

SYNTHESIS AND CHARACTERIZATION OF MANGANESE BASED ELECTRODE FOR APPLICATIONS IN METAL-ION BATTERIES

Submitted in partial fulfillment of the requirements for the award of
Master of Science in Chemistry

by

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INSTITUTE OF SCIENCE AND TECHNOLOGY
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This is to certify that this Project Report is the bonafide work of **A. THABIBA (39910019)** who carried out the project entitled **"SYNTHESIS AND CHARACTERIZATION OF MANGANESE BASED ELECTRODE FOR APPLICATIONS IN METAL-ION BATTERIES"** under my supervision from November, 2020 to March, 2021.

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DECLARATION

I, **A. THABIBA** hereby declare that the Project Report entitled “Synthesis and characterization of manganese-based electrode for application in metal-ion batteries” done by me under the guidance of **Dr. A. SHEIK MIDEEN, M.Sc., Ph.D.**, Professor, Department of Chemistry, Sathyabama Institute of Science and Technology, Chennai – 600119, India is submitted in partial fulfillment of the requirements for the award of **Master of Science in Chemistry** in April 2021.

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ABSTRACT

In the last five years, there have been unprecedented research efforts to identify electroactive materials for room temperature rechargeable aluminium-ion batteries. Manganese oxide nanoparticles (MnO_2 NPs) have piqued the interest of material scientists in recent years due to their wide range of applications. They're used in a variety of applications, including energy storage devices (aluminium-ion batteries, capacitors), catalysts, adsorbents, sensors and imaging, therapeutic activity, and so on. Because they have so many promising properties, a reliable protocol for producing cheap, stable, biocompatible, and environmentally friendly MnO_2 nanoparticles is required. They can be classified into various phases such as α , β , δ , and others. As a result of their unique nature, they could be used for a variety of purposes, depending on the mode of action and applications.

Manganese oxide (MnO_2) is gaining popularity as a potential cathode material for aqueous aluminium-ion batteries. As a result, this review has summarised traditional methods for the generation of α - MnO_2 nanoparticles, such as the co-precipitation method, Hummer's method for the synthesis of Graphene, and the simple mechanical method for the synthesis of MnO_2 /Graphene nanocomposites. The cathode MnO_2 /Graphene nanocomposite is made by mechanically doping Graphene nanoparticles into MnO_2 nanoparticles.

Characterization using various spectroscopic techniques is also discussed. XRD spectra values and graphs, FTIR peaks and graphs, EDX images and composition, and FESEM morphology are compared and examined for graphene nanoparticles, MnO_2 nanoparticles, and MnO_2 /Graphene nanocomposite. In the FESEM characterisation of α - MnO_2 nanoparticles, nanospheres are obtained.

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CHAPTER 1

INTRODUCTION

The rapid growth of energy demands, combined with a push for environmental sustainability, has prompted a shift toward non-exhaustive, long-term energy sources. Though conventional power sources remain the primary source of energy, demand for cleaner energy sources such as solar, tidal, and wind is growing. Solar photovoltaics is expected to surpass hydropower in installed capacity around 2030, and coal in installed capacity before 2040. The rapid deployment and falling costs of clean energy technology also reflect this shift in trend. [Srinivasan et al., 2019]

Unfortunately, due to the unpredictable and intermittent nature of such energy sources, direct use is inefficient, resulting in electricity overproduction or underproduction for extended periods of time. The integration of battery energy storage systems (BESS) into the electricity grid system is one logical solution to this problem, but the scales required mean that such systems must be sustainable, environmentally benign, safe, and inexpensive. Water as an electrolyte solvent is non-toxic, non-flammable, and inexpensive, so aqueous battery systems are gaining a lot of traction in this area. [Srinivasan et al., 2019]

The most advanced type of electrochemical ES is batteries. When a load is connected to the electrodes, the general working principle of a battery is the free transfer of electrons between electrodes caused by the oxidation-reduction reverse reaction occurring within the cells of the battery. When an electrode plate is placed in an electrolyte that facilitates the transfer of ions, energy is stored in electrochemical form. The number of active components that the electrolyte can accommodate determines how much energy is stored. The power rating of a battery is determined by the electrode surface area and cell resistance. Depending on the output voltage and energy capacity of the cells, the cells could be arranged in series, parallel, or combined. The variety of chemicals and materials that can be used as electrodes and electrolytes results in a

wide range of battery technologies that can be used to accomplish various tasks. Batteries are ES technologies with a high energy density and a low power density. Batteries are modular, allowing them to be tailored to specific site conditions and placed at various points throughout the grid. [Masebinu et al., 2017]

Traditional batteries are divided into two types: primary batteries, which are non-rechargeable and must be discarded once the stored energy has been depleted, and secondary batteries, which are rechargeable and can be used throughout the battery's life cycle. Primary batteries are less expensive than secondary batteries and have a lower discharge rate and higher energy density. They are not, however, suitable for bulk. Because they all have varying degrees of self-discharge losses, conventional batteries are primarily used for short-term storage. Their response time is approximately 20 milliseconds. They are useful for power quality management, short-term fluctuation reduction, spinning reserve application, and transmission deferral when integrated into RE. There are various types of batteries, each with its own set of advantages and disadvantages. [Masebinu et al., 2017]

1.1 ALUMINIUM-ION BATTERY

Despite the fact that Li-aqueous batteries have been extensively investigated, committing solely to Li-ion technology carries a high risk of material supply disruption due to geopolitical factors. As a result, securing BESS' long-term viability by pursuing non-lithium-ion chemistries such as Na, Zn, Mg, and Al is highly desirable. Aluminum-ion aqueous batteries (AIAB) are one of the most promising of these, as Al is inexpensive, abundant, and has a large volumetric capacity. This can significantly reduce the cost of the anode, lowering the overall cost of the battery. [Srinivasan et al., 2019]

Although Al^{3+} is smaller than Li^+ in the unsolvated state, it has the strongest electrostatic bonding with the host electrode materials, which, like many other di- and

trivalent ions, results in slower diffusion kinetics within the electrodes. Despite this, it has been discovered to intercalate and deintercalate successfully in certain compounds with good electrochemical properties [Wang et al., 2019]. Installation of auxiliary battery-type energy storage systems is a key design for power generators feeding on noncontinuous, nonfuel renewables, as modern cities demand a reliable supply of electricity when and where it is needed (BESS). Due to low cost and elemental abundance considerations, batteries containing Zn ions or Al ions in aqueous electrolytes are appealing, but achieving reversibility at a high energy density and long-life operation is complicated. The authors examine recent reports on reversible aqueous electrolyte batteries, with a focus on how electrochemical activation, insertion, and conversion mechanisms work. Key issues such as cation mobility, electrode stability, the formation of the electrode–electrolyte interface, and electrolyte decomposition are also discussed, as well as possible solutions or research directions for improving the performance of aqueous Zn-ion and Al-ion batteries. [Manalastas Jr. and Srinivasan et al., 2019]

Aluminium appeals to BESS because of its high volumetric capacity, low cost, and abundant supply. The development of a battery with Al metal as an anode and a cathode material that allows sufficient reversible (de)insertion of Al ion would be a huge step forward in the quest to lower the cost of energy storage devices while also ensuring long-term sustainability. Furthermore, using water instead of organics as the electrolyte solvent can significantly reduce the cost of such a battery. However, AIAB is still in its early stages of development and faces some challenges. 1) At the present, Al metal cannot be used as an anode in an aqueous electrolyte because its electrochemical plating/stripping voltage is too far away from the stable potential window of water. 2) The electrolyte (AlCl_3) developed for AIAB is highly acidic, promoting active material dissolution and auxiliary battery part corrosion. 3) In practice, no material has been reported that has demonstrated sufficient cycling stability to be used as a high voltage electrode material for AIAB. We summarise various implementations of rechargeable AIABs as reported in the literature in this section. We examine battery performance with a focus on electrode materials, including proposed

mechanisms for enabling electrochemical activity for each active material and characterization techniques for proving Al-ion insertion. [Manalastas Jr. and Srinivasan et al., 2019]

Aqueous intercalation batteries, given suitable electrode materials and aqueous electrolytes' high conductivity, may be capable of providing these characteristics in addition to being safe, non-toxic, and potentially low-cost when compared to nonaqueous systems like ionic liquids. The construction and testing of a fully functional aqueous Al-ion cell are described in this communication. The majority of Al-ion research focuses on room temperature ionic liquid electrolyte systems (RTILs), which theoretically allow the use of high-capacity aluminium metals via reversible deposition. The main goal of the research is to find positive electrode materials that do not severely limit cell capacity. In comparison to RTILs, using water as the solvent for an aluminium salt has the potential to provide a cheap, inherently safe, and more conductive electrolyte system. [Holland et al., 2018]

As a result, the demand for rechargeable batteries made from earth-friendly, non-toxic materials is greater than ever. In recent years, the allure of aluminium (Al) has not gone unnoticed in the world of rechargeable batteries. Al, as the third most abundant element in the Earth's crust, has a lot to offer in terms of overall battery performance, whether it's Al-metal or Al ion. There are two important electrochemical properties to mention. For starters, Al can exchange three electrons per cation. Second, when compared to its counterparts Li, Na, K, Mg, Ca, and Zn, Al has the highest storage capacity per volume. Furthermore, Al resources are cost-effective, and handling them in a natural setting is relatively simple. As a result, the electrochemical coupling of Al as an anode with a high-voltage cathode like graphene or graphite could be considered a noteworthy battery system. [Das et al., 2020]

CHAPTER 2

LITERATURE SURVEY

2.1 DIFFERENT TYPES OF CATHODE MATERIALS

Zhao et al. recently demonstrated the reversible electroplating or electrostripping of metallic Al in an aqueous environment, as well as its potential use as a direct anode material. However, in an aqueous environment, prospective cathode materials such as TiO_2 , CuHCF , V_2O_5 , MoO_3 , graphite, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, and MnO_2 have been reported to show only limited reversible cycling with Al-ions. The development of better electrode materials that can accommodate a higher charge capacity from aluminium ions in an aqueous electrolyte is therefore critical to making AIABs practical. There is a gap in existing AIAB research where typical conversion materials have yet to be explored for AIABs. [Srinivasan et al., 2019]

1. *TITANIUM DIOXIDE (TiO_2)*

The common polymorphs of TiO_2 are rutile, brookite, and anatase, which are found in eight different crystal structures. The anatase TiO_2 crystal structure is made up of stacked TiO_6 octahedrons that form tunnels, allowing cations to pass through. Apart from electronic conductivity, the electrolyte anion may also play a role in assisting Al ion insertion into host materials. The majority of nonaqueous Al-ion batteries studied so far cycle only in chloride-based electrolytes, whereas sulfate- and nitrate-based aqueous electrolytes show no or only weak electrochemical activity. [Manalastas Jr. and Srinivasan et al., 2019]

Lahan et al. observed weaker electrochemical activity for Al^{3+} insertion into TiO_2 in $\text{Al}_2(\text{SO}_4)_3$ electrolytes and no activity in $\text{Al}(\text{NO}_3)_3$ electrolytes, compared to the strong activity in AlCl_3 electrolytes, when they experimented with a variety of electrolytes. Liu et al. conducted a similar study on a TiO_2 nanotube array in electrolytes with various

anionic species in order to better understand the role of Cl ions. In $\text{Al}_2(\text{SO}_4)_3$ electrolytes, electrodes based on TiO_2 nanotube arrays were found to be electrochemically inactive for Al^{3+} insertion, whereas in AlCl_3 electrolytes, an obvious pair of reversible redox peaks was observed. Liu et al. also discovered that increasing the concentration of NaCl in $\text{Al}_2(\text{SO}_4)_3$ increased electrochemical activity, implying that Cl ions play a role in the intercalation process. However, XPS revealed no chloride peaks on the electrode surface, contrary to expectations. The mechanism by which Cl ions aid in the electrochemical insertion of Al ions is thus inconclusive and remains a mystery. Though Al-ion insertion into TiO_2 has been demonstrated, the intercalation occurs at low voltages in comparison to the SHE, making TiO_2 materials particularly susceptible to proton co-intercalation. [Manalastas Jr. and Srinivasan et al., 2019]

2. COPPER HEXACYANOFERRATE (CuHCF)

CuHCF nanoparticles were the first high voltage (0.72 V vs SHE) active material for AIABs to be reported [Manalastas Jr. and Srinivasan et al., 2019]. The electrode materials with Prussian Blue analogues (PBA) structures, such as CuHCF, showed a lot of potential for multivalent ion insertion/de-insertion. P and R ions are separated and bonded by CN ligands to form a face-centered cubic structure with open framework in PBAs with a generic formula of $\text{A}_x\text{PR}(\text{CN})_6$, and the large interstitial A sites are where guest ions can be inserted. For hydrogen storage, battery electrodes, and electrochromic applications, PBA's electrochemical properties have been extensively studied. Copper and nickel hexacyanoferrates with a PBA structure have recently been shown to electrochemically insert ions in aqueous solutions. Wessells et al., Cui et al., and Steingart et al. found that the capacity of CuHCF is unaffected by the intercalating species' ionic valency as long as the concentration of intercalating ions in the electrolyte is greater than the moles of active material, and this is because the number of ions inserted in the CuHCF is limited by charge balancing with the number of available Fe^{2+} in the crystal structure, limiting the cell capacity. [Guduru et al., 2016].

3. ***VANADIUM OXIDE (V₂O₅)***

It's an AIAB cathode because of its layered V₂O₅ structure and high V⁵⁺/V⁴⁺ redox potential. In a 1 m AlCl₃ aqueous electrolyte, González et al. demonstrated reversible intercalation of Al ions into V₂O₅ xerogels. In discharged V₂O₅ cathodes, XPS results confirmed the intercalation of Al ions and the resulting reduction in the average oxidation state of lattice vanadium. The results of ex situ XRD of electrodes obtained at various stages of discharging revealed progressive amorphization of V₂O₅. When cycling V₂O₅ at 60 mA g⁻¹, González et al. noticed a significant drop in gravimetric capacity, which worsened at a higher cycling rate of 200 mA g⁻¹. The structural amorphization caused by co intercalating Al³⁺ and H₂O, according to González et al., was the cause of the deteriorated stability. They proposed a side-reaction mechanism in which the Al ion reduces the proportionate stoichiometry of vanadium to a lower oxidation state, resulting in the formation of a hydrated Al–V complex that causes crystallinity loss. [Manalastas Jr. and Srinivasan et al., 2019]

4. ***GRAPHITE***

For nonaqueous Al-ion batteries, graphene in various forms, such as foam, film, and powder, has demonstrated exceptional power density and cycling stability. It can be engineered to accommodate large-sized intercalating ions by introducing defects or functional groups. Wang et al. reported a two-step process for producing exfoliated graphite for Al-ion batteries: first, H₂O and NO₃ molecules are electrochemically inserted into pristine graphitic layers; second, H₂O is oxidised to O₂ while NO₃ is reduced to NO, resulting in sufficient gaseous pressure to exfoliate graphitic layers under subsequent application of appropriate voltages. These exfoliated sheets were then processed into a cathode, paired with a Zn foil anode, and cycled successfully in an aqueous Al₂(SO₄)₃/Zn(CH₃COO)₂ electrolyte. Wang et al., on the other hand, did not observe CV peaks when the electrolyte was modified to remove all Al ions from solution. They concluded that the electrochemical activity in Al₂(SO₄)₃/Zn(CH₃COO)₂ was due solely to Al-ion intercalation, with no other spectator ions (Zn²⁺, H⁺, CH₃COO, or SO₄²⁻)

intercalating. Graphite sheets showed a 0.5 increase in interlayer distances after discharge, while SAED patterns revealed new phases that were not present before discharge. This showed that foreign species crystallographically inserted themselves into the graphitic layers. The high-resolution transmission electron microscopy (HRTEM) image and SAED pattern in the deep interior area of the discharged graphitic nanosheet, on the other hand, were identical to those of the pristine, implying that hydrated Al ion intercalation occurred readily on the surface but not in the interior graphite bulk. Nonetheless, Wang et al. demonstrated a charging time of 110 seconds for this material, with a discharge capacity of 60 mAh g⁻¹ at a rate of 2 A g⁻¹. Modified forms of graphene, as they have in the past for other materials, may help to improve capacity by allowing deep insertion of Al³⁺. [Manalastas Jr. and Srinivasan et al., 2019]

5. ***Na₃V₂(PO₄)₃***

Nacimientto et al. investigated NASICON-type Na₃V₂(PO₄)₃ (NVP) in great detail using 0.1 m AlCl₃ aqueous electrolytes. Wet ball-milling was used to create NVP/carbon nanocomposites to 1) improve conductivity, and 2) slow NVP dissolution in the electrolyte. Nacimientto et al. presented a convincing case of Al-ion insertion into NVP using multiple characterization techniques. First, the composition of raw, first charged, and discharged samples was determined using semiquantitative microanalysis, which agreed well with theoretical composition calculations based on electrochemical data. Second, ex situ XRD results for the crystallographic unit cell revealed a contraction/expansion cycle, which is consistent with ion intercalation/deintercalation. Third, XPS results showed that discharged samples had a high Al peak intensity, whereas vanadium peaks shifted reversibly to higher and lower energy values following battery charge and discharge, respectively. Fourth, an NMR study confirmed the presence of surface-accommodated Al ions as well as lattice-inserted Al ions. Based on these findings, Nacimientto et al. proposed a mechanism in which NVP loses sodium ions during the initial charging cycle, but subsequent discharging results in both bulk intercalation and surface storage of Al ions, both of which contribute to the measured specific capacity. Though the cycling stability of NVP in this study was not exceptional,

a successful Al-ion insertion was clearly demonstrated using multiple characterization techniques that complimented each other. [Manalastas Jr. and Srinivasan et al., 2019]

As a result, here we investigate FeVO₄ for Al-ion reaction in an aqueous electrolyte in an attempt to better understand the electrochemical behaviour of conversion-type materials. FeVO₄ 1) it has demonstrated exceptional capacity in non-aqueous Li-ion batteries, allowing up to 8 Li-ions to be inserted. 2) Its reaction potential allows for discharge/charge cycles while staying within the water's potential stability window, and 3) it has been reported to have a conversion-type reaction mechanism for various cations. In this paper, we describe the synthesis of FeVO₄ nanorods and show how they can be used as a cathode material in AIAB. We show that our material can deliver a capacity of 350 mA h g⁻¹ at 60 mA g⁻¹ in a pH- and concentration-modulated electrolyte, which is significantly higher than previously reported cathode materials for AIAB. The synthesis of FeVO₄ nanorods and show how they can be used as a cathode material in AIAB. We show that our material can deliver a capacity of 350 mA h g⁻¹ at 60 mA g⁻¹ in a pH- and concentration-modulated electrolyte, which is significantly higher than previously experimented cathode materials for AIAB. We also investigate the mechanism of Al-ion reaction with FeVO₄ using a variety of in-house and synchrotron-based analytical techniques, and provide definitive proof of concomitant Al-ion intake during electrochemical cycling. [Srinivasan et al., 2019]

2.2 MnO₂ AS A CATHODE MATERIAL

Nanomaterials, defined as materials with a length scale of less than 100 nanometers, are gaining popularity due to their fundamental scientific importance as well as the potential applications derived from their fascinating electrical, magnetic, and catalytic properties. [Liu et al., 2013]

In recent years, significant R&D investment in nanotechnology has resulted in nano-objects (particles with a size of less than 100 nm) with a diverse set of physical properties that differ from those of the bulk and are dependent on morphology,

polymorphism, particle size, coating, size distribution, and the precursor used in synthesis. In order to develop new systems for energy storage and/or conversion, these nano-substances have undergone extensive research in order to meet the demand for renewable energies. Transition-metal oxides, such as TiO_2 , MnO_2 , V_2O_5 , and others, are stable and robust materials with tuneable properties and large surface areas among them. [Julien et al., 2017]

Contaminant sensing, drug delivery, data storage, catalysis, and biomedical imaging all use manganese oxide (MnO_2) NPs. Because of the growing concern about pollution, green synthesis of NPs is critical. Because of its environmentally friendly nature, green chemistry-based NP synthesis is preferred. [Kumar et al., 2017]

Nanomaterials have more excellent electrochemical activity than bulk active electrode materials, such as higher capacities, larger surface areas, and lower current densities, and thus have a wild potential application in the electrochemistry field. MnO , MnO_2 , and Mn_3O_4 are manganese oxide composites that have been used in wastewater treatment, sensors, catalysis, supercapacitors, and alkaline and rechargeable batteries. [Liu et al., 2013]

Because of its structure flexibility, long cycle life, environmental compatibility, and low cost, manganese oxide (MnO_2) is a popular electrode active material for supercapacitors. Because of its crystal structure, particle size, and morphology, the performance of MnO_2 is dependent on various synthetic methods. MnO_2 has a clustered morphology and a low intrinsically electronic conductivity. Co-precipitation, micro emulsion, sol–gel, sonochemical, hydrothermal, and electrochemical methods were all used to create MnO_2 nanoparticles. [Gnana Sundara Raj et al., 2014]

The variety of structures and unique properties of manganese dioxides have piqued people's interest. Because of their low cost, earth abundance, environmental friendliness, and variable oxidation states, they have potential applications as catalysts,

solar cells, and electrochemical capacitors, as well as electrode materials for Li-ion and Li-air batteries. [Hashem, Abuzeid, Kaus, Indris, Ehrenberg et al., 2018]

To summarise, MnO₂ polymorphs, particularly the and polymorphs, have demonstrated high capacities and capacity retentions, making them better candidates for BESS. The Zn²⁺ storage mechanism for MnO₂ polymorphs, on the other hand, is still unknown. The synthesis precursors K⁺, Na⁺, Mg²⁺, and H₂O can intercalate into the MnO₂ crystals tunnels/layers and change the valence state of Mn in MnO₂, making a one-to-one comparison between studies much hard. Nonetheless, most polymorphs show a common trend of phase transformation to layered busenite or birnessite phases, implying that layered phases with large interlayer spacing are suitable for Zn²⁺ insertion in an aqueous electrolyte [Mahalastas Jr. and Srinivasan et al., 2019].

One way to avoid problems with aluminium substrate corrosion during the deposition of vanadium oxide (or any other functional layer) is to coat the aluminium surfaces with an initial layer that is sufficiently protective to allow the subsequent deposition of vanadium oxide. This intermediate layer must be stable in the acidic and oxidative environment required for vanadium oxide electrodeposition, and it would be ideal if the protective layer could be formed directly by electrodeposition, keeping the coating procedure simple and cost-effective. A layer of manganese oxide (MnO_x) was chosen in this study because at least MnO₂ should be stable in the pH/voltage window required for vanadium oxide deposition, and the MnO_x layer can be easily deposited using cathodic electrodeposition. This also avoids oxidation of the Al substrate, resulting in an all-electrochemical deposition method. The manganese oxide interlayer will be referred to as MnO_x in this study because it can undergo phase transformations due to ageing effects and oxidation during the subsequent vanadium oxide electrodeposition. The main purpose of this MnO_x layer is to initially slow down aluminium corrosion enough to allow electrodeposition of vanadium oxide on the aluminium microrods. The MnO_x layer does not need to form a perfect conformal layer on the microrods as long as it allows for vanadium oxide deposition, as the latter layer will act as a corrosion preventive measures layer later [Rehnlund, Valvo, Edstrom et al., 2014].

Manganese oxides (MnO_2) are known to be strong metal ion adsorbents and are found naturally in soils, aquifers, and sediments. Catalysis, ion sieves, rechargeable batteries, chemical sensing devices, magnetic devices, field-emission devices, hydrogen storage media, and microelectronics are just a few of the fields where synthetic manganese oxides with micro and nanostructures are still attracting interest. [Dand et al., 2015].

2.3 GRAPHENE

The synthesis, characterization, exploration, and exploitation of nanomaterials are the main topics of nanoscience and nanotechnology. Carbon, one of the most abundant atoms on the planet, occurs naturally in a variety of forms and as a component in a wide range of substances known as allotropes of carbon. Graphene, also known as the "wonder material," is the world's thinnest, strongest, and stiffest material, as well as an excellent heat and electricity conductor. It is the fundamental constituent of all other important allotropes. Because of its low cost, ease of access, and widespread ability to convert to graphene, graphene oxide (GO) is a hot topic. Another feature that is highly desired is scalability. [Paulchamy, Arthi, and Lignesh, 2015]

Graphene oxide is graphite that has been oxidised to intersperse carbon layers with oxygen molecules, then reduced to completely separate the carbon layers into single or few-layer graphene. Because the oxidising agents react with graphite, increasing the interplanar spacing between the layers of graphite, graphene oxide is effectively a by-product of this oxidation. Graphene oxide is then produced by dispersing the completely oxidised compound in a base solution such as water. [Paulchamy, Arthi, and Lignesh, 2015]

On both sides of a single graphite sheet, a large number of oxygen-containing functional groups have been introduced (namely, graphene). The implantation of functional groups overcomes the van der Waals force between the sheets and

increases interlayer spacing. An external force, such as sonication, is then used to easily pull the sheets in such an expanded structure open. Exfoliation is the process of separating expanded graphite into multi-layered or even single-layered sheets. Generally, the oxidised graphene sheets, namely, GO, acquire multiple defects and the degree of the defects is subject to the additive amount of oxidant and the oxidising time. Brodie, Hummers, and Staudenmeir developed one of the main methods for producing GO, which is the oxidative treatment of graphite. [Paulchamy, Arthi, and Lignesh, 2015]

2.4 ELECTROLYTES

Aqueous rechargeable batteries with mild electrolytes (containing metal salt as a solute, primarily aqueous metal-ion batteries with intercalation electrodes) have gained popularity in recent years, not only for grid-scale energy storage but also for wearable and biocompatible applications. Most intercalation-electrode materials for aqueous batteries can currently be traced back to a nonaqueous electrolyte equivalent. In contrast to nonaqueous systems, however, the choice of electrode materials in an aqueous electrolyte is severely limited due to the following issues: water's narrow stable electrochemical window (1.233 V), side reactions with water or oxygen, proton co-insertion with metal ion insertion, electrode material dissolution in aqueous electrolyte, and so on. [Wang et al., 2019]

Because of the solid research foundation in nonaqueous electrolyte, aqueous Li-ion batteries (ALIBs) are the most studied system. However, in recent years, other metal ions with abundant reserves, such as Na, K, Zn, Mg, Ca, and Al-ion batteries with mild aqueous electrolyte, have been proposed due to the limited Li resource. Aqueous rechargeable zinc batteries, in particular, have recently gotten a lot of attention because of their high theoretical capacity of 820 mAh g⁻¹, which is much higher than any other metal-ion battery anode material. [Wang et al., 2019]

Similarly, other multivalent metals (e.g., Al, Ca, Y, Ni, and Zn, among others) have several advantages in terms of ease of handling, abundance, low cost, high

storage capacity, and energy density, and many of them could be used as anodes in aqueous electrolytes, but they are all limited by the cathode and electrolyte materials available. For multivalent batteries, the electrolyte challenges are amplified, and the electrolyte choice is critical in terms of high ion mobility and easy (de)solvation of the ions at the electrode interfaces. [Guduru et al., 2016]

Aqueous-electrolyte batteries have several advantages over nonaqueous batteries in large-grid BESS applications: first, manufacturing costs are reduced due to the elimination of stringent drying protocols in battery assembly lines. Second, due to the higher ionic conductivity of water-based media and the use of inexpensive salts, aqueous systems are expected to enable higher power densities. Third, the replacement of toxic flammable organics in battery electrolytes with water reduces the risk of catastrophic incendiary failures. Because of the solvation properties, nonflammability, and nonvolatility of water, aqueous batteries would essentially offer better cost efficiency, ruggedness, and safety prospects. [Manalastas Jr. and Srinivasan et al., 2019]

Zn batteries with a mild aqueous electrolyte have recently gotten a lot of attention, so we did a thorough review of aqueous Zn batteries in the following areas: cathode materials (manganese oxides, vanadium oxide, Prussian blue analogues, and other materials, as well as Zn^{2+} storage mechanisms); Materials for anodes (from the development of zinc anodes in alkaline electrolytes to the most recent advances in mild electrolytes); electrolyte (including the selection of solute salt, additives in electrolyte and high concentration electrolyte). Third, K, Mg, Ca, and Al-ion aqueous batteries are still in the early stages of development. The history of these batteries, as well as their most recent developments, are briefly summarised to provide readers with a basic understanding of these batteries. [Wang et al., 2019]

Due to low cost and elemental abundance considerations, batteries containing Zn ions or Al ions in aqueous electrolytes are appealing, but achieving reversibility at a

high energy density and long-life operation is difficult. [Manalastas Jr. and Srinivasan et al., 2019]

There is also interest in using aqueous electrolytes, which have advantages in terms of cost, handling ease, toxicity, and environmental friendliness. In comparison to Li salts and organic solvents, the use of electrolytes based on Na, K, or Al salts benefits from their higher natural abundance and relative ease of processing. [Holland et al., 2019]. In 2012, a rechargeable multivalent Al-ion battery with aqueous electrolyte was proposed as a viable alternative to Li-ion batteries for high energy storage. It should be noted, however, that intercalation reactions in aqueous electrolytes are typically very complicated. Different side reactions could occur, such as proton co-intercalation into electrode materials alongside multivalent ion intercalation, electrode material reaction with water or oxygen, hydrogen/oxygen evolution reactions, and electrode material dissolution in water depending on pH. Proton co-intercalation can occur in positive electrode materials, and it is usually influenced by the electrodes' crystal structure and the electrolyte's pH. [Gurudu et al., 2016]

Aluminium appeals to BESS because of its high volumetric capacity, low cost, and abundant supply. Developing a battery with Al metal as an anode and a cathode material that allows sufficient reversible (de)insertion of Al ion would be a huge step forward in lowering the cost of energy storage devices and enabling long-term sustainability. Furthermore, using water instead of organics as the electrolyte solvent can significantly reduce the cost of such a battery. However, AIAB is still in its early stages of development and faces some challenges. 1) At the moment, Al metal cannot be used as an anode in an aqueous electrolyte because its electrochemical plating/stripping voltage is too far away from the stable potential window of water. 2) The electrolyte (AlCl_3) developed for AIAB is highly acidic, promoting active material dissolution and auxiliary battery part corrosion. 3) In practise, no material has been reported that has demonstrated sufficient cycling stability to be used as a high voltage electrode material for AIAB. We summarise the various implementations of rechargeable AIABs that have been reported in the literature in this section. We

examine battery performance with a focus on electrode materials, including proposed mechanisms for enabling electrochemical activity for each active material and characterization techniques for proving Al-ion insertion. [Manalastas Jr. and Srinivasan et al., 2019]

Apart from electronic conductivity, the electrolyte anion may also play a role in assisting Al ion insertion into host materials. The majority of nonaqueous Al-ion batteries studied so far cycle only in chloride-based electrolytes, whereas sulfate- and nitrate-based aqueous electrolytes show no or only weak electrochemical activity. Lahan et al. observed weaker electrochemical activity for Al^{3+} insertion into TiO_2 in $\text{Al}_2(\text{SO}_4)_3$ electrolytes and no activity in $\text{Al}(\text{NO}_3)_3$ electrolytes, compared to the strong activity in AlCl_3 electrolytes, when they experimented with a variety of electrolytes. Liu et al. conducted a similar study on a TiO_2 nanotube array in electrolytes with various anionic species in order to better understand the role of Cl ions. In $\text{Al}_2(\text{SO}_4)_3$ electrolytes, electrodes based on TiO_2 nanotube arrays were found to be electrochemically inactive for Al^{3+} insertion, whereas in AlCl_3 electrolytes, an obvious pair of reversible redox peaks was observed. Liu et al. also discovered that increasing the concentration of NaCl in $\text{Al}_2(\text{SO}_4)_3$ increased electrochemical activity, implying that Cl ions play a role in the intercalation process. XPS, however, revealed no chloride peaks on the electrode surface, contrary to expectations. The mechanism by which Cl ions aid in the electrochemical insertion of Al ions is thus inconclusive and remains a mystery. [Manalastas Jr. and Srinivasan et al., 2019]

A battery system with a Zn/Al metallic anode and a high-capacity cathode material in an aqueous electrolyte that has a long cycle life might meet the criteria for BESS. Metallic Zn anodes have been successfully cycled in mildly acidic aqueous electrolytes, but metallic Al anodes have not, owing to an electrochemical plating/stripping voltage that occurs too far outside of water's stable potential window. However, progress in broadening the electrochemical stability window of aqueous electrolytes and the use of protective interphases may soon allow Al metal to be used as an anode. [Manalastas Jr. and Srinivasan et al., 2019]

Table 3.1: Literature Survey on Synthesis Routes of the Vanadium Based Nano Compound

Synthetic Method	Reactants	Synthetic Conditions	Morphology	Particle Size	Characterization	Citation
Sol-gel Method	Sodium permanganate monohydrate, Perchloric acid	Stirring for 18 h 120°C for 3 hours	Manganese Oxide		XRD	Hibino et al.,
Sonochemical method	KMnO ₄ , Ca(NO ₃) ₂ PVdF, PEG	Ultrasonicated for 20 min 70°C for 8 h	MnO ₂ nanoparticles	10 -20 nm	FT-IR EDX SEM TEM	Gnana Sundara Raj et al.,2014
Electrochemical method	0.1 M KMnO ₄ , 6M HCl	650 °C 5 h 5 h at 400°C and 650 °C	Manganese oxides nanoscale	15-20 nm	SEM EDX TEM CV	Dang et al., 2015
Electrochemical method	Mn(NO ₃) ₂ silica sol KOH	300° C at a rate of 5°C/min for 1h	Mesoporous MnO ₂		XRD CV	Chang Zhao et al., 2015
Sol-gel Method	Li ₂ MnO ₃ solution, Li ₂ MnO ₃ sol-gel	80 – 90 °C for 4 to 6 h 12 hours at 120 °C 6 hours at 350 °C 850 °C for 12 hours	Li ₂ MnO ₃ nanoparticles		XRD EDAX SEM CV	Thangamuthu et al, 2020

Aqueous intercalation batteries, given suitable electrode materials and aqueous electrolytes' high conductivity, may be capable of providing these characteristics in addition to being safe, non-toxic, and potentially low-cost when compared to nonaqueous systems like ionic liquids. The construction and testing of a fully functional aqueous Al-ion cell are described in this communication. The majority of Al-ion research focuses on room temperature ionic liquid electrolyte systems (RTILs), which theoretically allow the use of high-capacity aluminium metals via reversible deposition. The main goal of the research is to find positive electrode materials that do not severely limit cell capacity. [Holland et al., 2018]

When compared to room temperature ionic liquid electrolyte systems, using water as a solvent for an aluminium salt has the potential to provide a cheap, inherently safe, and more conductive electrolyte system (RTILs). [Holland et al., 2018]

2.5 METHODS TO SYNTHESIS THE COMPOUND

1. *PRECIPITATION METHOD*

The solvent displacement technique is another name for the precipitation technique. It entails the precipitation of a preformed polymer from an organic solution, as well as the diffusion of the organic solvent into the aqueous medium near or in the absence of a surfactant. To begin, dissolve the precursor in di ionized water with a stirrer, then drop the reducing agent into the solution. Precipitates forms and settle in the bottom of the beaker after a while. Then drain the solution and filter out the precipitant and slag for further nano particle characterization. This strategy has several advantages, including the fact that it is a simple, low-cost, and one-stage process that allows for easy control of particle size and composition, as well as a variety of options for modifying particle surface state and overall homogeneity. [Iqbal et al., 2017]

2. SOLVOTHERMAL METHOD

In a solvothermal reaction, solvents are transported to temperatures well above their boiling points in a fixed vessel, such as a bomb or an autoclave. The solvothermal method involves dissolving the precursor and reducing agent in a beaker and then placing it in an autoclave to characterize the nanoparticles. Solvothermal synthesis is a versatile, convenient, and straightforward method that uses only a polar, oxygen-containing solvent and heat, but it is usually done in closed vessels, so temperature, pressure, and volume considerations are crucial. [Iqbal et al., 2017]

3. HYDROTHERMAL METHOD

Hydrothermal synthesis is primarily used for the aqueous synthesis of a single crystal. This procedure is also carried out in an autoclave, where a mineral is added to the water. A temperature gradient is maintained between the two ends of the chamber. To obtain the desired crystal, the hotter end dissolves the supplements and the cooler end deposits them on the crystal. The hydrothermal synthesis method is advantageous because it can produce large, high-quality crystals as well as crystals that are unstable near the melting point. However, this procedure necessitates the purchase of expensive equipment and is not suitable for crystal monitoring. [Iqbal et al., 2017]

4. SOL GEL METHOD

The sol-gel method can be used to make a variety of materials, including dense powders and thin films. It's simple and inexpensive. In this method, solution was added to the precipitate, which turned into clear sol and then gel over time. Benefits of Sol Gel i.e., it synthesizes nanoparticles at room temperature and has been found to be an efficient and mild route for large-scale industrial production of fine nano particles without the use of expensive chemicals or templates, but the stoichiometry of doped oxide nano particles is difficult to control, which is a disadvantage of this method. [Iqbal et al., 2017]

5. GREEN SYNTHESIS

Green synthesis is a plant-mediated synthesis of metal nanoparticles that is simple, inexpensive, quick, and environmentally friendly. The bio molecules found in plant materials have the potential to speed up nano synthesis or improve product stability. To begin, collect plant extract from boiling leaves of the concerned plant in deionized water. Use this extract in conjunction with a precursor to create nanoparticles. The surface morphology and size of metals are influenced by plant materials. Plant extracts could be used as a capping and reducing agent in nanoparticle synthesis. However, the particles produced by this method may be quite large. [Iqbal et al., 2017]

6. MICRO EMULSION METHOD

Water-in-oil (w/o) micro emulsions have water drops on the surface of the oil, which act as a source for the formation of nanoparticles. Form a micro emulsion first, which is either water in oil or oil in water, in this method. Then characterize the emulsion using the precursor. This method is advantageous because it produces particles of controlled size and does not necessitate the use of costly instruments. Metal nanoparticles, such as organic nanoparticles, metal oxides, and silver halides, have been synthesized using w/o micro emulsions. [Iqbal et al., 2017]

7. REFLUXING ROUTE

The refluxing method allows for in-situ crystallization of samples and requires atmospheric pressure and a temperature below the boiling point of the solvent. This method entails heating a solution with a condenser attached to prevent reagent loss. Many organic compounds, on the other hand, have low boiling points and will vaporise when exposed to such high heat. Large-scale preparations benefit from reflux treatment. [Julien et al., 2017]

8. CATALYTIC REACTION

A homogeneous catalyst can lower the potential energy of a chemical reaction (such as the oxidation of MnSO_4) while also controlling the growth of oxide materials. In situ electrochemical oxidation of Mn_3O_4 films composed of nano wall arrays with porous structure was used to create birnessite-type MnO_2 electrodes for supercapacitors. A simple room-temperature solution-based catalytic reaction using AgNO_3 was used to prepare a core-shell structure (γ - and β - MnO_2 forms) with spherically aligned nanorods. [Julien et al., 2017]

9. CO-PRECIPITATION METHOD

This technique, which has advantages such as simple and quick preparative synthesis, as well as easy control of particle size and composition, can be done without the use of surfactants. Currently, manganese salts with two different anions in equal concentration are used in the co-precipitation process. It's time to change the pH. [Julien et al., 2017]

10. WITZRMANN'S METHOD

In non-aqueous sol-gel chemistry, this is the reaction between KMnO_4 and small saccharides, such as glucose and sucrose, or other polyalcohols (alcoholic solution). Between tetra-alkyl ammonium permanganate and methanol, Ching et al. developed a modified sol-gel reaction. After a 2-hour calcination at 450°C , MnO_2 nanopowders were well crystallized. [Julien et al., 2017]

11. TEMPLATE APPROACH

Aerogel MnO_2 with an ultralow density (0.5 mg/cm^3) was made from nanosheet colloids using an ice-template method for use as a toxic reducing gas absorbent. [Julien et al., 2017]

2.6 MORPHOLOGY OF MnO₂ NANOPARTICLE

When the basic structural unit ([MnO₆] octahedron) is linked in different ways, MnO₂ can exist in various structural forms such as, α -, β -, γ -, δ -, ϵ - and λ -types. MnO₂ can be classified into three types based on the different [MnO₆] links: chain-like tunnel structures like the α -, β -, and γ -types, sheet or layered structures like the δ -MnO₂, and 3D structures like the λ -type. [Liu et al., 2013]

MnO₂ is found in a variety of crystal structures, including a-(hollandite), b-(pyrolusite), c-(nsutite), d-(birnessite), k-(akhtenskite), and so on, all of which have the same basic MnO₆ structure but are linked in different ways. The structure of MnO₂ NPs can be used to distinguish them. [Parajuli et al., 2020]

Edge-sharing of MnO₆ octahedral forms a double-chained structure in a-MnO₂, where corners are joined to form (1*1) and (2*2) tunnel structures. By doping alkali metal of large size into the tunnel structure, the stability of the (2*2) tunnel size can be maintained. The edge-sharing of the MnO₆ octahedral forms a single-chain (1*1) tunnel structure in the b-MnO₂ NPs. Positive ions cannot be accommodated in the structure of the (1*1) tunnel. The random growth of (1*1) and (1*2) domains produce c-MnO₂. The structure of d-MnO₂ is two-dimensional, with water or other cations like Na or K sandwiched between the two sheets. The three-dimensional structure of d-MnO₂ is well-known, with flower-like architecture and good crystallinity and order. Manganese is present in the octahedral sites in the ccp oxygen framework, resulting in a spinel-shaped 3D nanostructure of k-MnO₂. [Parajuli et al., 2020]

Several nanostructured objects, including nanosheets, nanotubes, nanorods, nanowires, nanoflakes, nanoflowers, nanourchins, and nanospheres, have been studied over the years. The SEM images depict the various morphologies of nanostructured MnO₂ materials. Because of the low crystallinity and small particle size, birnessite structures have been poorly defined in general. MnO₂ NPs come in a variety of crystal structures, each with its own set of properties and preparation methods. They are made

using a variety of methods, some of which are suitable for one crystalline structure but not for others. Different routes can be chosen depending on the requirements and availability. [Parajuli et al., 2020]

2.7 OBJECTIVES AND METHODOLOGY OF PRESENT INVESTIGATION

The major objectives of this project include:

- To synthesis Graphene nanoparticle by Hummer's method.
- To synthesis MnO₂ nanoparticle by Co-precipitation method.
- To synthesis MnO₂/Graphene nanocomposite by Mechanical method.
- To characterize Graphene nanoparticles, MnO₂ nanoparticles and MnO₂/Graphene nanocomposites by powder X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Energy Dispersive X-Ray (EDX) and Field Emission Scanning Electron Microscope (FESEM).

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS AND METHODS

1. GRAPHENE NANOPARTICLES

Hummer's method of synthesis

Graphene oxide was synthesized by Hummer's method through oxidation of graphite. Graphite flakes and NaNO_3 were mixed in 2:1 ratio. 50 mL of concentrated H_2SO_4 in a 500 mL volumetric flask kept under at ice bath ($10\text{--}15^\circ\text{C}$) with continuous stirring. The mixture was stirred continuously for 2 hours. A greyish colour mixture is obtained. The ice bath was then removed, and the mixture was stirred at 35°C for 90 minutes. It was kept for ageing. A brown colour mixture was obtained. The temperature was increased to 98°C for 60 minutes and to it 100 ml of distilled water is added gradually. Effervescence was seen and the mixture was cooled down to room temperature naturally. Then 10-15 ml of H_2O_2 added. Filter the mixture using 5% dilute HCl . Drying the sample at room temperature the graphene oxide (GO) was obtained as a powder [Fig. 3.1]. [Paulchamy, Arthi and Lignesh, 2015]



Figure 3.1: The Macroscopic Image of as Synthesized Graphene Nanoparticles

2. **MnO₂ NANOPARTICLE**

Co-precipitation method

The co-precipitation method was performed by using manganese salts of two different anions which are manganese (II) sulphate and manganese oxalate. Both salts of equal concentration i.e., 0.2M are mixed with continuous stirring at a constant temperature of 60°C. While stirring, NaOH solution was added till the pH of the solutions become 11.4. The stirring was continued for 1 hour at constant temperature of 60°C. Brown precipitates formed was then filtered and washed with ethanol. Precipitates were dried for 3 hours at 100°C. Then the precipitate was kept in muffle furnace at 450°C for 4 hrs [Fig. 3.2]. [Kumar et al., 2013]



Figure 3.2: The Macroscopic Image of as Synthesized MnO₂ Nanoparticle

3. **MnO₂/GRAPHENE NANOCOMPOSITE**

Mechanical method

MnO₂ nanoparticle and Graphene nanoparticle are mixed together by mechanical mixing using pestle and mortar. The mixture is kept in muffle furnace for 4 hours at 500°C . Thus MnO₂/Graphene nanocomposite was obtained [Fig. 3.3].



Figure 3.3: The Macroscopic Image of as Synthesized MnO₂/Graphene Nanocomposite

3.2 CHARACTERIZATION TECHNIQUES

The surface morphology of graphene, α -MnO₂ and the composite of α -MnO₂ and graphene samples were obtained with field emission scanning electron microscope (FESEM-SUPRA55, Carl Zeiss, Germany) coupled with X-ray energy dispersive spectrometer (EDS, Oxford INCA 250 silicon).

Further, the as synthesized graphene, α -MnO₂ and the composite of α -MnO₂ and graphene sample phases were characterized by using the X-ray powder diffraction (XRD) technique using a RigakuD/max-C diffractometer with Cu K α radiation source (λ = 1.5406 Å) and Fourier transform infrared spectroscopy (FTIR) was measured using a Bruker TENSOR27 FTIR.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 X-RAY DIFFRACTION (XRD) ANALYSIS

1. *GRAPHENE NANOPARTICLE*

The most widely used technique for general crystalline material characterization is X-ray diffraction (XRD). It is used to determine the orientation of a single crystal or grain by measuring the average spacing between layers or rows of atoms. Hummer's method yielded the XRD pattern for as synthesized Graphene nanoparticles is shown in Fig. 4.1 [Paulchamy, Arthi and Lignesh, 2015].

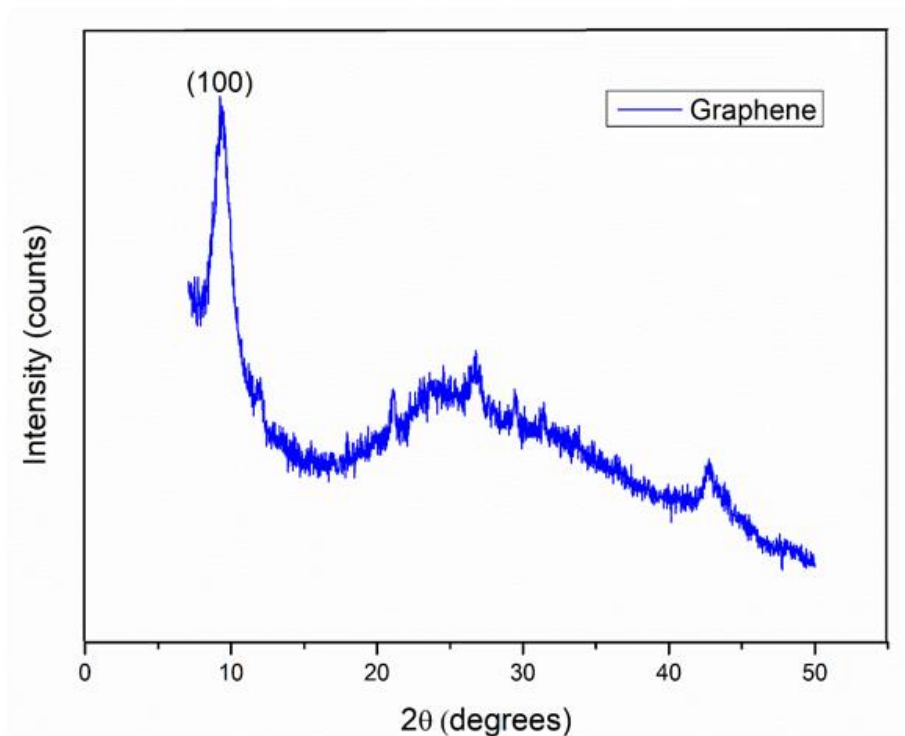


Figure 4.1: XRD pattern of Graphene nanoparticle

2. MnO_2 NANOPARTICLE AND MnO_2 /GRAPHENE NANOCOMPOSITE

XRD patterns of MnO_2 and MnO_2 /Graphene are shown in Figure 4.1.2. All peaks of MnO_2 /Graphene and MnO_2 are distinguishable in the pattern. The diffraction angles we obtained are at 18.4° , 29.3° , 36.4° , 44.6° , 51.2° , 59.0° , 60.3° and 64.9° . It is referred to diffraction angles at $2\theta = 12.7^\circ$, 18.1° , 28.8° , 37.5° , 42.1° , 49.9° , 56.2° , and 60.3° matched well with the diffraction peaks of (110), (200), (310), (211), (301), (411), (600), and (521) crystal planes of $\alpha\text{-MnO}_2$ standard data (JCPDS card PDF file no. 44-0141). Although the XRD peak positions and shapes of MnO_2 /Graphene are similar to those of MnO_2 , there are no obvious diffraction peaks of Graphene [Fig. 4.2]. [Feng et al., 2014]

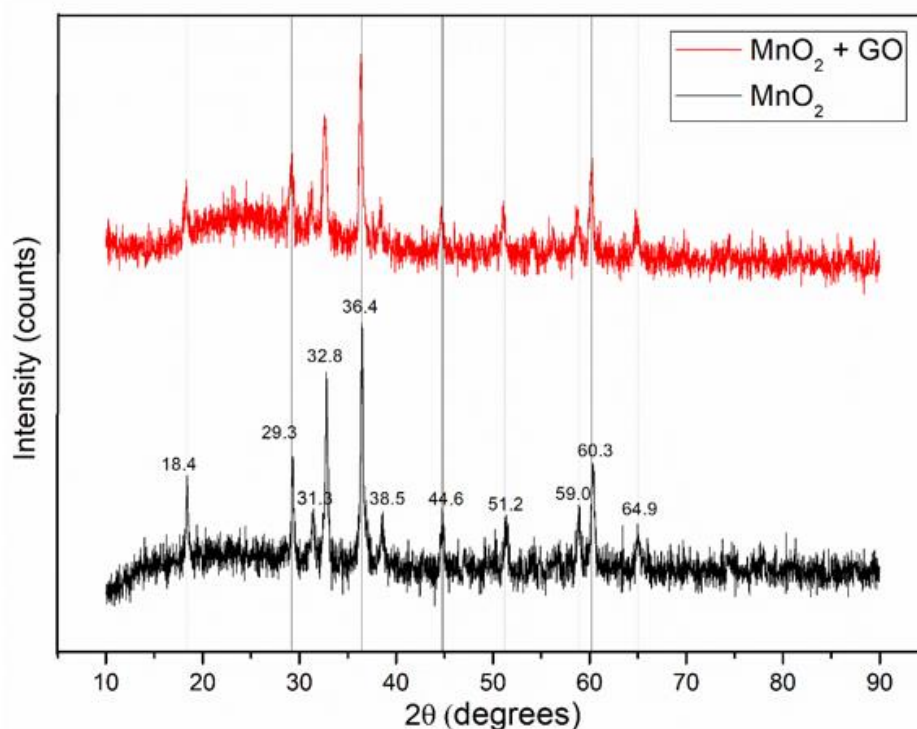


Figure 4.2: XRD patterns of MnO_2 nanoparticle and MnO_2 /Graphene nanocomposite

Table 4.1: X-Ray Diffraction analysis 2θ values obtained from graph and the reference values

OBTAINED DATA	REFERENCE [Feng et al., 2014]	
2θ	2θ	LATTICE PLANE
18.4°	18.1°	(200)
29.3°	28.8°	(310)
36.4°	37.5°	(211)
44.6°	42.1°	(301)
51.2°	49.9°	(411)
59.0°	56.2°	(600)
60.3°	60.3°	(521)

4.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) ANALYSIS

1. GRAPHENE NANOPARTICLE

It's a method for obtaining an infrared spectrum of a solid, liquid, or gas's absorption, emission, and photoconductivity. It can also be used to perform quantitative analysis on an unknown mixture. The bonding interactions in graphene before and after the oxidation process were investigated using FTIR measurements. It is assumed that the peak intensities are proportional to the amount of sample present.

Figure 4.3 shows that the C=O bond in synthesised graphene has a peak at 1514 cm^{-1} , confirming the presence of oxide functional groups after the oxidation process. The O-H stretch of H_2O molecules contributes to a broad peak at 2972 cm^{-1} to 3714 cm^{-1} , indicating absorbed water in graphene (bending absorption vibration peak). This confirms that graphene is a highly absorbent material, as evidenced by its ability to form a gel-like solution. [Paulchamy, Arthi and Lignesh, 2015]

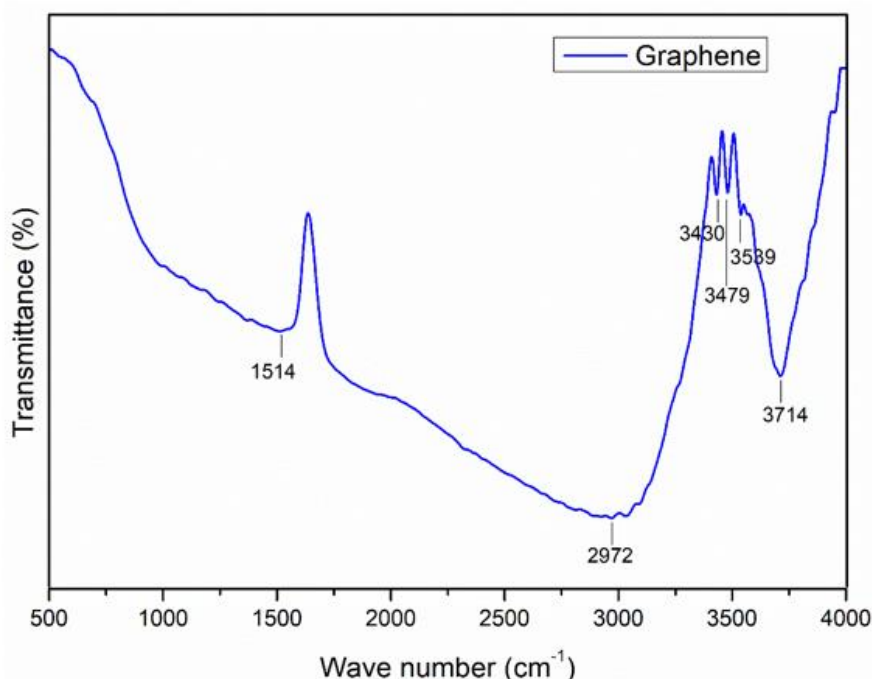


Figure 4.3: FTIR spectrum of Graphene nanoparticle

2. *MnO₂ NANOPARTICLE AND MnO₂/GRAPHENE NANOCOMPOSITE*

Figure 4.4 shows the FTIR spectra of Graphene and MnO₂/Graphene in the range of 4000-400 cm⁻¹. We can see that all of the peaks in the MnO₂ graph are present in the MnO₂/Graphene graph with minor changes. The typical peak characteristic of MnO₂/Graphene can be clearly seen at 629 cm⁻¹, which is commonly attributed to the Mn–O vibrations of the (MnO₆) octahedral. Mn–O vibrations are usually assigned to bands in the (400–800) cm⁻¹ range. The stretching collision of O–Mn–O, which indicates the presence of MnO_c, produces two absorption bands between 550 cm⁻¹ and 750 cm⁻¹. The birnessite structure and MnO₂ deposition on the graphite substrate are responsible for these peaks. The bands at 2700 cm⁻¹ and 2900 cm⁻¹ in the two graphs (Figure 4.2.1 and Figure 4.2.2) are attributed to C–H interaction in the graphene. Figures 4.2.1 and 4.2.2 MnO₂/Graphene show a strong peak at 1575 cm⁻¹, which corresponds to the C=C band and skeletal vibration of graphitic structure. A low peak at 3433 cm⁻¹ is due to O–H

absorption, which is caused by water molecules intercalating between MnO_2 molecules. [Doumbi et al., 2021]

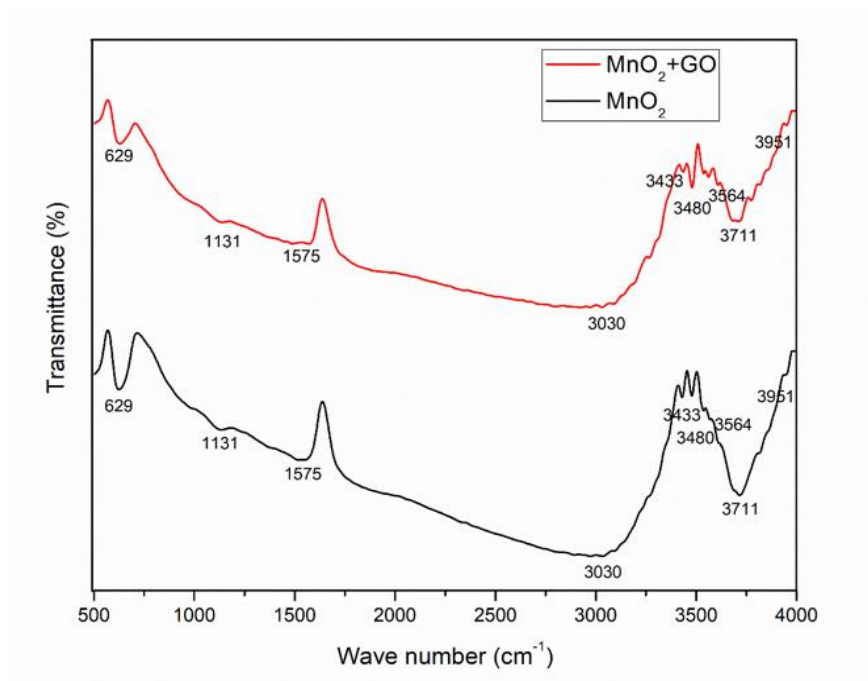


Figure 4.4: FTIR spectrum of MnO_2 nanoparticle and MnO_2 /Graphene nanocomposite

4.3 FIELD EMISSION SCANNING ELECTRON MICROSCOPE (FESEM) ANALYSIS

1. GRAPHENE NANOPARTICLE

A field emission scanning electron microscope was used to examine the surface morphology (FESEM). Figure 4.5 shows FESEM images of Graphene with well-defined and interconnected three-dimensional Graphene sheets, forming a porous network that resembles a loose sponge-like structure. [Paulchamy, Arthi and Lignesh, 2015]

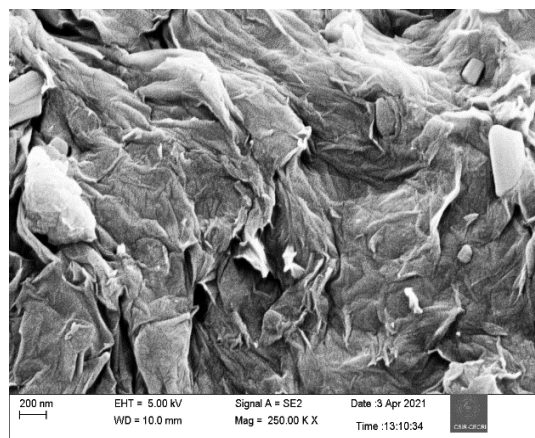
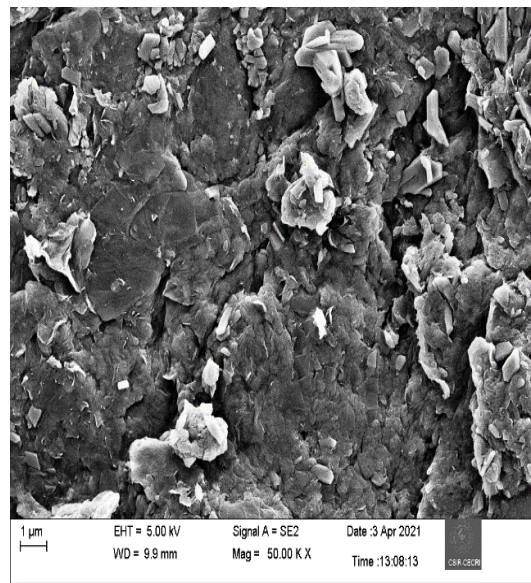
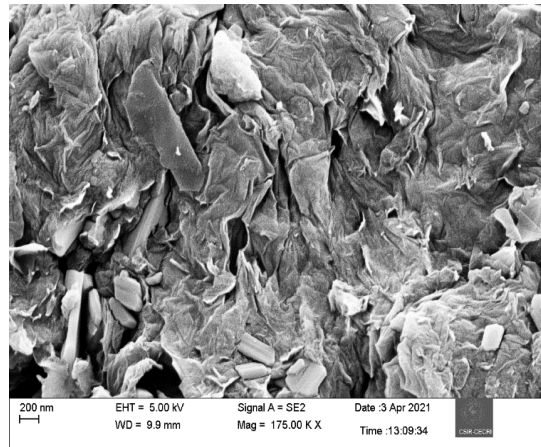


Figure 4.5: FESEM images of Graphene nanoparticle in different magnifications

2. *MnO₂ NANOPARTICLE*

The morphology of the as prepared MnO₂ nanoparticles are nanospheres [Fig. 4.6]. [Gnana Sundara Raj et al., 2014]

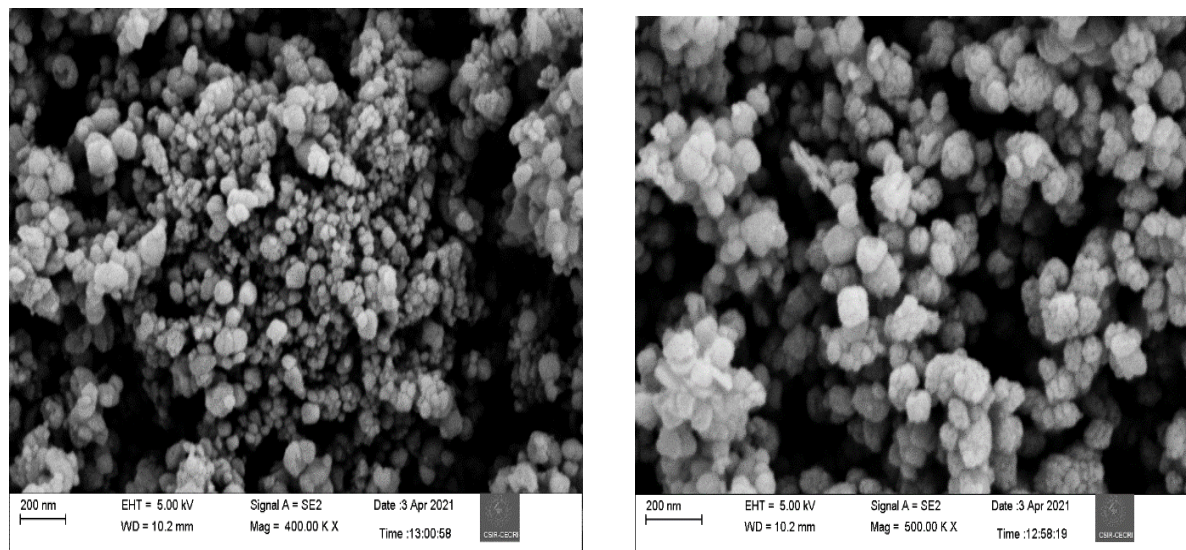


Figure 4.6: FESEM images of MnO₂ nanoparticle in different magnifications

3. *MnO₂/GRAPHENE NANOCOMPOSITE*

The morphology images of Graphene nanoparticles, MnO₂ nanoparticles, and MnO₂/Graphene nanocomposites are shown in Figures 4.3.1, 4.3.2 and 4.3.3 respectively. The α -MnO₂ was prepared by co-precipitation method. From Figure 4.3.3, the different magnifications of the MnO₂/Graphene nanocomposites are given. Graphene has a large flat surface which could avail for anchoring the MnO₂. [Wang et al.,2018]

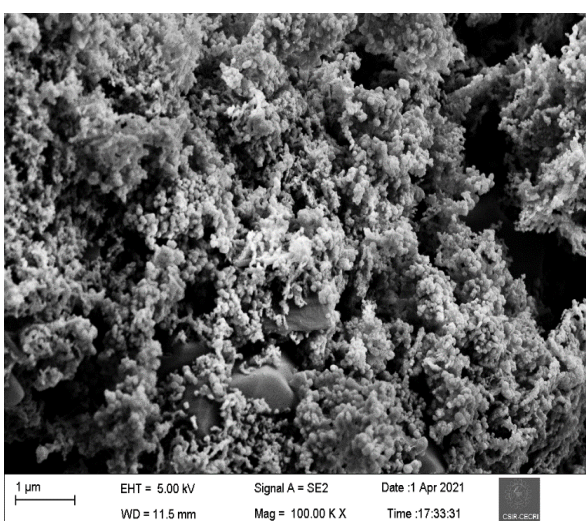
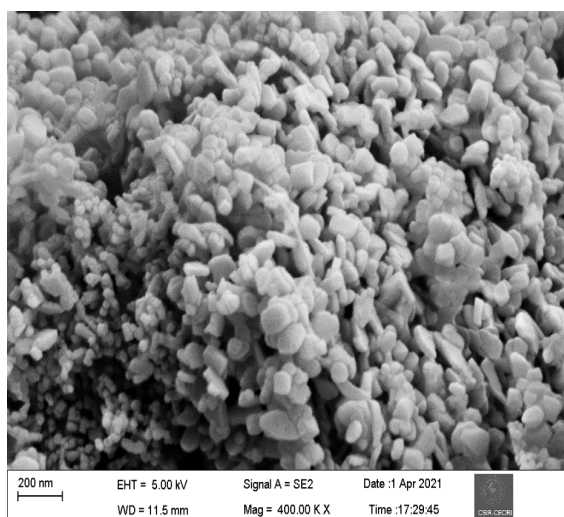
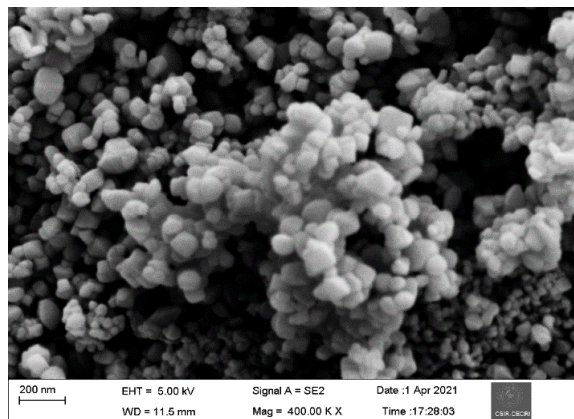
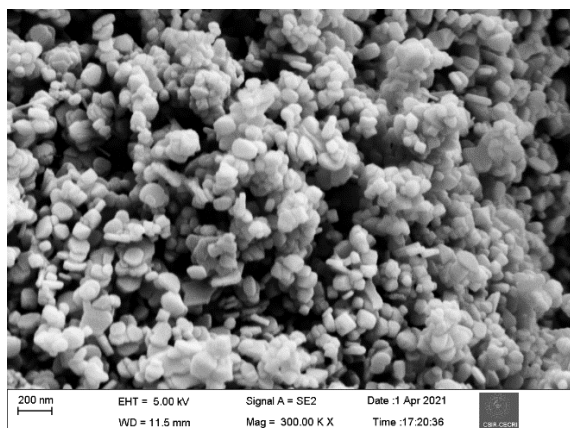
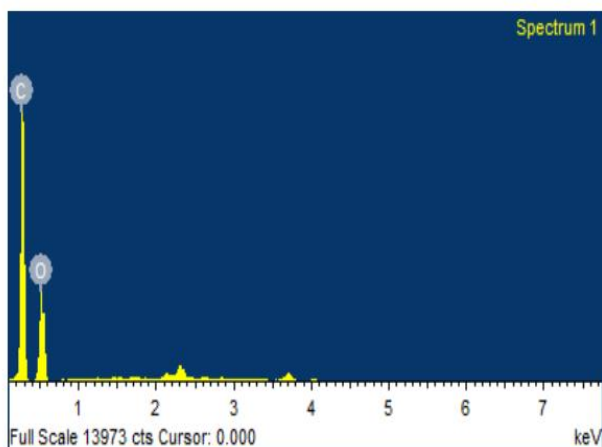
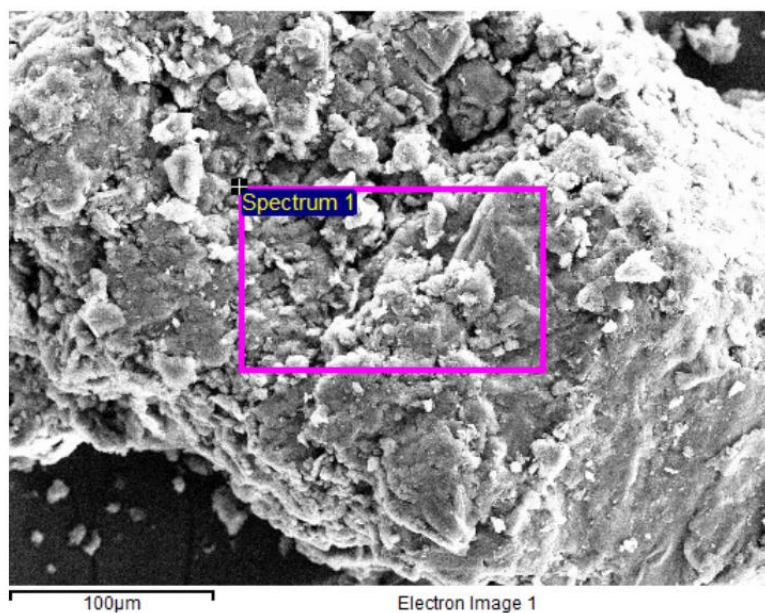


Figure 4.7: FESEM images of MnO₂/Graphene nanocomposite in different magnifications

4.4 ENERGY DISPERSIVE X-RAY (EDX) ANALYSIS

1. GRAPHENE NANOPARTICLE

EDX analysis of the sample depicted in Figure 4.8 exhibits that the final product comprises of only C and O, suggesting that the product is Graphene nanoparticle. [Wang et al., 2018] and [Tayel et al., 2018]

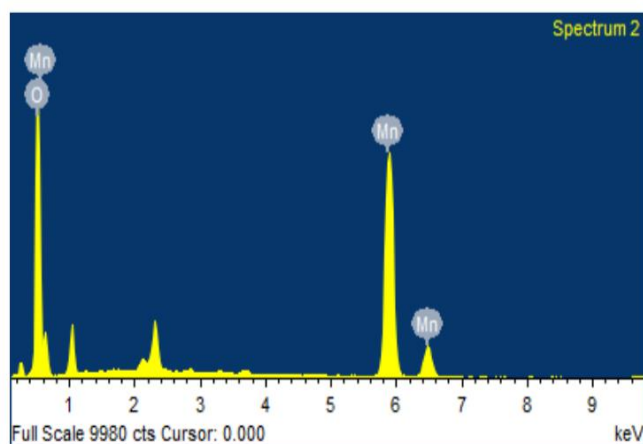
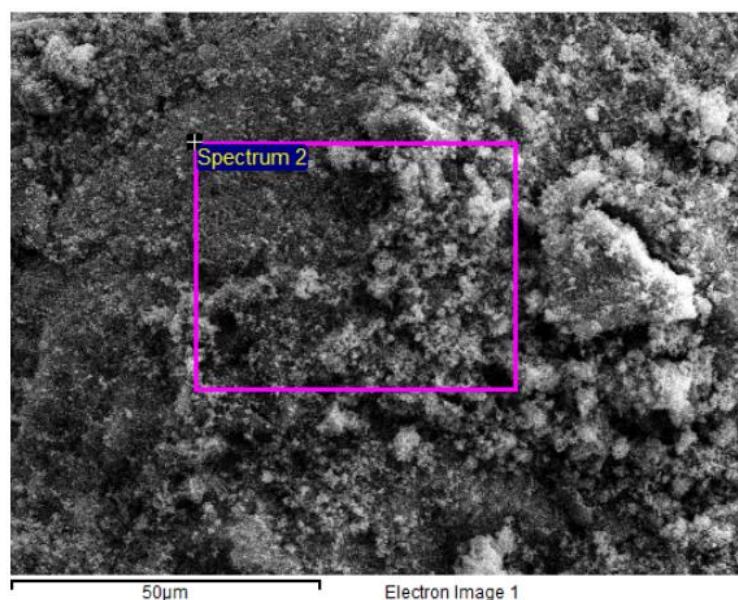


ELEMENT	WEIGHT%	ATOMIC%
C	59.41	66.09
O	40.59	33.91
TOTALS	100.00	100.00

Figure 4.8: EDX Analysis of Graphene nanoparticle

2. ***MnO₂ NANOPARTICLE***

EDX analysis of the sample depicted in Figure 4.9 exhibits that the final product comprises of only Mn and O, suggesting that the nanospheres are made of pure α -MnO₂. [Gnana Sundara Raj et al., 2014]



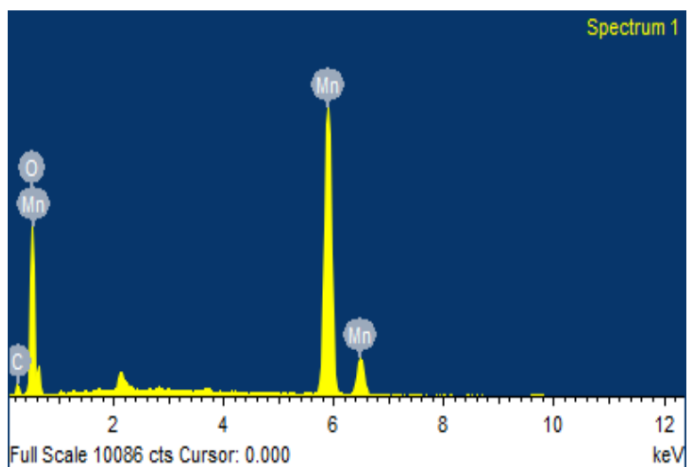
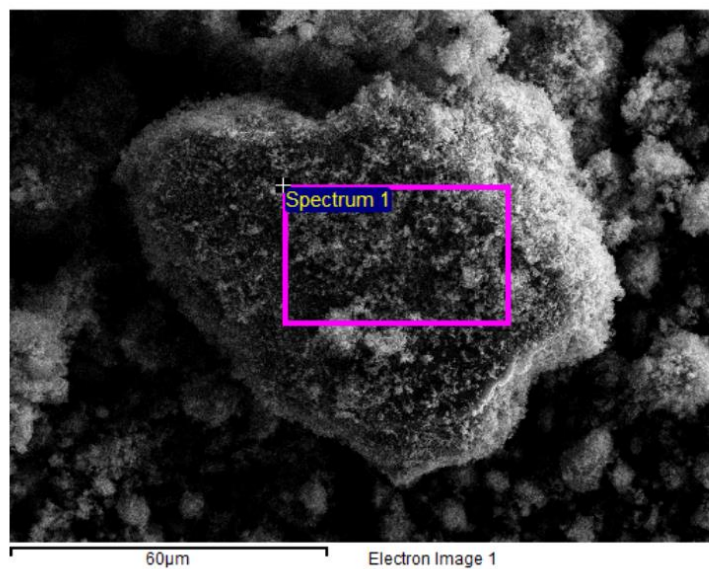
ELEMENT	WEIGHT%	ATOMIC%
Mn	64.44	34.55
O	35.56	65.45
TOTAL	100.00	100.00



Figure 4.9: EDX Analysis of MnO₂ nanoparticle

3. MnO₂/GRAPHENE NANOCOMPOSITE

EDX analysis of the sample depicted in Figure 4.4.3.2 exhibits that the final product comprises of C, O and Mn suggesting that there is carbon (C) peak in the EDX spectra which comes from Graphene. [Wang et al.,2018]



ELEMENT	WEIGHT%	ATOMIC%
C	5.00	13.25
O	22.55	44.82
Mn	72.45	41.93
TOTAL	100.00	100.00



Figure 4.10: EDX Analysis of MnO₂/Graphene nanocomposite

CHAPTER 5

CONCLUSIONS

Based on the experimental results and discussions, we conclude that:

- Rechargeable batteries are becoming increasingly important in today's world, and are becoming required for the majority of electronic devices that people use for communication, transportation, and monitoring. Aluminium-ion batteries need to improve their characteristics in order to be used in future applications that require high energy and power density as well as long-term stability. The characteristics of various types of cathode materials for Aluminum-ion batteries, as well as the electrolyte, synthesis methods, and characterization techniques, were summarised in this report.
- Thus, in this report we have demonstrated that Graphene nanoparticles were prepared using Hummer's method, MnO_2 nanoparticles were prepared using Co-precipitation, and MnO_2 /Graphene nanocomposites were prepared using Mechanical mixing.
- In comparison to crystal planes of $\alpha\text{-MnO}_2$ standard data, the X-Ray Diffraction (XRD) spectra confirms that the synthesised MnO_2 nanoparticles are a $\alpha\text{-MnO}_2$ (JCPDS card PDF file no. 44-0141).
- By comparing the obtained peaks with the valid research papers, Fourier Transform Infrared Spectroscopy (FTIR) peaks confirm the presence of Graphene nanoparticles, MnO_2 nanoparticles, and MnO_2 /Graphene nanocomposites.

- Images taken with a Field Emission Scanning Electron Microscope (FESEM) at various magnifications show that synthesised MnO_2 nanoparticles have the morphology of nanospheres.
- An Energy Dispersive X-Ray (EDX) analysis report that confirms with available researched data confirms the presence of elements required in synthesised Graphene nanoparticles, MnO_2 nanoparticles, and MnO_2 /Graphene nanocomposites.
- According to the above study results, the environmentally friendly electrode material for energy storage systems synthesised and characterized in this report has a good chance of competing with lithium-ion batteries and super capacitors.

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