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Structural effects on Pseudocapacitive response in Manganese oxide (MnO2) super capacitive system

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Structural Effects on Pseudo Capacitance in Manganese Oxide (MnO$_2$) Super Capacitive System

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Abstract

Electrochemical Super capacitors are high energy storage devices and the charge storage occurrence is due to double layer and pseudocapacitance phenomenon. These electrostatic and electrochemical phenomena aid for the production and storage of energy in eco-friendly way. The current study tries to explain the structural dependence on the capacitive behavior of Manganese oxide (MnO$_2$) electrodes. Manganese Oxide powders were produced in three different ways namely co-precipitation technique, modified Sol-gel technique and by reduction of potassium permanganate. Structural and microstructural features of the powders produced were compared and are correlated to the capacitive behavior of the material. In the co-precipitation technique we stabilized $\alpha$-MnO$_2$ phase which was believed to have double chain of edge sharing MnO$_6$ octahedron structure connected at the corners to give (2x2) and (1x1) tunnels. The powders obtained were heat treated at different temperatures to make them conductive enough for super capacitive application. Composite films of these powders with PEO/Graphite were made using a novel technique called Partial Solution Mixing. Electrochemical tests were then performed on these powders using the Three Electrode Gamry setup. Structural and microstructural analysis was performed on the powders using XRD, SEM and EDS techniques and was correlated to the super capacitive behavior. This study explains the structural dependence on the capacitive behavior of the MnO$_2$ powders produced and also gives an optimum way of producing $\alpha$- MnO$_2$ powders which were proved to be the best suited phase for super capacitive behavior.
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LIST OF ABBREVIATIONS

1. PEO – Poly Ethylene Oxide

2. PANI – Polyaniline

3. EIS – Electrochemical impedance spectroscopy
4. CV – Cyclic voltammetry
5. CP - Chronopotentiometry
6. H₂SO₄ – Sulfuric acid
7. Na₂SO₄ – Sodium Sulphate
8. KOH – Potassium hydroxide
9. SEM – Scanning electron microscope
10. XRD – X-ray diffraction
CHAPTER 1

1. INTRODUCTION:

1.1. Energy Crisis:

Energy crisis is one among the very serious issues faced by many countries around the world. There are multiple reasons for this but decline in the level of fossil fuels is one of the key causes. A direct effect on economy can also be seen due to the energy crisis. The central origin of energy crisis comes from depletion of oil deposits. Currently there is extreme need to work on exploring other fuels that can be harnessed efficiently and easily which can sustain on a longer run. Coal and natural gases are some of the good options available right now but near to the ground amounts of these reserves would make them perish in coming couple of decades. These resources are not just less abundant but also harmful to the environment. Usage of these carbon based fuels gives out emissions which has a high content of CO, CO$_2$ and other carbon remains [1]. These environmental factors laid a path for understanding the importance of greener energy. The idea of green synthesis of energy has gained popularity and became more important as the time progressed.

1.1.1 Alternative Sources of Energy:

As the primary sources of energy are depleting in a rapid pace there is inevitability of finding other sources of energy. Solar energy, tidal energy, wind and geothermal energies are other renewable forms of energy which can be worked on as an alternative. These are not as efficient as the primary fuels and the cost behind the setup for the usage of these natural energies makes things even inferior. Nuclear energy generated by usage of Uranium, Thorium, Plutonium can be categorized under non-renewable forms of energy. This nonrenewable form of energy has heaps of cost behind its production and more importantly the waste which comes out of the fusion and
fission reactions is very dangerous for the environment. The fusion and the fission reaction can only be conducted under controlled atmosphere which require very expensive nuclear reactors which takes nuclear energy out of resourceful alternative energy collection. Bio- Fuels is the other option available as an alternative energy resource, in this case microorganisms like algae and bacteria is used for the production of energy [2] [3]. Electro chemical energy is the other form of energy which can be generated and stored by means of Fuel cells, Batteries and Capacitors. They have a balanced combination of advantages and disadvantages which when used in a right way would give fruitful results. These energy production and storage devices work in tandem with other bigger devices and have the ability to drive the whole system.

Supercapacitors are high density power storage devices which can be effectively used when connected in series with a battery. Supercapacitors actually have a multiple advantages over a battery. Their high cyclic stability, very high reversibility and cycle life makes it superior device than a battery. These super capacitors charge much faster than a battery which makes it more efficient device than a battery. Charge discharge cycles are mostly surface phenomenon in supercapacitors which makes them act faster than other devices and these surface characteristics is the main cause of high power density of a super capacitor. As super capacitors have less energy density these devices as stated earlier are connected in series with batteries which has an higher specific energy than that of super capacitors. Alongside batteries super capacitors are used in Regenerative Braking Systems. These can also be used in systems using pulse power and bridge power applications such as military systems, automotive systems and memory devices. Work on developing electrochemical capacitor as a vital part of hybrid electric vehicles is vigorously done in the recent years [36], [37].
1.2. Electro Chemical Super Capacitors:

1.2.1 Background:

These are energy storage devices which can be used as a replacement of batteries. Electrochemical super capacitors are also called as electro chemical double layer capacitors (EDLC’s), ultra-capacitors and hybrid capacitors (specific cases). There are two ways through which charge can be stored in a supercapacitor. One of which being electrostatic charge separation (double layer capacitance) and the other is redox reactions (Pseudo capacitance). In a hybrid capacitor both of these phenomena transpire. These supercapacitors are either used separately or they can be used in a series connection with batteries, the systems which have both a battery and a super capacitor is termed as a hybrid system [4].

Electrochemical supercapacitors are also called as electrochemical double layer capacitors (EDLCs), ultracapacitors and also hybrid capacitors in certain cases; they are basically high energy storage devices that can be used as a replacement for batteries. The mechanism of charge storage is by electrostatic charge separation or by reversible redox reactions (as in battery) (pseudocapcitance) or a combination of both. The supercapacitors are either used separately or in a combination with batteries to produce a hybrid system. The EDLCs charging is similar to that happening in a common capacitor. But the amount of charge storage ability is higher compared to the electrolytic capacitors. This property is due to the high surface area of the electrode materials where the charges move towards the surface of the electrode and stay at the interface of the electrode and electrolyte. The charge storage mechanism is so fast that charging and discharging is rapid. Supercapacitors tend to have high power density and nominal energy density, which contrasts with the batteries and fuel cells [4].
Figure 1 Rogone plot, plotted between power density and energy density of different charge storage devices.

Figure 1, is a Ragone plot of specific energy and power of some charge storage devices. The electrochemical supercapacitors seem to bridge a gap between batteries and conventional capacitors. Supercapacitors cover a wide range of specific power and density values which depend on the materials selection for the electrode and electrolyte. Carbon based materials were used as supercapacitor electrodes for a long time due to its conductivity, ability to develop high surface area. Apart from carbon based materials a lot of others materials like conductive polymers, pure and doped metal oxide, aerogels and nano powders of metals are being used as supercapacitor electrodes.
1.3. Electrochemical Phenomenon:

1.3.1. Electrochemical Double Layer:

Formation of double layer at the electrode surface is mainly due to electrostatic and electrochemical interactions. Double layer interactions is one of the principles behind working of a supercapacitor (non-faradaic interactions) and the other being pseudocapacitance (faradaic interactions). Working on the single electrode interface enables us to understand the capacitive properties but addition of second electrodes explains the electrical circuit performance of the arrangement. The Electrode-Electrolyte interphase is the basis for the study of electrochemical double layer behavior. A drop in potential across the electrode electrolyte interphase is observed during the charged state. An IR or ohmic drop is observed inside and the solution during discharge state and vice versa on charge. Some of the key factors that affect the efficiency of double layer formed are surface porosity, electrode material and its surface area (particle size in the electrode). Figure 2(a) and 2(b) explain the charge separation in electrode-electrolyte interface and change in potential across the design of the discharge.

Fig 2(a): Double layer behavior with two electrodes and two double layers,
Different mechanisms of charge storage via double layer formation were suggested by different physicists. The three important models which explain the working of double layer are:

1. Helmholtz double layer model
2. Gouy – Chapman model
3. Stern model

According to Von Helmholtz the double layer of charges formed was a quasi-two dimensional model that consisted of two arrays of opposite charges, separated by atomic size distance. It was first studied on colloidal particle interface and had concludes that charges ascend from ionization, electrolytes or adsorption in case of non-aqueous colloids. The Helmholtz model does not hold good for complex conditions, because the ions present in the solution are non-static but are subjected to thermal fluctuations which will depend on the electrostatic forces present between the charged metal and ions. Figures 2 (a), (b), (c) explains the models proposed by Helmholtz, Gouy and Stern respectively.

Fig 2 (a): Helmholtz model, 3 (b) Gouy Model, 3(c) Stern Model [6]
Further advancements to the theory were done by Gouy and Chapman’s work which works with the details of counter ions. They have observed that counter ions get conjugated on the metal surfaces electron charge which when looked in a three dimensional view resembles a densely packed cation and anion stream. Two of the major issues with this model are incorrect local field around the electrode and the prediction of high capacitance being defined as the rate of change of net ionic charge on side of metal exposed to the electrolyte.

The limitations of the Gouy and Chapaman theory were overcome by Stern. In this theory the ionic ion distribution on the surface of the electrode exposed to the electrolyte was considered due to the adsorption of ions which follow Langmuir’s adsorption isotherm. The region formed between the inner layer and the electrolyte was called as the diffused layer of the distributed ionic charges [6], [7], [8] and [9]. Figure 3 gives the pictorial description of double layer formed by segregation of anions and cations on the surface.

![Diagram of double layer structure](image)

**Fig 3:** Pictorial representation of double layer structure formed by the adsorption of anions and cations on the metal surface [6]
According to the Stern theory, if the ions were of a specific or a finite size then the thickness of the inner layer can be deduced which was made to work according to the Helmholtz double layer with a capacitance of $C_H$. The region around the double layer is the diffuse region which has a capacitance of $C_{\text{diff}}$. The total capacitance is given by $C_{\text{dl}}$ which is the summation of $C_H$ and $C_{\text{diff}}$ in series. In this case $C_{\text{dl}}$ will be deduced from two smaller forms or components giving a higher value due to its reciprocal form. Therefore the potential of the electrode and the ionic concentration of the solution act as an important factor in deducing the double layer capacitance.

Initially it was assumed that in an equivalent circuit for a double layer capacitor the solution resistance $R_s$ is in series with double layer capacitance $C_{\text{dl}}$. Later it was found that another term $R_f$, which is the charge transfer resistance or faradic resistance is in parallel with $C_{\text{dl}}$. The arrangement is shown in figure 4.

![Fig 4. Equivalent circuit of a double layer capacitances (a) ideal polarizable capacitor (b) Interface with a series resistance (c) capacitor in series with a resistance $R_s$ and potential dependant faradaic resistance $R_f$ [10]](image)

### 1.3.2 Pseudocapacitance:

Pseudocapacitance is the other charge storage mechanism in supercapacitors alongside the double layer capacitance. Faradic charge transfer aids for pseudocapacitance $C_\Omega$. It was first
understood by Grahame in 1947 but he referred it as a reversible discharge of ions. Pseudocapacitance is basically due to movement of ions across the double layer aiding for the charge and discharge as seen in operation of a battery. Electron migration takes place between oxidized and reduced species. The basic cause of pseudocapacitance is given by:

- Redox reactions which are a function of electrode potential.
- Chemisorption of ions on the surface of the electrodes which leads to partial charge transfer from the migrants to the electrodes which is dependent on the potential of the electrode.

Due to the above interactions electrochemical reactions occur between the electrode and electrolyte. Usually these reactions are called REDOX reactions i.e., a combination of oxidation and reduction reactions. Oxidation reactions occur at the anode and the reduction reactions occurs at the cathode. The chief gears in electrochemical reactions are anode, cathode and the return path. Oxidation is referred as a process, in which electrons are removed, this transpires at the anode. Reduction is a process in which electrons are added and this befalls at the cathode.

- Oxidation reaction at the anode is given by:

  \[ M \rightarrow M^{n+} + ne^- \]

  This results in the generation of anodic current at specific potential where the reaction occurs.

- To maintain an equilibrium or neutrality the electrons released at the anode will be taken by the ions present in the solution and aids for their reduction. The reduction reaction is dependent on the medium (Acidic, Basic and Neutral medium) and these reactions are given by:
\[ 2H^+ + 2e^- \rightarrow H_2 \quad \text{Reduction of hydrogen} \]

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{Dissolved oxygen reduction in acidic medium} \]

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{Dissolved oxygen reduction in basic medium} \]

\[ Mn^+ + ne^- \rightarrow M \quad \text{Metal Reduction} \]

All these reactions occur at the cathode and the current generated due to these reactions is termed as cathodic current.

The charges produced due to these reactions account to the pseudocapacitance of the system. The reactions can be noticed with an increase in anodic or cathodic current in the cyclic voltammetry plot. This is because these reactions occur only at certain potentials which are independent to the electrode material used. These potentials are termed as oxidation and reduction potentials of the material.

So these reactions and the charges produced account to the pseudocapacitance of the system. The reactions are identified with the increase in the anodic and cathodic currents at particular potential values. Each oxidation and reduction reaction has its own characteristic potential.

One of the very good systems which can be used to explain the pseudocapacitive behavior is Ni – NiO system. It has Ni core and NiO shell and the charge storage or capacitance behavior arises due to the redox reactions on the surface and in the bulk. The nature and charge storage features of the Ni- NiO system can be understood using the CV plots. KOH is used as the electrolyte for CV analysis of Ni- NiO system. Figure 5 is the CV plot for Ni-NiO system, which shows the reduction and oxidation peaks.
The reaction corresponding to the redox peaks is given by:

\[
\text{NiO} + \text{OH}^- \quad \text{NiOOH} + e^-
\]

In the CV plot shown above the forward scan describes the oxidation cycle and the reverse scan describes the reduction cycle. And the resulting current generated in each cycle is termed as anodic and cathodic currents. The reaction given above is a combination of both anodic and cathodic reactions. This reaction can also be written separately as a combination of anodic (oxidation) and cathodic (reduction) reaction.

Oxidation: \( \text{Ni}^{2+} \rightarrow \text{Ni}^{3+} + e^- \) and the hydroxide ion from the solution form Nickel oxy hydroxide. This reaction occurs at a potential 0.45 V.

If the cycle is reversed:
Reduction: \( \text{Ni}^{3+} + e^{-} \rightarrow \text{Ni}^{2+} \) and the hydroxide ions go into the solution, the reaction occurs at a potential of 0.25V.

These are the typical reactions by which the charge storage takes place on the surface of the electrode.

In a complete double layer system at least 1 – 5% of charge storage is aided due to the pseudo capacitance and similarly in a pseudocapacitive system 1 – 5% of charge is stored due to double layer mechanism. The amount of double layer capacitance is proportional to the surface accessible to the ions to migrate. It can be concluded that there is always a presence of double layer capacitance in a pseudocapacitive system which aids for an enhanced charge storage potential for the system. Therefore it is vital to show the presence of this double layer capacitance in an equivalent circuit of pseudocapacitive system. This makes the circuit different from that of equivalent circuit generated for double layer capacitor. In an equivalent circuit the charge storage through pseudocapcitance is given by \( C_{\Omega} \), the faradaic resistance is given by \( R_{f} \) and another resistance which accounts to the discharge is given by \( R_{d} \). In the equivalent circuit for a pseudocapacitive device \( C_{\Omega}, R_{d}, \text{and } R_{f} \text{ are connected in series and the whole combination is in parallel with } C_{dl} \text{ which is the double layer capacity } [6], [11]. Figure 6 is the equivalent circuit for a pseudocapacitive capacitor.

![Equivalent circuit for a pseudocapacitive capacitor](image)

Fig 6 Equivalent circuit for a pseudocapacitive capacitor [11]
1.3.3 Hybrid Capacitors:

As the name suggests hybrid capacitors have the best of both the worlds. These capacitors use both double layer and pseudocapacitive behavior for storing charge. Recently a lot of study is been done because of the high charge storage capability of these hybrid capacitors. Metal oxides alongside carbon materials are a very good example for a super capacitive electrode. Carbon addition does not only aid for the double layer capacitance but it also provides a conductive path which leads to effective redox reactions to occur increasing the overall capacitance of the electrode.

Figure 7 is a good example of hybrid capacitors. Material ‘a’ which is graphite shows a complete double layer response and material b which is manganese oxide is a very good example of metal oxide showing pseudocapacitive behavior. When these two powders are mixed the response shown is much higher that the response of the individual ones. This is due to the summation of both double layer and pseudo capacitance towards the capacitance of the system.

![Figure 7](image.png)

Fig 7 Behavior of a hybrid capacitor, effect of double layer and pseudocapacitance together [47]
1.3.4. Cell Design:

The electrochemical system can be three electrode setup or a two electrode setup. In a two electrode system there are two working electrodes alongside a ion permeable membrane immersed in a bath of electrolyte. Each electrode electrolyte interface acts as a capacitor by itself. So the entire cell can be given as a set of capacitors in series [4] and the formation is given by the equation:

$$\frac{1}{C_{cell}} = \frac{1}{C_1} + \frac{1}{C_2}$$  \hspace{1cm} (1)

Where,

$C_{cell} – \text{Cell Capacitance, } C_1 – \text{Capacitance of electrode 1, } C_2 – \text{Capacitance of electrode 2.}$

The setup of a two electrode system is shown in the figure 2. It has a current collector over which the electrode material is mounted and there is a separator in between the electrodes. Entire setup is immersed in electrolyte [12]. In a three electrode setup, there are working electrode, counter electrode and a reference electrode. The capacitance value obtained from this setup is equivalent to capacitance obtained from a single electrode in a two electrode system (i.e., half the value of two electrode setup). Figure 8 show the two electrode system where the two capacitors are connected in series with the presence of interfacial resistance [4].
Fig 8: Two electrode system where the two capacitors are connected in series with the presence of interfacial resistance [4]

Highly conductive metals like silver, nickel, copper etc. are used as current collectors. The electrode materials is coated on the current collector by pressing a pellet with current collector or by coating the active material on the current collector using different coating techniques. The usage of current collector and production of active electrode is very essential part of electrochemical cell design. The resistance should be minimum which can be obtained by using highly conductive powders and lowering the resistance at the collector and powder interface enhances the efficiency of the electrode.

1.4. MATERIAL REQUIREMENT & PROPERTIES:

1.4.1. Materials used for electrodes:

Material used for the preparation of electrode plays a key role in the performance of supercapacitor. There are certain prerequisites which need to be certified in the material before using it an a supercapacitive material. Some of the main important features being high electrical
conductivity and high surface area. The other properties that need to be added on to the basic requirements are pore structure and size, wear resistance, cyclic stability, corrosion resistance, process ability and cost factor. These properties can be found in certain grades of materials like:

- Carbon and carbon based materials [4], [13], [14],
- Conducting polymers like polyaniline, polypyrrole, polythiophene [16], [15]
- Metal oxide/ceramic materials (RuO$_2$, NiO, Co$_2$O$_3$, VN etc) [17], [18], [19]
- Composite systems of the above three [20 – 35].

Carbon based materials like graphite, graphene and carbon nanotubes are highly preferred electrode materials due to their high conductivity and surface area. These conductive powders form a conductive path inside the electrode making it more conductive. Yan Wang et al. have developed graphene based electrodes which had a specific capacitance of 205 F/g in KOH electrolyte medium with energy and power density as 10kW/kg and 28.5 Wh/kg respectively [12]. The ceramic – carbon composite system and polymer – carbon conductive system have been extensively studied in the recent years. Polyaniline and mesoporous carbon composite has showed a specific capacitance of 470 F/g with an energy density of 76.4 Wh/kg [24].

1.4.2 Electrolyte:

Electrolyte is the main source of charge carriers in the super capacitor setup. There are organic, aqueous and solid state electrolytes available. Most of the commercial super capacitors use organic electrolytes (ease of packing). Aqueous electrolytes are generally ionic electrolytes; dissociation of electrolytic salts takes place on the application of potential. Ionic electrolytes can be acidic and basic in nature and used according to the properties or kind of electrode system dissociate at about 1.1V and are not reversible over this voltage limit. Organic electrolytes such
as tetraethyl ammonium tetrafluoro borate can are stable up to 3V. This wide potential window for organic electrolytes is one of the other reasons which make it suitable for commercial applications. Electrolytes are usually selected according to the compatibility with the electrodes used. Ni and NiO work extremely well in KOH electrolyte system, whereas MnO electrodes show good performance in sodium sulphate electrolyte [12], [27], [31], [32].

Voltammetric current density in cyclic voltagrams and longer charge discharge time in charge-discharge curves is dependent on the type of electrolyte used. The storage capacity is higher for the system containing bivalent ions in an electrolyte. Higher specific capacitance for bivalent system is attributed to the fact that each bivalent cation can reduce two Mn$^{4+}$ to Mn$^{3+}$. This doubles the number of electrons. Whereas, univalent cation reduces just one Mn$^{4+}$ to Mn$^{3+}$. In the current study Na$_2$SO$_4$ is used as an electrolyte which dissociates into Na$^{2+}$ ions and helps for higher capacitance.

1.5. Importance of Manganese Oxide:

Manganese oxides are widely known for their applications as molecular sieves, catalysts and electrode materials in batteries. Manganese oxides are traditionally used in primary Leclanc and also in commercially available secondary alkaline cells. In the current study Manganese oxide is used as the electrode material for super capacitive application. These metallic oxides are been considered good contenders for super capacitive study as they have very good theoretical super capacitance, their abundance, low cost and environmental friendliness. These metallic oxide powders are available in different forms and these structural forms of the oxide make it very versatile and applicable for wide range of applications [45].
Table 1: Crystal Structure details of Manganese Oxide [45]

<table>
<thead>
<tr>
<th>Type</th>
<th>Crystal Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>Rock Salt</td>
<td>Face centered cubic lattice with a 6:6 octahedral coordinates</td>
</tr>
<tr>
<td>Mn$_3$O$_4$</td>
<td>Tetragonal Spinel</td>
<td>Metal cations occupy 1/8 of the tetrahedral sites and $\frac{1}{2}$ of the octahedral sites and there are 32 oxygen anions in the FCC unit cell.</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>Body Centered Cubic</td>
<td>BCC unit cell with 16 formula units per unit cell</td>
</tr>
<tr>
<td>α- MnO$_2$</td>
<td>Monoclinic</td>
<td>Cross linking of double or triple chains of the MnO$_6$ octahedra resulting in 2-D tunnels with in the lattice.</td>
</tr>
<tr>
<td>β- MnO$_2$</td>
<td>Rutile Structure</td>
<td>Rutile structure with infinite chain of [MnO$_6$] octahedral sharing opposite edges; each chain in corner linked with four similar chains.</td>
</tr>
<tr>
<td>β- MnO$_2$</td>
<td>pbnm</td>
<td>Closely related to rutile except that the single chains of edge sharing octahedra are replaced by the double chains</td>
</tr>
<tr>
<td>γ- MnO$_2$</td>
<td></td>
<td>An irregular intergrowth of layers of pyrolusite and ramsdellite</td>
</tr>
<tr>
<td>η- MnO$_2$</td>
<td></td>
<td>Different from γ- MnO$_2$ only in crystallite size and the concentration of the micro domains of pyrolusite within the ramsdellite matrix</td>
</tr>
<tr>
<td>δ- MnO$_2$</td>
<td>Birnessite</td>
<td>Layered structure containing infinite 2-D sheets of edge shared MnO$_6$ octahedra</td>
</tr>
<tr>
<td>ε- MnO$_2$</td>
<td>Defective NiAs</td>
<td>Hexagonal close packing of anions with Mn$^{4+}$ statistically distributed over half the available octahedral interstices.</td>
</tr>
</tbody>
</table>

Alongside the features presented above manganese oxides show satisfactory energy storage performance in mild electrolytes and its environmental compatibility has made them one of the very promising materials showing pseudocapacitance. Manganese oxides also possess multiple valence states which can be used to trigger polaron conductivity by making minor physical and chemical modifications to the system. The ability to contain multiple valance states makes manganese oxide a very good candidate for super capacitor applications. For instance, a univalent cation or a bivalent cation can reduce Mn$^{4+}$ to Mn$^{3+}$ or Mn$^{2.7+}$ valance states which in turn leads to higher charge storage capacity. Recent studies state hollow micro and nano structure manganese oxide materials can be used in applications such as catalysis, lithium ion
batteries, chemical sensors and drug delivery systems as they possess high surface area, low
density and very high permeability.

The charge/discharge process in Manganese Oxide system is mainly due to
adsorption/desorption of ions and in three dimensional or in bulk phenomenon’s the energy or
charge storage is due to intercalation or redox reactions. These redox reactions aid for the
pseudocapacitive part of total capacitance stored by the material and charged stored on the
electrode/electrolyte interface aid for the double layer capacitance.

**Surface Phenomenon:** Aided by adsorption/desorption

\[
(MnO_2)_{Surface} + C^+ + e^- \rightarrow (MnOOC)_{Surface}
\]

**Bulk Phenomenon:** Aided by interculation/deinterculation

\[
MnO_2 + C^+ + e^- \rightarrow (MnOOC)
\]

Where C could be Na, H, K and Li ions. Manganese Oxide exists in different crystallographic
structures, like $\alpha$, $\beta$, $\gamma$, $\delta$ and $\lambda$. Each MnO$_2$ crystal consists of basic MnO$_6$ octahedron sub
units which are interlinked in dissimilar ways to give raise to different crystal forms of
Manganese oxide systems. The 1D, 2D and 3D tunnel structures of manganese oxide are formed
by sharing the vertices and edges of MnO$_6$ octahedron subunits. These crystallographic forms are
differentiated by the size of the tunnels formed and the number of octahedron subunits of MnO$_6$
($n \times m$) present in the constructure of crystal system. Figure 1 depicts the different
crystallographic systems of Manganese oxide with different sizes of tunneling.
α- MnO₂ is made by double chains of edge sharing MnO₆ octahedrons, which are connected at the corners to give (2 x 2) and (1 x 1) tunnels which extends in the direction of c – axis of tetragonal unit cell. Cations such as Na⁺, K⁺ and Li⁺ stabilize the α- MnO₂ structure. β- MnO₂ is made of single strands of MnO₆ octahedron sub units which are interlinked by edge sharing to form 1D(1 x 1) tunnel. Accommodation of cations is difficult in β- MnO₂ dude to narrow tunnel.
size. γ- MnO₂ has unsystematic intergrowth of ramsdellite (1 x 2) and pyrolusite (1 x 1) domains (ref pdf 22). δ- MnO₂ has a 2D layered structure with an interlayer separation of around 7Å. It has significant amounts of water and Na and K cations sandwiched between these layers. λ- MnO₂ has a 3D spinal structure. Size and types of the tunnels present in each crystal structure of Manganese Oxide is shown in table 2.

Table 2 : Size and types of tunneling in Mn Oxide Crystallographic forms [7]

<table>
<thead>
<tr>
<th>Crystallographic Form</th>
<th>Tunnel</th>
<th>Size/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>(1 x 1), (2 x 2)</td>
<td>1.89, 4.6</td>
</tr>
<tr>
<td>β</td>
<td>(1 x 1)</td>
<td>1.89</td>
</tr>
<tr>
<td>γ</td>
<td>(1 x 1), (1 x 2)</td>
<td>1.89, 2.3</td>
</tr>
<tr>
<td>δ</td>
<td>Interlayer distance</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Along with the size, morphology and composition, electrochemical activity of Manganese Oxide also depends on the crystal structure. The size of the tunnels present in the structure is directly proportional to the intercalation/de-intercalation of cations or protons in different crystallographic manganese oxide groups. These tunnels should be sufficiently spaced to accommodate the cations during the electrochemical cycle.

Micro structure also differentiates different manganese oxide systems and is responsible for the electrochemical behavior of Manganese oxide systems. α- MnO₂ contains spherical particle with interparticular separation between them. Thin plated or nano wires are also observed in manganese oxide crystal structure when they are made by using micro emulsion technique. Whereas β- MnO₂ contains 1 Dimensional Nano rods in which the diameter is about 50nm and the length is several micrometers. The morphology of γ- MnO₂ is spherical brushes with linear
and radially growing nano rods which are quite different from $\alpha$ and $\beta$ manganese oxide structures. $\delta$- $\text{MnO}_2$ is made of aggregated spherical particles which are made of short fibers which interlock them. $\lambda$- $\text{MnO}_2$ is made of polygon shaped particles with a size range of few nano meters to micro meters. Figure 10 shows the SEM micrographs of $\alpha$, $\beta$, $\gamma$, $\delta$ and $\lambda$ crystal forms of manganese oxides.

![Fig 10 SEM micrographs of a) $\alpha$, b) $\beta$, c) $\gamma$, d) $\delta$ and e) $\lambda$ crystal forms of manganese oxides [6]](image)

As per the literature $\alpha$- $\text{MnO}_2$ shows best specific capacitance due to its morphology, porosity and higher surface area. Specific capacitance of the manganese oxide varies in the subsequent
order of \( \alpha = \delta > \gamma > \lambda > \beta \). Environmental stability, high potential window and potential to be used in commercial applications makes manganese oxide a competitive material in super capacitor studies.

1.6. Production of Nano Powders:

Recent trends in nanotechnology enabled us manipulate particle properties both in atomic and molecular scale. The nanometer products which are used for super capacitive applications such as metal oxides can be processed in two different ways, i.e., Top–Down and Bottom–Up approach. In the top-down approach we start with the bulk material and break it down in to smaller fragments. In this method we use large structures, which are controlled externally in the development or production of nanostructures. This method includes ball milling, attrition and lithography.

In the bottom up approach we basically build the structure up from an atomic scale to nano scale. Some of the examples of this processing technique include Self-assembly, liquid- solid transformation. The liquid solid transformation can be sub classified in to co precipitation, sol gel processing, micro emulsion technique and solvothermal methods. In the coprecipitaion technique we dissolve the precursor salt (chlorides, nitrides) in water or other solvent mixtures to precipitate the oxohydroxide form using a base. Whereas, solgel processing techniques involve production of metal oxides via hydrolysis of precursors. Microimmulsion technique is based on the formation of micelles in a mixture containing water, surfactant and oil. During the production of nano metal oxide particles using the solvothermal method, the metal complexes are decomposed by applying thermal energy in an inert atmosphere under application of pressure.
Figure 11 is the schematic of the top-down and bottom-up approach with the techniques that are used. [6][13]

1.7. Ceramic- Carbon- Polymer Composites:

Graphite and other conductive carbon isotopes show good capacitive behavior. They show a very good double layer capacitance due to its ability of storing charge on the surface. Its high surface area makes it more suitable for super capacitive applications. Zhang et al have reports a specific capacitance of 120F/g for chemically reduced graphene oxide [38]. High surface area carbon black showed a specific capacitance of about 250 F/g in the work of F. Beck et al [39]. Other
carbon isotopes like CNT’s, Carbon fibers and graphene have shown very good ability to be super capacitive materials. These carbon isotopes can also be added as a filler material in metal oxides and non-conductive polymers. They form continuous interconnecting network in the oxide structure and aids for its conductivity.

Variable oxidation states, high conductivity and dielectric properties of metal oxides make them suitable for supercapacitive applications. Metal oxides like RuO₂, MnO₂, NiO, Fe₂O₃, Co₃O₄, SnO₂ and V₂O₅ have been used as supercapacitive materials. They show good pseudocapacitive behavior which aids for the charge storage property of these oxides. RuO₂ showed a specific capacitance of 720 F/g which made researchers to focus their study on metal oxides. These metal oxides have some disadvantages like low cyclic stability, limited conductivity and low potential window of operation. For these reasons metal oxides are usually used as super capacitor electrodes by either doping or by making composites [34].

Conductive polymers show extremely good pseudocapacitive behavior because of its ability to undergo redox reactions with varying potentials. Potentially good supercapacitive polymers can be made conductive by adding carbon based filler materials. These polymer based supercapacitive electrodes are more stable and have high cyclic stability with a decent potential window of operation. Conductive polymers derived from monomers such as pyrrole, aniline and thiophene show very good environmental stability and high electroactivity which makes these polymers suitable for electrodes used in super capacitor applications [34]. Polymer metal oxide composites is a very good field to study on as polymer aids for the excessive pseudocapacitance without disturbing the capacitive properties of metal oxides. These composites are also tough and rigid with good cyclic stability.
1.8 Objective:

Aim of the current study is to establish a structural co-relation to the electro chemical response obtained from the manganese oxide powders from three different production techniques. Manganese oxide powders are produced through modified sol gel technique, Co-precipitation and Reduction of KMnO$_4$ technique. $\alpha$− MnO$_2$ which has the (2x2) MnO$_6$ tunnel structure is stabilized in the co-precipitation technique. Efficient way of stabilizing $\alpha$− MnO$_2$ is explained in the current study. Tunnel size plays a vital role in electro chemical response obtained, as the tunnel size increases the electrolyte can penetrate deeper due to which the electrode electrolyte interaction sites increase. Structural and microstructural features of MnO$_2$ powders produced through co-precipitation, modified sol-gel and reduction of KMnO$_4$ techniques were compared and the corresponding electrochemical behavior is studied to establish a structural correlation with charge storage. Heat treatment steps are incorporated during the production to get the most suitable structure which gives maximum electro chemical response. Heat treatment also aids for the poloran conductivity due to the presence of multiple valence states of manganese. The basic response of the powders was studied by making pellets of the powders produced and testing them in a three electrode setup. PEO/Graphite/MnO$_2$ films were made using partial solution synthesis technique to compare the electro chemical response obtained. Na$_2$SO$_4$ is used as the electrolyte in the current study instead of traditional H$_2$SO$_4$ which suits the best for manganese oxide systems. The structural correlation to the electrochemical response is studied.

1.9. Approach

Manganese oxide has been applied as an electrode material for supercapacitor applications. These manganese oxide powders were produced using solution synthesis methods like co-
precipitation, Sol gel technique and reduction of potassium permanganate technique. These powders produced were there studied independently to understand the structural co-relation to the electro chemical response of the material. To make these powders conductive different heat treatment steps have been incorporated which involves both oxidizing and reducing atmospheres. These heat treatment steps are incorporated to get poloron conduction active in the electrode material. Poloron conductivity is obtained by forming Mn$^{3+}$ state in the lattice. This state of manganese is obtained by heat treatment in different environments for different production techniques. Pellets and composite films were made off of these powders to study the electro chemical response. PVDF and graphite is added to the powder to make the pellets. Composites films of these conductive powders and PEO are made which can be used as electrodes for supercapacitor applications. Addition of polymer aids for the pseudocapacitive nature of the electrode and also gives it strength and rigidity. PEO used is made conductive by mixing it with graphite using a novel technique called partial solution mixing technique. The graphite forms a continuous interconnecting path in the polymer lattice which makes it conductive. Composite films made of polymer and manganese oxide powders produced through three different techniques were studied and their electrochemical response is compared.
CHAPTER 2

2. CHARACTERIZATION

Electro chemical analysis techniques are used to characterize the performance of the super capacitor. The data obtained from electrochemical analysis should also be complimented by structural and optical data. Usually to understand the performance of electrode material electrochemical characterization techniques like impedance spectroscopy, cyclic voltammetry and chronopotentiometry are used. All the testing can be done in either two electrodes or three electrode setup. Three electrode system give in-depth details of the characteristics of the electrode where as two electrode system explains the efficiency of electrode.

2.1. Electro-Analytical Techniques:

Electro- analytical techniques record variation in current on application of potential and vice versa. These techniques are branched in to three sub categories:

- Voltammetry
- Potentiometry
- Coulometry

Electrochemical characterization for supercapacitive study mostly deals with voltammetry and potentiometry.

2.1.1. Cyclic Voltammetry:

Cyclic voltammetry is an electrochemical characterization technique which studies the kinetics of the electrochemical reaction. Response of current with study change in voltage is noted in this
characterization technique. Figure 9 shows the current vs voltage behavior of a material. The cyclic voltammetry response depends on the applied voltage, the rate at which the voltage is applied, electrode material and the electrolyte. The cyclic voltammetry plot thereby obtained can be used to understand the nature (capacitive or resistive) of the material. If the nature of the material is capacitive the area inside the curve is high. The area inside the curve is directly proportional to the charge stored. The mechanism which aids for the charge storage can be estimated with the help of cyclic voltammetry curve i.e., we can predict if the material is showing pseudocapacitance of double layer capacitance by looking at the shape of the curve (not always true) [40].

![Cyclic Voltammetry Plot](image)

"Fig 12 (a) Voltage pulse used in cyclic voltammetry, 9(b) CV plot"

Materials which show double layer capacitance usually have a rectangular CV plot with no anodic or cathodic peaks. The area inside the loop corresponds to the charge stored due to charge accumulation on the surface of the electrode. Figure 9(b) shows a typical CV plot for double layer capacitors.

The CV plot for pseudocapacitive materials consists of reduction and oxidation peaks. These peaks are dependent on the applied potential for specific material. At a given potential the activation energy for either reduction or oxidation reaction is reached and the reaction moves in
forward direction. Before the application of potential to the electrode system i.e., at t=0, the solution contains uniform bulk concentration. On application of potential the concentration of oxidized species go’s down at the surface. It results to a higher cathodic current as there will be more flux at the surface (Fick’s law of diffusion). The concentration eventually falls down to zero as potential becomes more negative. Similarly, the volume in the solution that is depleted of the oxidized species will increase and the concentration gradient will decrease.

![CV Plot](image)

**Fig 13. CV Plot of a pseudocapacitive electrode system with cathodic and anodic peaks**

If the concentration gradient decreases the amount of flux at the surface decreases and the current will begin to decrease. On reversing the voltage, the depletion of oxidized species at the surface is still noticed, but the surface concentration begins to rise so the current decreases further. And finally a region where anodic current dominates is reached.

As we know charge is the product of capacitance and the applied voltage. Therefore capacitance can be calculated by dividing the charge stored with the applied voltage.

$$C = \frac{q}{V}$$  \hspace{1cm} (2)
Where $C$ – Capacitance

$q$ – Charge stored

$V$ - Applied voltage

Specific Capacitance can be calculated from

$$C_{sp} = \frac{q}{m \Delta V}$$

$C_{sp}$ - Specific Capacitance

$q$ – Charge storage

$m$ – Mass of the electrode

$\Delta V$ – Voltage range

2.1.2. Chronopotentiometry:

In chronopotentiometry technique a constant current is applied to the electrode system and the corresponding voltage response is recorded. In case of a electrochemical capacitor setup, constant current is applied across the electrode for a particular time whose voltage response is recorded and then a reverse current of same value is applied for a particular time and its voltage response is recorded. Initial one is the charge Cycle and the later one is the discharge cycle. The cyclic stability of the electrode material can be estimated by knowing the charging and discharging behavior for higher number of cycles. Ideally the charge discharge curve should remain the same after certain number of cycles to prove its cyclic stability. Characteristics like capacitance, power density and energy density can also be estimated using the chronopotentiometry.
Figure 11 shows the charge discharge behavior of G-COOMn from the work of park et al. The sudden drop in the potential is due to ohmic drop which occurs due to the resistance from electrode, electrolyte and the current collector. It is same as the equivalent resistance which can be obtained from Nyquist plot.

Specific capacitance value for a specific electrode system can be estimated by using the below equations:

\[ C_{sp} = \frac{I \Delta t}{\Delta V m} \]

Energy density \( E = 0.5 C_{sp} (\Delta V)^2 \)

Power density, \( P = \frac{E}{\Delta t} \)
\( C_{sp} \) – Specific capacitance

I – Current

\( \Delta t \) – Discharge time

\( \Delta V \) – Change in voltage during discharge

m – Mass of the electrodes

E – Energy density

P – Power density

The cyclic stability of the super capacitor and its supercapacitive efficiency can be estimated using cyclic voltammetry and chronopotentiometry. The energy and power density obtained through chronopotentiometry enables us to understand the application of the super capacitor.

2.2. Scanning Electron Microscopy:

Scanning electron microscopy (SEM) is a type of electron microscopy in which the sample is scanned using an electron microscope. The output is in the form of images which can be further analyzed for particle size dimensions, surface to volume ratios, to study the morphology and for chemical composition analysis. The electrons are made incident on the sample surface which then are scattered by the surface and detected by various signal detectors. These scattered electrons contain information about the sample which can be further analyzed for surface topology and composition.

Scanning electron microscopy is widely used in the field of material sciences for microstructural analysis of the sample. A typical schematic of an SEM is as shown in figure 12. As shown in the figure SEM consists of electron gun which produces the electrons required for scanning. Electromagnetic lenses and apertures are used to focus and define the path of the electron beams.
The instrument consists of high vacuum environment in order to limit the scattering of the electrons. The signal detection and processing system enable real time image of the sample [41].

The electron beam is incident onto the surface of the sample and it interacts with sample surface and scatters. The interaction can divided into two main categories, elastic and inelastic interactions. In elastic scattering the incident electron may have been deflected by the nucleus of the sample or the electron of same energy as that of incident in the outer shells of the sample. The scattered electron might have not lost much energy due to interaction and are usually deflected at wide angles [41]. Some of the incident electron may be backscattered due
electrostatic attraction between the positively charged nucleus of the sample and the negatively charged electrons. The backscattered electrons might scattered at angle greater than 90° and gives useful information about the image of the sample. In inelastic interactions there are many different types of interactions between incident electrons and the electrons and the atoms of the sample in which the incident electron beam transfers energy to the atom. The amount of energy transferred depends on the binding energy of the electrons to the atoms and on whether the electrons in the sample get excited singly or collectively.

The excitation of the electrons leads to generation of secondary electrons which usually have energy less than 50eV and are used to visualize the sample. A number of other signals are also produced like characteristic x ray, Auger electrons and cathode luminescence when electron beam is incident on the sample as shown in figure 13. When an incident beams strikes the sample instead of it bouncing off the sample surface it might penetrate into then sample up to certain depth before it encounters a specimen atom and collides with it, by doing so it produces a region of primary excitation which may be originating point of many signal waves. The shape and size of the excited region depend on the energy of the excited beam and atomic number of the sample as shown by figure 16.

Depending on the accelerating voltage, region of interaction surface the shape of interaction region can be a tear drop or hemisphere for low atomic number specimen and high atomic number specimen respectively. The depth of penetration increases with an increase in the energy of the incident beam. The depth may decrease with increase in atomic number of the sample since higher atomic number sample will have more particles to stop the electrons from penetrating.
The secondary electrons are very important source of information. When incident beam strikes the surface of the sample it causes ionization of the sample atoms and the loosely bound electrons may be emitted and are known as secondary electrons. They usually escape from a
region very close to the material surface since they have very less energy. Hence secondary electrons give accurate information about the position of the beam of the electron incident on the surface of the sample and topographic information about the surface with good resolution. They are mainly used for topographic contrast in SEM and can be used to resolve surface structure of order of 10 nm. The secondary electrons which are produced from the specimen beam interaction contribute to the SEM image. Back scattered electrons (BSE) are most valuable source for SEM image production. It provides compositional and topographical information about the sample. Sometimes BSE are defined as the one which leaves the sample surface with energy greater than 50 eV or the one which might have undergone multiple or single scattering events. The BSE have a large energy compared to the secondary electrons which prevents it from being absorbed by the sample and the region of the sample which produced BSE is larger compared to secondary electrons.

Surface analysis of the electrode is done using the SEM. Important features of the electrode like the porosity and the particle size can be estimated using this microscopy technique.

2.3. X-Ray Diffraction:

Crystals are known to have regularity and symmetry and hence their study can give us vital information about specific properties of the materials. X ray crystallography has led to better understanding of crystal structures, chemical bonds and non-covalent interactions. X rays like light and ultraviolet radiations can be categorized as electromagnetic waves. The accompanying magnetic field plays no role in x ray diffraction and hence it can be imagined as an electric field oscillating in a single plane, where the plane is perpendicular to the direction of propagation as shown in figure 15. X ray wavelengths generally lie between 0.1 Å and about 100 Å [42].
X rays are produced by bombarding a metal target with high energy electrons. The electrons are emitted from a heated filament held at a high negative potential and are accelerated towards the target held at positive potential as shown in figure 16. These components are assembled into an evacuated chamber to avoid scattering of electrons.
When a high energy electron beam meets the target it is scattered many times and photons are produced as it decelerates. A large faction of these is X rays which forms a continuous distribution of energies. Now bombarding of electron ejects an electron from the atom of material in the form of an x ray photon. The radiations emitted are mixture of x-rays of various wavelengths, in order to obtain monochromatic x rays it is necessary to eliminate unwanted wavelengths, this can be achieved by using filters which will absorb the unwanted wavelengths.

In 1912, German physicist von Laue found that if atoms in crystals were regularly spaced, and if the wavelength of the x-rays were equal to the interatomic distance in crystals, then diffraction of x-rays by crystals should be possible. His hypothesis proved to be successful. Later two English physicists named W. H. Bragg and W. L. Bragg successfully analyzed Laue’s experiment and formed a mathematical expression which explains the condition for diffraction from a crystal. It is given by the following:

\[ \lambda = 2d \sin \theta \]  \hspace{1cm} (3)

Where \( \lambda \) is the wavelength of the X-Ray beam, \( 2\theta \) is the angle between the diffracted beam and the transmitted beam, and \( d \) is the interplanar spacing between the atoms of the crystal [43]. Diffraction occurs whenever Bragg’s law is satisfied.

The above mentioned principle is widely applied in characterizing the materials like metals, ceramics and polymers. This technique is mainly used to determine the lattice parameters, degree of crystallinity, size of the crystallites, and crystalline orientation [44]. In the current study XRD is used to understand the crystal structure of the produced powders, their phase distribution and degree of crystallinity with respect to temperature.
CHAPTER 3

3. EXPERIMENTAL

3.1. Materials

3.1.1. Polyethylene oxide:

Polyethylene oxide has a chemical formula \((\text{C}_2\text{H}_4\text{O})_n\) and is an oligomer or polymer of ethylene oxide. PEO is a low melting solid and its melting point is dependent on the molecular weight of the polymer. PEO is widely used in the field of medical sciences and it is one of the most efficient carriers of protein into the blood. PEO used in the current study is PEO lend H-6000.

\[
\begin{align*}
\text{H} & \quad \text{O} \\
& \quad \text{nOH}
\end{align*}
\]

Fig 20 Structure of Polyethylene Oxide [48]

Properties like glass transition temperature and flow temperature depend on the molecular weight of the polymer.

3.1.2. Manganese Oxide:

Manganese oxide powders used in the current study are synthesized through three different techniques. These production techniques involve co-precipitation of Mn(OH)\(_2\) from manganese nitrate and sodium hydroxide precursor solutions, reduction of KMnO\(_4\) using Mn(NO\(_3\))\(_2\) precursor solution and modified sol-gel technique which involves manganese acetate and manganese nitrate as precursor solutions.

3.1.3 Graphite:

Highly conductive and very fine graphite powders are acquired from Asbury Graphite Mills Inc. The graphite powders used in the study has a very high surface area 115 m\(^2\)/g.
3.2. Synthesis of Manganese Oxide Powders:

Manganese oxide powders are produced through modified sol gel technique, Co-precipitation and Reduction of KMnO₄ technique. α– MnO₂ which has the (2x2) MnO₆ tunnel structure is stabilized in the co-precipitation technique. Structural and microstructural features of MnO₂ powders produced through co-precipitation, modified sol-gel and reduction of KMnO₄ techniques were compared and the corresponding electrochemical behavior is studied to establish a structural correlation with charge storage.

3.2.1. Reduction of Potassium permanganate:

Manganese oxide (MnO₂) powders are synthesized by reduction of KMnO₄. This is a solution techniques which involves potassium permanganate solution and manganese nitrate as precursor solutions. Potassium Permanganate (KMnO₄, F.W 158.05, Fisher Scientific) was dissolved in 95:5 solution (95% De-ionized water. 5% Iso propyl alcohol). While the solution was stirred Mn(NO₃)₂ was slowly added to the initial solution. Molar ratio of 2:3 was maintained. A purple KMnO₄ solutions turns brown on addition of Mn(NO₃)₂. The solution was allowed to stir for few hours for homogenous distribution of Mn²⁺ ions in the solution. Formation of the precipitate can be explained according to the equation,

\[ 2Mn^{7+} + 3Mn^{2+} \rightarrow 5Mn^{4+} \]

The solution was allowed to stir and then filtered using filter papers of different grades. The powders were then washed with distilled water and were filtered out again. This process was repeated several times to obtain purer powders. These powders were further dried in a vacuum oven at around 60°C overnight. These dried were them separated in to batches and were heat treated in reducing atmospheres at different temperatures fixed as per TGA analysis data. N₂ gas is used as the reducing medium for heat treatment of the powders.
3.2.2 Co- Precipitation Technique:

MnO\textsubscript{2} powders were produced by co-precipitation of Mn(OH)\textsubscript{2} using Mn(NO\textsubscript{3})\textsubscript{2} and NaOH as precursor solutions. Mn(NO\textsubscript{3})\textsubscript{2} precursor solution was made by dissolving in 95:5 solution (95% De-ionized water. 5% Iso propyl alcohol). While the solution is stirred concentrated NaOH is added drop wise to the solution. NaOH was added to the solution till the pH of the solution reaches 9. Instant precipitation is seen by the addition of NaOH in the solution slowly the solution turns brown and precipitate is clearly seen. The solution is allowed to stir for few hours for equal distribution of ions. After the solution was stirred the powders were filtered using filter paper. The powders were then washed with distilled water and were filtered out again. This process was repeated several times to obtain purer powders. These powders were further dried in a vacuum oven at around 60\textdegree{}C overnight. These dried powders were then separated in to batches and were heat treated in reducing atmospheres at different temperatures fixed as per TGA analysis data.

3.2.3 Modified Sol- Gel Technique:

Manganese oxide powders were produced using Manganese Acetate, Citric Acid and Ammonium Hydroxide as precursor solutions. Precursor solution of manganese acetate and citric acid was made by dissolving them in in 95:5 solution (95% De-ionized water. 5% Iso propyl alcohol). Molar ratio of manganese acetate to citric acid was maintained at 1:2 in the precursor solution. Ammonium hydroxide is then added drop wise to the solution and was allowed to stir during this process. Immediate formation of brown precipitate is observed and the solution was allowed to stir for several hours for homogenous distribution of ions. After the solution was stirred the powders were filtered using filter paper. The powders were then washed with distilled
water and were filtered out again. This process was repeated several times to obtain purer powders. These powders were further dried in a vacuum oven at around 60°C overnight. These dried powders were then separated into batches and were heat treated at different temperatures fixed as per TGA analysis data.

3.3. Preparation of Electrode:

The basic response of the powders was studied by making pellets of the powders produced and testing them in a three electrode setup. PEO/Graphite/MnO$_2$ films were made using partial solution synthesis technique to compare the electro chemical response obtained.

3.3.1 Pellet preparation:

Pellets of the synthesized powders were made to study the natural response of the powders. All the pellets used for the study were made by using the same composition. 85% of the active powders, 10% Graphite and 5% PVDF. Required amount of powders as per the composition and few drops of IPA were added in to a Petra dish and were mixed thoroughly. The mixture is then dried and pellets were made off this mixture.

3.3.2 Film Preparation:

Synthesized manganese oxide powders were dispersed in PEO/Graphite solution made by using partial solution synthesis technique. This Manganese oxide dispersed solution is used to make PEO/MnO$_2$/Graphite films. 0.6g of active metal oxide powder is dispersed in 14ml of PEO/Graphite solution. This solution is mixed thoroughly for complete dispersion of active ceramic powders. The solution is then spin coated on stainless steel substrates. Pyrolysis of these films is done at a temperature range of 240 – 250°C.
3.4. Electrochemical Cell Design:

Two different types of cell setup could be used to perform the electrochemical analysis one of which is three electrode cell and the other is two electrode cell. In the current study we used three electrode systems to perform the analysis. A three electrode cell consists of a working electrode (electrode under study), a reference electrode which could be either a standard calomel electrode or hydrogen electrode and a counter electrode. We used carbon electrode as the counter electrode in this study. Three electrode system gives a better idea of the redox reactions going on in the system. Whereas, in a two electrode system a material under study is used alongside the standard reference electrode.

3.5. Electrochemical Characterization:

All the electrochemical analysis in the current work is performed in a three electrode setup using Gamry Potentiostat 300G. The software used in the potentiostat is called the Gamry Framework. All the analysis done is recorded directly in the computer by this software. The electrochemical tests performed on this potentiostat to characterize the supercapacitive material include cyclic voltammetry and chronopotentiometry.

3.5.1. Cyclic Voltammetry (CV):

Cyclic Voltammetry is either performed on a two electrode system or a three electrode system. This technique enables us in understanding the redox reactions going on in the cell. In the current study CV data is collected over a potential window of -0.8V to +0.8 V for a required number of cycles.

3.5.2. Chronopotentiometry (CP):
Charge/ discharge behavior of the supercapacitive material can be estimated using chronopotentiometry technique. A constant current is applied on the material and the voltage response is recorded. The area under the curve gives the charge stored and the slope of the lines gives the rate of charge and discharge. In the current study the voltage response is measured on application of constant current of 1mA and 5mA. During the discharge cycle the equal amount of current in applied but with negative amplitude.

3.5.3. Echem Analyst:

Echem analyst is the analysis software used to analyze all the data obtained from Gamry. Charge discharge potentials, charge stored and specific capacitance can be estimated using this analysis technique.

3.6. Structural Characterization:

3.6.1: X- Ray Diffraction:

X- Ray diffraction technique is used to do the qualitative and quantitative analysis of the material. It is also used to understand the crystalline state and size, structure, the amount of phases present and the lattice parameters of the material. X- Ray diffraction is operated on the basis of Bragg’s law. A diffraction pattern of the monochromatic beam which hits the sample at different angles is used to understand materials in this technique.

3.6.2. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS):

SEM is an electron microscopy technique used to study the morphology and surface properties of the materials. It is a highly sophisticated technique which has a very high resolution and magnification. Microstructures of as produced and heat treated Manganese oxide powers were
obtained using SEM. Energy Dispersive Spectroscopy is used to determine the elemental composition of the material. It helps in obtaining the distribution of elements at a certain region on the sample area.
CHAPTER 4

4. RESULTS AND DISCUSSION:

4.1. Manganese Oxide Powders produced using Modified Sol-Gel Technique:

4.1.1: X-Ray Diffraction analysis

The X-Ray Diffraction analysis on the Manganese Oxide powders using the Modified Sol Gel Technique is performed to understand the phase distribution of the powders and its variation with respect to the heat treatment temperatures. Crystallinity with respect to temperature and crystalline size can also be calculated using the XRD technique. The X-Ray diffraction analysis is performed on the as prepared powder samples and also powders which were heat treated at different temperatures. During the analysis we used Cu Kα radiation with a wavelength of 0.154 nm at 2θ range of 20° - 75°. It was observed that the powders consisted of two different phases, one being MnO₂ and the other being Mn₂O₃. The presence of MnO₂ phase was confirmed with obtained diffraction patterns at 20, 25, 30, 35, 37, 39, 45 and 60 with diffraction planes 200, 211, 321, 222, 400, 411, 422 and 431. Similarly the presence of Mn₂O₃ was confirmed by diffraction patterns at 32, 39, 43, 55, 60, 66, 68 and 70 with diffraction plane and traces of Mn₃O₄. The powders turned completely crystalized at 300°C. As the temperature increased the amount of amorphous phase in the powder increased. XRD pattern at 300°C showed completely crystallized phase.
Fig 21(a) XRD patterns for powders heat treated at a) 180 b) 240 and C) 300°C in reducing atmosphere for 1 hour which are produced using modified solgel Technique.

Fig 21(b) XRD patterns for powders heat treated at a) 180 b) 240 and C) 300°C in reducing atmosphere for 1 hour which are produced using modified solgel Technique.
The crystallite size can be calculated from Debye – Scherer equation, which is,

\[ d = \frac{n \lambda}{\beta \cos \theta} \]  \hspace{1cm} (3)

where,

\( d \) – crystallite size

\( n \) – shape factor (constant = 0.9)

\( \lambda \) – Wavelength of the X - ray source

\( \beta \) – Full width and half maximum of the 100% intensity peak in radians

\( \theta \) – Angle between the incident ray and the scattering planes.

From the XRD pattern of the different BaTiO\(_3\)s the crystallite size can be calculated. Thus XRD data helps in the detection the material formation, doping and also crystallite size.
The intensity of peaks changed with respect to the heat treatment temperature which indicated the change in the amount of phases present with respect to the temperature. It was observed that as the temperature increased the peak intensity of MnO₂ decreased and the peak intensity of Mn₂O₃ increased.

As the heat treatment temperature increased the powders composition changed respectively. Mn₂O₃ is a more stable oxide and was stabilized with increase in temperature. At around 300°C the powders completely transformed into Mn₂O₃. The second important factor which could be observed with the XRD data is the amount of crystallinity change with respect to the heat treatment temperature. The powders looked amorphous at lower temperatures and the crystallinity of the powders increased with respect to the increase in temperature. At 180°C the powders looked amorphous and at higher temperatures the powders totally transformed to crystalline.
4.1.2 Microstructural Analysis:

Figure 22, 23 and 24 gives the microstructural details of MnO2 powders obtained through solgel technique heat treated at 180°C for 1hr in reducing atmosphere created using forming gas.

Fig 22 shows the micrographs of MnO2 at 2000x, powders obtained through solgel technique heat treated at 180°C for 1hr in reducing atmosphere created using forming gas.

Fig 23 shows the micrographs of MnO2 at 2000x, powders obtained through solgel technique heat treated at 240°C for 1hr in reducing atmosphere created using forming gas.
Fig 24 (a) shows the micrographs of MnO2 at 35000X powders obtained through solgel technique heat treated at 180°C for 1hr in reducing atmosphere created using forming gas.

Fig 24 (b) shows the micrographs of MnO2 at 10000 powders obtained through solgel technique heat treated at 180°C for 1hr in reducing atmosphere created using forming gas.
SEM and EDS analysis was performed on HITACHI Scanning Electron Microscope at University of Cincinnati. It was observed that the powders contained spherical particles along with some strands of nano wires. These spherical particles seen reciprocate to the presence of $\alpha$-MnO$_2$ phase whereas the nano wires represent the $\beta$-MnO$_2$ phase. The presence of $\alpha$-MnO$_2$ was also proved by the XRD patterns obtained. Particle size change with respect to temperature is also seen in these micrographs.

4.1.3 Cyclic Voltammetry:

Fig 25 CV response of the pellet made from MnO$_2$ powders obtained from modified solgel technique, heat treated for 1 hr in reducing atmosphere.

![Graph showing the CV response of MnO$_2$ powders](image)

Fig 25 a CV response of the pellet made from MnO$_2$ powders obtained from modified solgel technique, heat treated for 1 hr in reducing atmosphere.
Fig 25 (b) CV response of the pellet made from MnO2 powders obtained from modified solgel technique, heat treated for 1 hr in reducing atmosphere

Fig 25 CV response of the pellet made from MnO2 powders obtained from modified solgel technique, heat treated for 1 hr in reducing atmosphere
The cyclic voltammetry response of the powders heat treated at 180°, 240° and 300° C which were made using modified solgel technique is shown above. The storage of charge is due to both double layer and pseudocapacitance behavior shown by the powders. Energy storage due to double layer phenomenon is due to accumulation of charged particles around the electrode during each half of the cycle. The charge storage aided by pseudo capacitance is due to the oxidation and reduction of the manganese oxide present on the surface. Most of the charge stored is due to bulk oxidation and reduction phenomenon taking place in the electrode made. This can be explained by the dependency on the charge storage with respect to the scan rate. As the scan rate increases the response obtained varies. At higher scan rates the charge stored is due to the double layer phenomenon and the redox reactions occurred on the surface of the electrode. As the scan rate decreases the time for electrode and electrolyte interactions increases which results in efficient penetration of electrolyte in to the electrode resulting in bulk redox reactions which there by leads to higher charge storage.

**Surface Phenomenon:** Aided by adsorption/desorption

\[
2\text{(MnO}_2\text{)}_{\text{Surface}} + 2\text{Na}^{2+} + 4\text{e}^- \rightarrow 2\text{(MnOONa)}_{\text{Surface}}
\]

**Bulk Phenomenon:** Aided by intercalation/deintercalation

\[
2\text{MnO}_2 + 2\text{Na}^{2+} + 4\text{e}^- \rightarrow 2\text{(MnOONa)}
\]

H₂SO₄ is widely used acidic electrolyte for the study of Manganese oxide electrodes. In the current study we have used Na₂SO₄ instead of the usual sulphuric acid. Voltammetric current density in cyclic voltagrams and longer charge discharge time in charge-discharge curves is dependent on the type of electrolyte used. We chose Na₂SO₄ over H₂SO₄ for the availability of bivalent ions. The storage capacity is higher for the system containing bivalent ions in an
electrolyte. Higher specific capacitance for bivalent system is attributed to the fact that each bivalent cation can reduce two Mn$^{4+}$ to Mn$^{3+}$. This doubles the number of electrons. Whereas, univalent cation reduce just one Mn$^{4+}$ to Mn$^{3+}$.

Fig 26 (a) CV response of the MnO2/PEO/Graphite film made from MnO2 powders obtained from modified solgel technique, heat treated at 180°C for 1 hr in reducing atmosphere.

- Modified Sol-gel technique
  Temp: 180°C 1hr, Reducing atm
  Sp. Cap= 824 F/g

- Modified Sol-gel technique
  Temp: 225°C 1hr, N2/H2
  Sp. Cap = 385 F/g
Figure shows the cyclic voltammetric response of films made using spin coating technique. These composite films were made by using MnO₂ powders produced using modified solgel technique and PEO/Graphite solution made using novel partial solution mixing technique. The cyclic voltammetry response shown for these electrodes is due to double layer capacitance which is due to immigration of charges around the electrode, pseudo capacitance offered by manganese oxide powders and also pseudo capacitance offered by PEO/Graphite. Higher charge storage is seen in the composite electrodes due to the redox reactions in offered from PEO. Graphite present in the solution forms a continuous path for charge transfer which makes the electrode suitable for efficient charge discharge behavior.

Heat treatment temperature plays an important role in the CV response obtained. As the heat treatment temperature increases the amount of Mn(OH)₂ phase present decreases. Removal of
these hydroxides gives a layered structure which is suitable for super capacitive applications as it offers higher surface area for intercalation/deintercalation. Also as the temperature increases the crystallinity of the powders increases. Higher crystallinity is not suitable for super capacitive applications. As the temperature increases the amount of Mn$_2$O$_3$ phase present also increases. Presence of Mn$_2$O$_3$ in the powders helps in two ways, it increases the conductivity of the powders as it most conductive phase in among all the manganese oxides and also presence of two different valence states aids for the polaron conductivity of the powders. Table 3 gives the specific capacitance values obtained at different temperatures.

Table 3 Specific Capacitance obtained at different temperatures:

<table>
<thead>
<tr>
<th>S.No</th>
<th>Temperature (C)</th>
<th>Specific Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
<td>824</td>
</tr>
<tr>
<td>2</td>
<td>225</td>
<td>385</td>
</tr>
<tr>
<td>3</td>
<td>240</td>
<td>302</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>137</td>
</tr>
</tbody>
</table>

Table gives the specific capacitance obtained at different heat treatment temperatures used for production of manganese oxide powders.

**4.2 Manganese Oxide Powders produced using Co-Precipitation Technique:**

4.2.1: X-Ray Diffraction analysis

X-Ray Diffraction analysis is performed on the as prepared and the heat treated powder to understand the composition of phases present and the crystallinity of the powders. These two factors directly correlate to the electrochemical performance of the powders. We used Cu Kα radiation with a wavelength of 0.154 nm at 2θ range of 20° - 75°. It was observed that the powders consisted of two different phases MnO$_2$ and the other being Mn$_2$O$_3$. As the heat treatment temperature changed the composition of the phases changed evidently.
These powders were heat treated in reducing atmosphere and the phase change with increasing temperature is observed in the XRD plots obtained. As the temperature increased the amount of Mn$_2$O$_3$ phase present increased. Low intensity Mn(OH)$_2$ peaks were observed at lower temperature but they gradually disappeared as the temperature increased. Amount of Mn$_2$O$_3$ phase increased with increase in the temperature this is concluded by observing the change in peak intensities of Mn$_2$O$_3$.

The crystallinity of powders increased with increase in heat treatment temperatures the powders heat treated at 180°C showed highly amorphous behavior and as the heat treatment temperature increased the crystallinity of the powders increased.

Fig 27 (a) XRD patterns for powders heat treated at 150°C in reducing atmosphere for 1 hour which are produced using Co-precipitation technique.
Fig 27 (b) XRD patterns for powders heat treated at 250°C in reducing atmosphere for 1 hour which are produced using Co-precipitation technique.

<table>
<thead>
<tr>
<th>Co-precipitation technique</th>
<th># Mn2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>* MnO2</td>
<td></td>
</tr>
<tr>
<td>o Mn(OH)2</td>
<td></td>
</tr>
<tr>
<td>Temp = 250°C, 1hr, N2/H2</td>
<td></td>
</tr>
</tbody>
</table>

Fig 27 (c) XRD patterns for powders heat treated at 300°C in reducing atmosphere for 1 hour which are produced using Co-precipitation technique.

<table>
<thead>
<tr>
<th>Co-precipitation</th>
<th># Mn2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>* MnO2</td>
<td></td>
</tr>
<tr>
<td>o Mn(OH)2</td>
<td></td>
</tr>
<tr>
<td>Temp = 300°C</td>
<td></td>
</tr>
</tbody>
</table>
4.2.2 Micro Structural Analysis:

Figure 28, 29 and 30 are the SEM micrographs of Manganese oxide powders obtained through co-precipitation route.

Fig 28 shows the micrographs of MnO2 at 2000X powders obtained through co-precipitation technique heat treated at 250C for 1hr in reducing atmosphere created using forming gas

Fig 29 shows the micrographs of MnO2 at 2000X powders obtained through co-precipitation technique heat treated at 300C for 1hr in reducing atmosphere created using forming gas
Fig 30 (a) shows the micrographs of MnO2 at 15000X powders obtained through co-precipitation technique heat treated at 250C for 1hr in reducing atmosphere created using forming gas.

Fig 30 (b) shows the micrographs of MnO2 at 35000X powders obtained through co-precipitation technique heat treated at 250C for 1hr in reducing atmosphere created using forming gas.

SEM and EDS analysis was performed on HITACHI Scanning Electron Microscope at University of Cincinnati. It was observed that the powders contained spherical particles which
represent $\alpha$- MnO$_2$ phase presence. There are no nano wires present in the microstructure which shows the stabilization of $\alpha$- MnO$_2$. Nano wires represent the $\alpha$- MnO$_2$ phase. There by the stabilization of $\alpha$- MnO$_2$ in the co-precipitation technique was obtained due to the presence of the Na ions. The size of the Na ions widens up the tunnel size in the MnO$_6$ octahedron structure and makes it (2x2) spaced instead of (1x1) which is in the case of $\alpha$- MnO$_2$. Completely crystalline phase formation at high temperatures is observed in the micrographs taken.

4.2.3 Cyclic Voltammetry:

Fig 31 CV response of the pellet made from MnO$_2$ powders obtained from co-precipitation, heat treated for 1 hr at different reducing atmospheres.

Fig 31(a) CV response of the pellet made from MnO$_2$ powders obtained from co-precipitation, heat treated for 1 hr at 150°C in reducing atmosphere.
Fig 31 (b) CV response of the pellet made from MnO2 powders obtained from co-precipitation, heat treated for 1 hr at 250°C in reducing atmosphere

The cyclic voltammetry response of the powders heat treated at 250°C which were made using so-precipitation technique using Na as α-MnO2 stabilizer is shown above. The storage of charge is due to both double layer and pseudocapacitance behavior shown by the powders. Energy
storage due to double layer phenomenon is due to accumulation of charged particles around the electrode during each half of the cycle. The charge storage aided by pseudo capacitance is due to the oxidation and reduction of the manganese oxide present on the surface. Most of the charge stored is due to bulk oxidation and reduction phenomenon taking place in the electrode made. This can be explained by the dependency on the charge storage with respect to the scan rate. As the scan rate increases the response obtained varies. At higher scan rates the charge stored is due to the double layer phenomenon and the redox reactions occurred on the surface of the electrode. As the scan rate decreases the time for electrode and electrolyte interactions increases which results in efficient penetration of electrolyte in to the electrode resulting in bulk redox reactions which there by leads to higher charge storage.

**Surface Phenomenon:** Aided by adsorption/desorption

\[2(MnO_2)_{\text{Surface}} + 2Na^{2+} + 4e^- \rightarrow 2(MnOONa)_{\text{Surface}}\]

**Bulk Phenomenon:** Aided by intercalation/deintercalation

\[2MnO_2 + 2Na^{2+} + 4e^- \rightarrow 2(MnOONa)\]

Na is added to stabilize \(\alpha\)-MnO\(_2\) phase. The size of the Na ions widens up the tunnel size in the MnO\(_6\) octahedron structure and makes it (2x2) spaced instead of (1x1) which is in the case of \(\alpha\)-MnO\(_2\). As the tunnel size is high the amounts of electrolyte penetrating increases give rise to higher charge storage values.

During the production of powders using co-precipitation technique Mn(OH)\(_2\) phase forms which on further heat treatment gives manganese oxide powders. Conversion of Mn(OH)\(_2\) to MnO\(_2\) gives rise to layered structure which suits best for super capacitive applications. Layered
structure suits best for super capacitive applications as the amount of bulk interactions increases due to penetration of electrolyte between the layers.

Fig 32 (a) CV response of the MnO2/PEO/Graphite film made from MnO2 powders obtained from co-precipitation technique, heat treated at 150°C for 1 hr in reducing atmosphere.

Fig 32 (b) CV response of the MnO2/PEO/Graphite film made from MnO2 powders obtained from co-precipitation technique, heat treated at 150°C for 1 hr in reducing atmosphere.
Figure shows the cyclic voltammetric response of films made using spin coating technique. These composite films were made by using MnO₂ powders produced using modified solgel technique and PEO/Graphite solution made using novel partial solution mixing technique. The cyclic voltammetry response shown for these electrodes is due to double layer capacitance which is due to immigration of charges around the electrode, pseudo capacitance offered by manganese oxide powders and also pseudo capacitance offered by PEO/Graphite. Higher charge storage is seen in the composite electrodes due to the redox reactions in offered from PEO. Graphite present in the solution forms a continuous path for charge transfer which makes the electrode suitable for efficient charge discharge behavior. Higher capacitance values obtained is due to stabilization of alpha manganese oxide structure which suits best for super capacitive applications. Table 4 Specific Capacitance obtained at different temperatures for co-precipitation technique.
Table 4 Specific Capacitance obtained at different temperatures for co-precipitation technique:

<table>
<thead>
<tr>
<th>S.No</th>
<th>Temperature (°C)</th>
<th>Specific Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>1197</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>300</td>
</tr>
</tbody>
</table>

The capacitance value suddenly drops down at 300°C as the powders become completely crystalline at that temperature. Complete crystallinity is not suitable for super capacitive applications. This proves that best pseudo capacitive behavior is shown when the heat treatment temperature is restricted under 300°C.

4.3. Manganese Oxide Powders produced using reduction of KMnO₄ Technique:

4.3.1 X-Ray Diffraction Studies:

X-Ray diffraction analysis on reduced KMnO₄ technique is performed to understand the phase composition, distribution of phases, crystallite size and crystallinity of the powders. Phase composition, crystallite size and crystallinity of the powders directly reflect its electro chemical performance. We used Cu Kα radiation with a wavelength of 0.154 nm at 2θ range of 20° - 75°. These powders were heat treated in reducing atmosphere and as the heat treatment temperature changes a change is composition and crystallinity in the powders was observed.

As the temperature increased the efficiency of reduction activity increased. As produced powders was composed mostly on MnO₂ powders. Reduction of these powders aided for the formation of Mn₂O₃ phase in the powders. As the temperature of heat treatment increased the amount on Mn₂O₃ phase formation increased. The crystallinity change in the powders was also observed.
with respect to the change in heat treatment temperatures. As the temperature increased the crystallinity of the powders increased. The powders turned completely crystalline at 300°C.

Fig 33 (a) XRD patterns for powders heat treated at 180°C in reducing atmosphere for 1 hour which are produced using reduction of KMnO4 technique

Fig 33 (b) XRD patterns for powders heat treated at 240°C in reducing atmosphere for 1 hour which are produced using reduction of KMnO4 technique
Fig 33 (C) XRD patterns for powders heat treated at 300 C in reducing atmosphere for 1 hour which are produced using reduction of KMnO4 technique

4.3.2 Micro Structural Analysis:

Figure 34, 35 and 36 are the SEM micrographs of Manganese oxide powders obtained through co-precipitation route.

Fig 34 shows the micrographs of MnO2 powders obtained through reduced KMnO4 technique heat treated at 240C for 1hr in reducing atmosphere created using forming gas.
Fig 35 shows the micrographs of MnO2 powders obtained through reduced KMnO4 technique heat treated at 300C for 1hr in reducing atmosphere created using forming gas.

Fig 36 (a) shows the micrographs of MnO2 powders obtained through reduced KMnO4 technique heat treated at 240C for 1hr in reducing atmosphere created using forming gas.
Fig 36 (b) shows the micrographs of MnO2 powders obtained through reduced KMnO4 technique heat treated at 240°C for 1hr in reducing atmosphere created using forming gas.

SEM images reveal the presence of β-MnO2 phase. It was observed that the powders contained spherical particles along with some strands of nano wires. These spherical particles seen reciprocate to the presence of α-MnO2 phase whereas the nano wires represent the β-MnO2 phase.
4.3.3 Cyclic Voltammetry Study:

Fig 37 shows the CV response of the pellet made from MnO2 powders heat treated for 1 hr at 250°C in reducing atmosphere obtained through reduction of KMnO4 route.

Fig 37 (a) shows the CV response of the pellet made from MnO2 powders heat treated for 1 hr at 180°C in reducing atmosphere obtained through reduction of KMnO4 route.

Fig 37 (b) shows the CV response of the pellet made from MnO2 powders heat treated for 1 hr at 250°C in reducing atmosphere obtained through reduction of KMnO4 route.
Fig 37 (c) shows the CV response of the pellet made from MnO2 powders heat treated for 1 hr at 300C in reducing atmosphere obtained through reduction of KMnO4 route.
Fig 38 CV response of the MnO2/PEO/Graphite film made from MnO2 powders obtained from reduction of KMnO4 technique, heat treated at 240C for 1 hr in reducing atmosphere. 

![Reduction of KMnO4 technique](image)

The cyclic voltammetry response obtained for reduced KMnO4 system is not as good as the other two systems. The response obtained from the composite electrode shows that manganese oxide powders added are just acting as a conducting phase in the electrode. The charge storage in due to the double layer capacitance offered by the electrode and pseudo capacitance of the polymer/graphite composite system. Manganese oxide powders had very little effect on the charge storage.
4.4 Chronopotentiometry Study:

Figures 33, 34 and 35 are the Chrono- potentiometry studies for co-precipitated, modified sol-gel and reduced KMnO4 systems at different temperatures.

Fig 39 Continous CP curve for powders made through co-precipitation technique which were heat treated at 250°C for 1 hr in reducing atmosphere

Fig 40 Continous CP curve for powders made through Modified Sol-Gel technique which were heat treated at 225°C for 1 hr in reducing atmosphere
Fig 41 Continous CP curve for powders made through reduction of KMnO4 technique which were heat treated at 240 °C for 1 hr in reducing atmosphere

Chronopotentiometry is an electrochemical technique where a constant current is applied across the electrode for a particular amount of time and its voltage response is recorded. In case of an electrochemical capacitor setup, constant current of 1Amp is applied across the electrode for a particular time whose voltage response is recorded and then a reverse current of same value is applied for a particular time and its voltage response is recorded. The response shows that all the three systems show good cyclic stability as the CP curves remained the same for all three cycles. The slope of first two systems increased with increasing time but the rate of increase got lowered with time. Whereas for the third system the slope increased until a point and remained constant. This proves that the presence of α- MnO₂ phase enhanced the storage ability of the powders. And also from the CP data obtained we can see that the IR drop is more for the reduced potassium permanganate system when compared to the first two.
4.5 Factors Influencing Charge storage:

4.5.1 Effect of Scan rate on the amount of charge stored:

Figure 36 explains the effect of scan rate on the amount of charge stored in co-precipitated system, modified sol-gel system and reduced KMnO4 system.

Figure 42 explains the effect of scan rate on the amount of charge stored in co-precipitated system, modified sol-gel system and reduced KMnO4 system.

It was observed that the scan rate is inversely proportional to the amount of charge stored. At higher scan rates as the charge discharge cycles are very fast, due to which only the double layer capacitance behavior of the electrode can be seen and minute amount of charge stored due to redox reactions on the surface of the electrode. As the scan rate lowers down the electrode electrolyte interaction time increases which leads to efficient redox reactions and high charge storage. As the scan rate decreases the electrolyte which got penetrated into the electrode gives out response which corresponds to the bulk interaction of the electrolyte with electrode. Due to these interactions as the scan rate decreases the amount of charge stored in an electrode electrolyte system increases.
4.5.2 Effect of Temperature on charge storage:

Figure 37 explains the effect of temperature on the amount of charge stored in co-precipitated system, modified sol-gel system and reduced KMnO4 system.

![Graph showing effect of temperature on charge storage]

Figure 43 explains the effect of temperature on the amount of charge stored in co-precipitated system, modified sol-gel system and reduced KMnO4 system.

Temperature directly affects the charge storage ability of the super capacitive systems. This affect is due to the structural modification of the powders with respect to temperature. In all the three systems as the heat treatment temperature increases the amount of amorphous phase decreases and crystallinity increases. This structural change plays a vital role in charge storage behavior of the electrodes. If the powders are completely amorphous the conductivity of the electrode is less and charge storage behavior observed is not ideal. If the powders are completely crystalline the porosity in the structure is minimal and charge storage is not obtained as the structure provides minimum charge transfer resistance.

In this case all three systems showed the formation of secondary phase which aids for the conduction of the powders due to phenomenon called poloron conduction. The amount of Mn$_2$O$_3$ is optimum for temperature ranging from 180–240°C. As the temperature increases further
completely crystalline $\text{Mn}_2\text{O}_3$ phase is formed which is not suitable for supercapacitive applications.

4.5.3. Effect of Ball Milling:

Bottled manganese stannate powders obtained from sigma Aldrich were heat treated at 250$^\circ$C. A batch separated from this heat treated powders were ball milled in 60-40 solution (60% Distilled Water and 40 % IPA). The electrochemical response of the powders before and after was studied. Figure 38 shows the CV response of just the heat treated powders and figure 39 shows the CV response of heat treated and ball milled powders.

Fig 44 CV response of $\text{MnSnO}_3$ powders heat treated in reducing atmosphere at 250C for 1 Hr
Fig 45 CV response of MnSnO3 powders heat treated in reducing atmosphere at 250°C for 1 Hr and ball milled in 60:40 solution for 4 hrs.

It was observed that the heat treated and ball milled powders showed a better CV response when compared with just the heat treated ones. The peak positions of the response have changed after ball milling, this might be due to functionalization of stannate sites. This shows that ball milling aids for the functionalization which in turn reflects the electro chemical response. Ball milling also reduces the particle size in the powders. Lower the particle size higher is the surface area. As the surface area increases the electrode electrolyte interaction sites increase giving a much higher electro chemical response.
4.6 EDAX Analysis:

Figure 46 below shows the Energy Dispersive X-Ray Spectroscopy analysis of powders produced using co-precipitation technique. Elemental analysis of the powders is done using this technique and the data obtained shows the presence of manganese and oxygen in the system proving the formation of manganese oxide phase in the powders. Na which aids for the stabilization of alpha phase is also observed. Presence of minute amounts of Na in the system is a good sign as this might control the structural modifications during the electro chemical cycles.

Fig 46 shows the EDAX data of as prepared MnO2 powders obtained using co-precipitation technique

Figure 47 below shows the Energy Dispersive X-Ray Spectroscopy analysis of powders produced using reduced potassium permanganate technique. Elemental analysis of the powders is done using this technique and the data obtained shows the presence of manganese and oxygen in the system proving the formation of manganese oxide phase in the powders. Traces of potassium is observed in the system. Presence of potassium is seen due to the use of potassium permanganate as the precursor solution for the production of manganese oxide powders using the reduction of potassium permanganate technique.
4.6 Discussion:

XRD data of the three powders showed the phases present in the powders produced and the effect of heat treatment temperatures on these phases. As the temperature increases the crystallinity of all the three powders made through three different techniques increased. This showed that temperature had similar effect on all the three phases present. As the temperature increased the crystallinity of the powders increased and all the powders reached complete crystallinity at around 300°C. All the heat treatments were carried out in reducing atmosphere which was created using forming gas. The reason for using reducing atmosphere for heat treatment is to incorporate Mn$_2$O$_3$ phase which is formed by the reduction of MnO$_2$ as prepared powders. All the powders were heat treated for 1 hour in reducing atmosphere. XRD data showed the presence of Mn$_2$O$_3$ phase in the heat treated powders. As the heat treatment temperature increased the amount of Mn$_2$O$_3$ phase increased.
SEM images gave the crystal structural and morphology details of the powders prepared through all three techniques. SEM micrographs for powders made from modified solgel technique and reduced KMnO4 technique showed the presence of nano wires in the structure. These nano wires represent the presence of $\beta$- $\text{MnO}_2$ phase. Powders obtained through co-precipitation technique showed spherical particles which represent presence and complete stabilization $\alpha$- $\text{MnO}_2$ phase. At higher temperatures that is at around 300°C complete crystallization of powders is observed in the micrographs. All the powders turned crystalline at 300°C and this can be understood from both XRD and SEM data obtained. As the temperature increased the size of the particles increased which can be seen in the micrographs. As the particle size increases the surface area of the powder decreases affecting the electro chemical response of the powders. Powders obtained through modified sol-gel technique and reduced KMnO4 techniques are in micron scale and the powders obtained through solgel technique are on nano scale. Powders made through co-precipitation technique are very fine and spherical, these features suit best for the pseudo capacitance behavior.

CV data for all the powders was collected using both and pellets and films. Pellets were made to understand the response of the as prepared heat treated powders without any external influence. This data enables us to understand the pseudocapacitive response obtained from manganese oxide powders. Films were made through spin coating technique. PEO/Graphite solution made using partial solution mixing technique is used to make the films. These films showed an enhanced response when compared to the as prepared and heat treated manganese oxide powders. This attributes to the fact that PEO/graphite enhances the capacitive behavior of the composite electrode system. This system now acts like a hybrid super capacitive system where both Manganese and PEO enhances the pseudo capacitance of each other and thereby giving a
much higher response. Powders prepared using co-precipitated technique showed best charge storage behavior out of all three powders used. This is due to the stabilization of $\alpha$- MnO$_2$ phase obtained by using Na in the precursor solution. $\alpha$- MnO$_2$ phase has (2x2) octahedron tunnel structure which gives more room for electrolyte to penetrate in to the electrode system there by showing much higher pseudo capacitive response.

It was observed that the scan rate is inversely proportional to the amount of charge stored. At higher scan rates as the charge discharge cycles are very fast, due to which only the double layer capacitance behavior of the electrode can be seen and minute amount of charge stored due to redox reactions on the surface of the electrode. As the scan rate lowers down the electrode electrolyte interaction time increases which leads to efficient redox reactions and high charge storage. As the scan rate decreases the electrolyte which got penetrated into the electrode gives out response which corresponds to the bulk interaction of the electrolyte with electrode. Due to these interactions as the scan rate decreases the amount of charge stored in an electrode electrolyte system increases.

Temperature directly affects the charge storage ability of the super capacitive systems. This affect is due to the structural modification of the powders with respect to temperature. In all the three systems as the heat treatment temperature increases the amount of amorphous phase decreases and crystallinity increases. This structural change plays a vital role in charge storage behavior of the electrodes. If the powders are completely amorphous the conductivity of the electrode is less and charge storage behavior observed is not ideal. If the powders are completely crystalline the porosity in the structure is minimal and charge storage is not obtained as the structure provides minimum charge transfer resistance.
In this case all three systems showed the formation of secondary phase which aids for the conduction of the powders due to phenomenon called polaron conduction. The amount of Mn$_2$O$_3$ is optimum for temperature ranging from 180- 240˚C. As the temperature increases further completely crystalline Mn$_2$O$_3$ phase is formed which is not suitable for supercapacitive applications.

It was observed that the heat treated and ball milled powders showed a better CV response when compared with just the heat treated ones. The peak positions of the response have changed after ball milling this might be due to functionalization of stannate sites. This shows that ball milling aids for the functionalization which in turn reflects the electro chemical response. Ball milling also reduces the particle size in the powders. Lower the particle size higher is the surface area. As the surface area increases the electrode electrolyte interaction sites increase giving a much higher electro chemical response.

5. SUMMARY

Electrochemical Super capacitors are high energy storage devices and the charge storage occurrence is due to double layer and pseudo capacitance phenomenon. These electrostatic and electrochemical phenomena aid for the production and storage of energy in eco-friendly way. The current study tries to explain the structural dependence on the capacitive behavior of Manganese oxide (MnO$_2$) electrodes. MnO$_2$ powders were synthesized using three different techniques, one of which included the stabilization of alpha MnO$_2$ structure using Na as a stabilizing agent. α- MnO$_2$ is stabilized because it has (2x2) MnO$_6$ tunnel structure whereas β-MnO$_2$ has (1x1) MnO$_6$ tunnel structure. Tunnel size plays a vital role in electro chemical response obtained, as the tunnel size increases the electrolyte can penetrate deeper due to which the electrode electrolyte interaction sites increase. Na salt was incorporated as a precursor salt
instead of adding Na as an external stabilizing agent in the co-precipitation technique to stabilize the \( \alpha \)- MnO\(_2\) structure. Structural and microstructural features of MnO\(_2\) powders produced through co-precipitation, modified sol-gel and reduction of KMnO\(_4\) techniques were compared and the corresponding electrochemical behavior is studied to establish a structural correlation with charge storage. Na\(_2\)SO\(_4\) is used as the electrolyte in the current study instead of traditional H\(_2\)SO\(_4\) which suits the best for manganese oxide systems. The structural correlation to the electrochemical response is studied.

6. CONCLUSIONS:

MnO\(_2\) powders were successfully synthesized using co-precipitation, Modified Sol-Gel and Reduced KMnO\(_4\) technique. Presence of MnO\(_2\) phase alongside minute quantities of other oxide phase was proved using XRD data. \( \alpha \)- MnO\(_2\) phase was successfully stabilized by using NaOH as a precursor solution in the co-precipitation technique and this was proven by the XRD data and the microstructural analysis. Presence of \( \beta \)- MnO\(_2\) phase in the powders produced from modified sol gel technique and reduced KMnO\(_4\) was observed from the XRD and microstructural data. Cyclic voltammetry response of manganese oxide powders produced from co-precipitation technique showed a specific capacitance of 1197 F/g. This high value of charge storage is due to the (2x2) MnO\(_6\) octahedron tunnel structure stabilized by the addition of Na to the system which serves as a \( \alpha \)- MnO\(_2\) phase stabilizer. Layered structure which is usually obtained during co-precipitation technique also aids for the high storage values obtained. Presence of \( \beta \)- MnO\(_2\) structure is powders produced using modified solgel technique and reduced KMnO\(_4\) technique is proven by the presence of nano wires in the microstructural data obtained. Easy and efficient way of producing MnO\(_2\) powders with completely stabilized \( \alpha \)- MnO\(_2\) phase is showcased in the current study. Structural dependence of electrochemical response of the
manganese oxide powders is successfully explained. MnO$_2$ powders produced using modified solgel technique showed a specific capacitance of 824 F/g due to the layered structured formed when Mn(OH)$_2$ was heat treated to form MnO$_2$. Effect of temperature on the charge storage behavior is successfully explained. Effect of scan rate on the charge storage is successfully explained. Importance of electrolyte in the electro chemical response obtained is effectively described.

7. Future Work

- Study on doping the powders with cobalt.
- XPS study to understand the valence changes occurring during the charge discharge cycles on the electrodes.
- Usage of organic electrolyte to increase the potential of application.
References:


5. Holmberg, Sunshine, Alexandra Perebikovsky, Lawrence Kulinsky, and Marc Madou.


46. Chen, Yuanzhen, Yongning Liu, and Wei Yan. "Preparation of Porous (Ni,Co)$_3$(BO3)2/Ni(OH)2 Nanosheet Networks as Pseudocapacitor Materials with


