SYNTHESIS AND CHARACTERIZATION OF MnO₂ and NiO₂ FOR SUPERCAPACITOR APPLICATIONS

M.Sc. Thesis

By ANJALI CHAUDHARY



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SYNTHESIS AND CHARACTERIZATION OF MnO₂ and NiO₂ FOR SUPERCAPACITOR APPLICATIONS

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Submitted in partial fulfilment of the Requirements for the award of the degree

Of

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By

ANJALI CHAUDHARY



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "SYNTHESIS AND CHARACTERIZATION OF MnO₂ and NiO₂ FOR SUPERCAPACITOR APPLICATIONS" in the partial fulfilment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2016 to June 2017 under the supervision of Dr. Parasharam M. Shirage, Associate Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date

(Anjali Chaudhary)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Signature of the Supervisor of M.Sc. thesis

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ABSTRACT

The basic key points for an electrode of a supercapacitor are porous structure and high electrochemical surface area. Keeping this in mind, in this work we have successfully synthesised MnO₂ and NiO₂ over Nickel foam using a facile and efficient hydrothermal method and first time reporting the supercapacitor application. Ni foams show a good morphological porous structure of compromising rods and flower type that is a key parameter for supercapacitor studies. As the high surface area has been manifested as an important and necessary parameter in supercapacitor to store the charges, these structures provides efficient electrochemical surface area which is anticipated as a reason for good value of specific capacitance.

The physio-chemical characterization of synthesized material was carried out by X-ray diffractometer (XRD) which shows the purity of the material, Field Emission Gun Scanning Electron Microscope (FESEM) showing the rod and flower shape structure and electrochemical performance was carried out by Cyclic Voltammetry (CV), Galvanostatic Charging Discharging (GCD) and Electrochemical impedance Spectroscopy (EIS) methods. CV analysis shows a specific capacitance of 2229 F/g at a scan rate of 1mV/s and 1833 F/g at a current density of 10mA, which proves that the synthesised material is suitable for the supercapacitor application.

LIST OF PUBLICATION

Comparative Study with a Unique Arrangement to Tap Piezoelectric Output to Realize a Self-Poled PVDF Based Nanocomposite for Energy Harvesting Applications, M. Pusty, A. Sharma, L. Sinha, A. Chaudhary, P. Shirage, Chemistry Select, (2017), 2, 2774-2782

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Acronyms

β	Beta
α	Alpha
Cu	Copper
BSE	Backscattered
WE	Working Electrode
CE	Counter Electrode
RE	Reference Electrode
CV	Cyclic Voltammetry
DC	Direct Current
AC	Alternating Current
EIS	Electrochemical Impedance Spectroscopy
GCD	Galvanostatic Charging Discharging
%	Percentage
Ni	Nickel

CHAPTER 1: INTRODUCTION

1.1 Introduction:

Demand for energy consumption has significantly increased because of the rapid growth of population and global economy. Based on the surveys on total world energy consumption conducted by Energy Information Administration (EIA), fossil fuels (petroleum, coal, natural gas, etc.) make up the bulk of the world's current primary energy sources. The scarcity of fossil fuels generated an intensive search for alternative natural energy sources. Sustainable and renewable energy sources have attracted great interest nowadays due to the decrease of natural reserves. Therefore, the possibility to collect energy from wind, sun, water etc. is a subject of extensive research. ^[1, 2]A big drawback of these sources is the time periodicity of energy generation, for example a change of sunlight from day to night and wind is not blowing continuously. An important intermediate step ^[3, 4] between these energy resources and versatile energy application is energy storage and thus has attracted significant attention. The introduced batteries, even with recent modifications, do not have the desired efficiency in applications; specifically the full charge/discharge time takes up to an hour, which is too long for electronic systems. ^[5, 6]This problem can be overcome by supercapacitors.

Energy crisis and environmental pollution have triggered the development of clean and renewable energy storage systems. Supercapacitors, also called electrochemical capacitors, are a novel type of charge energy storage devices in between traditional capacitors and batteries. Compared with traditional capacitors, supercapacitors possess higher specific capacity and specific energy. Meanwhile, they exhibit higher specific power, shorter charging time, more efficient discharging than batteries, and they cause no pollution in the environment. Although their energy density is 10 to 50 times lower than lithium ion batteries now, supercapacitors with a near unlimited cycle life are useful in the

field of power system, memory storage, and vehicle assistant equipment.

The search of new materials for electrodes of Supercapacitor is growing attention in terms of energy storage applications. The introduced batteries, even with recent modifications, do not have the desired efficiency in applications; specifically the full charge/discharge time takes up to an hour, which is too long for electronic systems. This problem can be overcome by supercapacitors. A major shortcoming of current supercapacitors is their low energy density (typically 5-10 Wh/kg), ^[7, 8] lower than the batteries. Supercapacitors are more useful for energy related application if their energy density can be increased. Their performance can be increased by modifying the structure of the material of electrode used.

So the material that has large power density as well as can store enough large amount of energy seems to be very novel for supercapacitor applications. They are known to be supercapacitor since the mechanism by which they can store charge is different from that of batteries and ultracapacitors. They physically store the charge by the formation of electrochemical double layer or ^[7, 8] by faradaic reactions which gives them a high value of power density and longer life.

For example, combining a supercapacitor and a battery in a single unit can create an electric vehicle with longer life, lower costs and more power. Based on the principle of energy storage, supercapacitors can be classified into electric double layer capacitors (EDLCs) ^[9, 10] and pseudo-capacitors. EDLCs store charges using the very thin double layer structure formed at the interface between electrode and electrolyte, while pseudo-capacitors use fast and reversible redox reactions on the surface and bulk near the surface of electrodes for energy storage. Compared with EDLCs, pseudo-capacitors capacitors exhibit higher capacitance and higher energy density.

A supercapacitor consists of electrode, electrolyte and separator, where electrode plays a key role for the performance of supercapacitor. It is a crucial task to explore electrode materials with excellent performance. According to the work principle of pseudo-capacitors, electrode materials and electrolyte should contact effectively, meanwhile, ions/charges should transport fast in the bulk of electrode and at the interface between electrode and electrolyte in order to achieve excellent properties. Therefore, transition metal oxides with mesopores ^[11, 12] (between 2 and 50 nm) are favourable for building supercapacitors with high performance due to their large specific surface area and suitable pore size distribution.

Transition metal oxides and hydroxides are proven to be good materials for pseudo capacitors. According to reported literature individually MnO₂ and NiO₂ show good value of specific capacitance (nearly 600 F/g and 800 F/g respectively) but there mixture on Ni substrate ^[13, 14] has not been reported till now. So to explore the properties of both the material on Ni foam this work has been done to measure various characteristics which support its use in supercapacitor. In this thesis MnO₂ and NiO₂ materials synthesis on Ni foam with simple and economical method is carried out.

CHAPTER 2: EXPERIMENTAL TECHNIQUES

2.1 Material Synthesis:

2.1.1 Treatment of Nickel foam:

Several Nickel foams (1cm x 1cm) were treated using conc. HCl (20% dilution), acetone with the assistance of ultra-sonication in order to remove dirt and oxidation film from the surface of Nickel foam ^[15, 16]. Then deionized water was used to wash them several times. After that, Ni foams were dried and mass of Ni foam has been measured using weighing balance.

2.1.2 Preparation Method:

Firstly, (S1) 125 mg Manganese Nitrate Hydrate ($Mn(NO_3)_2.xH_2O$), 250 mg Nickel Nitrate Hexahydrate ($Ni(NO)_3.6H_2O$), 4.4 mg Urea, 5.5 mg Ammonium Chloride (NH_4Cl), 0.2 g CTAB (Hexadiethyltrimethylammonium Bromide, $C_{19}H_{42}BrN$) were added in 70 mL solvent containing 40 mL deionized water and 30 mL ethanol ^[17, 18]. Then the solution was kept for stirring on magnetic stirrer for 60 minutes.

A Teflon coated autoclave was washed properly and cleaned using ethanol and distilled water. Then dry it using dryer.

After that the treated Ni foam (two) along with the solution were placed in Teflon coated autoclave. The autoclave was sealed and maintained at temperature of 90°C for 4 hours and subsequently raised the temperature to 110°C for 10 hours. Next the autoclave was cooled ^[19, 20] to room temperature. Take the Ni foam out of the autoclave and washed it with deionized water to remove ions. Then it is dried ^[22, 23]. The difference of mass of Ni foam initially and after deposition gives the amount of mass deposited on Ni foam. These deposited Ni foam were used for various characterization and measurement. (S2) An another solution containing 125 mg Manganese Nitrate Hydrated (Mn (NO₃)₂.xH₂O), 4.4 mg Urea, 5.5 mg Ammonium Chloride (NH₄Cl), 0.2 gm. CTAB (Hexadiethyltrimethylammonium Bromide, C₁₉H₄₂BrN) were added in 70 mL solvent containing 40 mL deionized water and 30 mL ethanol. Again the solution was kept for stirring for 60 minutes. After that two Ni foams were placed in Teflon and repeat the same procedure as earlier for this solution also.



Fig.2.1.1 Various Steps involved in the preparation process, (a) Ultrasonication of Nickel foam, (b) Weighing of chemicals, (c) Magnetic stirring of prepared sample, (d) Setup of autoclave with solution and Ni foam, (e) Autoclave placed in a furnace for a particular set of time.

2.2 Structural Techniques:

2.2.1 X-Ray Diffraction (XRD):

Principle:

In 1913 W.H. and W.L. Bragg ^[24, 25] found that substances whose macroscopic forms were crystalline diffract the x-rays when fall upon them. It is because the spacing of atoms of crystalline solids is comparable to the wavelength of x-ray that is the required condition for the diffraction to occur.

Crystalline solids act as a diffraction grating for x-rays and constructive interference of monochromatic x-rays and crystalline sample thus gives a diffraction pattern.

In 1895 ^[26, 27] Wilhelm Roengten found that a highly penetrating radiation of unknown nature is produced when fast electrons impinge on matter. These radiation (known to be x-rays) were found to be unaffected by electric and magnetic fields, to pass readily through opaque materials.

The faster the original electrons, the more penetrating the resulting x-rays and greater the number of electrons, the greater the intensity of x-ray beam.

The x-ray spectrum consists of Bremsstrahlung (Braking radiation) and Characteristic x-ray (radiation involving the transition of inner shell electrons). ^[26, 27]



Fig.2.2.1 X-Ray Spectrum showing the variation of number of x-rays with x-ray energy.



Fig.2.2.2 (a) and (b) shows Different ways by which high energy electron interact with an atom and give rise Bremsstrahlung, characteristic X-ray and Auger electron ejection.



Fig.2.2.3 Diffraction of X-ray by a crystal lattice due to the periodicity of the crystal.

Light rays of wavelength λ incident on a crystal at an angle Θ whose crystal planes are separated by a distance "*d*".

The total path difference travelled by the wave from incidence to detection is

=N'B'+B'N

 $= BB'Sin\Theta + BB'Sin\Theta$

=dSin Θ +d Sin Θ

 $=2dSin\Theta$

For the constructive interference to occur, the total path difference should be an integral multiple of the wavelength of the incident light. i.e.,

 $2dSin\Theta = n\lambda$

Where n is an integer.

This law known as Bragg's law of diffraction which relates the interplanar spacing of the crystal to the wavelength of light used. ^[4, 5]

Instrumentation:

X-ray Diffractometer consists of three parts:

1. X-ray tube: It usually contains filament tube (containing cathode to eject electrons, metal target) which produces X-rays.

- 2. Sample Holder
- 3. Detector



Fig.2.2.4 Bruker D8 XRD apparatus showing the position of sample holder, source of x-ray and detector.

The X-rays are produced in cathode ray tube by heating filament to produce electrons, accelerate the electrons towards the target by applying electromagnetic field and bombarding the target material with electrons.



Fig.2.2.5 Schematic diagram of X-ray Diffractometer which shows how x-ray is diffracted by passing through the sample and then detected by a detected by x-ray detector.

When electrons have sufficient energy to dislodge inner shell electrons of target material, characteristic spectra of X-rays are produced. The spectra consists of several components of rays, the most common are K_{α} and K_{β} lines. Copper is the most common material used for production of X-rays with Cu-K_{α} radiation of wavelength 1.5418 A°, ^[28, 29] these X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the crystal satisfies the Brag's condition then diffraction peak occurs which is recorded.

In X-ray diffraction pattern, positions of the peaks gives information about the size and shape of unit cell of the sample while intensity of the peaks reveals about atomic position within the unit cell.



2.2.2 Field Emission Scanning Electron Microscopy (FE-SEM):

Fig.2.2.6 Various Components of Field Emission Scanning Electron Microscope.

FE-SEM is one of the most widely used instruments in material research. It is heavily used for microstructural characterization. In this technique, electrons are used instead of light waves to see the microstructure of surface of a specimen. However since electrons are excited to high energy (KeV), so wavelength of electron waves quite small and resolution is quite high. The electromagnetic lenses ^[29, 30] used in it are not a part of image formation system, but just helps to focus the electron beam on specimen surface.

This gives two of the major benefits of SEM: range of magnification and depth of field in the image, giving three dimensional information of image. In a typical SEM, electrons are thermionically

Emitted from a tungsten or lanthanum hexaboride (LaB₆) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 Kev, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5µm [33, 34] into the surface. The size of the interaction volume depends on the beam accelerating voltage, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation which can be detected to produce an image, as described below.

The most common imaging mode monitors low energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometres from the surface. The electrons and electromagnetic radiation which can be detected by a scintillator-photomultiplier device and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a Digital image. This process relies on a raster-scanned primary ^[35, 36] beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus

steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three dimensional appearance. Using this technique, resolutions of 1 nm are possible. Backscattered electrons consist of high energy electrons originating in the electron beam that are reflected or back scattered out of the specimen interaction volume. Backscattered electrons may be used to detect contrast between areas with different chemical compositions, especially when the average atomic number of the various regions is different, since the brightness of the BSE image tends to increase with the atomic number. This image can be used to determine the crystallographic structure of the specimen.

There are fewer backscattered electrons emitted from a sample than secondary electrons. The number of BSE leaving the sample surface might be significantly lower than those follow trajectories toward the sides. In contrast, with the case with secondary electrons, the collection efficiency of BSE cannot be significantly improved by a positive bias common on Everhart-Thornley detectors. ^[37, 38]This detector positioned on one side of the sample has low collection efficiency for backscattered electrons due to small acceptance angles.



Fig.2.2.7 FE-SEM instrument setup in laboratory.

2.3 Electrochemical Techniques:

2.3.1 Cyclic Voltammetry (CV):

Voltammetry is a category of electrochemical methods used in analytical chemistry. In voltammetry, information about an analyte is obtained by measuring current as a function of potential.

Amperometry is a kind of analysis by which we can measure the various values of voltages ^[42, 29] as a function of applied current.

A. 1) there are four electrodes which we will use for measurement of any electrochemical process. These electrodes are following:

1. Working Electrode: It is the electrode in an electrochemical process on which the reaction of interest is occurring. Working electrode can be made of inert materials such as Au, Ag, Pt and film electrodes etc. For corrosion applications, the material for working electrode is the material under investigation (which is actually corroding). The size and shape of the working electrode also varies and it depends on application.

2. *Counter/Auxiliary electrode:* It is an electrode which is used to close the current circuit in the electrochemical cell. It is usually made of an inert material (e.g. Pt, Au, graphite, glassy carbon) and usually it does not participate in the electrochemical reaction. Because the current is flowing between the 'WE' and the 'CE', the total surface area of the 'CE' must be higher than the area of the 'WE' so that it will not be a limiting factor in the kinetics of the electrochemical process under investigation.

3. *Reference Electrode:* It is an electrode which has a stable and wellknown electrode potential and it is used as a point of reference in the electrochemical cell for the potential control and measurement. The high stability of the reference electrode potential is usually reached by employing a redox system with constant concentrations of each participants of the redox reaction. Moreover, the current flow through the reference electrode is kept close to zero (ideally, zero) which is achieved by using the 'CE' to close the current in the cell together with a very high input impedance on the electrometer.

Reference electrode ^[36, 40] is an electrode used as a half cell to build an electrochemical cell. This allows the potential of other half to be determined. SHE (Standard Hydrogen Electrode), Standard Calomel electrode, Silver-Silver Chloride electrode is generally used as reference electrode as they remain unaffected during the whole electrochemical process.

4. Sense (S): It is mostly connected along with working electrode.

5. *Ground Connection:* This electrode is usually of green colour and connected to dummy cell while measurements are taken.



Fig.2.3.1 Various Electrodes of Auto lab Instrument whose combination can be used as three or two electrode system for various electrochemical processes.

A. 2) There are two types of electrode system that are practically use for various electrochemical measurements e.g. CV, EIS, GCD and chronoamperometry etc.

A.2.1 Two Electrode Setup: In a two-electrode setup, 'CE' and 'RE' are shorted on one of the electrodes while the 'WE' and 'S' are shorted on the opposite electrode. The potential across the complete cell is measured. This includes contributions from the CE/electrolyte interface and the electrolyte itself. The two-electrode configuration can therefore be used whenever precise control of the interface potential across the 'WE' electrochemical interface is not ^[25, 32] critical and the behaviour of the whole cell is under investigation. This setup is typically used with energy storage or conversion devices like batteries, fuel cells, photovoltaic panels etc. It is also used in measurements of ultrafast dynamics of electrode processes or electrochemical impedance measurements of high frequencies.

A.2.2 Three electrode setup: The three-electrode cell setup is the most common electrochemical cell setup used in electrochemistry. In this case, the current flows between the 'CE' and the 'WE'. The potential difference is controlled between the 'WE' and the 'CE' and measured between 'WE' and 'RE'. This is frequently used as compared to two electrode setup because in this the voltage between 'RE' ^[37, 39] and 'WE' electrode is not affected because of the presence of 'CE' as it passes all the current through it.



Fig.2.3.2 Combination of various electrodes to form three electrode and two electrode system.

In Cyclic Voltammetry experiment, the working electrode is ramped linearly versus time. Unlike in linear sweep voltammetry after the set potential is reached in a CV experiment, the working's electrode potential is ramped in the direction to return to its original value. These cycles of ramp may be repeated as many time as you want by changing the values of number of repetitions in CV staircase profile. The rate of change of voltage during each phase is known as scan rate.

In Cyclic Voltammetry we used three electrode setup and we measure the values of voltage and current with different values of scan rate. After that as plot was plotted in ORIGIN and area was calculated for measurement of specific capacitance value.

Capacitance is given by charge divided by voltage and it is termed to be specific when divided by mass. ^[26, 30] Charge can be written as a product of current and time. The Specific capacitance is given by the formula $C = \frac{1}{mv\Delta V} \int IdV$ where, C is specific capacitance, m is deposited mass, v is scan rate, ΔV is potential window, and $\int I dv$ is the area of the I-V graph plotted from the data received.

It can be seen that with increasing scan rate the value of specific capacitance decreases.



Fig.2.3.3 Autolab instrument with the setup arrangement of electrode contained in 1M KOH solvent in a three electrode system.

2.3.2 Electrochemical Impedance Spectroscopy (EIS):

When the conduction is only by electrons then it is easy to measure the resistivity and thus conduction (as it is a reciprocal of resistivity). In a DC conductivity measurement process, current from a DC source should flow through the sample and the potential difference that develops across the sample must be measured. Using Ohm's law the resistance of the sample can be determined, and then using the dimensions of the sample, [3,4] the conductivity can be determined using the relationship

R = V/I

 $\rho = R * A/l$

Where, R is the resistance

V is the potential difference

I is the current

A is the area of cross section

ρ is the resistivity of material

But in AC conductivity charge carriers are electrons as well as ions. The challenge in measuring ionic conductivity is that most of our measuring instruments such as voltmeters and ammeters use electron as charge carriers.



Fig.2.3.4 Phasor diagram of Inductor showing that voltage is ahead of current in phase by 90° and Phasor diagram of Capacitor showing that voltage is lag of current in phase by 90°.

EIS is a tool to measure AC conductivity, in this the concept of Resistance is replaced by Impedance (consists of Resistance, Inductor, Capacitor). In capacitive circuit current leads voltage by 90° whereas in inductive circuit current lags voltage by 90°. Thus when we measure the impedance of a circuit a phase angle will come into the picture with the application of sinusoidal voltage.

 $V(t)=V_{o}\sin \omega t$

V(t) is the potential at time t, V_o is the amplitude of the signal and ω is the ^[4, 5] radial frequency. The relationship between radial frequency ω and frequency *f* is expressed as

 $\omega = 2\pi f$

In a linear system, the response signal, the current I(t), is shifted in phase (Θ) and has a different amplitude

 $I(t)=I_{o}sin(\omega t+\Theta)$

An expression analogous to Ohm's law allows us to calculate the impedance, given as Z(t)=V(t)/I(t)

= $V_o \sin \omega t / I_o \sin (\omega t + \Theta)$

= $Z_0 \sin \omega t / \sin (\omega t + \Theta)$

The impedance is thus represented by magnitude Z_o and a phase shift Θ .



Fig.2.3.5 Nyquist plot (variation of real impedance on x axis with the imaginary impedance on y axis).

EIS is a recent tool in corrosion and solid state laboratories that is slowly making its way into the service environment as units are decreased in size and becomes portable.

The usefulness of EIS lies in the ability to distinguish the dielectric and electric properties of individual contributions of components under investigation. EIS is a non-destructive technique and so can provide time dependent information about ongoing processes such as corrosion, discharge of batteries. Only disadvantage it has the complex data analysis for quantification. Impedance with a magnitude and phase shift can be written as

$$= Z_{o} (\cos \varphi + i \sin \varphi)$$

The expression of Z is composed of a real and an imaginary part. If the real part is plotted on X axis and the imaginary part on Y axis, we get a "Nyquist Plot".

On the Nyquist Plot the impedance can be represented as a vector of length |Z|. The angle between this vector and the X axis is *f*.

Nyquist plots have one major shortcoming. ^[12, 13] When you look at any data point on the plot, you cannot tell what frequency was used to record that plot. This shortcoming was overcame by using Bode plot in which log frequency is plotted on X axis and both the absolute value of impedance and phase shift on Y axis



Fig.2.3.6 Bode plots (variation of logarithmic of impedance in a circuit with logarithmic of frequency)

Variation of phase (φ) *with logarithmic of frequency.*

2.3.3 Galvanostatic Charging Discharging (GCD):

It is a type of electrochemical measurement technique by which one can evaluate the specific capacitance value by passing a constant value of current through the electrode, ^[12, 38] then measures the time the electrode required to charge to a particular potential (cut off potential) and then also calculating the time it required to discharge to come to zero potential.

The value of specific capacitance can be calculated with the help of GCD curve using the formula C= I Δ T/M Δ V,

Where I is current, ΔT is discharging time, M is the mass deposited, ΔV is the potential.

Galvanostatic refers to an experimental technique ^[28, 35] whereby an electrode is maintained at a constant rate in an electrolyte. This technique is used to measure corrosion rate and electrochemical reactions.

Galvanostatic like potentiostatic and potentiodynamic, ^[27, 41] is a polarization technique that allows for the controlled polarization of metal/ electrode surfaces in electrolytes, in order to directly observe cathodic and anodic behaviour.

In Galvanostatic test, the change is plotted in potential versus time at constant current.

In Galvanostatic mode, the current between working electrode and counter electrode is controlled. In potentiostatic mode, potential of CE against WE is controlled so as the potential difference between WE and RE is measured.

Chapter 3: RESULTS AND DISCUSSION 3.1. STRUCTURAL PROPERTIES:

3.1.1. XRD (X-Ray Diffraction):



Fig.3.1.1 XRD pattern of samples S1, S2 and Ni foam showing the diffraction peak at various scattering angles.

The crystal structure of the as prepared films was examined by X-ray diffraction (XRD). The XRD patterns were recorded in a Rigaku Smart Lab, Automated Multipurpose x-ray diffractometer with Cu K α radiation ((λ) =0.154nm) from 10 to 80. Fig 3.1.1 shows the XRD pattern of (*c*) only

Ni foam, (b) MnO_2 deposited over Ni foam and (c) mixture of both MnO_2 and NiO₂ over Ni foam, which is deposited by hydrothermal method at temperature 90°C for 4 hours followed by 110°C for 10 hours.

The determined characteristic 2 Θ values and (*hkl*) planes of all the three samples are given in the table below. The values are confirmed with the respective JCPDS Card.

Ni Fo	oam	MnO ₂ (S	52)
2 0	(hkl)	20	(hkl)
(degree)		(degree)	
44.58	(110)	22	(110)
51.77	(200)	31.15	(101)
76.36	(220)	55.25	(211)

Table 3.1.1 Diffraction angle (Θ and (hkl) values of Ni foam and MnO_2 (Sample S2).

MnO ₂ and NiO ₂ (S1)						
2Θ (degree)	(hkl)					
22	(110)					
31.15	(101)					
55.25	(211)					
37.86	(-111)					
50.05	(-203)					

Table 3.2. 2 Diffraction angle (Θ and (hkl) values of NiO₂ and MnO₂ (Sample S1).

Fig.3.1.1 (c), shows the XRD pattern of pure Ni foam. The peaks with their corresponding planes as written in the table 1 can be indexed to pure Ni face centered cubic (fcc) structure [space group-fm-3m (225), JCPDS 04-0850].

Fig.3.1.1 (b) represent the XRD pattern of MnO₂ and their corresponding planes as written in table 1 confirms the deposition of MnO₂ on Ni foam. The peaks can be indexed to pure tetragonal phase [space group-42/mnm (136)] of MnO₂ [JCPDS 10-0713]. The values of lattice parameters of MnO₂ are a=b=4.44 Å, c=2.89Å and $\alpha=\beta=\gamma=90^{\circ}$

Fig. 3.1.1 (a) displays the deposition of both the structure MnO₂ and NiO₂ on Ni foam. The peaks with their corresponding planes *i.e.*, 22.00°, 31.15°, 55.25° (please see table 2) of the MnO₂ can be indexed to pure tetragonal phase [space group-42/mnm (136)]of MnO₂ [JCPDS 10-0713], The values of lattice parameters of MnO₂ are a=b=4.44 Å, c=2.89Å and $\alpha=\beta=\gamma=90^{\circ}$ and the peaks at 37.86°, 50.05°) (table 2) of NiO₂ can be indexed to pure monoclinic phase [space group-c2/m(12), JCPDS 89-8397] of NiO₂ and the lattice parameters are a=4.85Å, b=2.81Å, c=5.58Å and $\alpha=\gamma=90^{\circ}$, $\beta=125.836^{\circ}$.

So the above results confirms that the MnO_2 and NiO_2 materials are formed in phase pure.

3.1.2. FE-SEM (Field Emission Scanning Electron Microscopy):

FE-SEM analysis is done on Field- Emission Scanning Electron Microscope (FE-SEM), Supra55 Zeiss. In fig. 3.1.2, we observe that MnO_2 and NiO_2 that are formed have agglomerated and the particle size is in nanometer range.



Fig.3.1.2 FE-SEM images of sample S1 (a) 288X (b) 17.42 KX (c) 1.88 KX (d) 6.2 KX (e) 10.72 KX (f) 11.89 KX.

The FE-SEM images indicates the flower like structure with highly porous nature of the material, which is one of the essential parameter for the supercapacitor applications. Please note that higher the surface area, higher the specific capacitance expected due to large amount of charge storage in electrochemical performance. From above figure, it is very clear that our samples are highly porous in nature with large surface area 95 m²/g, which were confirmed by BET measurements.



Fig.3.1.3 FE-SEM images of sample S2 (a) 14.11 KX (b) 19.27 KX.

Fig. 3.1.3 shows that the agglomeration of nanorods takes place along with the flakes type structure which gives high surface area ($35 \text{ m}^2/\text{g}$) and accessible surface for the electrolytic ions to interact with the electrodes surface during the electrochemical reaction.

From above FE-SEM image it is clear that MnO_2 and NiO_2 composite has more surface area than MnO_2 materials hence, the high electrochemical performance is expected from sample-S1.

3.2 ELECTROCHEMICAL PROPERTIES:

3.2.1. Cyclic Voltammetry (CV):

CV analysis of both samples were done in a potential window of -0.2V to 0.6V at various scan rates ranging from 1mV/s to 50 mV/s. The electrolyte used for both samples was 1M KOH (Potassium Hydroxide) prepared in 50mL distilled water. The samples were kept in a 1X1 holder of a stainless steel electrode that works as a working electrode. Calomel electrode was used as a Reference electrode while Platinum electrode was used as a Counter/Auxiliary electrode in a three electrode electrochemical cell system. Then various electrochemical measurements (CV, EIS, GCD, and Stability Test) were carried out.



Fig. 3.2.1 CV curve of sample S1 showing the cyclic voltammograms at 1 mV/s, 2 mV/s, 5 mV/s, 10 mV/s, 20 mV/s, 30 mV/s, 40 mV/s, 50 mV/s with potential window of -0.2 to 0.6 V.



Fig. 3.2.2 CV curve of sample S2 showing the cyclic voltammograms at 1 mV/s, 2 mV/s, 5 mV/s, 10 mV/s, 20 mV/s, 30 mV/s with potential window of -0.2 to 0.6 V.

Current between the sample and platinum electrode was plotted against \mathbf{Y} axis and potential of working electrode v/s standard calomel electrode was plotted against \mathbf{X} axis and then area was calculated using ORIGIN software.

The Specific Capacitance is given by the formula $C = \frac{1}{mv\Delta V} \int IdV$ where, C is specific capacitance, m is deposited mass, v is scan rate, ΔV is potential window, and $\int I.dV$ is the area of the I-V graph plotted from the data received. It can be seen that with increasing scan rate the value of specific capacitance decreases. Generally when we increase the scan rate, we are increasing the electronic field within the cell setup, which will alter both faradaic and non-faradaic processes. As the scan rate increases the diffusion of electrolyte ion into electrode internal structure and pore become difficult (diffusion limitation) and ineffective interaction between the electrolyte and electrode materials occurs therefore the specific capacitance is decrease.

Sr. No.	Scan rate	Mass	Mathematical	Specific
	(V/s)	deposited	Area (m ²)	Capacitance
		(g)		(F / g)
1	0.001	0.0014	0.0002	2229.29
2	0.002	0.0014	0.0048	2163.10
3	0.005	0.0014	0.0011	1978.13
4	0.01	0.0014	0.0193	1727.92
5	0.02	0.0014	0.0325	1451.04
6	0.03	0.0014	0.0415	1237.14
7	0.04	0.0014	0.0462	1031.85
8	0.05	0.0014	0.0488	872.21

 Table 3.2.1 Comparison of Specific Capacitance v/s Scan Rate of sample S1.

In table 3.2.1, specific capacitance of S1 sample at various values of scan rate is represented with its mathematical area. With increasing value of scan rate, specific capacitance decreases according to the formula

$$C = \frac{1}{m\nu\Delta V} \int I dV.$$

S. No.	Scan	Mass	Mathematical	Specific
	Rate	Deposited	Area (m ²)	Capacitance
	(V/s)	(g)		(F / g)
1	0.001	0.002	0.0017	1068.15
2	0.002	0.002	0.0024	753.12
3	0.005	0.002	0.0044	571.25
4	0.01	0.002	0.0058	368.12
5	0.02	0.002	0.0065	205.93
6	0.03	0.002	0.0062	130.62

Table 3.2.2 Comparison of specific capacitance v/s scan rate of sample S2.

From table 3.2.2, comparative study of S2 sample was done to measure the values of specific capacitance at various scan rates. It can be easily shown from the above tables that the sample that contains both MnO_2 and NiO_2 deposited on Ni foam has higher values of specific capacitance 2229.29 F/g (nearly two times) as compared to MnO_2 deposited on Ni foam 1068.15 F/g. Both MnO_2 and NiO_2 deposited on Ni foam have a large surface area which contributes to high value of specific capacitance of sample.

Whereas formation of MnO_2 has less surface area than S1, thus the electrodes made from MnO_2 deposited on Ni foam has lesser specific capacitance in comparison with S1. These results demonstrates that S1-sample (Surface area ~95 m²/g) has two times higher capacitance than S2 (Surface area ~35 m²/g) sample due to higher surface area.



Fig. 3.2.3 Plot of specific capacitance v/s scan rate of (a) S2 and (b) S1 sample.

From the fig.3.2.3 it can be easily shown that in S1, specific capacitance gradually decreases with scan rate as compared to S2, indicating S1 sample is much better for supercapacitor applications.

3.2.2 Galvanostatic Charging Discharging (GCD):



Fig.3.2.4 GCD curve of sample S1 with cutoff potential of 0.45 V at current of 10 mA, 12 mA, 14 mA, 15 mA, 18 mA, 20 mA and 30 mA.

In fig.3.2.4, the GCD cycles of sample S1 is shown at current 10mA, 12mA, 14mA, 15mA, 18mA, 20mA and 30mA. At all values of current the value of cut-off voltage is 0.45 Volt. At 10mA, the discharging time is nearly 118 seconds, at 12mA the discharging time is nearly 68 seconds, at 14mA the discharging time is nearly 56 seconds, at 15 mA the discharging time is nearly 51 seconds, at 18mA the discharging time is 41 seconds, at 20mA the discharging time is nearly 36seconds and at 30mA the discharging time is nearly 21 seconds.

The value of specific capacitance can be calculated with the help of GCD curve using the formula $C = I\Delta T/M\Delta V$,

Where I is current, ΔT is discharging time, M is the mass deposited, ΔV is the cut-off potential. The value of specific capacitance calculated using CV curve and GCD curve is nearly same to some extent.



Fig.3.2.5 GCD curve of sample S2 with cutoff potential of 0.45 V at current of 10 mA, 12 mA, 14 mA, 15 mA, 16 mA, 18 mA and 20 mA.

In fig.3.2.5, the GCD curve of sample S2 is shown at current values of 10mA, 12mA, 14mA, 15mA, 16mA, 18mA and 20mA. At all values of current the cut-off potential is 0.45Volt. At 10mA the discharging time is nearly 40 seconds, at 12mA the discharging time is nearly 31 seconds, at 14mA the discharging time is nearly 25 seconds, at 15mA the discharging time is nearly 20 seconds, at 16mA the discharging time is nearly 19 seconds, at 18mA the discharging time is nearly 16 seconds and at 20mA the discharging time is nearly14 seconds.

The value of specific capacitance is also calculated using GCD curve in this case and it quiet resemble to values calculated using CV curves using the formula $C = I\Delta T/M\Delta V$.

S.No.	I (A)	T2 (s)	T1 (s)	ΔT (s)dis	Mass	ΔV	Specific
					Deposited	(V)	Capacitance
					(g)		(F / g)
1	0.01	247	131	115	0.0014	0.45	1833.49
2	0.012	142	73	68	0.0014	0.45	1296.95
3	0.014	116	60	55	0.0014	0.45	1242
4	0.015	106	55	51	0.0014	0.45	1215
5	0.018	84	43	40	0.0014	0.45	1154
6	0.02	73	38	35	0.0014	0.45	1118.09
7	0.03	44	23	20	0.0014	0.45	991.90

Table 3.2.3. Specific capacitance calculated using charging discharging cycle of sample S1.

In table 3.2.3, I is the current, T2 and T1 denotes for initial and final values of time on discharging curve, ΔT is the discharging time, M is the mass deposited on the sample and ΔV is the cut-off potential. For various values of current, specific capacitance is calculated using discharging time, cut-off potential and mass deposited in units of Farad/gram. With increasing value of current, specific capacitance decreases since specific capacitance depends on the product of current and discharging time, not alone on the value of current. Two factors will decide the value of specific capacitance at a particular value of current.

S.No.	I(A)	T1(s)	T2(s)	ΔT(s)dis	Mass	$\Delta V(V)$	Specific
					Deposited		Capacitance
					(g)		(F/g)
1	0.01	145	184	39	0.002	0.45	439.11
2	0.012	116	146	30	0.002	0.45	410
3	0.014	98	123	25	0.002	0.45	392
4	0.015	79	99	19	0.002	0.45	321.67
5	0.016	77	95	18	0.002	0.45	321.78
6	0.018	109	126	16	0.002	0.45	330

 Table 3.2.4. Specific capacitance calculated using charging discharging cycle of sample S2.

In table 3.2.4, I is the current, T2 and T1 denotes for initial and final values of time on discharging curve, ΔT is the discharging time, M is the mass deposited on the sample and ΔV is the cut-off potential. For various values of current, specific capacitance is calculated using discharging time, cut-off potential and mass deposited in units of Farad/gram. With increasing value of current, specific capacitance decreases since specific capacitance depends on the product of current and discharging time, not alone on the value of current. Two factors will decide the value of specific capacitance at a particular value of current. In this we do not get a close relation of specific capacitance value calculated using CV curve with that of GCD curve.



3.2.3 Electrochemical Impedance Spectroscopy (EIS):

Fig. 3.2.6 Nyquist plot of sample S1 showing the variation of imaginary impedance value with real impedance value.

In order to understand the superior performance of the electrode material, comparative EIS study was performed before and after CV in frequency range 10 mHz 100 kHz at AC potential bias of 10mV. The solution resistance (R_s) is due to the cumulative effect of ionic resistance of electrolyte, intrinsic resistance of electrodes and diffusion of ions. Whereas the charge transfer resistance (R_{ct}) is due to electronic resistance of electrode material and contact resistance at various interfaces.

In after CV Nyquist Plot, the imaginary part of impedance increases more rapidly as compare to that of before CV Nyquist Plot, which is due to typical more capacitive behaviour of the electrode after the experiment because of formation of double layer on both electrodes and thus increases its capacitive behaviour.



Fig. 3.2.7 Nyquist plot of sample S2 showing the variation of imaginary impedance value with real impedance value.

The EIS plot of sample S2 was also taken in order to understand the superior performance of the electrode material, comparative EIS study was performed before and after CV in frequency range 10 mHz 100 kHz at AC potential bias of 10mV. The solution resistance (R_s) is due to the cumulative effect of ionic resistance of electrolyte, intrinsic resistance of electrodes and diffusion of ions. Whereas the charge transfer resistance (R_{ct}) is due to electronic resistance of electrode material and contact resistance at various interfaces.

In Nyquist Plot of before and after CV experiments, there is not so much difference in their impedance behavior, at higher frequencies there is slight difference in their capacitive behavior.

3.2.4 Stability Test:

Stability test for Charging and Discharging Cycles were performed in order to test its performance so that it can be used further for making energy storage devices. It was initially designed for 500 cycles, but stopped after 300 cycles as the performance of the electrode was degrade with number of cycles. The electrolyte used was 1M KOH (Potassium Hydroxide) in 50 mL of distilled water. The fig. 3.2.8, below shows the stability test for sample S1 for 300 cycles.



Fig. 3.2.8 Stability curve of sample S1 showing the variation of efficiency with number of charging discharging cycles.

				Specific		
S. No.	T2(s)	T1(s)	ΔT(s)dis	(Fg-1)	No.Of Cvcles	%age
	((, g .
1	2518	2467	51	1375	25	95.5
2	5322	5269	53	1440.21	50	100
3	8061	8009	52	1413.04	75	98.1
4	10777	10725	52	1413.04	100	98.1
_		1.0000	~~		105	0.0.1
5	14041	13989	52	1413.04	125	98.1
6	1(200	1(22)	50	1412.04	150	00.1
6	16288	16236	52	1413.04	150	98.1
7	20475	20427	48	1304.34	175	90.6
8	21269	21221	48	1304.34	200	90.6
9	23996	23950	46	1250	225	86.8
10	26118	26071	47	1277.17	250	88.7
11	28486	28441	45	1222.82	275	84.9
12	30784	30740	44	1195.65	300	83.1

Table 3.2.5. % efficiency of specific capacitance with number of cycles ofsample S1.

In table 3.2.5, the specific capacitance of the sample was calculated with the help of GCD curves using the formula C= $I\Delta T/M\Delta V$, where the symbols have their usual meanings.

The (S1) sample that was deposited on Nickel foam was 1.4 mg, cut off potential was set to 0.45V at a current of 10mA to test the stability of the sample against charge discharge cycle in order its lifetime that it can withstand when we use the electrode for making the device.

It can be easily concluded from the table that the specific capacitance is at maximum after 50 cycles which is 1440.21F/g and then its value decreased to 98.1% up to 150 cycles and after that its value continuously decreasing and it retained to 83.1% of its original value (1440.21 F/g) after 300 cycles which may be due to material degradation in the solvent (1 M KOH in 50 mL distilled water) or due to decrease in electrical conductivity of the deposited material on the Ni substrate or due to low adhesion between Ni substrate and the material that was deposited using hydrothermal deposition method.



Fig. 3.2.9 Stability curve of sample S2 showing the variation of efficiency with number of charging discharging cycles.

S.No.	T2(s)	T1(s)	$\Delta T(s)$ dis	Specific	No. of	%age
				Capacitance (F/g)	Cycles	
1	53	81	28	317.2	25	95.2
2	1509	1539	30	333.3	50	100
3	3070	3100	30	333.3	75	100
4	4640	4670.2	30	333.3	100	100
5	6210	6240	30	333.3	125	100
6	7780	7808	28	311.1	150	93.3
7	9349	9377	28	311.1	175	93.3
8	10939	10966	27	300	200	90
9	12540	12567	27	300	225	90
10	14077	14104	27	300	250	90
11	15739	15765	26	288.8	275	86.6
12	17335	17360	25	277.7	300	83.3

Table 3.2.6. % efficiency of specific capacitance with number of cycles ofsample S2.

The (S2) sample that was deposited on Nickel foam was 2.0 mg, cut off potential was set to 0.45V at a current density of 10mA/g to test the stability of the sample against charge-discharge cycle in order its lifetime that it can withstand when we use the electrode for making the device.

It can be easily concluded from the table 3.2.6 that the specific capacitance is at maximum after 25 cycles, remain to this value up to 125 cycles, then its value decreased to 93.3% up to 175 cycles and after that its value continuously decreasing and it retained to 83.1% of its original value after 300 cycles.

Chapter 4: SUMMARY, CONCLUSION AND FUTURE SCOPE

Summary:

In recent times, Nanostructured electrode materials based supercapacitors have become remarkable because of their superior rate property and efficiency than conventional (carbon) materials. The transport of ions become simple once the distance between the electrode and electrolyte becomes smaller. Recently, transition metal oxides, carbon materials and conducting polymers have been comprehensively accepted as electrode materials with outstanding capacitive properties. Very recently, composites of metal oxides and carbon nanotube (MWNTs) materials have fascinated extensive recognition based on the combination of the distinctive properties of both individual materials and their great cooperative effects for electrode materials of supercapacitors. Here this master thesis we have carried out MnO₂ and NiO₂ based supercapacitance measurements. The summary of the work carried out as follows:

- The S1 (MnO₂ and NiO₂) and S2 (NiO₂) samples are prepared by using simple and economical hydrothermal method on nickel foam.
- The XRD patterns of S1 and S2 samples reflect that the prepared materials are phase pure.
- SEM results indicates formation of flower like morphology in S1 sample while rod like morphology in S2 sample. S1 sample has surface area of 95 m²/g and S2 sample has surface area 35 m²/g.

- The electrochemical performance studied using CV reveal the specific capacitance of samples S1 and S2 are 2229 F/g and 1068 F/g, respectively. While taking the advantage of charging discharging time, specific capacitance of the samples were 1833 F/g and 1439 F/g, respectively.
- From GCD curves repeated nearly for 300 cycles, the samples' efficiency reduces to 83% at the end of 300 cycles.

Conclusion:

- An electrode for supercapacitor application (MnO₂ and NiO₂ deposited on Ni foam substrate) was prepared successfully using simple and economical hydrothermal method in pure form.
- The composite of MnO₂ and NiO₂ shows very high specific capacitance (2229 F/g), reflecting that this is promising material for the future supercapacitor device fabrication.

My Learning and understanding through the project work:

- The powdered as well as film samples were prepared using various methods (chemical bath deposition method, hydrothermal deposition method, electrochemical deposition method).
- Understanding the mechanism of various methods involved in the sample preparation.
- Structural and morphological characterization has been done using XRD and SEM.
- Electrochemical characterization (CV, EIS, GCD, Stability test) has been done using Auto lab instrument.

Future Scope:

Present work deals with synthesis of electrode material for supercapacitor application and its characterization has been done using XRD, SEM, and Auto lab instrument. There are some possible scopes to extend this work further in future as:

- > Maximize the stability of the electrode material
- Design a device using the electrode and then use it to measure its energy and power density.

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