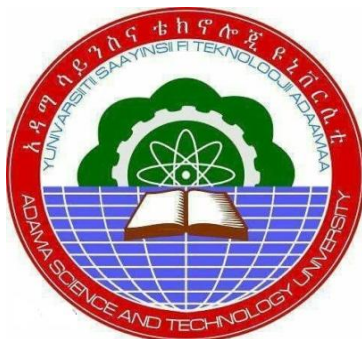


Manganese Dioxide/Water Hyacinth Based Activated Carbon Nanocomposite for Electrochemical Supercapacitor



Tilahun Temesgen Oli

A Thesis Submitted to the Department of Applied Chemistry

School of Applied Natural Science

**Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Applied
Chemistry (Physical Chemistry)**

Office of Graduate Studies

Adama Science and Technology University

October, 2023

Adama, Ethiopia

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Declaration

I declare that this thesis research entitled “**Manganese Dioxide/Water hyacinth Based Activated Carbon Nanocomposite for Electrochemical Supercapacitor**” is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

Tilahun Temesgen Oli

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Recommendation

This is to certify that the thesis entitled “**Manganese Dioxide/Water hyacinth Based Activated Carbon Nanocomposite for Electrochemical Supercapacitor**” submitted in partial fulfillment of the requirement for the degree of Master of Science in Applied Chemistry (Physical Chemistry), the Graduate program of the Department of Applied Chemistry, and has been carried out by Tilahun Temesgen, under my advises. Therefore, I recommend the submission of a revised version of the thesis to the department following the applicable procedures.

Yilkal Dessie (Ph.D.)

Advisor

Signature

Date

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I, the advisor of the thesis entitled “**Manganese Dioxide/Water hyacinth Based Activated Carbon Nanocomposite for Electrochemical Supercapacitor**” and developed by Tilahun Temesgen, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Yilkal Dessie (Ph.D.)

Advisor

Signature

Date

We, the undersigned, members of the Board of Reviewers of this thesis by Tilahun Temesgen have read and evaluated the thesis research entitled “**Manganese Dioxide/Water hyacinth Based Activated Carbon Nanocomposite for Electrochemical Supercapacitor**” and assessed the understanding of the candidate about the thesis research. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Applied Chemistry (Physical Chemistry).

Defaru Negera (Ph.D.)

Chairperson

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Date

Fedlu Kedir (Ph.D.)

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Sisay Tadesse (Prof.)

External examiner

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Date

Final approval and acceptance of the thesis is contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

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List of Acronyms and Abbreviations

AC	Activated carbon
BET	Brunauer-Emmett-Teller
CBD	Chemical bath deposition
C_{dl}	Double layer Capacitance
C_s	Specific Capacitance
CV	Cyclic Voltammetry
ED	Energy Density
EDLCs	Electrical double layer capacitors
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series Resistance
FT-IR	Fourier-Transform infrared,
GCD	Galvanostatic Charge Discharge
HK	Horvath-Kawazoe Method
LF	Leaf
MO	Metal Oxides
NL-DFT	Non-local-density functional theory
NS	Nanostructure
PCs	Pseudocapacitors
PD	Power Density

RT	Room Temperature
SCs	Supercapacitor
SEM	Scanning electron microscopy
SSA	Specific Surface Area
TGA-DTA	Thermo gravimetric-Differential thermal analysis
UV-Vis	Ultraviolet Visible Spectroscopy
XRD	X-ray diffraction
WH	Water hyacinth

List of Symbols

α –MnO ₂	Alpha-phase manganese dioxide
β –MnO ₂	Beta-phase manganese dioxide
γ –MnO ₂	Gamma-phase manganese dioxide
δ –MnO ₂	Delta phase manganese dioxide
ϵ -	Dielectric permittivity
ϵ_0 -	Permittivity of vacuum
λ –MnO ₂	Lamda phase manganese dioxide
Δt	Time interval
ΔV	Voltage interval (Potential Window)

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Abstract

Using electrode materials that are inexpensive, abundant, renewable, and ecologically benign for clean energy sources like Supercapacitor (SCs) is an efficient way to build a sustainable future. This study is aimed at the synthesis, characterization, and electrochemical SCs performance testing of a manganese dioxide (MnO_2) nanostructure and its composite with activated carbon (MnO_2/AC). In the green synthesis of MnO_2 and MnO_2/AC nanocomposite, *Eichornia crassipes* (water hyacinth) leaf extract was employed as reducing and capping agents, and its stem part was used as the precursor to prepare activated carbon (AC) through the chemical activation method in self-generated atmospheric conditions. The biosynthesized MnO_2 and MnO_2/AC nanocomposite were characterized using TGA-DTA, X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV-Vis spectroscopy, Brunauer-Emmett-Teller (BET) analysis, and FT-IR spectroscopy. XRD analysis identified the formation of the δ - MnO_2 phase structure with crystallite sizes of 2.75 nm, 2.22 nm and 2.78 nm for metal to plant extract ratios of 1:3, 1:1, and 3:1 nanostructures (NS), respectively. The band gap energy changed from 1.51 to 1.37 eV, with the corresponding BET specific surface area (SSA) values of $498 \text{ m}^2 \text{ g}^{-1}$ and $601 \text{ m}^2 \text{ g}^{-1}$ for MnO_2 and when it was composited with AC, respectively. SEM micrograms and FT-IR analysis revealed the presence of MnO_2 and its composite in a cluster of spherical NS with an oxygenic functional group-rich surface. A three-electrode system with an IVIUM electrochemical workstation was employed to measure their SCs performances in a 6M KOH aqueous electrolyte. The result showed that an excellent specific capacity (Cs) of 224 F g^{-1} was obtained using MnO_2/AC nanocomposite as compared to the capacitance of individual components WH_3 (75 F g^{-1}) and Mn (1:1) (108 F g^{-1}) samples of activated carbon and MnO_2 , respectively, at 3 A g^{-1} current density. It also showed its original capacitance retention of 95% after 2000 galvanostatic charge discharge (GCD) cycles. Thus, green synthesized MnO_2 NS and its composite with AC, derived from water hyacinth stem are a promising for use as electrode materials in electrochemical SCs.

Key words: Supercapacitor, Water hyacinth, Activated carbon, electrode materials, green synthesis and chemical activation

CHAPTER ONE

INTRODUCTION

1.1. Background of the Study

Due to the expanding human population and quick industrial development, there is an urgent need for green, highly efficient, sustainable, and renewable energy supplies. To date, many energy conversion and storage technologies, such as the solar cell (Al-Ezzi & Ansari, 2022), fuel cells (Fan et al., 2021), super capacitors (SCs) (Ping et al., 2019) and battery (Ling, 2022), have been developed with the ultimate goal of utilizing renewable energy sources. Due to their high power density, quick charge/discharge, cycle stability, and safe operation, SCs have been recently attracted a lot of attention as a promising energy storage device (Anil Kumar et al., 2023). Since SCs performance is heavily reliant on the activity and kinetics of the electrode material, it is crucial to choose an electrode material with an optimized structure, increased activity, and enhanced kinetics in order to improve SCs electrochemical performance.

Pseudo-capacitors (PCs) electrode materials like transition metal oxides (TMO) have received a lot of attention since they can undergo reversible redox reactions that result in the generation of charges that could meet the demands of high energy SCs (Yu et al., 2020). Manganese dioxide (MnO_2) has emerged as a desirable candidate metal oxide for efficient electrode material for SCs among several of the known TMOs. This is due to its abundant sources, strong electrochemical activity, diverse morphologies, large theoretical capacitance (1370 F g^{-1}), and environmental friendliness (Zhang et al., 2020). However, the major limitation of MnO_2 electrode in SCs is its low chemical stability and low ionic conductivity, which makes it difficult to sustain its long cycle life and high rate charge-discharge processes, respectively (Wang et al., 2015). Recently, electrochemical double layer capacitors (EDLCs) electrode materials such as porous carbons (ACs) have gained an interest since they are produced from renewable, inexpensive, and abundantly available biomass (Gao et al., 2017). Although porous carbons are remain stable and possess large SSA, but their specific capacitance and energy density are still relatively small as compared with their theoretical capacitance. Making a hybrid composite with MnO_2 electrode material and porous carbon electrode material is a good way to combine their advantages and thus, increase their capacitance. For instance, the introduction of porous carbon accelerates electrolyte ion transport due to its high porosity and results better life cycle of the material in

SCs since no chemical reaction is involved (Zhai et al., 2022). The introduction of PCs electrode materials, on the other hand, can achieve high energy densities because the electrode materials in these devices can undergo reversible redox reactions that generate charges and cause a faradic current to flow through the SC cell when potential is applied (Zhang et al., 2015).

Recent studies have shown that it is possible to synthesize nanoparticles using a green chemistry method and a variety of plant extracts for a variety of applications. However, there are few or no reports of the green synthesis of MnO_2 nanomaterial and its composite with AC employing Water hyacinth (*E. crassipes*) plant leaf extract as a reducing and capping agent for SCs application. Water hyacinth is the worst aquatic plant that has a number of negative ecological and economic effects on freshwater habitats (Degaga, 2019). Its leaf extract contains a variety of bio-molecules, including phenolic, alkaloids, flavonoids, sterols, and saponins, which may have significant reducing or stabilizing effects in green synthesis method, as previously reported (Netai et al., 2016). In addition, Water hyacinth-based AC has a well-designed hierarchical structure that results in a large specific surface area (SSA), good electrical conductivity, and significant electrochemical characteristics (Zheng et al., 2017). Consequently, using water hyacinth plant for preparing AC and nanomaterials is a viable strategy for creating affordable, eco-friendly, and high-performance electrode materials for SCs application. In this thesis work, a composite of MnO_2 with AC was made using a simple green synthesis method using water hyacinth plant extract, and the resulting nano-composite displayed excellent specific capacitance.

To date, an inert gas or controlled atmospheric condition has been used to carry out the carbonization process during AC preparation. This typically requires a furnace with the proper installation to regulate the flow of inert gases like nitrogen. As a result, the process becomes more expensive when scaled up to an industrial level because large amounts of gas are required. However, according to earlier studies, it is possible to prepare an efficient activated carbon by chemical activation without using a controlled atmosphere during carbonization (Anisuzzaman et al., 2015; Yousfi et al., 2020). This will allow a non-negligible savings in the preparation costs of porous carbons such as AC. Thus, in this study, AC were prepared by chemical activation methods using self generated atmospheric condition employing the stem part of Water hyacinth as a renewable and readily available carbon source for SCs application.

1.2. Statement of the Problem

Scientists are encouraged to look for renewable energy supplies that can replace fossil fuels because of the release of polluting gases from them. Due to their high power density, quick charge/discharge, cycle stability, and safe operation, SCs have recently attracted a lot of attention as a promising energy storage device (Anil Kumar et al., 2023). However, their characteristic low energy density is still the problem that needs further research to be solved. Recently, Pseudocapacitors (PCs) electrode materials such as transition metal oxides (TMO) have been emerged as desirable candidates for SC since it can undergo redox reaction that enhances energy density of SCs. Compared to other TMO, RuO_2 has a higher specific capacitance, but it is also quite expensive, toxic, and rare (Godlaveeti et al., 2021). MnO_2 is regarded as a viable electrode material for SCs due to its excellent electrochemical characteristics, abundant found, low cost, and environmental friendly (Shen et al., 2018). MnO_2 nanomaterial can undergo fast and reversible Faradaic redox reactions which is characteristics of its excellent electrochemical performance and results high specific capacitance. However, poor life cycles (low chemical stability) still the problem which needs further research to improve. On the other hand, porous carbons possesses large specific surface area (SSA), remain stable, long cycle life and high rate charge-discharge, but their specific capacitance (Cs) and energy density (ED) are relatively low (Zhang et al., 2020). Hence, making a hybrid composite with MnO_2 electrode material and AC electrode material is a good way to combine these advantages and improve their energy storage capacitance.

1.3. Objective of the Study

1.3.1. General Objective

The overall objective of this study is to synthesize and characterize MnO_2/AC nanocomposite using Water hyacinth as AC precursor for electrochemical SCs applications.

1.3.2. Specific Objective

- To synthesis MnO_2 nanostructures using Water hyacinth leaf extract for comparative purpose.

- To prepare porous activated carbons (ACs) through chemical activation method derived from Water hyacinth stem by KOH and K_2CO_3 as chemical activation agents to obtain high SSA carbons.
- To prepare MnO_2 based ACs nanocomposites with different forms of carbon samples through green synthesis method using Water hyacinth leaf extract.
- To evaluate the supercapacitive performance of all electrode materials loaded on the nickel foam through drop casting method without any addition of conductive additive agent.

1.4. Significance of the study

This study helps to utilize renewable biomass and their derivative, such as (ACs) as promising alternatives to replace traditional with non-sustainable electrode materials particularly in SCs devices. Since water hyacinth is affecting water bodies like lakes etc. so, utilizing it indirectly reduces its disadvantage. It also aimed to improve reliable, inexpensive, limitless eco-friendly energy sources in order to construct a sustainable future. Generally, this study provides information regarding the application of MnO_2 nanostructure composited with Water hyacinth based AC for potential electrochemical SCs. Moreover, the findings of this study will be used as a baseline by other researchers for further study in this area.

1.5. Scope of the Study

This study is limited to synthesize AC using water hyacinth stem as a precursor employing KOH and K_2CO_3 as activating agent in self-generated atmospheric condition, green synthesize of MnO_2 nanostructure and MnO_2 /AC composite *via* water hyacinth leaf extract, fabrication of electrodes from as-synthesized AC, MnO_2 and MnO_2 /AC composite, characterization of as-synthesized materials using SEM, XRD, TGA-DTA, BET, UV-Vis and FT-IR spectroscopy and electrochemical investigation using CV, GCD and EIS method in standard three electrode system workstation and examination of the performances of as-synthesized material for SCs application.

CHAPTER TWO

LITERATURE REVIEW

2.1. SCs and Their Charge Storage Mechanism

SC is an electrochemical energy storage device with much higher power density (PD) than batteries and much higher energy density (ED) than conventional capacitors. The SCs has several advantages such as low ohmic equivalent series resistance (ESR), higher PD which describes how quickly the device can deliver energy, long cycle life, charging and discharging in seconds without termination of charge required, and high coulombic efficiency as compared to batteries (Maher et al., 2021).

Based on the mechanism of the charge storage, SC can be divided into three types, including EDLCs, PCs, and hybrid capacitors. Here, EDLCs store charge electro-statically (no chemical reaction), PCs store charge *via* redox reactions involving transferring charge between electrolytes and electrodes, and hybrid capacitors store charge through a combination of faradic and non-faradic materials (Lokhande et al., 2020).

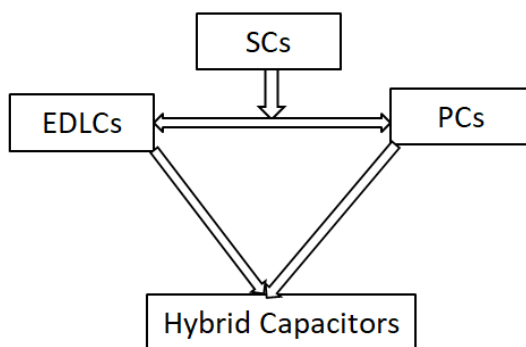


Figure 1: Types of SCs

Table 1 Comparison between PCs, EDLCs and Hybrid capacitors (Maher et al., 2021)

Parameters	EDLCs	PCs	Hybrid capacitors
Storage mechanism	Non faradic/electrostatic	Faradic, reversible redox	Both faradic and non faradic

		reaction	
Specific capacitance	Lower	Higher	Higher
Energy density	Lower	Higher	Higher
Power density	Higher	Lower	Higher
Stability	Higher	Lower	Higher
Electrode material	Carbon based material	MO and Conductive polymers	MO/Carbon based material and Conductive polymer/Carbon based material

2.1.1. Electrochemical Double Layer Capacitors (EDLCs)

The electrostatic physical adsorption and desorption of electrolyte cations and anions onto electrode surfaces is the fundamental process in EDLCs when the electrode is charged without transferring charge between the electrode material (Inagaki et al., 2014). During charging the negative and positive ions in the electrolyte attracted to the positively and negatively charged electrodes surfaces, respectively. The stored charge is released through the external circuit to power the load as the cation and anion leave the solid electrode's surface during discharge and return to the electrolyte body (Ma et al., 2023). This process results in the storage of charge between the electrode's surface and the electrolyte ion, as depicted in Figure 2. Since the EDLCs materials can react to potential changes quickly, they can rapidly deliver energy during the discharging process (Sagadevan et al., 2021). Equation 1 below illustrates how the small distance (d) (often less than 0.5 nm) between electrolyte ions and the large electrode surface area (A) provide EDLCs a larger electric capacity than conventional capacitors (Sagadevan et al., 2021; Siraj et al., 2020).

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (1)$$

Where, C is capacitance, ϵ_0 is electrical permittivity of vacuum, d is thickness of the double layer ϵ_r is dielectric constant of electrolyte, and A is surface area of electrode.

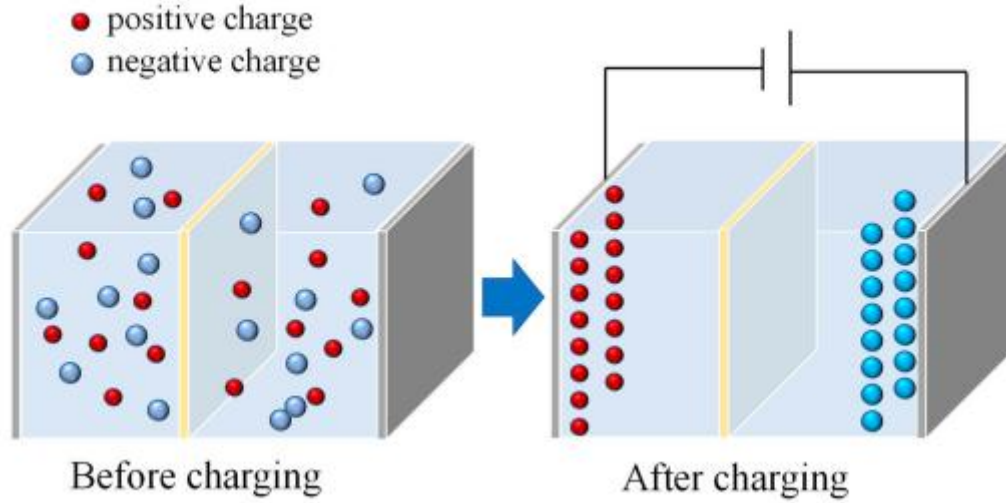
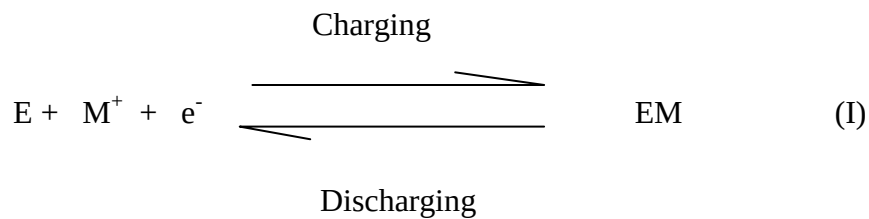


Figure 2: Operating principle of EDLCs (Ma et al., 2023)

2.1.2. Pseudocapacitors (PCs)

In contrast to EDLCs, PCs operate through charge transfer between the electrolyte and the electrode arising from redox reactions when potential is applied on the electrode (Bhat et al., 2020). The Faradic process, which results in a buildup of electrons at the electrode, involves the transmission of electrons produced by the redox reaction across the electrolyte/electrode contact. Reactions are reversed when it is discharged as shown by reaction (I) below (Arumugam et al., 2023). During discharging, there is a reversal of reactions then electrons are released.



Where, E stands for electrode, M^+ metal ion and e^- electron.

The capacity of a PCs is larger than that of an EDLC of the same volume or weight, thus it will be able to deliver higher ED; however these suffer from relatively lower PD than EDLC types due to Faradaic reactions (C. Yang, 2021).

2.1.3. Hybrid capacitor

Hybrid capacitors technology is aimed to achieve SCs with high performance through combining the EDLCs and PCs storage principles. Hybrid capacitors produce higher Cs using EDLCs and other PCs electrode materials. This combination has the advantage of generating higher PD and higher ED than the individual components while minimizing the shortcomings of the combining components (Muzaffar et al., 2019a). Compared to PCs, EDLCs have a lower capacitance but a higher PD due to the absence of a chemical reaction during the charge/discharge process. Therefore, both Faradic and non-Faradic methods can be used in combination to produce high power densities and eliminate the drawbacks of EDLC and PCs. As a result, these hybrid SCs can reach higher ED and PD as well as longer cycle stability of the material (Lokhande et al., 2020; Sharma & Chand, 2023).

2.2. Electrode materials in Electrochemical SCs

For improved SCs performances, electrode materials must be carefully selected and designed. SCs electrode materials must possess high electrical conductivity, great chemical stability, excellent corrosion resistance, wide specific surface area, and environmental friendliness in order to make SC that work properly (Forouzandeh et al., 2020; Salleh et al., 2023). Here, they can be categorized into three subsections, including EDLC, PCs, and Hybrid SCs electrode materials.

2.2.1. EDLCs electrode materials

These materials store electrical energy by ions adhering to high SSA carbons at the electrode surface without undergoing a redox reaction (Jiang et al., 2020). In EDLCs, the electrode materials are primarily carbon-based materials such ACs, graphene, and carbon nanotubes. Carbon nanotubes are a type of long, hollow, one-dimensional (1D) carbon nanostructure with a diameter below 10 nm (Venkataraman et al., 2019). Graphene is a two dimensional (2D) carbon nanomaterial, and one promising candidate for SC electrodes due to its large theoretical SSA ($2630 \text{ m}^2 \text{ g}^{-1}$), superior conductivity and chemical durability, and considerable theoretical Cs (550 F g^{-1}) (Chen et al., 2019). Although porous carbons are remain stable and possess large SSA, but their Cs and energy density are still relatively small as compared with their theoretical capacitance. Carbon nanotube and graphene carbon nanomaterials have high surface area and better conductivity. But because it is less expensive and easier to produce, AC (3D porous

carbon) has emerged as the ideal electrode material for EDLCs and is widely applied in commercialized SCs (S. Saini et al., 2021; Zou et al., 2018). Carbon nanotubes and graphene are more energy consuming and expensive to prepare than ACs, because they are prepared under high vacuum and high temperature (Abbas et al., 2022).

2.2.2. PCs electrode materials

Pseudo-capacitors (PCs) electrode materials can achieve high energy densities as these materials can undergo reversible redox reactions, generating charges and resulting in a faradic current passing through the SC cell when potential is applied, which could satisfy the needs of high-energy SCs (M. Huang, Li, Dong, Zhang, & Li, 2015).

Transition MOs such as RuO_2 , Co_3O_4 , MnO_2 , and NiO and conductive polymers like polyaniline (PANI) and polypyrrole (PPy) are extensively studied as PCs electrode materials due to their ability to undergo fast and reversible redox reaction (P. Saini, 2023; Singu & Yoon, 2017). Despite the advantages of CP, such as its higher electrical conductivity, low cost, and excellent charge density, this material's structural degradation (shrinking/swelling) during the charging/discharging process can seriously damage the rate capability performance and cycling stability of SCs (Jalal et al., 2021). From the various metal oxides, RuO_2 has high specific capacitance than other metal oxides/hydroxide but it is very expensive (Godlaveeti et al., 2021). Manganese oxide (MnO_2) is considered as a promising electrode material for supercapacitors because of its outstanding electrochemical properties, abundant resource, low cost and environmental compatibility (Shen et al., 2018).

PCs electrode materials provide excellent capacitance and ED in comparison to the electrode material of EDLCs. However, poor life cycles frequently served as a counterbalance to such important features. This is owing to the possibility that repeated chemical reaction cycles are degrading the pseudo-capacitive materials and causing undesirable morphological changes, which eventually leads to a decline in performance. In response, it was recommended that using carbon materials would be a great way to solve this issue (Jalal et al., 2021).

2.2.3. Hybrid capacitor electrode Materials

The hybrid capacitors formation results from coupling of different redox and EDLC materials like graphene or graphite, MOs, conducting polymers and AC that are offering chemical and physical charge storage process together in one electrode (Muzaffar et al., 2019b). This combination yields higher Cs than that of PCs and EDLC as well as conventional capacitors. Transition MOs improve the pseudocapacitance capability, thus enhancing the Cs of porous carbon (AC) materials, while the introduction of AC materials accelerates electrolyte ion transport and the life cycle of the material (Ramirez-castro & Soc, 2015). For example, (Qiu et al synthesized MnO₂/graphene composite electrodes employing the sonochemical technique for SCs and showed Cs of 156.1 F g⁻¹ at 100 mV s⁻¹ (Qiu et al., 2019). As-fabricated MnO₂/graphene hierarchical composite electrodes exceed the MnO₂ electrode in terms of Cs and rate capability. These outstanding electrochemical performances are credited to the strong composite structure and synergetic contribution of petal-like MnO₂ arrays and conductive graphene sheets. The increment in the capacitance of the composite is due to the combined effects of transition MOs nanomaterials that undergo fast surface redox (pseudocapacitive) reactions and double layer capacitance (Doloksaribu et al., 2017). Diantoro et al. also prepared composite-based activated carbon with a different mass of 0–20% MnO₂ to improve the performance of activated carbon (Diantoro et al., 2022). They found that with the addition of 15% MnO₂, an excellent Cs of 79.43 F g⁻¹ sustaining 88.88% after 1000 test cycles in 1 M Et₄NBF₄ organic electrolyte.

2.3. Synthesis of AC

Physical activation and chemical activation are mostly employed for activation process to prepare AC from carbon-rich organic precursors such as peanut shells (Qiao et al., 2021), stink bean pod peel (Taer et al., 2021), Willow Wood (Phiri et al., 2019), coke (Lee et al., 2015), rotten carrot (S. Ahmed et al., 2018), Moringa oleifera Leaves (Taslim et al., 2022), and etc.

Physical activation is a common two-step process that involves controlled gasification at relatively higher temperatures while being exposed to oxidizing gases such carbon dioxide, steam, air, or a mixture of these (Wang et al., 2017). Chemical activation has a number of advantages over physical activation, including lower conversion temperatures, quicker activation times, more carbon yield, bigger SSA, and porosity (Abioye & Ani, 2015).

In chemical activation, the material is first impregnated with some chemically activating agents such as KOH (Phiri et al., 2019), ZnCl_2 (Wang et al., 2017), H_2SO_4 (Siraj et al., 2020), K_2CO_3 (Abdulhameed et al., 2021) and then subjected heat treatment under inert condition (Din et al., 2017). Overall, these two processes can result in significant increases in SSA and porosity as well as the development of porous structures with a range of sizes, from nano porous (2–50 nm) to micro porous (>50 nm). For example, Lee et al. prepared coke based AC electrode materials for SCs through physical activation using CO_2 as activating agent. To investigate the impact of CO_2 activation, the electrochemical performance of the obtained activated carbons was investigated (Lee et al., 2015). According to the experimental findings, mesopores grew and micro pores reduced as CO_2 activation progressed, increasing the specific capacity from 13.9 F g^{-1} to 18.3 F g^{-1} .

Farzana et al. also prepared AC from waste compact discs as precursors through the physical activation method for SC application (Farzana et al., 2018). The prepared material exhibited a Cs of 51 F g^{-1} and a PD of 0.7 kW kg^{-1} at a current density of 10 mV s^{-1} in a non-aqueous electrolyte. KOH is the most frequently utilized activating agent in chemical activation processes due to the fact that char materials are more amenable to KOH activation and as a result lead to a larger degree of mesopore and micropore growth, which results in a high SSA but yields low product. Due to its benefits, including its ability to boost AC yield, eco-friendliness, and ability to create oxygen functional groups, K_2CO_3 is also chosen for the preparation of AC (Abdulhameed et al., 2021).

2.4. Synthesis methods of MnO_2 Nanostructure

The preparation method and process parameters govern the activity of MnO_2 nanostructure. MnO_2 has been produced in a variety of morphologies with different sizes, and the electrochemical characteristics of each are being studied. It is possible to synthesize manganese oxide nanostructure both top-down and bottom-up method. Due to expensive preparation costs and consume high energy, the top-down method is not frequently utilized (Bloch et al., 2021; Sahib & Naser, 2021). Thus, most researchers prefer the bottom-up method. To date, a number of techniques, including electro deposition, green synthesis, microwave assisted synthesis, hydrothermal synthesis, and chemical precipitation have been developed for synthesis of MnO_2 nanostructure (Du et al., 2023).

2.4.1. Microwave Synthesis

When compared to conventional heating, microwave heating results in better energy savings because the material's interior temperature is directly affected (Dos Reis et al., 2020). Thus, there are fewer energy losses to the surroundings. As a consequence, conventional heating techniques for the production of nanostructures have been gradually replaced by microwave irradiation. By uniformly heating the reactants, this method can be used to improve the structure and properties of the materials in reactions with slow reaction rates and high activation energies (Baral et al., 2021). For instance, Bello et al. synthesized manganese oxide on nickel foam graphene using a hydrothermal microwave irradiation approach, studied its electrochemical performance, and found that it displayed outstanding cycle stability and Cs of 305 F g^{-1} at 1 A g^{-1} (Bello et al., 2013). The microwave synthesis process has a number of benefits, such as faster reaction times, higher yields, selective heating, and strong repeatability, but it also has some significant drawbacks, such as relatively high reactor costs and challenges with scaling up or reaction monitoring (Mikrovalov et al., 2011).

2.4.2. Hydrothermal synthesis

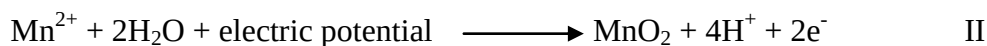
In the hydrothermal synthesis process, an aqueous solution is employed as a reaction system in a particular closed reaction vessel (autoclave) at high temperature and pressure (G. Yang & Park, 2019). A chemical that is weakly soluble or insoluble under normal circumstances is dissolved and then re-crystallized. At high temperatures and pressures, solvents also dissolve and re-crystallize into the desired materials, where variables like reaction temperatures, reaction periods, and solvent amounts all significantly affect the end product's shape and structure. The hydrothermal method has the benefits of a single step, single-phase material manufacturing, good morphology, and product ratio adjustment (T. T. Liu et al., 2013). Additionally, under controlled physical and chemical conditions, it entails the fabrication of electrode materials with great homogeneity and purity (Sharma & Chand, 2023). However, the reaction requires high temperature operation and takes a long time to complete (Kaur et al., 2020). Taranu et al. synthesized rod-like $\alpha\text{-MnO}_2$ nanostructure with the various diameter by hydrothermal method employing $\text{Mn}(\text{CH}_3\text{COO})_2$ and KMnO_4 as reactants (Taranu et al., 2022). In addition, Zhao et al. synthesized urchin-like MnO_2 nanostructure and investigated its electrochemical properties for

SCs (S. Zhao et al., 2015). The electrochemical test of the produced MnO₂ demonstrates optimal cyclic voltammetry behavior, high Cs (151.5 F g⁻¹ @ 1 A g⁻¹ current density), and outstanding cycling stability (93.4% capacitance retention after 1000 cycles), which points to its promising use as SC.

2.4.3. Electrochemical deposition

Electro deposition typically occurs in a three-electrode system in which a metal electrode is immersed in a specific electrolyte solution and an electric field is applied to deposit the desired substance (M. Miao et al., 2022). Working electrode has good electrical conductivity and chemical inertness. In electrochemical deposition, the desired material is deposited on the working electrode, where an electro catalytic reaction takes place, while a reference electrode maintains the working electrode's potential throughout the process.

According to reaction II, the production of manganese dioxide takes place at the electrode (Affrald et al., 2023).



In order to investigate the effects of changing the electrodeposition time on the material's microstructure and electrochemical properties, Dai et al. roduced nanobelt-shaped MnO₂ using the electrochemical deposition method (Dai et al., 2020). They obtained that the optimum time for sample deposition was 50 s, and the material exhibited a Cs of 291.9 F g⁻¹ at the current density of 1 A g⁻¹ and lowest charge transfer. Della Noce et al. also prepared MnO₂ nano flakes by room temperature electro-deposition method and investigated the influence of applied current density on the structure and capacitive performance of MnO₂ electrodes (Della Noce et al., 2017). They noticed that SC significantly decreased as the current density increased, and this effect seemed to be more prominent in samples processed at low current density levels. By adjusting the synthesis conditions, it is possible to control the topologies and morphologies of electrode materials during electrochemical deposition; however, this technique cannot be used for large scale production (Lokhande et al., 2020)

2.4.4. Green Synthesis via Plant Extract

The green synthesis method is a synthesis process resulting in metal nanomaterials using natural components originating from both land- and sea-based organisms (plants and microbes) (Nandiyanto et al., 2021). Green methods are favored and accepted as effective alternatives to producing nanomaterials in a manner that it is safe, economical, and environmentally friendly while chemical methods, which are more expensive and use toxic chemicals that lead negative impacts (Sivanesan et al., 2017). Their stabilizing and capping properties also aid in preventing a dense aggregation, which could results the creation of small-scale nanostructures (Sila et al., 2019). Microorganisms or plant extracts may be employed in this procedure. However, using microorganisms has its own drawbacks in comparison to using green plant extract because they need specialized tools and equipment to be cultured and enhanced for their growth before being used for synthesis (Tilahun Bekele et al., 2021). They also need various parameters to be optimized in order to achieve and maintain growth before being used in the synthesis process. Due to the wide variety of plants, the synthesis of nanomaterials from plant extract has become a popular topic of study all over the world as numerous plant species are being rapidly explored and used in the process. MnO₂ were biosynthesized utilizing different plant extracts including Aloe vera (Joshi et al., 2020), ficus leave (Hasan et al., 2023), Viola betonicifolia (H. Lu et al., 2021), and Hypericum perforatum (Ghorbani et al., 2023). For example, Abuzeid et al. successfully synthesized two MnO₂ nanostructure by cost-effective and environmentally friendly green synthesis approach using orange juice and peel extracts as reducing agents (Abuzeid et al., 2019a). Compared to samples made with orange juice extract (OJ-MnO₂), those made with orange peel extract (OP- MnO₂) have a higher surface area (Abuzeid et al., 2019a). The electrochemical characteristics of OP-MnO₂ exhibits greater capacitance of 139 F g⁻¹ than OJ-MnO₂ 50 F g⁻¹ at 0.5A g⁻¹ current density.

2.4.5. Other methods

There are many synthesis techniques to fabricate nanostructure materials which include Chemical Bath Deposition, Chemical Vapor deposition, sol-gel method and etc. Sol-gel is a dip coating method that often starts with an inorganic solution as a precursor. The method includes a difficult step like gravitational draining with concurrent solvent drying, evaporation, and

condensation. The method allows for homogeneous material composition, textural control, and cost savings over chemical vapor deposition (Ahmad et al., 2018). The main drawbacks include a long reaction period, which is time-consuming, and the formation of a precipitating agent, which reduces a solute's solubility and makes the final substance hard to solve (Varshney et al., 2016). The production of active materials for SCs in the form of powder can also be achieved simply and easily *via* chemical precipitation. In this process, solute concentrations in solution are held above solubility limits to allow precipitation to occur owing to SCs (Lokhande et al., 2020). This precipitate is then removed from the solution, cleaned with distilled water, and dried at necessary temperatures in suitable atmospheres to produce the final product.

Table 2: Advantage and disadvantage of different synthesis methods

Method	Advantage	Disadvantage	References
Top down approach (physical method)	High speed, no use of toxic chemicals, purity, uniform size and shape	High cost, require high energy, temperature and pressure, large amount of waste generation, difficult size and shape tenability	(Bloch et al., 2021)
Electrochemical deposition	Less time required, Low cost, precise control over the thickness of film and deposition rate	Unsuitable for large scale production	(Lokhande et al., 2020)
Hydrothermal method	Easy control of morphology	High temperature operation and time consuming	(Kaur et al., 2020)
Sol-gel	Large-scale production	Time consuming	(Varshney et al., 2016)
Chemical precipitation	Fast process	Difficult to control morphology	(Ahmad et al., 2018)

Microwave synthesis	Faster reaction times, higher yields and selective heating	high reactor costs, challenges with scaling up or reaction monitoring	(Mikrovalov et al., 2011)
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2.5. Factors affecting performance of the AC-based materials

The performance of the AC electrode in the SC is influenced by the SSA (Gao et al., 2017), pore structure (Yang et al., 2019), pore size distribution (Largeot et al., 2008), surface chemistry (Dos Reis et al., 2020) and etc., which are mostly influenced by chosen activation processes and their biomass precursors. At the interface between the carbon and the electrolyte, the energy is stored via reversible ion adsorption on high SSA carbons. The SSA of these carbons is further enhanced by the creation of porosity in the bulk of the carbon materials. Pore structures (macropore, mesopore and micropore) and pore size distribution also have great effects on the performance of the electrode in the SC. In the electrochemical charge/discharge process, each pore structures serve a different function. For instance, the ion buffer reservoir for the mesopore and micro pore structures is the macropore structure. Mesopore provide abundant transport channels for ion, while micropore provides available sites for ion storage, enabling high performance in SCs (Dos Reis et al., 2020; H. Yang et al., 2019). From literature it is found that interconnected pores of different structures, micropore with higher volumes and diameters closer to the size of ions are preferred for SC electrodes (Diantoro et al., 2022; Ghosh et al., 2019a). When pore size is increased, the average distance between the pore wall and the center of the ion (d) increases and the capacitance decreases in accordance with equation 1 above. Conversely, when pore size is decreased, the average distance between the pore wall and the center of the ion (d) decreases and the capacitance increases (Largeot *et al.*, 2008; Dos Reis et al., 2020). The pore structures depends on the type of carbon source biomass precursors employed or the activation parameters, such as the activation temperature and activation agent to carbon ratio (Xu et al., 2017).

2.6. MnO₂ Nanostructure and MnO₂/AC composites in SCs

Why MnO₂ is so appealing for SCs applications? First, it is redox-active (Wayu & Wayu, 2021), among many of transition MO, it founds abundantly (Wu et al., 2020), have a special tunnel structure that enables bulk redox reactions (Shin et al., 2020), various morphologies (Jabeen et al., 2016), large theoretical capacitance (1370 F g^{-1}) (Zhang, 2015a) and environmental

friendliness (Ping et al., 2019). MnO_2 can exist in various crystal structures such as α -, β -, γ -, δ -, and λ -type as depicted in figure 3, and the different structures can be described by the size of their tunnels determined by the number of octahedral subunits ($n \times m$) and leads different specific capacitance (Zhang et al., 2015b).

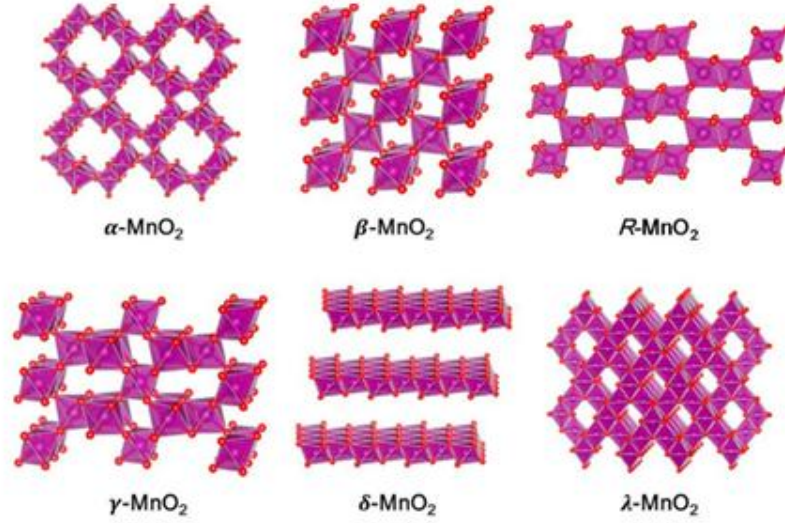
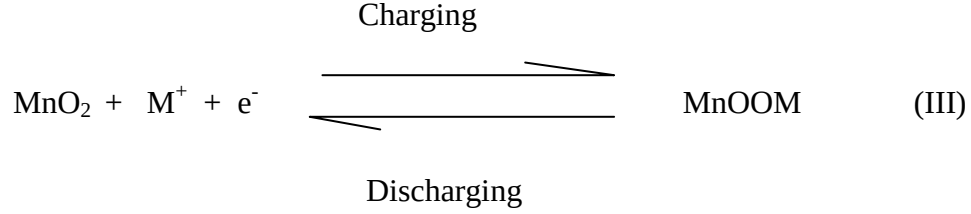


Figure 3: Crystal structures of MnO_2 polymorphs (Mn: magenta and O: red (Shin et al., 2020)

For example, Zhao et al Prepared MnO_2 with different crystal structure as electrode materials by hydrothermal method and investigated its effect on performance of SC (X. Zhao et al., 2017). The experimental results showed that Cs of the synthesized MnO_2 were in the following order: δ - $\text{MnO}_2 > \text{amorphous MnO}_2 > \alpha$ - $\text{MnO}_2 > \beta$ - MnO_2 . The porous nano sheet structure, which increases the SSA of δ - MnO_2 , offers abundance of active sites and contact area between the electrode and the electrolyte, and permits charges and ions to travel quickly in three directions result high SC performance. δ - MnO_2 has a good ion-exchange and oxidation-reduction capacity due to its 0.7 nm interlayer gap, which is stabilized by some cations and water molecules (Xia et al., 2019). Shuttle redox processes between Mn^{4+} and Mn^{3+} on outer active surface sites, which are facilitated by the insertion of electrolyte cations and protons, are thought to be the mechanism for the charge storage of the MnO_2 electrode. The reversible Faradaic reaction can be carried out via the adsorption/desorption of ions from the electrolyte according to the reaction (III) below, which is regulated by the SSA of MnO_2 (Abuzeid et al., 2019; Hu et al., 2018; J. Liu et al., 2022).



Where, ($\text{M}^+ = \text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+$)

The capacitance values of pure phase MnO_2 can only be achieved at 14–43% of the theoretical capacity, despite the fact that MnO_2 based electrode materials exhibit quick and reversible redox reactions (J. Liu et al., 2022). Thus, to increase the capacitance of MnO_2 electrodes for use in SCs application, numerous attempts are currently being made. For example, nano structuring the electrode and producing hetero junction materials with other substances have shown to be the most effective ways to maximize the capacitance of MnO_2 electrodes. By boosting SSA and exposing effective active sites through nano structuring the electrode, a wider electrode/electrolyte interface is created, enhancing surface charge storage (Rodriguez-Romero et al., 2022). The kinetics of charge transfer are improved, porous structures are created, and the structural stability of MnO_2 -based electrode materials are all increased when hetero junction materials are made using 3D porous carbon materials such as AC (Ramirez-castro & Soc, 2015).

Specifically, MnO_2/AC composites as electrode materials for super-capacitors can significantly enhance the Cs through the combination of fast faradic reactions (Sudhakar., 2016) and double-layer charging (Y. Liu et al., 2016). For optimal MnO_2 use, carbonaceous materials combined with nano-structured MnO_2 offer a high electro-active surface area (Wang et al., 2015). Furthermore, the combination of MnO_2 and AC may also take advantage of improved charge/discharge rate capability and chemical stability of AC and the high specific capacitance of MnO_2 (Sudhakar, 2016). An appropriate amount of MnO_2 nano structure in MnO_2/AC composite electrode material enhances the Cs of SCs. However, further raising the electrode's MnO_2 content resulted in a decrease in capacitive performance and a reduction in the electrode's SSA, primarily as a result of MnO_2 particle aggregation inside the composite (Doloksaribu et al., 2017).

2.7. Performance Parameters of SCs Electrode Materials

For the evaluation of the super-capacitor's electrochemical performance, the commonly used techniques are Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV) and Galvanostatic charge/discharge (GCD) (Reza et al., 2020).

CV is an electrochemical method employed for measuring the current response of redox-active solutions at specified potential sweep rates and plotted as measured current versus applied potential (Majumdar, 2021a). It enables in determining the reversibility of charging and discharging operations as well as the operational voltage range or potential window. Under controlled current conditions, GCD method is a reliable way to assess the electrochemical capacitance, energy density, power density, and cyclic stability of materials. This method differs from cyclic voltammetry in that the current is controlled and the voltage is measured as a function of time (Licht et al., 2020). In order to evaluate a material's frequency-response properties, particularly its power limiting internal resistance, electrochemical impedance spectroscopy (EIS) is frequently employed. In contrast to other methods, this method uses a sinusoidal signal with a small voltage amplitude (a few mV or less) and alternating current that is measured at various frequencies. This indicates that the technique can be used to measure the current by adjusting the voltage. Higher voltage windows, excellent cyclic stability, higher mechanical stability, faster charge/discharge rates, and other factors listed in Table 3 can all be used to evaluate the performance of optimal SCs. (Majumdar, 2021a).

Table 3: Performance parameters for evaluation of electrode materials in SCs

Parameters	Information derived	References
Specific capacitance	Charge storage ability of the material per its unit mass under a given voltage range	(Shao et al., 2018)
Energy Density	Energy stored per unit mass of the system	(Majumdar, 2021b)
Power Density	A measure of how the material can quickly discharge its energy	
Rate capability	Response of capacitance at varying potential scan rates or current densities	
Operating potential	Range of potential within which electrolyte and	

(potential window)	electrode faces no irreversible redox reaction	
Cycle stability	Capacitance retention efficiency after nth GCD charge/discharge cycle	(Ntakirutimana et al., 2020)
Equivalent series resistance	Intrinsic resistance of the current collector, electrode materials and contact resistance between The electrode material and current collector	(Arulraj & Nishanthi, 2020)
Charge transfer resistance	Resistance associated with flow of charge between electrolyte and electrode interface	(Mei et al., 2018)
Diffusion resistance	Ionic resistance when it diffuse into the micro pores	(Pilathottathil & Thayyil, 2017)

Furthermore, certain additional crucial factors, including as mechanical stability, environmental friendliness, operating temperature limits, self-discharging rates, etc. are also frequently evaluated to assign the performance of SCs electrode materials (Majumdar, 2021b).

CHAPTER THREE

MATERIALS AND METHODS

3.1. Chemicals and Reagents

In this study, analytical grade chemicals and reagents were received and employed without further treatment. Polyvinyl alcohol (PVA, 98%), Potassium carbonate (K_2CO_3 , >99.0%), and hydrochloride acid (HCl, 37 %) from Alpha Chemika, Mumbai India, Potassium permanganate ($KMnO_4$, 99% Sigma Aldrich), Potassium hydroxide (KOH) pellets (>85.0% Sigma aldrich). Nickel foam (> 99.99%; 3 cm x 1 cm area with thickness of 1.6 mm) received from Korea. All experimental runs were conducted using distilled water.

3.2. Instruments

Instruments that were employed during this research work were: TGA-DTA (DTG-60H detector, Shimadzu, Japan), XRD diffractometer (XRD-7000, Shimadzu, Tokyo, Japan), SEM (JCM-6000 plus, Shimadzu, Japan), UV-Vis spectroscopy (Shimadzu– double beam P9), and Potentiostat (Iviumstat, Eindhoven, Netherlands) at Adama Science and technology University, FT-IR (FT/IR-6600typeA, Jasco, Tokyo, Japan) and BET (Nova 4200 Quantachrome Instruments, Boynton Beach, USA) at Bahir Dar University.

3.3. Sample Collection and Preparation

3.3.1 Collection and preparation of Plant leafs

The leaves of water hyacinth (*Eichhornia crassipes*) were collected from Lake Koka, Oromia, Ethiopia. The botanical identification of the collected plant were conducted at Addis Ababa University. The plant leaf was properly washed with tap water followed by distilled water to remove muds and other impurities. The leaf was then dried for about seven days at room temperature in an open air and in the shade to get rid of any moisture content. The dried leaf of this plant was crushed by using an electrical grinding machine to produce a fine powder. Finally, the dried fine powder was stored for further use.

3.3.2. Preparation of Leaf Extract.

The extraction of the plant leaf was carried out by adopting procedure from the literature (Zelekew et al., 2021). Briefly, 10 g of the powdered leaf of the water hyacinth was placed into a 1000 mL Erlenmeyer flask followed by addition of 400 mL of distilled water. The flask containing the mixture was placed on a hot plate and the mixture was heated at 50 °C for 1 hr with continuous stirring. Then the boiled suspension formed in the solution was allowed to cool and filtered. Finally, the filtrate was stored in airtight glass bottle covered with aluminum foil and placed at 4 °C in a refrigerator for further use.

3.4. Synthesis of MnO₂ nanostructure

MnO₂ naomaterials were prepared by the reported procedure (Hasan et al., 2023) with slight modification. Briefly, 0.1 M KMnO₄ precursor solution was added drop wise to the water hyacinth leaf extract in three different ratios (1:1, 1:3 and 3:1) by volume, and then labeled as Mn(1:1), Mn(1:3) and Mn(3:1), respectively. Then after, the three solutions were stirred continuously for 5 hr that resulted in brown-black suspension formation. The resulting nanomaterial was centrifuged at 3000 rpm for 30 min to separate it from the reaction mixture. To eliminate any impurities, all suspensions were washed with ethanol-distilled water-ethanol order three times before being dried in an oven at 80 °C for 3 hr. The oven dried samples was characterized by TGA/DTA to determine the stable thermal temperature. Based on the thermal evidence, the biosynthesized nanomaterial was calcined at 450 °C for 2 hr, finely powdered, and kept in a glass bottle for future characterization and application.

3.5. Synthesis of AC

Portion of the water hyacinth stem sample was washed with tap water followed by distilled water and then chopped using knife and air dried in the laboratory at room temperature for two weeks. The dried pieces with a size of 1-2 cm were grinded using an electrical grinding machine at constant speed. In addition, the powder size was also controlled by using 150 µm (mesh #100) sized sieve mesh. Then, the three different ratios of stem powder with three different coupled chemical activators were mixed separately in three separated 1000 mL beakers and labeled as WH₁, WH₂, and WH₃. Then, the precursors was treated using potassium hydroxide (KOH) and potassium carbonate (K₂CO₃) in a 1:2 (w/w) (WH component/KOH) ratio (i.e., WH₁ (15 g WH +

10 g K_2CO_3 + 20 g KOH), WH_2 (15 g WH + 20 g K_2CO_3 + 10 g KOH) and WH_3 (15 g WH + 15 g K_2CO_3 + 15 g KOH)). All the contents was kept in closed beaker for about 24 hr. K_2CO_3 generates more mesopores structures scattered on the surface of the AC with high yield, whereas KOH emerges the development of AC with more microporous structure and high SSA as a previous reports, which is why they were utilized jointly in this study (Abdulhameed et al., 2021; Harimisa et al., 2022; Garba et al., 2016). (Garba et al., 2016)The mixture were placed in 1000 mL of beaker separately, filled with distilled water, and left for overnight to soaking properly. After that, the clear solution was decanted and the precipitated sample was washed using distilled water until its pH nearly neutral and then dried at about 120 °C for 2 hr in an oven. After its thermal stability analysis using TGA-DTA, the dried samples were heated at 500 °C for 1hr in a furnace using self generated atmospheric condition with controlled temperature to an accuracy of $\pm 5^\circ C$ by means of a temperature controller by following previous methods (Srinivasakannan & Abu Bakar, 2004; Yousfi et al., 2020). The resulting black powders were cooled, washed by 1M HCl solution for 1h and then washed by hot and cold distilled water for several times to remove residual inorganic impurities, till neutral pH solution was reached. Finally, the samples were collected and ready for further use.

3.6. Synthesis of MnO_2 /AC composite

The three MnO_2 /AC nanocomposites ratios were prepared by adopting from previously published method (Albo & Allah, 2023). First, 50 mL of water hyacinth leaf extract was placed in three separate 500 mL of beakers and labeled as MnH1, MnH2 and MnH3. Afterwards, 150 mL of 0.05 M $KMnO_4$, 1 M $KMnO_4$, and 2 M $KMnO_4$ precursor solution was added to the beaker containing extract that labeled as MnH1, MnH2 and MnH3 in drop wise way, respectively. Then, the solution was steadily agitated on the hot plate at room temperature for 2 hr. Afterwards, 0.5 g of previously prepared AC was added into the each solutions, while the stirring time was continuing for an additional 4 hr at room temperature. The resulting product was washed and centrifuged at 3000 rpm for 30 min followed by drying in the oven at 80 °C for 3 hr. Finally, after TGA/DTA identification, the sample was calcined at about 450 °C for 2 hr, collected in to the sample holder and kept it for further use. The synthesis process of MnO_2 /AC nanocomposite is schematically illustrated in figure 4.

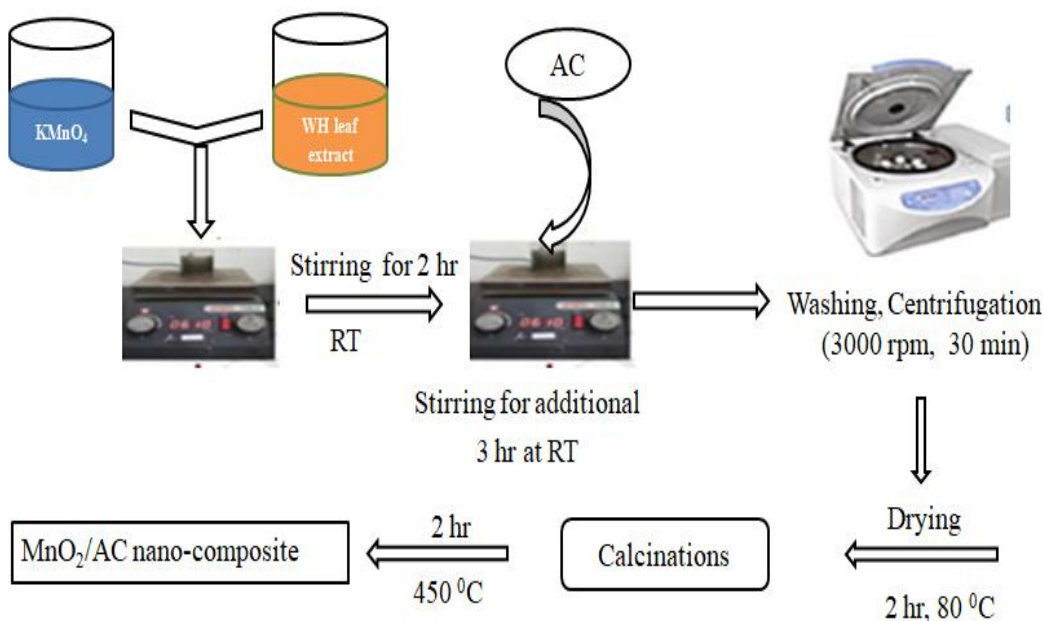


Figure 4: Schematic diagram of MnO₂/AC nanocomposite synthesis process

3.7. Electrode Preparation

Rectangular shaped Ni foam (3 cm and 1 cm) as a current collector was first etched using 1 M HCl for 30 min, in order to remove surface oxides (Abou- Elyazed et al., 2022). The etched Ni foam was rinsed thoroughly with distilled water, ethanol, and then dried at room temperature. Fabrication of all electrodes using AC, MnO₂, and MnO₂/AC nano-composite were performed by following previous report with some modifications (Shrestha, 2022). Briefly, electrode fabrication was done by preparing a paste from mixing of active materials and polyvinyl alcohol (PVA) as a binding agent in 9:1 ratio by mass. First, 50 mg of binder was taken in to 100 mL beaker and then 10 mL of distilled water was added. In order to dissolve the PVA completely, the solution was placed on the hot plate and continuously stirred at 45 °C for 2 hr. After that, 11.3 mg of active material was thoroughly grinded in a mortar to get fine powder and then 250 µL of already prepared PVA solution was added in order to disperse active materials. Further, only 1cm² area of the etched nickel-foam was coated homogeneously by applying about 100 µL of the slurry by using a micropipette and dried at 70 °C for overnight. Mass was measured before and after mass loading of active materials by a four-digit electronic balance for electrochemical measurements.

3.8. Characterization of as-synthesized materials

The crystalline structure was determined using XRD (Cu K = 1.5406) with a voltage of 40 kV and a current of 30 mA in the range of (10^0 - 80^0) angle of diffraction. Thermo gravimetric-differential thermal analyses (TGA-DTA) were used to conduct the thermal stability analysis. A double beam UV-Vis spectroscopy was employed to measure the optical properties in the range of 200-800 nm. For surface functional groups analysis, FT-IR spectroscopy measurement was done in the spectral range of 4000 - 400 cm^{-1} . Surface area measurement was performed using Brunauer-Emmett-Teller (BET) by nitrogen adsorption analyzer. Surface morphology analysis of the synthesized electrode materials were done by employing scanning electron microscopy (SEM).

3.9. Electrochemical Measurement

All electrochemical characterizations was performed in a standard three electrode system IVUM potentiostat while using the as-synthesized AC, MnO_2 , and MnO_2/AC composite electrode as a working electrode (WE), Pt wire as the counter electrode (CE), and Ag/AgCl electrode as the reference electrode (RE) in the presence of 6 M KOH electrolyte solution. The cyclic voltammetry (CV) experiments were performed at varying scan rates from 10 to 100 mV s^{-1} at the range of voltage (0-0.5V). The galvanostatic charge/discharge (GCD) tests were recorded from 1 to 10 A g^{-1} currents density within (0-0.5 V) voltage window. Electrochemical impedance spectroscopy (EIS) was performed at 10 mV voltage in the frequency range from 1 MHz to 0.01 Hz.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1. Physical Characterization

4.1.1. X-ray Diffraction (XRD) Analysis

XRD pattern analysis of the MnO₂, AC and MnO₂/AC nanocomposite was carried out to examine their crystalline and phase structure. Figure 5A shows XRD of MnO₂ nanostructure synthesized within three different volume ratios (Mn(1:3), Mn(1:1) and Mn(3:1)). The diffraction peaks were observed at 2θ values of ≈12.5, 25.48, 37.46, and 66.14 along with their Miller index planes of (001), (002), (111), and (020), respectively with JCPDS card number of 80-1090. The presence of these diffraction peaks is indexed to the δ-MnO₂ (K-Birnessite) crystal phase. These peaks of the XRD spectra are in good agreement with the literature reported before (Cremonozzi et al., 2020; Huang et al., 2022; Wan et al., 2014). The weak and broad peaks indicate a poor or polycrystalline feature of the layered δ-MnO₂. This δ-MnO₂ structure is composed of layers with tetragonal holes, stabilized by water molecules stored between the sheets (Rodriguez-Romero et al., 2022).

The crystallite size (D) was determined by Debye Scherer formula according to equations 2 (Bekru et al., 2021).

$$D = \frac{k\lambda}{\beta \cos \theta} \text{ (nm)} \quad 2$$

where D is the crystallite size in nm, k is Scherrer's constant (0.94) depending on the miller index of the reflecting plane and the shape of the crystal, λ is the XRD wavelength (nm), β is the full width at half maximum (FWHM) of crystallite peak (measured in radians) and θ is Bragg's angle (°) of the XRD peak. As a result, the calculated crystallite size of three ratios of the as-synthesized MnO₂ nanostructures from the most intense peaks were 2.75 nm, 2.22 nm and 2.78 nm in case of Mn(1:3), Mn(1:1) and Mn(3:1), respectively.

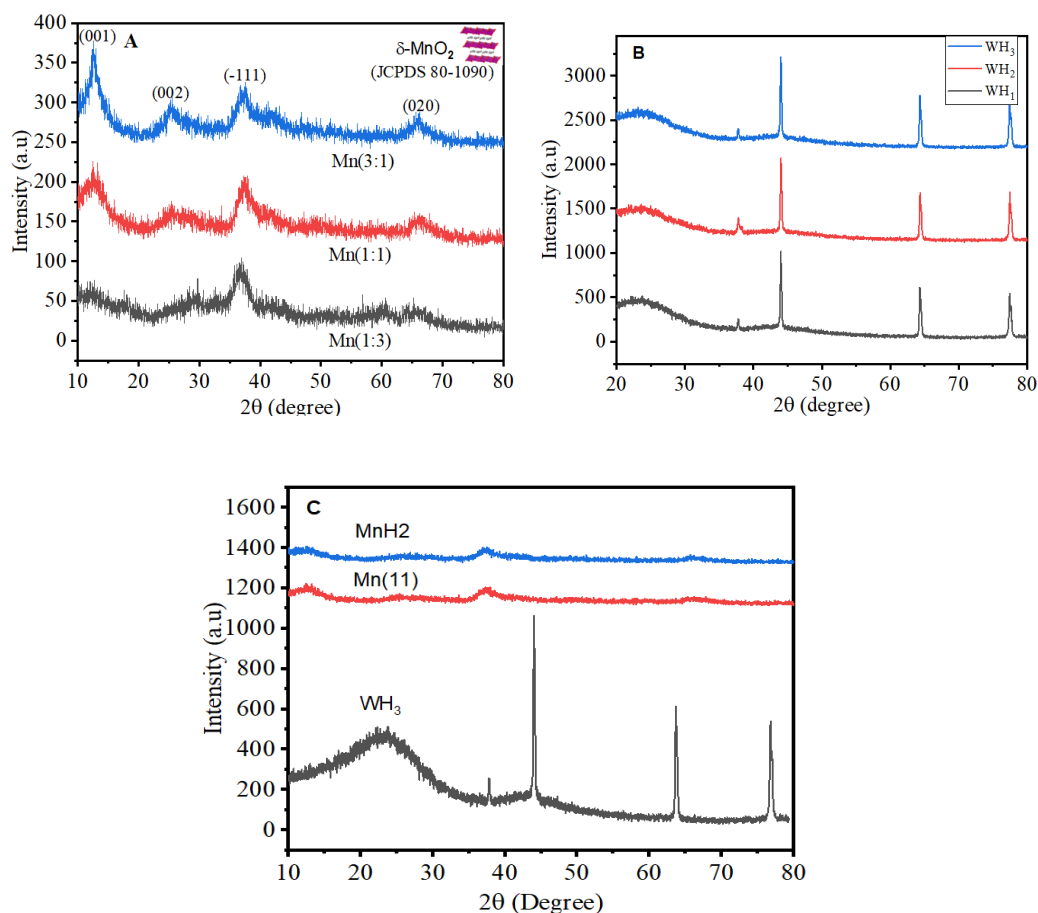


Figure 5: XRD patterns of Mn(1:1), Mn(1:3) and Mn(3:1) nanostructures (A), WH₁, WH₂ and WH₃ (B), and XRD pattern comparison of Mn(1:1), WH₂ and MnH₂ (C)

Again figure 5B and C shows XRD of activated carbon (AC) synthesized within three different ratios and its composite with MnO₂. Broad peaks at $2\theta = 24.12$ and 43.60 in the XRD pattern of AC are allocated to the amorphous structure and correspond to the (002) and (100) planes of carbon, respectively. However, some additional peaks were still visible, possibly because some chemical activating agents were not completely removed during washing procedures to neutralize the produced activated carbon (Rahma et al., 2019). The XRD spectra of the MnO₂ and MnO₂/AC samples revealed identical diffraction peaks, illustrating that surface modification and combination had no impact on the crystal structure of MnO₂, which could be attributed to the amorphous structure and the low content of AC in the composite (Albo & Allah, 2023; Chen et al., 2020).

4.1.2. Fourier Transform Infrared (FT-IR) Analysis

As depicted in figure 6, all the samples showed a broad absorption band of FT-IR spectra peak around 3361 cm^{-1} and 1030 cm^{-1} . This peak is mainly the characteristic of the stretching and bending vibration band of the $-(\text{OH})$ bond in physical adsorbed water molecules and oxygenic functional groups such as phenols, carboxyl, and alcohols found in AC and plant extract (Feng et al., 2020; Wang et al., 2015). For the chemical adsorption, these oxygenic functional groups might serve as active sites. The peak that is present at 1633 cm^{-1} can also be related to $\text{C}=\text{O}$ stretching of carboxylic acids, and the peak at 2925 cm^{-1} is ascribed to the existence of aliphatic C-H stretching of CH , CH_2 and CH_3 groups (Mojoudi et al., 2019; Shen et al., 2018). The peaks located between 537 and 750 cm^{-1} are attributed to Mn-O vibrations which justifies the formation of MnO_2 nanostructure (Racik et al., 2019). The spectra of MnO_2 exhibits low absorption peaks of carboxyl and Mn-O stretching vibration with slight shift to the lower wave number band region, which indicate that AC are grafted onto the MnO_2 nanostructure. It can be conclude that the primary oxygen-containing groups are evidently present in the FT-IR spectrum of the as synthesized sample.

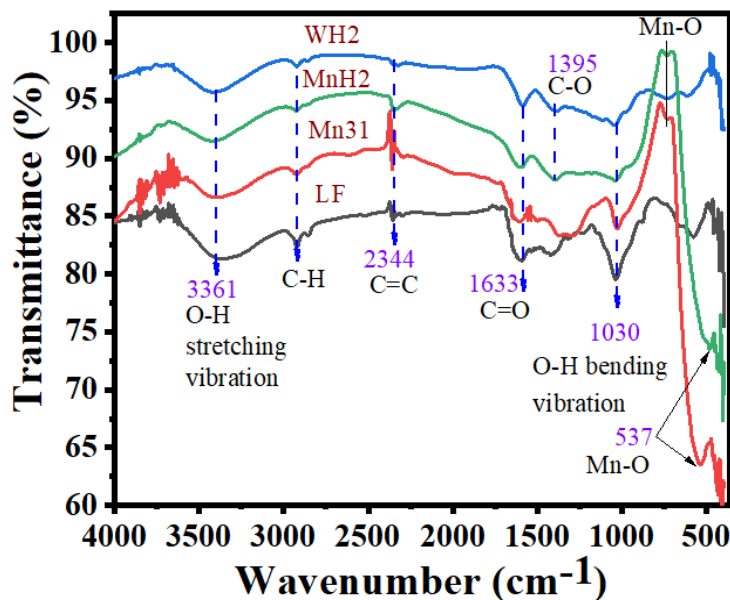


Figure 6: FT-IR spectra comparison of $\text{Mn}(1:1)$, WH_2 , MnH_2 and LF (water hyacinth leaf powder)

4.1.3. Thermal analysis

As depicted in figure 7A, the TGA-DTA curve of MnO_2 nanostructure reveals some weight loss steps in the tested temperature range (20–1200 °C) of which are associated with the degradation of the main component of the synthesized MnO_2 nanostructure. The first small weight loss associated with one peak of the DTA curve at about 100 °C; indicating the removal of surface adsorbed water molecule. The second stage which initiates around 150 °C and ends around 350 °C corresponds to the removal of the plant extract residues. The strong endothermic peak of the DTA curve at about 241 °C may associate with the conversion of the MnOOH to MnO_2 (Hashem et al., 2018).

The calcination temperature for the synthesized MnO_2 nanostructure was set at the temperature above which weight loss becomes constant (350–500 °C). The Purity of MnO_2 nanostructure is increased by the calcination temperature, which also eliminates undesirable plant extract residues. As a result, MnO_2 nanostructure was purified by calcination at 450 °C to eliminate undesirable plant extract residues. Above 500 °C, weight loss about 1.7 % and increased TGA curve after 620 °C were attributed to the phase transformation from MnO_2 to Mn_3O_4 and oxidation of Mn_3O_4 to Mn_2O_3 respectively (A. Kumar & Maitra, 2020). The last decomposition occurred at about 850 °C and shows the decomposition of M_2O_3 to MnO .

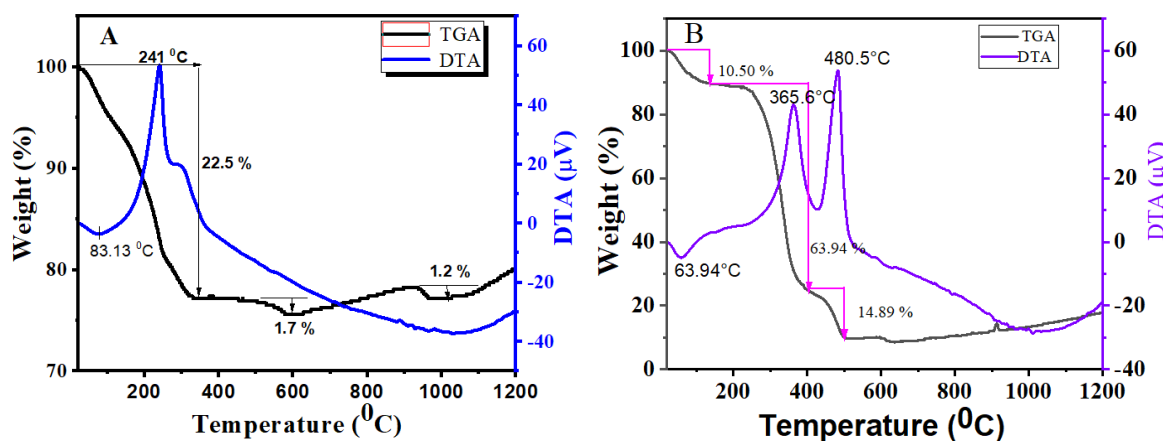


Figure 7: TGA-DTA curve of as-synthesized MnO_2 nanostructure (A), TGA-DTA curve of the Water hyacinth based AC (B)

Three major stages were also observed in the thermal degradation components for water hyacinth based AC samples as depicted in figure 7B. The first stage, which started from room temperature to 120 °C, involves removal of moisture content present in the water hyacinth, with approximately 10.5% weight loss. The most weight loss (63.94%) with two DTA endothermic peaks were observed at 365.6°C, 480.5°C in the second stage, which depicts the combined decomposition of the hemicelluloses and cellulose molecules (Salgado et al., 2018). The third and last stage of decomposition which occurred above 400 °C was due to lignin degradation (Alves et al., 2019). Above 500 °C, no weight loss was observed as a result, it was fixed as the activation temperature for AC preparation in this study. The results showed good agreement with previously reported results (Emamy et al., 2021; Lawtae & Tangsathitkulchai, 2021; Shokry et al., 2020).

4.1.4. Brunauer, Emmett and Teller (BET) analysis

BET is the most common method used to describe specific surface area (SSA) using the nitrogen adsorption on the surface of the substance to be analyzed in the lower relative pressure (p/p^0) range of (0.05–0.30). SSA measurements of the synthesized materials was performed using BET analyzer via nitrogen adsorption isotherm at 77 K and the results are shown in figure 8 and table 5.

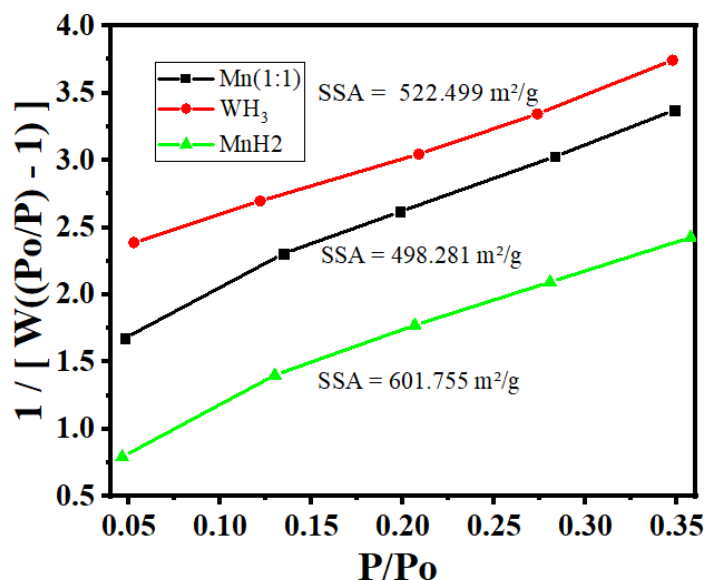


Figure 8: multipoint BET Plot of Mn(1:1), WH₃ and MnH₂

The BET equation also employed to estimate cumulative pore volume and average pore size. BET calculate SSA according to equation 3 and 4 below (Thommes et al., 2015):

$$\frac{1}{W \left(\frac{P_0}{P} - 1 \right)} = \frac{1}{Wm * C} + \frac{C-1}{Wm * C} \left(\frac{P}{P_0} \right) \quad 3$$

$$SSA = \left(\frac{N * A}{(slope + intercept)} \right) \left(\frac{1}{M * m} \right) \quad 4$$

Where, slope = $\frac{C-1}{Wm * C}$, intercept = $\frac{1}{Wm * C}$, W= weight of gas adsorbed, P/P^0 = relative pressure P^0 = minimum pressure required to condense absorbed gas, Wm = weight of adsorbate as monolayer, C = BET constant, N = Avogadro's number (6.023x10²³), A = Adsorbate cross sectional area (16.2Å²) for nitrogen gas, M = molecular weight of nitrogen gas and m = mass of analyzed sample.

Table 4: SSA, cumulative pore volume and average pore radius (size) of Mn (1:1), WH₃ and MnH₂

Physiochemical properties	Sample materials		
	Mn(1:1)	WH ₃	MnH ₂
BET surface area (m ² g ⁻¹)	498.3	522.5	601.8
NL-DFT method cumulative pore volume (cm ³ g ⁻¹)	0.18	0.16	0.25
NL-DFT average pore radius (nm)	0.88	0.92	0.18

The electro-active characteristics of the electrode material in SC application are directly impacted by SSA and pore volume. From literature it is proved that the material with high SSA, interconnected pores of different structures, micropore with higher volumes and diameters closer to the size of electrolyte ions are preferred for SC application (Diantoro et al., 2022; Ghosh et al., 2019; Gao et al., 2017). BET analysis showed that the presence of the AC in its composite with MnO₂ showed higher SSA and Non-local-density functional theory (NL-DFT) cumulative pore volume. High SSA results in a higher value of the capacitance since the redox reactions responsible for the capacitive response take place on the surface (Rodriguez-Romero et al.,

2022). Because of its porous structure and greater SSA generated, these results showed that a green-synthesized MnO_2/AC composite utilizing water hyacinth leaf extract has a promising activity for energy storage applications. As a result, AC, MnO_2 and their composite with high porosity and valuable surface texture was prepared using inexpensive natural resources.

4.1.5. UV-Vis Spectroscopy analysis

Figure 9A displays the UV-Vis absorption spectra of the Mn (1:1), WH_3 , and MnH_2 materials in the wavelength range of 200–800 nm. In the case of AC, there was an absorption peak at 278 that is associated with electronic transitions between the bonding and anti-bonding orbitals ($\pi\text{-}\pi^*$) (Sathish-Kumar et al., 2012). On the other hand, the bio-synthesized nanostructure shows a sharp absorption peak at 267 nm, which is due to electron transition from un-paired electron to anti-bonding ($n\rightarrow\pi^*$) (Dessie et al., 2020). The emergence of absorption edges at this peak clearly demonstrates the formation of MnO_2 nanostructure, which is consistent with what has previously been reported (Sherin et al., 2017).

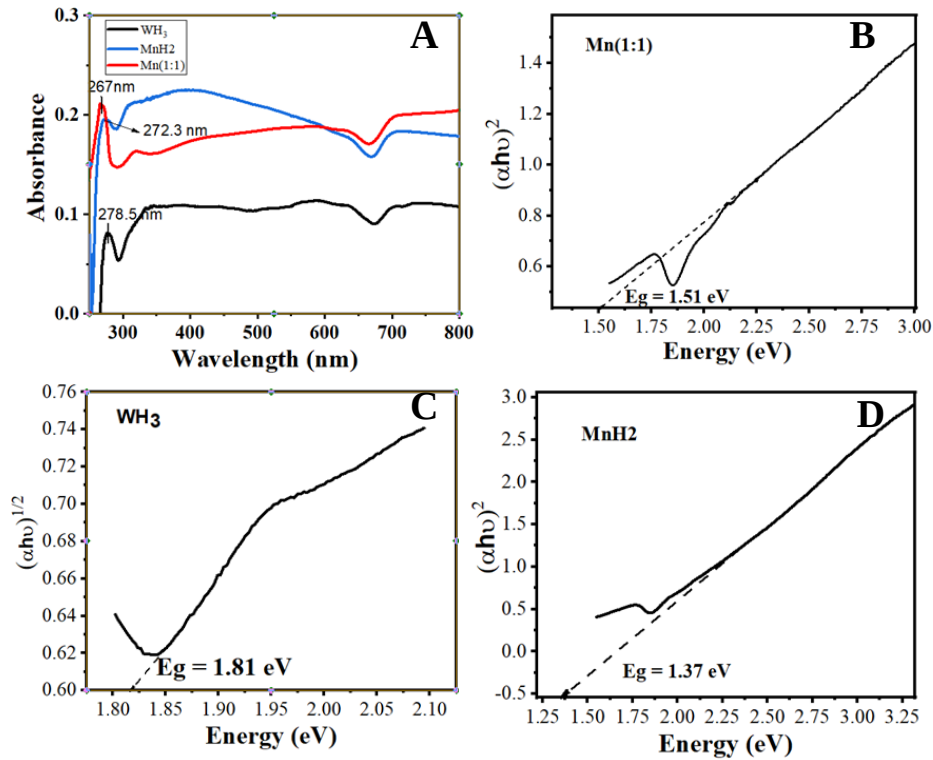


Figure 9: UV-Vis absorption spectrum of Mn(1:1), WH_3 and MnH_2 (A), Tauc plot of Mn(1:1) (B), WH_3 (C), and MnH_2 (D)

With the addition of AC in the composite, the intensities of these peaks decreased and shifted to a longer wavelength (272 nm), which confirms the interaction of MnO₂ and AC in the composite. The band gap energy (E_g) of magnetite nanoparticles was determined using the general equation of the Tauc plot method , as shown in equation 5.

$$(\alpha h\nu)^n = C(h\nu - E_g) \quad 5$$

where α is the absorption coefficient, h is the Planck constant (4.136×10^{-15} eV s⁻¹), C is the energy constant of the model, ν is frequency of incident light (s⁻¹) , E_g is the energy of the band gap (eV), $n = 1/2$ for indirect allowed transitions and $n = 2$ for direct allowed transitions.

According to the Tauc plot, the linear region in the graph of $(\alpha h\nu)^n$ versus the energy of the photon is extrapolated to the x-axis to predict the energy of the band gap. In this study, the graph $(\alpha h\nu)^n$ versus the energy of the photon has a linear region in the case of Mn (1:1), MnH₂ when $n = 2$, and WH₃ when $n = 1/2$, as depicted in figure 9(B-D). Based on this plot, the band gaps of WH₃, Mn(1:1), and MnH₂ were obtained to be 1.81, 1.51, and 1.37 eV, respectively. The compositing of MnO₂ with AC results in a narrowing of the band gap, which is likely due to the presence of carbon-oxygen bonds and the formation of new molecular orbitals in the system, accompanied by a reduction in the energy between the HOMO and LUMO orbitals (Chen et al., 2017).

4.1.6. Scanning Electron Microscopy (SEM) analysis

SEM analysis for as-synthesized materials was performed by employing SEM as shown in figure 10 to reveals information about the external morphology. The micrograms indicated that MnO₂ and its composite were found in a cluster of spherical-like nanomaterial. By comparing the SEM images of the Mn(1:1) and AC (WH₁, WH₂ and WH₃), it was found that abundant pore structure were observed in case of AC which provide fast electrolyte ion diffusion pathways. The surface of AC is full of cavities and in a honeycomb-like structure. However, the MnH₂ surface showed a reduction in the size of some pores, disappearance of some pores, and roughening after addition of the MnO₂ due to the resulting heterogeneity.

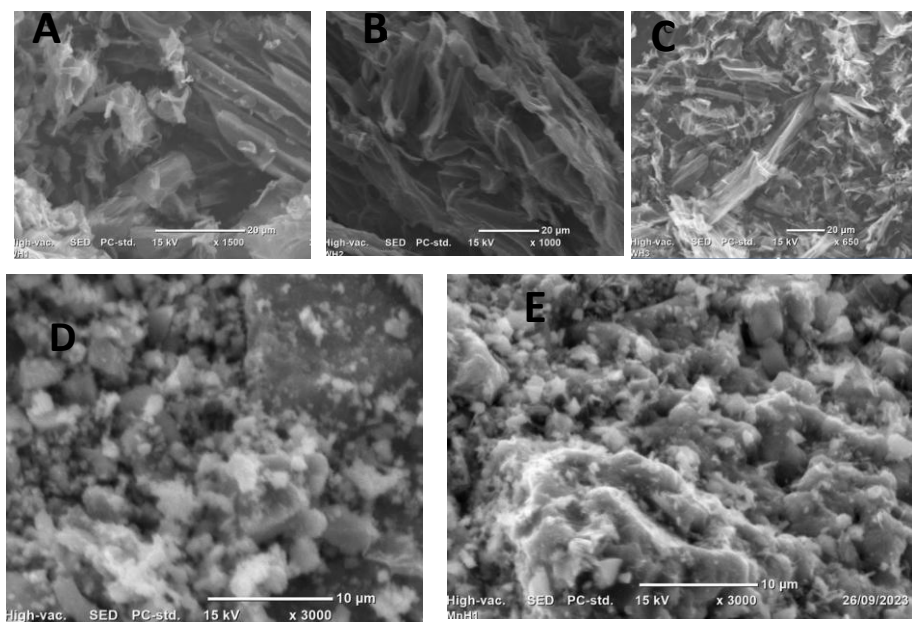


Figure 10: Scanning electron micrographs of WH₁ (A), WH₂ (B), WH₃ (C), Mn(1:1) (D) and MnH₂ (E)

4.2. Electrochemical Supercapacitor test

The electrochemical SC tests of all prepared electrodes were studied by CV, GCD and EIS in 6 M KOH solution in three electrode system with IVIUM electrochemical workstation.

4.2.1. Cyclic voltammetry (CV) analysis

CV is an electrochemical method employed for measuring the current response of redox-active solutions to a linearly cycled potential sweep and plotted as measured current versus applied potential. Figure 11 shows the cyclic voltammograms of AC-electrode, MnO₂ and their hybrid composite electrode materials at 20 mV s⁻¹ scan rate. As it is observed, area of cyclic voltammogram of Mn(1:1) and MnH₂ are larger than that of other three ratios of MnO₂, and its composite respectively which indicates their higher charge storage capability. This shows that as the electrode's MnO₂ concentration increased further, capacitive performance decreased. This may have happened as a result of decrease of SSA and porosity of the material as concentration increased, which in turn increases the ionic resistance value (Shrestha, 2022). In case of AC,

WH₃ showed that larger CV area and this could be attributed to its hierarchical structure. The hierarchical porous structure connects various pore size configurations, facilitating the flow of the electrolyte ions in the bulk of the material. Generally, CV area of all composite is larger than that of pure AC and MnO₂ this shows improved their Cs. This could be attributed to its high SSA and the synergistic effects arising from AC and MnO₂ nanostructure. High SSA provides enough electrode/electrolyte interfaces for adsorption of the ion on the surface of the electrode.

MnH1 has a lower specific capacitance than MnH2 because to the lesser amount of MnO₂ that may cause EDLC behavior to dominate pseudocapacitive (redox) behavior. However, when MnO₂ concentration was further raised in the case of the MnH3 composite electrode, capacitive performances was reduced, which may have been caused by MnO₂ particle aggregation within the material, which leads increased the bulk resistance value (Shrestha, 2022).

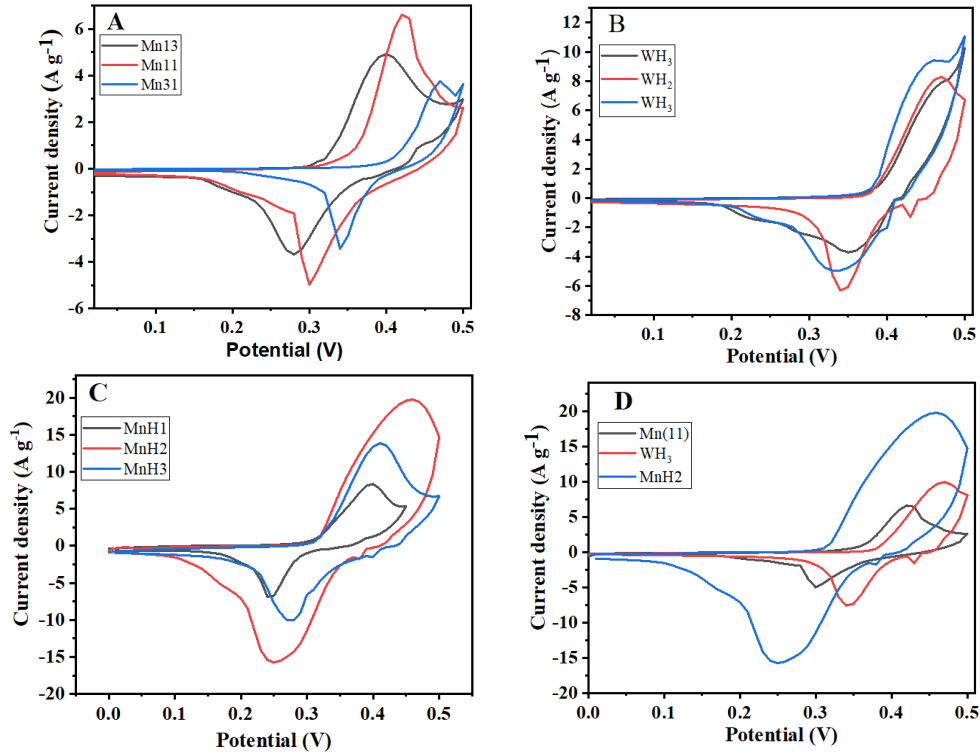
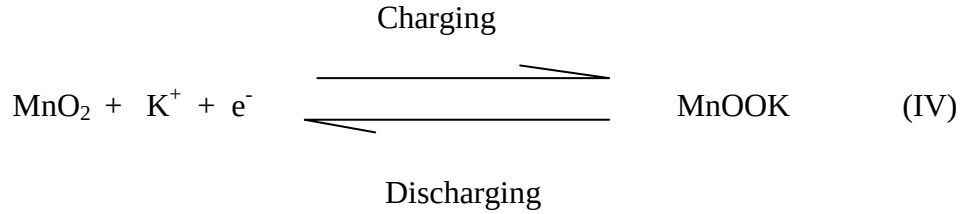


Figure 11: CV curves of three samples of (a) MnO₂ nanomaterial, (b) AC, (c) MnO₂/AC nanocomposite, and (d) their optimized CV curve comparison at 20 mV s^{-1}

The CV curve of MnO₂/AC and MnO₂ consists of two redox peaks in the (0-0.5) V potential window. This indicates that the capacitance is mainly governed by faradic reactions, as shown in reaction 1 below (Abuzeid et al., 2019).



The cathodic peak in the potential range 0.25–0.35 V may be associated with the reduction of MnO₂ to MnOOK (forward reaction), while the anodic peak that appears in the potential range 0.4–0.5 V may be attributable to the oxidation mechanism that is described in the backward reaction. Whereas the current gradually increases from 0.3 V to 0.4 V and from 0.45 V to 0.5 V on the CV curves for the water hyacinth-based AC electrodes, this is because of the pseudocapacitive behavior caused by the redox reactions on oxygen functional groups (Zheng et al., 2017).

Figure 12 (A-C) shows the CV curves of MnO₂, an AC electrode, and their hybrid composite at different scan rates ranging from 20 to 100 mV s⁻¹. The linearity of peak current vs square root of scan rate is shown using Randles-Sevcik equation (6).

$$I_p = (2.69 \times 10^5) \times n^{3/2} \times A \times D^{1/2} \times C \times v^{1/2} \quad 6$$

I_p is the peak current (A), v is the scan rate (Vs^{-1/2}), n is the number of electron lost or gained in the process, A is the surface area of the electrode (cm²), D is the diffusivity of the reactant (cm² s⁻¹) and C is the initial reactant concentration (mol cm⁻³) (Ghosh et al., 2019a).

All the synthesized materials linearly depend on square root of scanning rates on both anodic and cathodic sides as depicted in figure 12D, which confirms the good reversibility and high-speed capabilities of the synthesized electrode materials (Ghosh et al., 2019b). However, as the scan rate increases, the potential of the anodic and cathodic peaks is shifted slightly to the more positive and negative sides, respectively, because of the electrode polarization due to the quick electronic and ionic motions at the electrode's surface (Sasikumar et al., 2023).

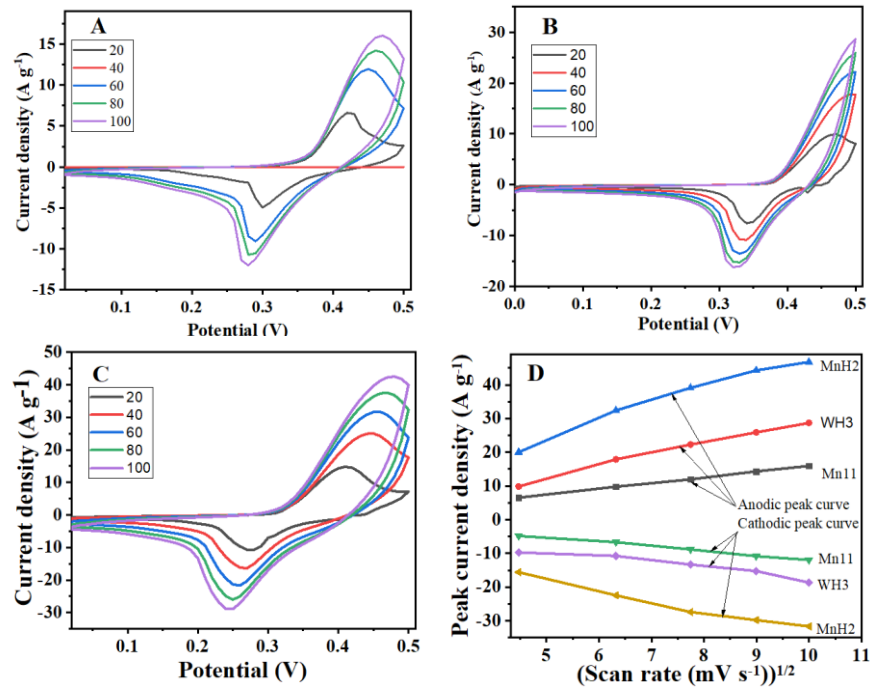


Figure 12: CV curves of the Mn(1:1) (A), WH₃ (B), MnH₂ (C) at different scan rates, and plots of their peak current density as a function of the square root of the scan rates (D)

4.2.2. Galvanostatic charge/discharge (GCD) analysis

The electrochemical properties of all the electrodes were also further investigated employing the galvanostatic charge/discharge (GCD) process and are shown in figure 13 under the 0–0.5 V potential window in the 6M KOH aqueous electrolyte. The Cs of a SC electrode material can be calculated from the the GCD curve according to equation (7) (S. Saini et al., 2021).

$$C_s = \frac{i\Delta t}{m\Delta V} \quad (\text{F g}^{-1}) \quad 7$$

Where, i is the set current, t is the discharge time, and V is the voltage window and m is mass of active material.

As a result, the maximum Cs of 108 F g⁻¹, 75 F g⁻¹, and 224 F g⁻¹ were calculated in the case of the Mn(1:1), WH₃, and MnH₂ electrode materials, respectively, at a 3 A g⁻¹ current density. As compared to the single AC and MnO₂ samples, the composite of AC and MnO₂ materials showed a higher value of capacitance. This could be due to the high SSA and synergistic effect of AC

and MnO₂ nanostructures in the composite. A high surface area provides more active sites for the physiochemical interaction of electrolyte ions with electrodes, which results in a higher value of capacitance.

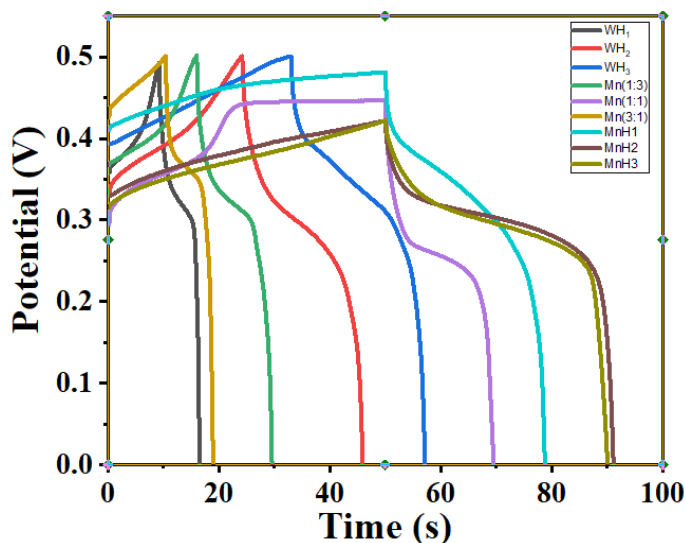


Figure 13: The GCD curve comparison of all samples of MnO₂ nano materials, AC and MnO₂/AC nano composite electrodes at constant current densities of 2 A g⁻¹.

The GCD curves of the optimized materials are shown in figure 14 at various current densities. Figure 14 (A-C) revealed charging and discharging times decreased as the current density increased. This showed that the time required for charging and discharging electrode materials was lowered as the current density increased. The relationship between this current density and specific capacitance is shown in figure 14D. As it is observed, Cs increased as the current density increased up to 3 A g⁻¹. This is due to the fact that most of the as-synthesized electrode material's surface could efficiently participate in the electrochemical redox reactions at high current density, resulting in a high capacitance value. This confirms the high-speed capabilities of the synthesized electrode materials. However, as current density was further increased, Cs gradually decreased with increasing current density for all materials, and this could be due to the diffusion-limited process. At slower current densities, SC's electrode materials have more time to be occupied by the electrolyte ions, resulting in greater diffusion and larger Cs. In contrast, at higher current densities, the electrolyte ions do not get sufficient time for diffusion into the inner pores, resulting in lower.

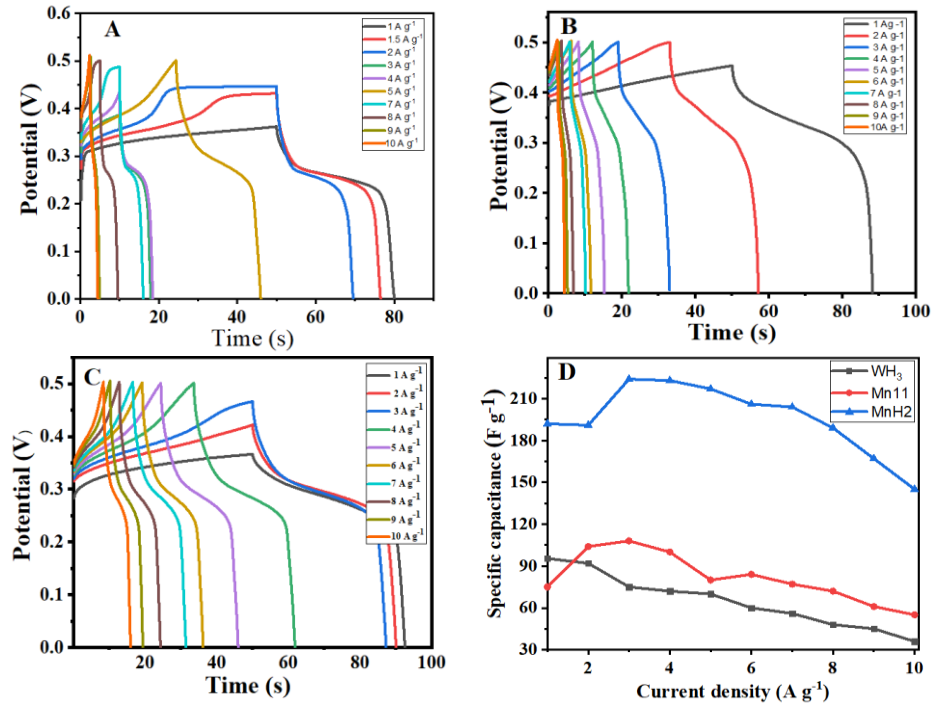


Figure 14: GCD curve of WH₃ (B), Mn(1:1) (B) and MnH₂ (C) of samples with their plots of specific capacitance as a function of current density (D)

The energy density (ED) and power density (PD) of all the electrode's materials were calculated using the equations (8) and (9), respectively (A. N. Ahmed et al., 2022; Yaashikaa et al., 2020).

$$ED = \frac{0.5 C_m (\Delta V)^2}{3.6} (\text{W h kg}^{-1}) \quad (8)$$

$$PD = \frac{3600 ED}{\Delta t} (\text{W kg}^{-1}) \quad (9)$$

Where, C_s is specific capacitance (F g⁻¹), ΔV operating potential range (potential window) in volt (V), and Δt is the time of discharging (s) for a cycle of the SC. As a result, the maximum ED of (3.8, 2.6 and 7.8) Wh kg⁻¹ with the corresponding PD of (740, 780, and 758 W kg⁻¹) was achieved in the case of optimized MnO₂ nanostructure, AC, and their hybrid composite, respectively, at a current density of 3 A g⁻¹.

Generally, the electrochemical properties indicated that the composite of the electrode materials revealed an excellent performance in SC application. This could be attributed to its high SSA and the synergistic effects arising from AC and MnO₂ nanostructure. According to table 5, the Cs are equivalent to those found in the literature and higher. The electrode material also offered a more affordable alternative to more expensive synthetic materials.

Table 5: Comparative electrochemical performance of various MnO₂/carbon nanocomposite materials reported previously in the literature

Material	Retention capacitance (cycles)	Cs (F g ⁻¹)	ED (W h kg ⁻¹)	PD (W kg ⁻¹)	References
MnO ₂ /AC		221 1 A g ⁻¹	-	-	(T. Huang et al., 2015)
MnO ₂ /AC		77.6 5 mV s ⁻¹			(Dutta et al., 2016)
AC- MnO ₂	88 % (1000)	84.28	14.88	96.68	(Diantoro et al., 2022)
AC- MnO ₂ 15%//AC	91.97% (1000)	98.45	21.07	103.98	(Diantoro et al., 2022)
MnO ₂ /Carbon Cloth	97.3% (2000)	67.8	18.46	699.54	(J. Miao et al., 2021)
MnO ₂ /MWCNT//AC	94% (2000)	52 2 A g ⁻¹	18.7	8000	(Sivakumar et al., 2022)
MnO ₂ /graphene	75% (10,000)	133 (10 mV s ⁻¹)	-	-	(Amade et al., 2019)
MnO ₂ -PVA	98% 500	12.5 at 0.14 A g ⁻¹	42.0	192	(Z. Lu et al., 2019)
MWNT/ MnO ₂	116% at 10,000	152 at 0.2 A g ⁻¹	14.1	202	(Z. Lu et al., 2017)
MnO ₂ /AC	95% (2000)	224 at 3 A g ⁻¹	7.8	758	This work

Cyclic ability is also a key factor in the selection of better materials, and it is employed to evaluate the durability of the electrode to maintain its maximum Cs. It is the capacitance retention of the devices or electrode materials at the nth cycle under certain test conditions (Ntakirutimana et al., 2020). In this study, 2000 continuous charge/discharge cycles were applied at a 4 A g^{-1} current density. Figure 15 reveals the capacity retention and life cycle stability of MnH2 composite electrode. As can be seen, MnH2 has high capacity retention of 95% and can sustain 2000 prolonged cycles without noticeably degrading.

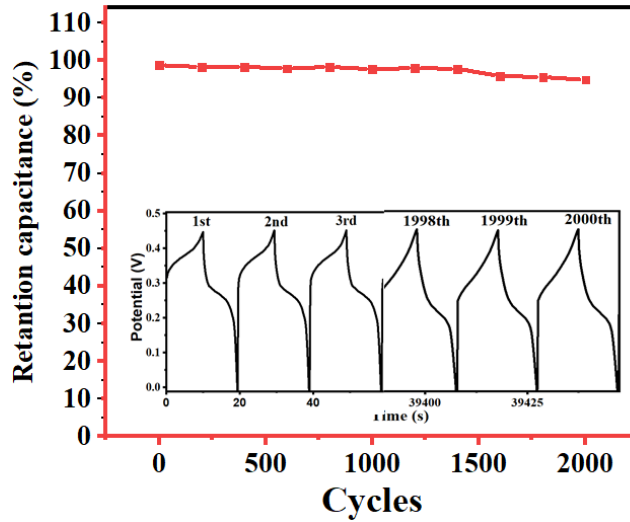


Figure 15: Cyclic stability of MnH2 at 4 F g^{-1} for 2000 cycles with its specific capacitance and retention capacitance

4.2.3. Electrochemical impedance spectroscopy (EIS) analysis

EIS analysis provides a fundamental understanding of the electrode/electrolyte interface behavior, the charge-transfer resistance (R_{ct}), and ionic diffusion in different recorded frequency regions (Pilathottathil & Thayyil, 2017). Figure 16 represents the Nyquist plot of EIS measurements of electrodes with rundles circuit fit model using IVIUM software. In the graphic, the horizontal axis represents the real impedance while the vertical axis represents an imagined impedance. It shows how the EIS charts behave differently depending on the frequency range employed. For instance, intercept on the real axis at high frequency reveals the internal resistance (R_s) associated with intrinsic resistance of the current collector, electrode materials and contact resistance between the electrode material and current collector (Arulraj & Nishanthi, 2020).

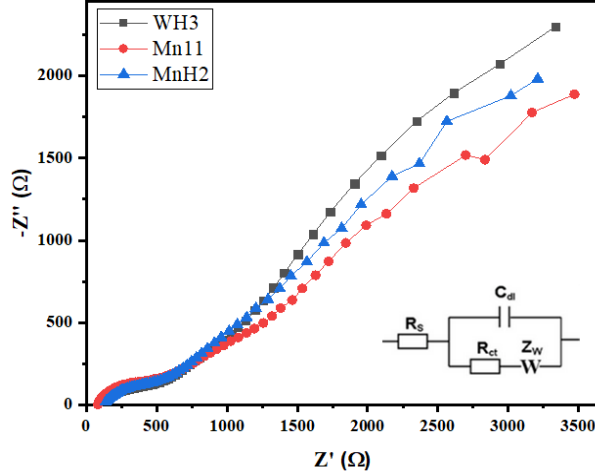


Figure 16: Nyquist plots of EIS curves for WH₃, Mn(1:1) and MnH₂

The presence of the semi circle at the middle frequency region shows the induced charge transfer resistance associated with electrode/electrolyte ion chemical interaction (Mei et al., 2018). The larger diameter of the semi-circle indicates higher electron transfer resistance, which is a sign of the poor conductivity of the material (Ghosh et al., 2019b). Whereas when the ions from the electrolyte travel into the pores of the electrode material, the presence of a straight line at low frequency regions demonstrates ionic diffusion resistance. A linear zone with a steep slope corresponding to electrodes that effectively allows ions to easily diffuse into the micropores (Pilathottathil & Thayyil, 2017). The presence of the straight line and semi-circle in the plot shows both capacitive and the resistive properties of the studied electrode, respectively. For WH₃, Mn(1:1), and MnH₂, the fitted R_{ct} values were 277Ω, 372Ω and 295Ω , respectively. From the graph one can observe that, adding AC material to the composite resulted in a lower R_{ct} and ionic resistance than using a single MnO₂ nanostructure. This could be due to high porosity of AC, thus accelerates electrolyte ion transport. In addition, the presence of the AC can prevent the agglomeration of MnO₂ and reduces its charge transfer resistance (Wu et al., 2020).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5. 1. Conclusion

In this research thesis, novel electrode materials such as AC, MnO₂ and their composite have been synthesized and tested for SCs application. Water hyacinth stem was employed to prepare AC as precursor through K₂CO₃ and KOH chemical activation process in self generated atmospheric condition. Additionally, its leaf extract was used as reducing and capping agents in green synthesis of MnO₂ nanostructure and MnO₂/AC nanocomposite. As-synthesized electrode materials were systematically characterized and revealed good physicochemical properties, such as high SSA, poly functional groups and amorphous structure. The optimal ratio of water hyacinth derived AC, MnO₂ nanostructure and their composite showed excellent Cs of 75 F g⁻¹, 108 F g⁻¹, and 224 F g⁻¹ respectively at a current density of 3 A g⁻¹ in 6M KOH aqueous electrolyte. This indicated that the composite electrodes displayed higher Cs than pure MnO₂ and AC electrodes. The composite electrode also demonstrated good cycle stability, 95% retention of the original capacitance after 2000 cycles of charge/discharge at a current density of 4 A g⁻¹. Furthermore, it also possesses high energy density of 7.8 Wh kg⁻¹ and power density of 758 W kg⁻¹ at 3 A g⁻¹. Green synthesized MnO₂ nanostructure and its composite with AC derived from water hyacinth stem are a promising for use as electrode materials in electrochemical SCs.

5.2. Recommendation

The following recommendations are made to help individuals who want to concentrate on this field of study based on the current findings of AC, MnO₂, and MnO₂/AC nanocomposite manufactured by using the water hyacinth plant. To compare their performance to that of SC, these materials could be evaluated for fuel cells and water splitting applications. In addition, they can be tested as adsorbent for toxic heavy metal removal efficiency.

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Appendixes

Table S1: Crystallite sizes of As-synthesized electrode materials.

Materials	2 θ value ($^{\circ}$)	FWHM (deg)	Miller index (hkl)	Mean crystal size (nm)
Mn (1:3)	12.5	0.29	001	2.75
	25.78	1.20	002	
	37.46	0.88	111	
	66.54	1.02	020	
Mn(1:1)	12.5	0.11	001	2.22
	25.48	0.31	002	
	37.46	0.56	111	
	66.14	0.77	020	
Mn(3:1)	12.8	0.38	001	2.78
	25.5	0.21	002	
	37.96	0.90	111	
	66.72	1.00	020	
WH ₁	12.5	1.32	001	25.82
	25.48	1.54	002	
WH ₂	12.5	2.00	001	28.36
	25.48	0.76	002	
WH ₃	12.5	1.54	001	21.17
	25.48	0.89	002	
MnH1	12.7	1.92	001	16.85
	25.59	1.55	002	
	36.46	0.79	111	
	67.14	0.33	020	
MnH2	12.56	1.54	001	13.64
	25.7	1.06	002	
	37.46	0.23	111	

	66.18	0.15	020	
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MnH3	12.1	0.29	001	15.02
	25.27	1.07	002	
	37.40	2.1	111	
	66.3	1.76	020	

Table S2: Specific capacitance, energy density and power density value of all prepared electrodes at 2 A g⁻¹

Material	Mn(1:3)	Mn(1:1)	Mn(3:1)	WH ₁	WH ₂	WH ₃	MnH1	MnH2	MnH3
Cs (Fg ⁻¹)	55.28	86.93	34.96	30.12	86.64	96.48	117.5	195.9	190.4
ED (Wh Kg ⁻¹)	1.92	2.75	1.21	1.04	3.00	3.35	3.76	4.80	4.66
PD (Wkg ⁻¹)	417	449	419	510	500	500	480	420	421

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