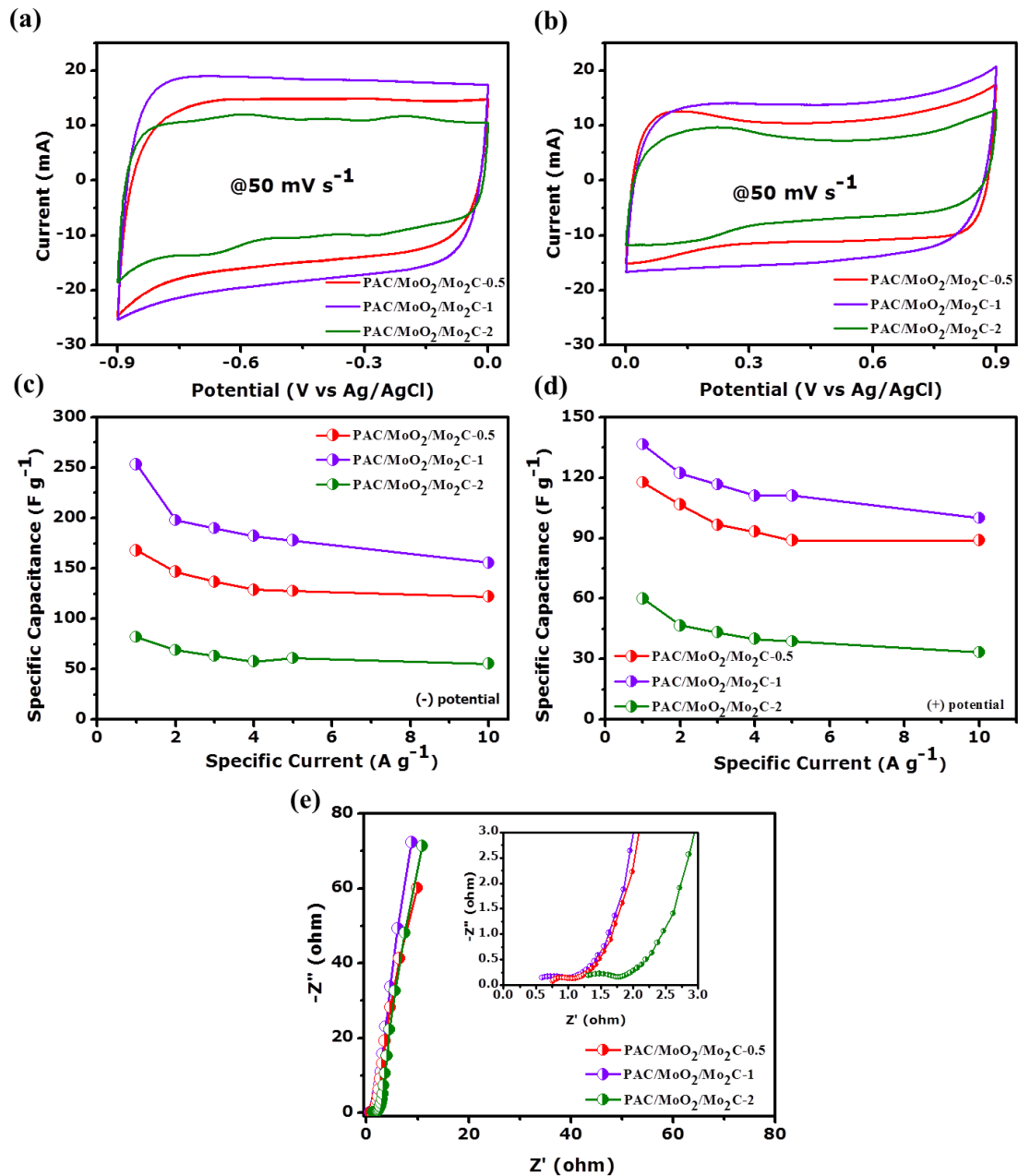


Fig. 8. (a, b) Cyclic voltammetry at scan rate of 50 mV s⁻¹, (c, d) specific capacitance at different specific current values in (-0.9 - 0.0 V) and (0.0 - 0.9 V) operating potential windows and (e) Nyquist plots of the PAC/MoO₂/Mo₂C ternary composites in a three-electrode configuration.

The corresponding specific capacitance (C_s) as function of the specific current in the range of 1 - 10 A g⁻¹ are presented in figure 8(c-d) in the negative (-0.9 - 0.0 V vs. Ag/AgCl) and positive (0.0 - 0.9 V vs. Ag/AgCl) operating potential windows for all three composites, respectively. The C_s of the ternary composites was determined from the discharge period of GCD patterns using equation (1).

From both figure 8(c-d), it is observed that the PAC/MoO₂/Mo₂C-1 electrode depicted the highest C_s value in both potential windows reflecting longer charge-discharge pattern which is consistent with the highest current response from the CV curve. However, the smallest C_s value of PAC/MoO₂/Mo₂C-2 in both potential windows can be explained by the fact that further increasing the molybdenum precursor content could lead to the blockage of some pores in the porous carbon matrix as evidenced by a decrease in SSA of 301 m² g⁻¹ and thus limit the ion diffusion at the electrode/electrolyte interface [95].

Electrochemical impedance spectroscopy (EIS) analysis of the as-synthesized PAC/MoO₂/Mo₂C ternary composites was evaluated at open circuit voltage (V_{OC}) in the frequency range of 100 kHz to 10 mHz. The EIS data are provided using Nyquist plot which illustrates the variation of the impedance as a function of the frequency as shown figure 8(e).

The Nyquist plots of all ternary composites exhibit a semi-circle at high to medium frequency region corresponding to the charge transfer resistance (R_{ct}) and a quasi-straight line slightly tilted to Z'' imaginary axis at low frequency region indicating the ion diffusion throughout the electrolyte [96][97]. The Nyquist curves of the ternary composites further confirms the capacitive characteristic. The intercept of the Z' real axis (beginning of the arc) at high frequency depicts the equivalent series resistance (ESR) which represents the combination of resistance at electrode/electrolyte and electrode/current collector interfaces [98][99]. As seen in the inset to figure 8(e), PAC/MoO₂/Mo₂C-1 electrode depicts smaller ESR and R_{ct} values of 0.59 and 1.01 Ω as compared to PAC/MoO₂/Mo₂C-0.5 (0.76 and 1.10 Ω) and PAC/MoO₂/Mo₂C-2 electrodes (1.31 and 1.84 Ω), respectively. In addition, PAC/MoO₂/Mo₂C-1 electrode also has the shortest diffusion path length and closest to the Z'' axis suggesting a quicker ion diffusion of the interfacial electrode and KNO₃ electrolyte and shows better capacitive features among the ternary composites.

Considering all the above results, the as-prepared PAC/MoO₂/Mo₂C-1 electrode recorded superior electrochemical performance among the other ternary composites. This might be ascribed to the synergistic effect of the MoO₂, Mo₂C and porous carbon obtained after the reaction of ammonium molybdate and porous carbon at equal mass ratios during the pyrolysis route. This is also supported by the at.% of all the deconvoluted peaks in Table S1 where for this particular sample MoO₂ and Mo₂C show higher at.% as compared to the rest of the composites. The formation of the MoO₂ and Mo₂C nanoparticles embedded into the porous PAC provided abundant electro-active sites for the charge transfer ability and quick ion diffusion of the electrolyte which improve the wettability and the electrical conductivity, thus the charge storage of the electrode.

The electrochemical measurement of the PAC/MoO₂/Mo₂C-1 ternary composite electrode was further performed in a two-cell configuration by assembling a symmetric device using identical electrolyte. Figure 9(a-b) displays the CV features of the as-fabricated symmetric supercapacitor (PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1) under an operating cell potential of 0-1.8 V. The CV features of the ternary composite device reveals a quasi-rectangular behaviour whereas the current response increased upon increasing the scan rates from 10 to 400 mV s⁻¹ (figure 9(a)) suggesting quasi-reversible electron transfer kinetics and dominated electrical double layer. A slight redox peak was observed in the CV curves due to the pseudocapacitive contribution from the molybdenum oxide. The CV curves of the PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 device still maintain the rectangular-like feature upon increasing the scan rate to high rate from 0.5 to 2.5 V s⁻¹ (as seen in figure 9(b)) which demonstrated a high rate capability [100].

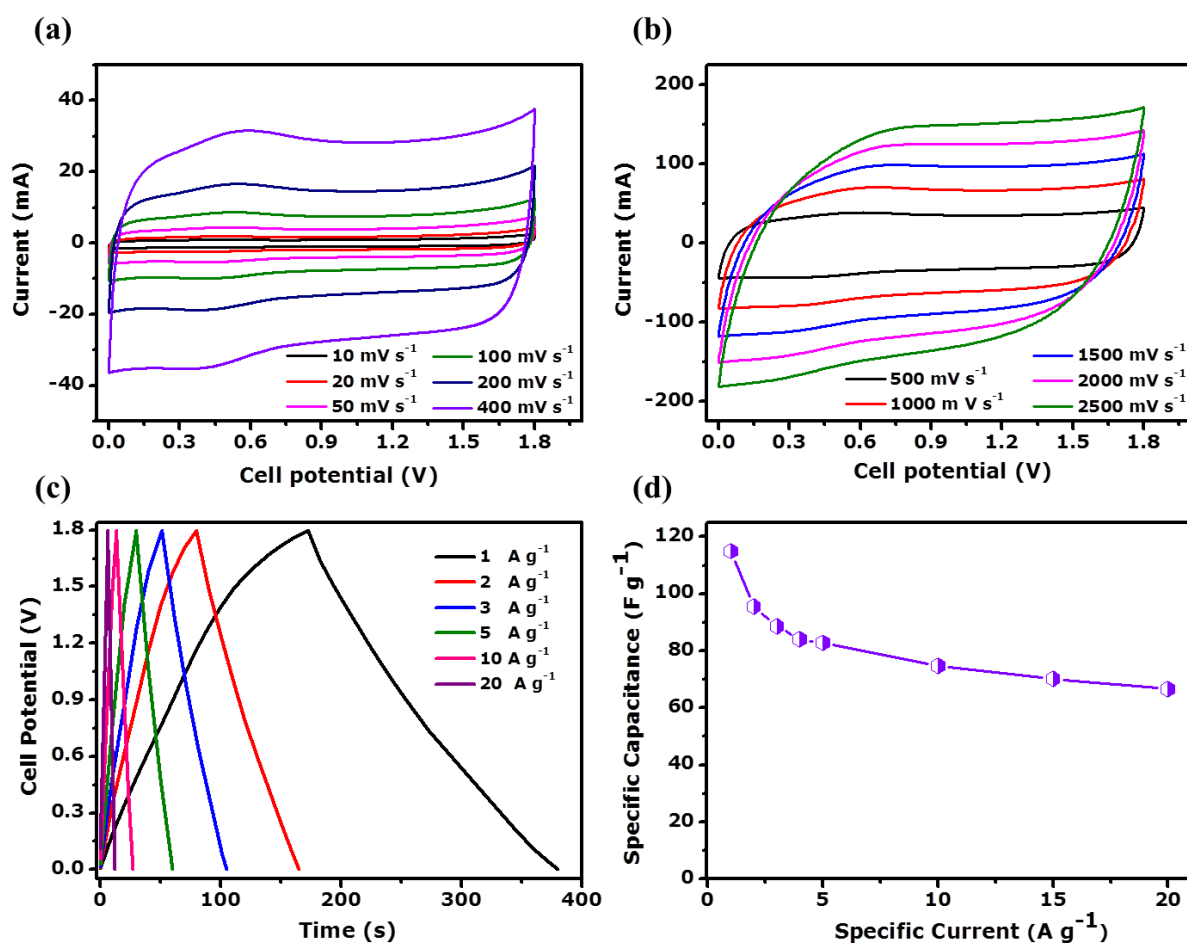


Figure 9: (a, b) Cyclic voltammetry at scan rates variant from 10 - 400 mV s⁻¹ and from 500 - 2500 mV s⁻¹, respectively, (c) galvanostatic charge-discharge profiles at various specific currents from 1 to 20 A g⁻¹ and (d) specific capacitance as a function of specific current for PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 symmetric cell.

GCD plots of the assembled device in the operating potential of 0 - 1.8 V are shown in figure 9(c). A typical triangular behaviour was recorded for all GCD plots at various specific currents from 1 to 20 A g⁻¹ confirming the capacitive charge storage mechanism of the symmetric ternary composite device [101]. The plot of the obtained specific capacitance (C_s) calculated using equation (2) against the specific current from 1 to 20 A g⁻¹ is depicted in figure 9(d). The recorded value C_s of the ternary composite device was found to be 115 F g⁻¹ at 1 A g⁻¹ specific current. The ternary composite PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 device still delivered a high C_s of 67 F g⁻¹ even after a twentyfold increase of specific current which confirms the good rate capability of 58.3% obtained from the symmetric supercapacitor.

Figure 10(a) depicts the specific energy against specific power (Ragone plot) measured at various specific currents (1 - 20 A g⁻¹). The symmetric ternary composite device recorded high specific energy of 51.8 W h kg⁻¹ with an associated power of 0.9 kW kg⁻¹ at 1 A g⁻¹. Interestingly, the symmetric ternary composite device can maintain up to 30 W h kg⁻¹ of specific energy with a corresponding specific power of 18 kW kg⁻¹ even at 20 A g⁻¹ increase of specific current. These specific energy/power values recorded for the PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 symmetric cell are better than reports on Mo-based/C composites for supercapacitors applications as shown in Table S2.

To investigate the stability of the PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 device, the cycling test based on the long-term galvanostatic charge-discharge was performed at 10 A g⁻¹ specific current as shown in figure 10(b). The ternary composite device recorded a columbic efficiency of 99.8% up to 25,000 charge-discharge cycles and a capacitance retention found to be 94%, 92% and 83% after 7,000, 15,000 and 25,000 constant charge-discharge cycles, respectively. These results indicate that even up to 25,000 continuous cycling the ternary composite device still maintains good stability with a specific capacitance loss of 17% as compared to the initial value. The good long-term stability of the symmetric device is owed to the rapid electron transfer kinetics offered by the ternary composite electrode.

An additional stability performance, floating test (or voltage holding) has been investigated on the PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 symmetric supercapacitor. Figure 10(c) displays the variation of the specific capacitance versus the floating time of each 10 h during 150 h at a maximum potential cell of 1.8 V at 10 A g⁻¹. An increase of 21 % from the initial value of the specific capacitance is observed during the first 60 h of floating subsequently stabilizing up to 150 h floating time. The specific capacitance of the ternary composite device was enhanced from 74.7 to 90 F g⁻¹ after the floating time which also highlights an improvement of the specific energy from 33.7 to 40.2 W h kg⁻¹.

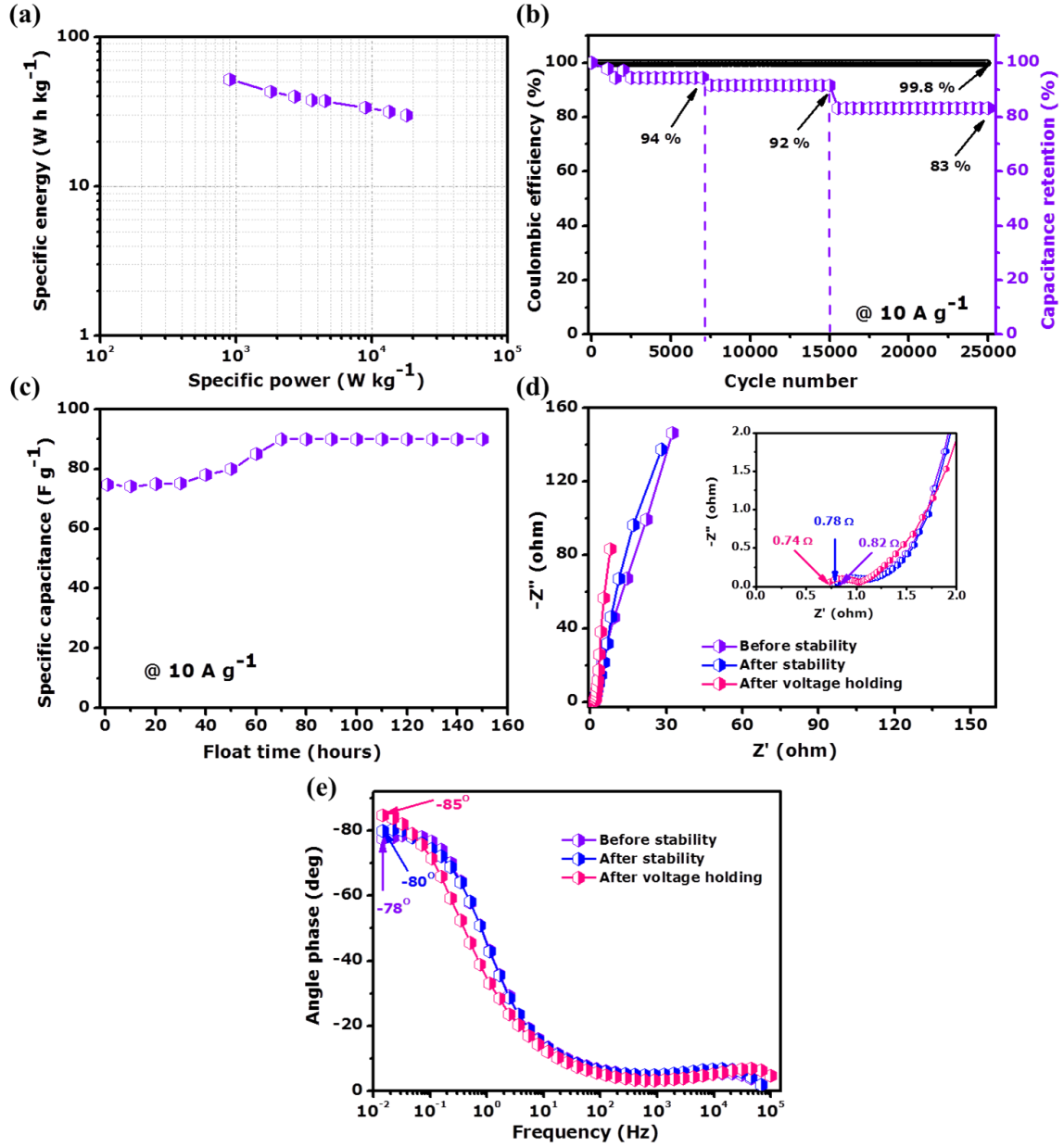


Figure 10: (a) Ragone plot, (b) cycling stability up to 25,000 cycles, (c) specific capacitance as function of voltage holding time up to 180 h, (d) Nyquist plots and (e) Bode plot of PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 symmetric cell.

The improvement of the PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 device in the specific capacitance and specific energy could be ascribed to more penetration of ions electrolyte into the network of MoO₂ and Mo₂C nanoparticles embedded in the porous carbon. This could consequently increase the electrode wettability and enable faster diffusion of electrolyte ions at the electrode/KNO₃ electrolyte interface, hence enhancing the charge storage [102][103].

In brief, the as-fabricated PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 device revealed a good stability performance in terms of long-term cycling up 25,000 cycles and floating time over 150 h thereby implying a superior electrochemical performance of the entire device.

Figure 10(d) illustrates the Nyquist plots of PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 symmetric supercapacitor before and both after long-term cycling and holding test. All Nyquist plots exhibit a nearly vertical feature at low frequency referring to the ideal capacitive characteristic and the great electrical conductivity of the PAC/MoO₂/Mo₂C-1 ternary composite. A slight decrease of the *ESR* values was observed from the original value of 0.82 Ω to 0.78 Ω and 0.74 Ω for both after 25,000 cycles and 150 h floating test respectively as shown in the inset to figure 10(d). Similarly, the *R_{ct}* value depicted also a small decrease from the initial value of 1.14 Ω to 1.11 Ω and 1.04 Ω after cycling and holding tests, respectively. These small *ESR* and *R_{ct}* values demonstrate a fast charge transport capability and rapid ion diffusion through the full symmetric device which got improved by the stability tests as indication that the electrode had better wettability after stability [104].

The Bode plot of the as-fabricated-symmetric device which defines the plot of the angle phase versus frequency is shown in figure 10(e) before and after cycling stability and voltage holding. The phase angle values increased from -78° to -80° and -85° after cycling and holding test, respectively. These values are close to -90° which confirm the ideal capacitive behaviour of the PAC/MoO₂/Mo₂C-1 ternary composite [105].

According to these results, the as-fabricated symmetric supercapacitor demonstrated a superior electrochemical performance after cycling and holding test in aqueous electrolyte which could be due to the fact that the electrodes wettability had been improved and hence ions have more access to the pores. The high performance of the PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 symmetric supercapacitor is based on the synergistic effect of the ternary composite with the following benefits:

(i) High electrical conductivity of Mo₂C, (ii) pseudocapacitor effect of MoO₂ and (iii) large surface area of porous carbon (PAC). Owing to these advantages, the PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 can be used as an excellent charge storage device.

4. Conclusion

A ternary peanut shell activated carbon/molybdenum oxide/molybdenum carbide (PAC/MoO₂/Mo₂C) composite was successfully synthesized via a facile in-situ pyrolysis route of ratio of porous carbon to different mass loading of ammonium molybdate (1:0.5; 1:1; 1:2). All as-synthesized materials display the in-situ formation of MoO₂ and Mo₂C nanostructures into the porous carbon based on the XRD, Raman, HRTEM, SAED, EDX mapping and XPS analysis. The ternary composite with the mass ratio of 1 to 1 (PAC/MoO₂/Mo₂C-1) provided a superior electrochemical characteristic in a neutral 2.5 M KNO₃ electrolyte. The as-assembled PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 symmetric device delivered an excellent specific capacitance of 115 F g⁻¹ at 1 A g⁻¹ with a good rate capability (58 % at 20 A g⁻¹) and cycling stability (99.8% columbic efficiency after 25000 cycles). Moreover, a specific energy of 51.8 W h kg⁻¹ with a corresponding power of 0.9 kW kg⁻¹ was recorded for the symmetric device within an operating potential window of 1.8 V at 1 A g⁻¹ specific current. Interestingly, the electrochemical results of the device show a significant enhancement of 21 % from its initial specific capacitance value after 160 h holding test. These remarkable performances are linked to the great synergistic effect of the different components into the ternary composite by supplying favourable properties: Pseudocapacitor behaviour of the MoO₂, highly conductive Mo₂C and high surface area of the porous carbon. This study provides a simple and low cost way to enhance the electrochemical performance of carbons by incorporating Mo-based components into porous activated carbon.

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4.3.3 Concluding Remarks

In summary, ternary composite PAC/MoO₂/Mo₂C was successfully designed through a simple one-step pyrolysis of PAC to various mass ratios ammonium molybdate at 850 °C. The structural, morphological characterizations have confirmed that the MoO₂ and Mo₂C nanostructures are well embedded into the porous PAC. PAC/MoO₂/Mo₂C-1 ternary composite with the optimal mass ratio of PAC to molybdenum precursor has shown the best electrochemical features. In three-electrode configuration, PAC/MoO₂/Mo₂C-1 electrode superior electrochemical performance with a specific capacitance of 253 F g⁻¹, low internal resistance and good rate capability as compared to PAC electrode with 167 F g⁻¹ at 1 A g⁻¹ in 2.5 M KNO₃ aqueous electrolyte. This enhanced performance is correlated to the synergistic effect of each component of the ternary offering additional active sites, faster ions diffusion rate and chemical stability. The as-fabricated symmetric device delivered a high specific energy 51.8 kW h kg⁻¹ with an associated specific power of 0.9 kW kg⁻¹ within a cell voltage of 1.8 V at 1 A g⁻¹ specific current. Moreover, a long-term cycling stability up to 25,000 cycles with a capacitance retention 83% was recorded. This research work suggests a simple and sustainable way to enhance the supercapacitive performance of carbon based materials by incorporating Mo-based components.

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5.0 General conclusions and future works

5.1 Conclusions

In the desire to obtain a single energy storage technology that combines low cost, high specific energy power, this work has addressed some of the research questions on activated carbons derived from peanut shells and their molybdenum-based nanocomposites for supercapacitor applications. Their physicochemical, surface and electrochemical properties have been successfully achieved using various techniques. All activated carbon materials were synthesized using chemical vapour deposition (CVD) and characterized by N₂ adsorption-desorption, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), high resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS). The electrochemical analysis of the as-synthesized materials was performed in three-electrode and two-electrode configurations using cyclic voltammetry (CV), galvanostatic charge discharge (GCD), electrochemical impedance spectroscopy (EIS) and stability tests. The obtained results from this study led to the conclusions below:

➤ Activated carbon derived from peanut shell waste (APSW) has been successfully prepared through two-step process: Pre-carbonization followed by a chemical activation using potassium-based activating agents (AAs) at various mass concentrations. The effect of the KHCO₃, K₂CO₃ and KOH and their mass concentrations on the morphological, structural, textural and electrochemical properties of the APSW has been investigated.

The APSW prepared with KOH at a the optimal mass ratio of carbonized PSW to KOH (1:4) (APSW-KOH4) resulted in the formation of hierarchically porous carbon with the highest specific surface area of $2547 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $1.2 \text{ cm}^3 \text{ g}^{-1}$ as compared to the other samples. The APSW-KOH4 electrode showed excellent electrochemical performance which can be explained by the favorable accessibility of the electrolyte ions within the surface of the electrode and easy ion transport related to large SSA associated with the combination of micro-, meso- and macro-pores.

This study demonstrated the effect of the potassium-based AAs on the microstructures and electrochemical properties of the APSW materials which contributed to the way to design and tune the properties of the porous carbon by choosing the appropriate AAs.

➤ To further enhance the electrochemical properties of best activated carbon that was achieved from the varying AA, nitrogen-doped porous peanut shell activated carbon (NPAC) was synthesized by two-step procedure: First chemical activation of the PSW with KOH followed by post nitrogen-doping of porous peanut shell activated carbon (PAC) using melamine. The impact of the mass ratio of KOH to raw material (PSW: KOH) on the physicochemical and electrochemical properties of the NPAC has been compared and evaluated. The best electrochemical performance was obtained with NPAC-1 prepared with an equal mass ratio of KOH to PSW. Through the comparison between the electrochemical of the N-doped and non-doped electrodes, it turns out that the NPAC-1 electrode showed higher specific capacitance of 216 F g^{-1} as compared to 167 F g^{-1} for PAC-1 electrode at 1 A g^{-1} in a 2.5 M KNO_3 . The introduction of the nitrogen into the porous carbons enhanced their physicochemical characteristics and provided more electrochemical active sites leading to an increase of performance in supercapacitors.

This study emphasized that the N-doped porous carbon is a promising approach to enhance the surface chemistry and capacitive properties, thus an increase in the energy storing capability.

➤ The second approach of improving the electrochemical properties of the best activated carbon from PSW was to introduce pseudocapacitive materials to it by making composite. In this regard, ternary composite of porous peanut shell activated carbon/molybdenum oxide/molybdenum carbide (PAC/MoO₂/Mo₂C) has been prepared via one-step pyrolysis route by varying mass ratios of PAC to ammonium molybdate tetrahydrate (1:0.5; 1:1; 1:2).

The influence of the mass loading of the molybdenum precursor on the surface chemistry, the structural and textural properties of the ternary had been studied. PAC/MoO₂/Mo₂C-1 with a mass ratio of 1: 1 exhibited superior electrochemical performance. The incorporation of MoO₂ and Mo₂C nanostructures into the PAC has led to a significant improvement on the electrochemical performance with a specific capacitance of 253 F g⁻¹ higher than the pristine PAC-1 (167 F g⁻¹) at 1 A g⁻¹ in a 2.5 M KNO₃. These excellent results are attributed to the good synergistic effect of the properties of each component such as high surface area associated with the porous structure of PAC, pseudocapacitance effect from the faradaic reactions of MoO₂ and good electrical conductivity and chemical stability of Mo₂C.

This study demonstrated a sustainable and eco-friendly one-step pathway of synthesising a ternary composite PAC/MoO₂/Mo₂C as advanced electrode material for supercapacitors. Moreover, this study also emphasised on an efficient strategy to improve the electrochemical properties towards incorporating Mo-based components into the porous carbon materials.

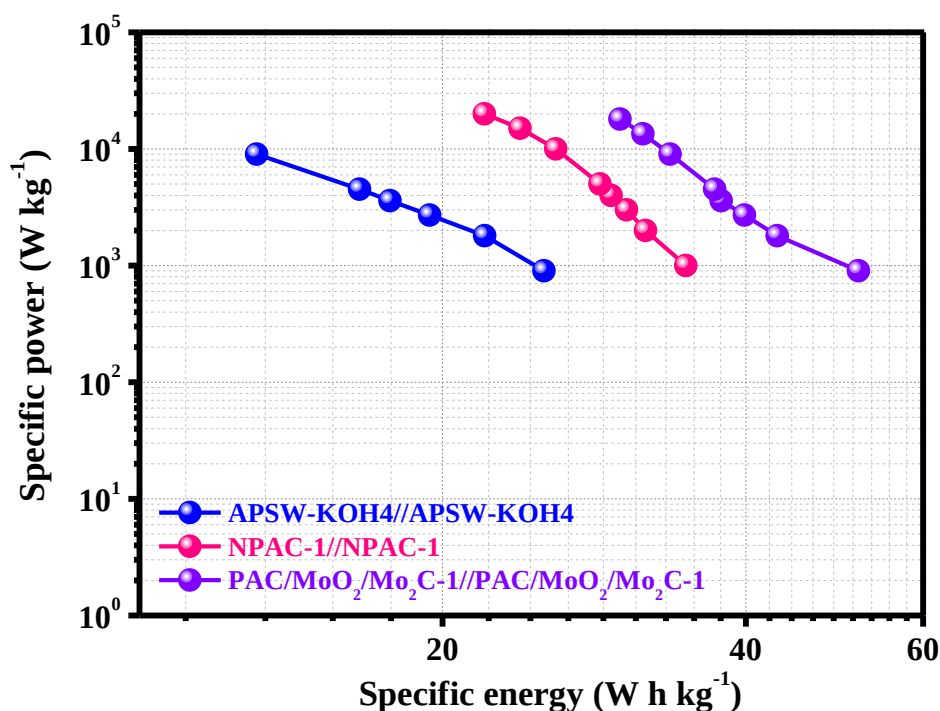


Figure 5.1: Ragone plot of APSW-KOH4// APSW-KOH4, NPAC-1//NPAC-1 and PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 symmetric devices.

The electrochemical performance of the best as-synthesized electrodes materials have been tested in symmetric devices in 2.5 M KNO₃ aqueous electrolyte: APSW-KOH4// APSW-KOH4, NPAC-1//NPAC-1 and PAC/MoO₂/Mo₂C-1//PAC/MoO₂/Mo₂C-1 and their results are compared and summarized in the Ragone plot as shown in figure 5.1. It is clearly shown that all symmetric devices based-carbon material exhibit good electrochemical performance with a wide cell potential in the range of 1.8 - 2V. In particular, the PAC/MoO₂/Mo₂C-1 electrode reveals the highest electrochemical performance as compared to others.

This dissertation highlights low cost, eco-friendly and efficient strategies to improve the electrochemical properties via a novel post nitrogen-doping route and incorporating Mo-based components into the porous activating carbon nanostructures for high-performance energy storage.

5.2 Future works

In future work, the electrochemical performance of PAC/MoO₂/Mo₂C ternary composite will be further investigated in hybrids capacitors. The as-assembled device with PAC/MoO₂/Mo₂C as negative electrode and faradaic material as positive electrode will combine both merits of capacitive and faradaic properties and extend the operating potential which will result to further improvement of their specific energy storing capability while still retaining their high specific power. The investigation of their electrochemical performance in various aqueous and ionic liquid electrolytes can be explored for supercapacitors.

Another study to be considered will be on the investigation molybdenum titanium carbide (Mo₂Ti₂C₃T_x) electrode material which belongs to two dimensional transitional metal carbides (MXenes) for supercapacitor applications