

# **Synthesis and Characterisation of Manganese Oxide Nanoparticles for Supercapacitor Applications**

*Submitted By*

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*In partial fulfillment for the award of the degree of*

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in  
Physics**



Under the supervision of

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## BONAFIDE CERTIFICATE

This is to certify that this dissertation titled “*Synthesis and Charcterisation of Manganese Oxide Nanoparticles for Supercapacitor Applications*” is a bonafide work carried out by **Muhammed Nihal**, **Register Number NG20CPHR25** in partial fulfillment of the requirement for the award of the degree of Bachelor of Science in Physics under my guidance.

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Examiners

1.....

2.....

## Declaration

I, hereby declare that this dissertation is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning except where due acknowledgement has been made in the text.

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# **Chapter 1**

## **Introduction**

Super capacitor is a potential energy storage device that has been used in various fields like automobile industries, energy harvesting systems, grid stabilizations, solar arrays, Uninterruptible Power Supplies(UPS), electronic devices for back-up memory (SRAM) etc. It is used in regenerative braking system [1] in electric vehicle, trolley busses and electric power transit to generate a fast & smooth acceleration.

### **1.1 Supercapacitors v/s Batteries**

Supercapacitors are promising replacement of batteries. It acts as bridge between batteries and electrochemical capacitors in terms of electrochemical properties. It has excellent power density which reduces the charging period, longer life cycle than batteries and environmentally friendly compared to batteries.

However, super capacitors lack in energy density compared to batteries, hence it is used as a short term energy storage device and hence, efforts are on to synthesize and optimize materials which can provide enhanced energy density, without compromising power density and cycle life.

Batteries generally have excellent energy density in range of 200 Wh/kg to 300 Wh/kg. It excels in energy density as they store charges through the mechanism of redox reactions which takes place in the bulk of the material. Hence, metal oxides are being looked upon as potential candidates for developing supercapacitors as they offer pseudocapacitance through surface redox reactions.

### **1.2 Types of supercapacitors**

Super capacitors are divided into three groups depending on their charge storage mechanisms as:

1. Electric Double – Layer Capacitors (EDLC)
  - EDLC uses carbonaceous material and thus it has splendid stable charge - discharge cycles.
  - High power density & specific capacitance.

- Energy density is lowest among the three types.
- Charge storage: Electrostatically (in the Helmholtz layer)
- To generate electric double layer, carbon based high porosity materials (AC, CNT, Graphene, Carbon aerogels, Carbon foam) are used.

## 2. Pseudo capacitors

- It uses metal oxides or conducting polymer electrodes with a high amount of electrochemical pseudocapacitance.
- Pseudocapacitance is achieved by Faradaic electron charge – transfer with redox reactions, intercalation or electrosorption.
- Poor cycle stability and low power density compared to EDLC.
- High energy density compared to EDLC.
- Charge storage: Electrochemically (Faradaically).

## 3. Hybrid capacitors

- Combination of both EDLC & pseudocapacitors.
- Three types:
  - (i) Assymmetric
  - (ii) Battery type
  - (iii) Composite hybrid
- Use electrodes with differing characteristics, one exhibiting mostly electrostatic capacitance and other mostly electrochemical capacitance.
- Charge storage: Electrostatically & electrochemically.

## 1.3 Components of supercapacitors.

- 1) Electrodes
- 2) Electrolytes
- 3) Separators
- 4) Current collectors
- 5) Binders, etc.

**Electrodes:** Nature and characteristics of electrode material determines the capacity and how well the material supports the charge or energy storage mechanism.

- i) Carbon based materials: Activated Carbon (AC), Carbon Nano Tubes (CNT), Graphene, Carbide Derived Carbon, Carbon foam & Carbon aero gel.
- ii) Metal based materials: Metal oxides, non-metal oxides & conducting polymers.

**Electrolytes:** Five types of electrolytes are used in super capacitors.

- i) Aqueous electrolyte
- ii) Organic electrolyte
- iii) Ionic electrolyte
- iv) Solid state/Quasi solid-state electrolyte
- v) Redox active electrolyte

**Separators:** It is a semi permeable material, which is responsible for ionic charge compensation between the electrodes. It electrically isolates the two electrodes.

**Current Collectors:** It is used to conduct and bridge the flow of electrons between the active material and external battery terminal. Nickel foam, Aluminium foil, Copper foil, Carbon cloth etc. are commonly used as current collectors because of their high current carrying capability, chemical stability and low cost.

**Binders:** A substance used to make other substances or materials stick or mix together is generally termed as a binder. Polyvinylidene fluoride (PVDF) is a common binder used in electrode fabrication being a highly non reactive thermo plastic fluoro polymer.



## Chapter 2

### Literature Review

A number of different synthesis techniques have been employed to fabricate supercapacitors using manganese oxide and its composites as active material. Some of them are discussed below.

There have been multiple previous attempts to study the electrochemical behavior of transition metal oxides (TMOs) and their derivatives as energy storage devices. Over the past decade, research in this area has been primarily focused on increasing the energy density of devices without compromising power density and cycle life. This can be achieved by enhancing the specific capacitance (F/g) and using electrolytes with wide operating potential window (V). Great emphasis is laid on the optimization of related parameters during sample preparation and cell fabrication.

Among TMOs, RuO<sub>2</sub> having a very high theoretical capacitance of 1,300 - 2,200 F g<sup>-1</sup> is the first reported and one of the widely studied pseudocapacitive materials [2]. However, high cost, low abundance and toxic nature limits its use practically [3]. Hence, the current research focus is on other transition metal oxides which are cost effective and environmentally benign.

The exceptionally high theoretical specific capacitance (~ 1370 Fg<sup>-1</sup>) [4], low cost, nontoxic nature and high natural abundance make manganese oxides as one of the promising candidates to overcome the limitations of ruthenium oxides [5-7]. Of the transition metals, Mn has the greatest number of oxidation states, most of which have a special tunnel structure that enables bulk redox reactions [8]. Diverse crystal morphologies such as nanospheres [9], nanorods [10], nanowire [10], nanoflowers [11], nano urchin [9] etc. and the associated variation in electrochemical properties exhibited by them offers the possibility of designing novel electrode materials with desirable energy storage characteristics. Owing to the existence of Manganese oxide in several phases and crystallographic forms such as MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, MnO etc., research on manganese oxides is challenging yet promising. Moreover, the low intrinsic electron conductivity of manganese oxides is an issue to be addressed [12].

## Chapter 3

### Experimental Techniques

#### 3.1 Preparation Method.

Several methods have been developed to synthesis manganese oxide nanoparticles like sol gel process, hydrothermal process, low pressure spray pyrolysis, simple liquid phase process and other techniques. Among various methods for controlled synthesis, Solution Combustion method was used here to synthesis Manganese Oxide nanoparticles. In this method, different parameters like the nature of the fuel and oxidizer, fuel to oxidizer ratio, reaction temperature and concentration of the initial solution have important role on getting powders with desired shape and size.

##### 3.1.1 Solution Combustion Synthesis

Solution combustion synthesis (SCS) has emerged as an attractive technique for the production of homogeneous, high-purity, and crystalline oxide powders at significantly lower temperatures than that of the conventional synthesis methods. SCS as a complex self-sustained chemical process, which takes place in a homogeneous solution of precursors. SCS starts with dehydration and thermal decomposition of the homogeneous solution of an oxidizer and a fuel and involves several thermally coupled exothermic reactions, which result in the formation of at least one solid product and a large amount of gas. Typical oxidizers are hydrated metal nitrates, while fuels represent a broad range of compounds including urea, glycine, citric acid, etc.[13]

##### 3.1.2 Synthesis of Manganese Oxide by Solution Combustion Method

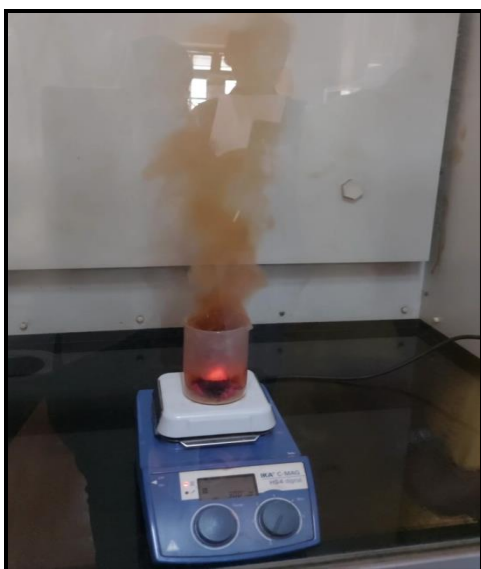
Manganese nitrate  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Emsure, 98% pure) and Urea  $\text{NH}_2\text{CONH}_2$  (Loba Chemie, 98% pure) were used as the oxidiser and fuel respectively to synthesise manganese oxide nanoparticles by solution combustion method. Manganese Nitrate Tetrahydrate is accurately weighed to about 2.517 g using an analytical balance. It is then dissolved in 3 ml of de ionized water. 1.4040 g of urea, is also weighed in an analytical balance. It is then dissolved in 10 ml of water. These

two precursors were mixed together and is magnetically stirred to get a homogenous solution.

This mixture is then heated in fume hood. The solution is heated initially at 50°C for five minutes. Then the temperature is raised to 100°C and boiled for five minutes. The vapors formed around the beaker are continuously cleaned using a soft tissue paper. It is observed that the solution was heated well and the elimination of vapors turned the solution into the form of a gel.

Then the temperature is raised to 200°C and then to 300°C until the mixture exceeds the ignition temperature of the reaction and combustion occurred. This reaction was ignited in a flaming manner. The entire process of combustion took around 35 minutes. The final black products were collected, powdered well using a pestle and mortar and denoted as “NITU-1”. It is then taken for X-Ray Diffraction (XRD) with radiation of wavelength 0.15406 nm. The XRD patterns were recorded using Rigaku software.

The as prepared sample was then calcined at 450°C for around one hour in the muffle furnace and labeled as “NITU-1B”. The PXRD of the sample was obtained once again.



(a)



(b)

**Figure 1:** (a) Solution-combustion synthesis of manganese oxide (b) Calcination in muffle furnace

### **3.1.3 Preparation of the electrode.**

The manganese oxide sample prepared by solution combustion method was used as the active material (AM), acetylene black as the conducting material (CM) and polyvinylidene fluoride (PVDF) as binder (BM) to prepare the ink. AM, CM and the BM were weighed in the ratio 8:1:1. The AM and CM were mixed well in a mortar. The binder was dispersed in N-Methyl-pyrrolidone (NMP) and was sonicated for 15 minutes. The binder dissolved in NMP was added drop by drop with constant stirring to the mixture of AM and CM taken in a mortar, until a homogeneous, ink like slurry is obtained.

The as-prepared ink containing manganese oxide as the active material was coated onto a pre-cleaned Nickel foam (1 cm x 2 cm) and dried in hot air vacuum oven at 60°C for sixteen hours. The nickel foam was weighed before and after coating to obtain the mass loading of the electrode material. This manganese coated nickel foam was used as the working electrode in Cyclic Voltammetry (CV) analysis.

## **3.2 Characterisation**

The structural characteristics of the Manganese Oxide sample synthesized by solution combustion method were studied by using XRD technique. Electrochemical (Supercapacitor) properties were studied by employing CV technique.

### **3.2.1 X-ray Diffraction Techniques**

X-ray diffraction (XRD) is one of the powerful methods for the study of nanomaterials. X-rays have the wavelength on the atomic scale, so X-ray diffraction (XRD) is a primary tool for examining the structure of nano-materials. XRD offers exceptional accuracy in the measurement of atomic spacing and is the technique of choice for determining strain states in thin films. The intensities measured with XRD can provide quantitative, accurate information on the atomic arrangements at interfaces. With lab-based equipment, surface sensitivities down to a thickness of  $\sim 50\text{\AA}$  are achievable, but synchrotron radiation allows the characterization of much thinner films and for many materials, monoatomic layers can be analyzed.

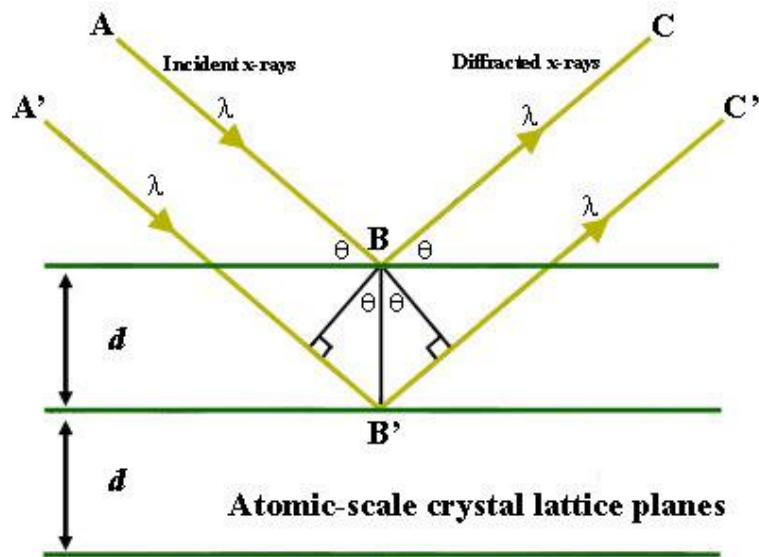
In X-ray diffraction work, we normally distinguish between single crystal and polycrystalline or powder applications. The single crystal sample is a perfect (all unit cells aligned in a perfect extended pattern) crystal with a cross section of about 0.3 mm. Powder diffraction is mainly used for various solid materials, e.g. asbestos, quartz. In powder or polycrystalline diffraction, it is important to have a sample with a smooth plane surface. If possible, we normally grind the sample down to particles of about 0.002 mm to 0.005 mm cross section. The ideal sample is homogeneous and the crystallites are randomly distributed. The sample is pressed into a sample holder so that we have a smooth flat surface.

A typical powder XRD instrumentation consist of four main components such as X-ray source, receiving optics, specimen stage and X-ray detector. The detector and source with its associated optics lie on the circumference of focusing circle and the sample stage at the center of the circle.

Bragg's law is the basis of XRD analysis. With this law it is possible to make accurate measure of experimental results in the determination of crystal structures. The angle between the X-ray source and the plane of the specimen is taken as  $\theta$ , known as Bragg's angle and the angle between the detector and the projection of X-ray is  $2\theta$ .

A typical diffraction spectrum consists of a plot of reflected intensities versus the detected angle  $2\theta$ . For the XRD analysis, fine powder samples are mounted on the sample holder and the powder is assumed to consist of randomly oriented crystallites.

When a beam of X-ray is incident on the sample, X-rays are scattered by each atom in the sample. If the scattered beams are in phase, these interfere constructively and one gets the intensity maximum at that particular angle. The atomic planes from where the X-rays are scattered are referred to as 'reflecting planes'.



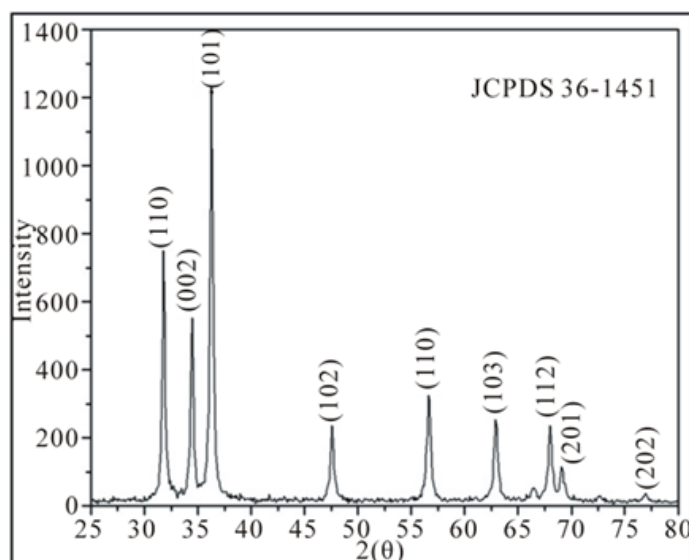
**Fig 3.1** Schematic diagram of Bragg's law

The Bragg's law relates the wavelength ( $\lambda$ ) of the reflected X-ray, the angle of diffraction ( $\theta$ ) and the spacing between the atomic planes ( $d$ ) as follows:

$$2d \sin \theta = n \lambda \quad (1)$$

The angle between the transmitted and diffracted beams will always be equal to  $2\theta$ . This angle can be obtained readily in experimental situations and the results of X-ray diffraction are therefore given in terms of  $2\theta$ . It is however very important to remember that the angle that is used in the Bragg's equation must correspond to the angle between the incident radiation and the diffracting plane, i.e.  $\theta$ . For the first order diffraction,  $n = 1$ , and knowing  $\theta$  and  $\lambda$ , one can calculate the interplanar spacing  $d$ -value for a particular plane.

A lot of information can be obtained from an XRD pattern. A schematic of XRD pattern and a diffractometer is shown below.



**Fig 3.2** Schematic XRD spectrum of ZnO



**Fig 3.3** Rigaku Miniflex 600 X-Ray Diffractometer.

The powder diffraction data consists of a record of photon intensity versus detector angle  $2\theta$ .

The peaks in the graph show the Bragg reflection from different planes of atoms. Only for certain planes the Bragg condition is satisfied. These planes can be determined by several methods, depending on the structure of sample.

For a known material, there is a standard database maintained by the International Center for Diffraction Data (ICDD) or Joint Committee on Powder Diffraction Standards (JCPDS) for the identification of organic and inorganic materials with a crystal structure. We can identify the unknown materials by comparing their diffraction patterns and the database. Also, the XRD pattern can be

used for (a) estimating crystalline size (b) Identification of crystalline phases and their degree of crystallization and (c) Residual strain. The most common wavelength used in XRD is 1.54 Å which is the wavelength of Cu K $\alpha$ . We used Rigaku Miniflex 600 with Cu K $\alpha$  line of 1.54056 Å.

The average crystallite size of nanoparticles can be calculated using Scherrer formula which is given below.

$$D = K \lambda / \beta \cos\theta \quad (2)$$

Where;

D - the average particle size,

$\lambda$  - the is wave length of the radiation

$\beta$  - the FWHM (full width at half maximum) of the reflection peak

K - Scherrer constant

$\theta$  - Bragg's angle of the peak

The Scherrer constant (K) in the formula accounts for the shape of the particle and is generally taken to have the value 0.9. The FWHM is obtained by fitting a Gaussian profile to each of the peaks in the XRD pattern. The size obtained from the Scherrer formula yields the apparent or average particle-size for a material. Powders of materials are generally aggregates of smaller particles, and thus consist of a distribution of particle sizes.

### 3.2.2 Cyclic Voltammetry (CV)

The normal method to carry out material capacitance measurements is to coat the material onto an inert substrate like nickel foam, then measure this electrode in the chosen electrolyte using electrochemical cyclic voltammetry and record cyclic voltammograms of the material. In the present work, CV curves were recorded using the NOVA Software 2.1.4 provided with the Metrohm Autolab PGSTAT 302N Potentiostat/Galvanostat in the three-electrode configuration. The prepared sample coated on Nickel foam was used as the working electrode (WE), Ag/AgCl as the reference electrode (RE) and Platinum wire as the counter electrode (CE). 3 M KOH



was used as the electrolyte. CV curve was obtained for a scan rate of 0.005 Vs<sup>-1</sup> within a potential window from -0.1 V to 0.5 V. The specific capacitance C<sub>s</sub> (F/g) was calculated using the equation,

$$C_s = Q/m\Delta E \quad (3)$$

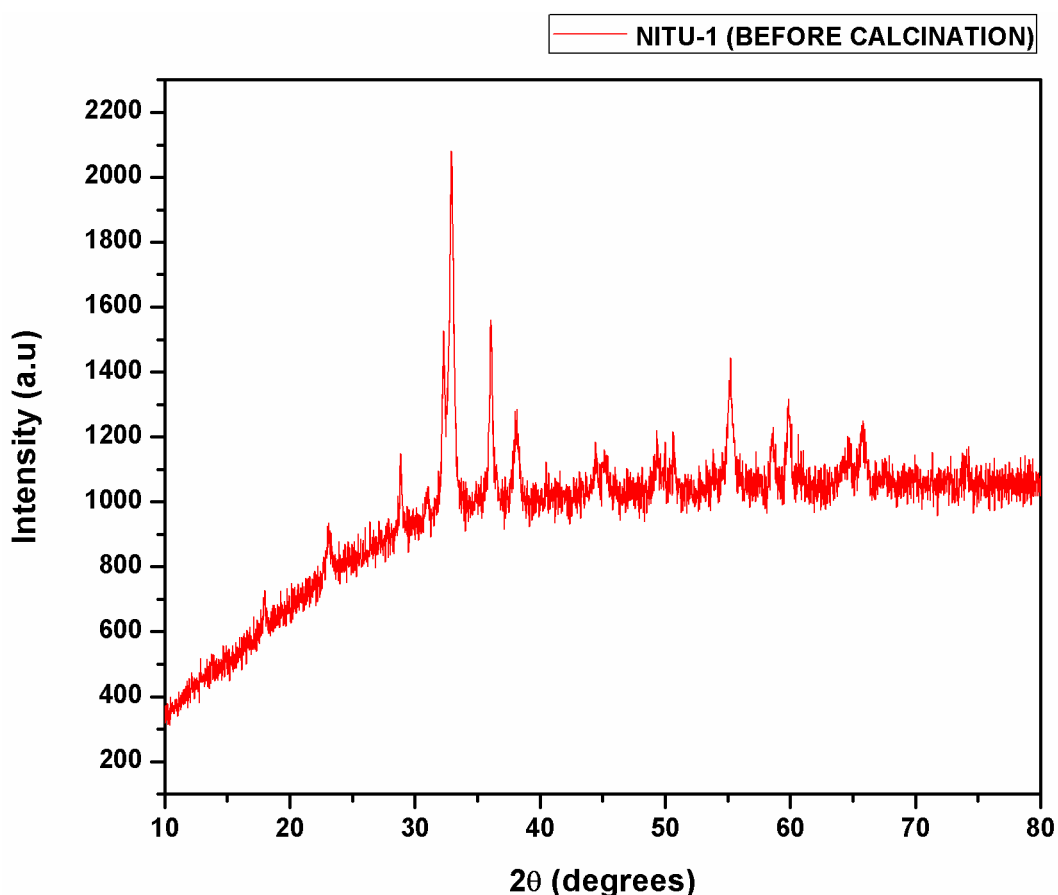
where, Q is the charge accumulated inside the electrode layer given by the area under the cyclic voltammogram in either direction in a potential window, m is the mass loading of the electrode,  $\Delta E$  is the potential window[14].

## Chapter 4

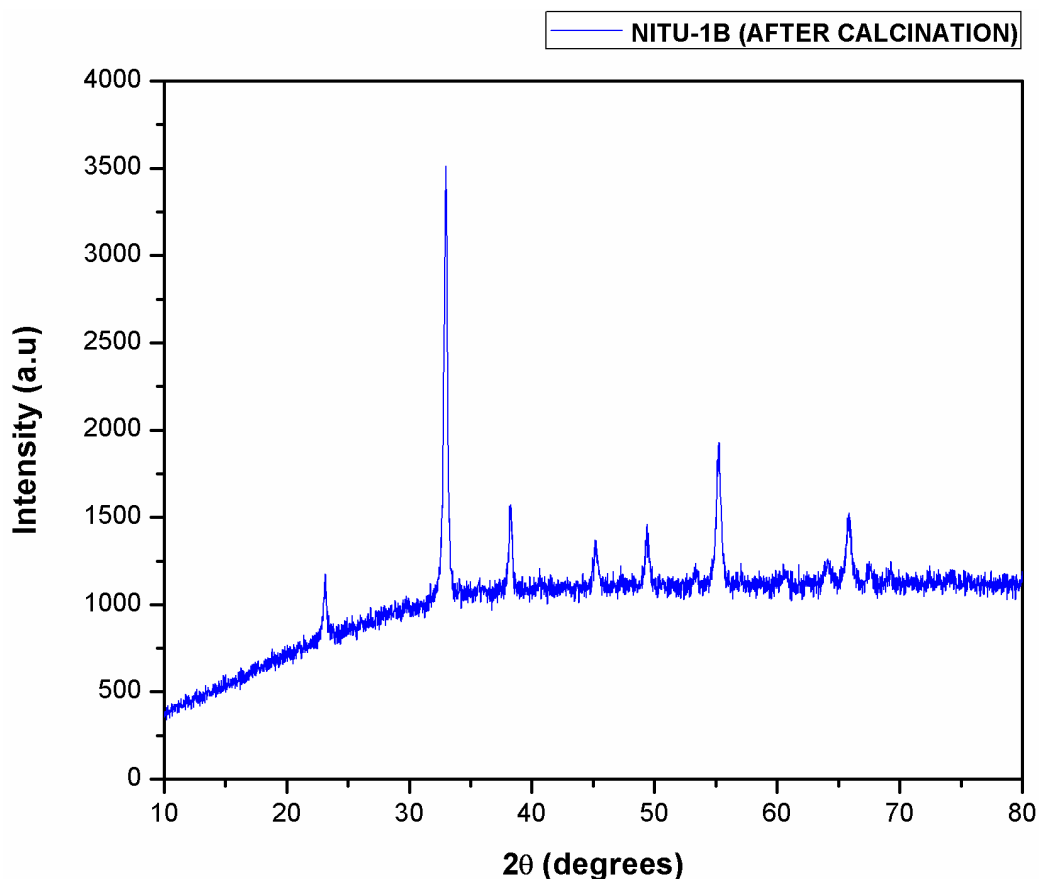
### RESULTS AND DISCUSSION

#### 4.1 PXRD Analysis:

The crystallinity and phase composition of the sample were investigated by X-ray powder diffraction method using Rigaku Miniflex 600 with Cu K $\alpha$  line of 1.54 Å. Data were collected over a range of  $2\theta$  of 20° - 80° with a step 0.02 and scan speed of 2°/min. The diffraction pattern of the as prepared sample obtained is shown in fig. 4.1. Prominent peaks are observed at 32.9°, 55.2° and 59.8° which are in good agreement with the characteristic peaks of cubic  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> phase. The peak at 36.1° corresponds to Mn<sub>3</sub>O<sub>4</sub>, whose intensity is low [15]. The XRD analysis thus confirmed the formation of a mixed phase of Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> nanoparticles.



**Figure 4.1.** PXRD pattern of Manganese oxide sample before calcination.



**Figure 4.2.** PXRD pattern of Manganese oxide sample after calcination at 450°C.

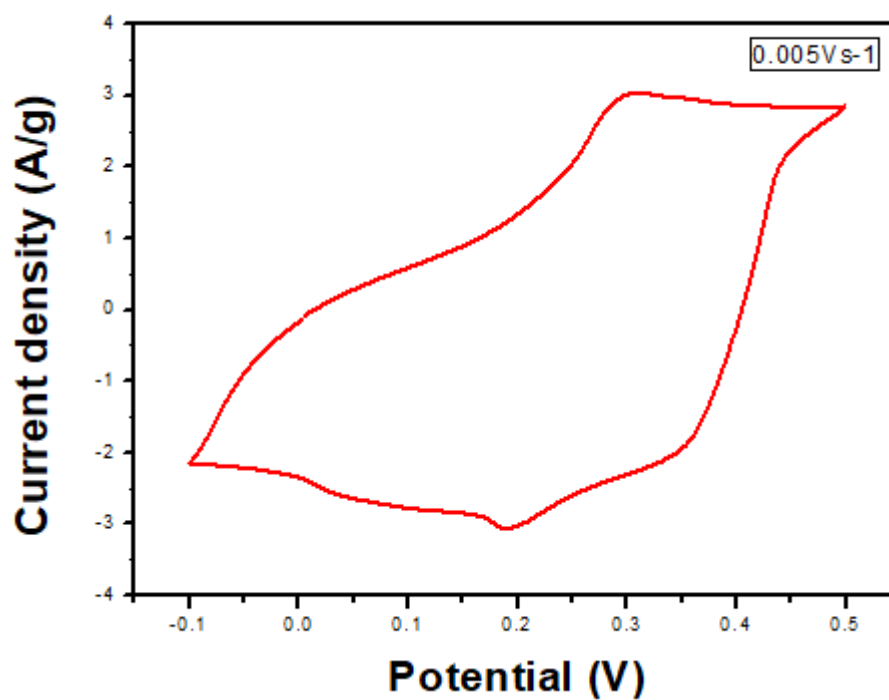
After calcination, prominent PXRD peaks are observed at 23.2°, 32.9°, 38.26°, 55.2° and 65.84° which is different from that of the as prepared sample. Absence of the characteristic peak at 36.1° indicates that the impurity phase of  $\text{Mn}_3\text{O}_4$  has been converted into  $\alpha\text{-Mn}_2\text{O}_3$  following calcination. The observed peaks are in good agreement with the JCPDS Card No.78-390 corresponding to that of  $\alpha\text{-Mn}_2\text{O}_3$ .

The average crystallite size of the as prepared (before calcination) manganese oxide nanoparticles calculated using equation (2) is 23.8 nm, whereas the size increased to 25.32 nm, following calcination at 450°C. The increase in average crystallite size is attributed to the possible agglomeration of particles on calcination. The PXRD results also indicate that thermal treatment has a significant influence on the phase composition of the product.

## 4.2 Cyclic Voltammetry

Cyclic voltammetry (CV) test was employed to characterize the supercapacitor performance of the prepared electrode.

Fig. 4.3 shows the cyclic voltammogram of the prepared electrode with a sweep rate of  $0.005 \text{ Vs}^{-1}$  in a potential range between  $-0.1 \text{ V}$  and  $0.5 \text{ V}$  (vs.  $\text{Ag}/\text{AgCl}$ ). The area under this curve represents the voltammetric charge accumulated during a cycle. The specific capacitance of the electrode corresponding to a mass loading of  $0.00232 \text{ g}$  calculated using equation (3) gives  $226.70 \text{ Fg}^{-1}$ .



**Figure. 4.3.** Cyclic Voltammogram of the  $\text{MnO}$  electrode at a scan rate  $0.005 \text{ Vs}^{-1}$

## Chapter 5

### Conclusion

Supercapacitors provide promising solutions to future energy storage requirements. A variety of methods and materials are available for the development of supercapacitors. Among the various electrode materials manganese oxide characterized by high capacitance, low cost, abundance and environment friendly nature has emerged as a promising candidate. The full potential of manganese oxide based electrochemical supercapacitors has not been realized yet, but innovative manufacturing process have been developed to make chemical and structural modifications to manganese oxide materials to introduce more electrochemically active sites.

This work focussed on understanding the concept of supercapacitors with an emphasis on the solution-combustion synthesis of Manganese oxide nanoparticles and the study of supercapacitive behaviour of the electrode fabricated using the prepared sample.

Nanocrystalline  $\alpha$ - $\text{Mn}_2\text{O}_3$  samples with the average crystallite size of around 24 nm were synthesized by solution combustion method followed by calcination at 450°C and studied by X-ray diffraction to evaluate their structure and phase composition. It was observed that the sample synthesized at a fuel to oxide ratio of 1.4 (fuel rich condition) contained mainly of  $\alpha$ - $\text{Mn}_2\text{O}_3$  phase with trace amount of  $\text{Mn}_3\text{O}_4$  as an impurity phase. Upon calcination at 450°C, pure  $\alpha$ - $\text{Mn}_2\text{O}_3$  was obtained. The electrochemical properties of the  $\alpha$ - $\text{Mn}_2\text{O}_3$  sample were probed by cyclic voltammetry and the specific capacitance was obtained as 226.70  $\text{Fg}^{-1}$  at a scan rate of 0.005  $\text{Vs}^{-1}$ , confirming the charge storage ability of the prepared sample.

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