Synthesis and Characterization of Nano-Material for Supercapacitor Application

M.Sc. Thesis

By

Rohit Yadav



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2018

Synthesis and Characterization of Nano-Material for Supercapacitor Application

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree of Master of Science

By

Rohit Yadav



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2018



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Synthesis and Characterization of Nano-Material for Supercapacitor Application** 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 2018 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 (Rohit Yadav)

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 (**Dr. Parasharam M. Shirage**)

Convener, DPGC

Rohit Yadav has successfully given his M.Sc. Oral Examination held on 22 June 2018.

Signature of Supervisor of MSc thesis Date:

Signature of PSPC Member Date: **Dr. Krushna R. Mavani** Signature of PSPC Member Date: **Dr. Santosh S. Hosmani**

Date:

Dedicated to;

My Country

And

My Teachers and Parents

Acknowledgements

It is always an immense pleasure to remind the fine people for their sincere support and encouragement I received to uphold my project work. This work will not have been completed without their kind help.

I take this opportunity to express my deep sense of thank and profound gratitude to my supervisor, **Dr. Parasharam M. Shirage** for giving me opportunity to work in AFMRG. His exemplary guidance, monitoring and constant encouragement helped me in successful completion of this work well on time. I am thankful to my PSPC members Dr. Krushna R. Mavani and Dr. Santosh Hosmani, for their valuable suggestions which helped me to enhance my experimental skills.

I am deeply indebted to Prof. Pradeep Mathur (Director, Indian Institute of Technology, Indore) for allowing me to carry out my research in this institution. I greatly appreciate the support and motivation of all physics department of IIT Indore.

I am heartily thankful to Dr. Mahesh Verma and Mr. Prateek Bhojane for their kind support and help to accomplish my project successfully. I extend my thanks to complete AFMRG lab for their kind help throughout the project work. I am highly thankful to SIC, IIT Indore for FESEM and XRD measurements as without their support this report would not have been possible.

I am in short of words in expressing my heartful gratitude to my family who paved the path before me upon whose shoulders I stand. To my parents, sisters and brothers, for their continuous support, encouragement and motivation in every phase of life, I won't be this strong without you all as my inspiration.

Rohit Yadav

Abstract

With the constantly increasing worldwide need for energy, fossil-based fuels (coal, petroleum, and natural gas) as our main energy sources are rapidly decreasing, while their combustion is increasing the output of greenhouse gases and other pollutants in our environment. Therefore, there is an urgent need to seek renewable clean energy sources like, solar energy, wind energy etc. as alternatives. Energy storage devices are employed to reduce the rate of mismatch between energy source and energy demand. Although great efforts have been made on development of high performance Li-ion batteries and fuel cells in the past, high maintenance cost and the slow power capability have kept them away from applications. Recently, supercapacitors have drawn attention because of their high charge storage capacity, long life cycle and outstanding power density. Thus considering the importance of the supercapacitors as energy storage devices, in the present project proposal, it is aimed to focus on the synthesis and characterization of nanostructured materials for the supercapacitor applications. Electrode materials possessing the high capacity, long cycling stability, and excellent rate capability are highly desirable, also surface area plays a very crucial role since charges are stored on the surface. The aim of this project is to obtain nanomaterial of high surface area with controlled surface morphology for supercapacitor application.

Here we report the synthesis and supercapacitive property of Nickel sulphide, Cobalt sulphide and Manganese Sulphide (NiCoMnS) composite nanostructure synthesized by fast, cost-effective and facile electrochemical technique. Physio-chemical characterizations were carried out such as; X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) for phase purity, surface morphology of electrode material and particle size distribution.

The electrochemical measurements were carried out by cyclic (CV). galvanostatic charging-discharging voltammetry (GCD), electrochemical impedance spectroscopy (EIS). The synthesized material exhibits enhanced electrochemical performance in 2M KOH electrolyte, CV exhibits the specific capacitance of 5420 Fg⁻¹ at 1 mVs⁻¹ scan rate and GCD exhibits 5008.08 Fg^{-1} at a current density of $5Ag^{-1}$. The material shows an excellent stability and capacitive retention of 48% after 3500 cycles at a current density of 100 Ag^{-1} . Moreover, excellent energy density of 36 Wh/kg and power density of 24975 W/kg has been Hence these electrochemical results of NiCoMnS calculated. nanostructured composite demonstrate its application for energy storage devices at high current density.

List of Publication

List of paper published/submitted:

 Mahesh Verma, Rohit Yadav, Lichchhavi Sinha, Sonal Mittal, Sawanta S Mali, Chang Kook Hong, Parasharam M Shirage*, "Hierarchical Interconnected Nanosheets of Nickel Cobalt Manganese Sulfide (NiCoMnS) Synthesized by Electrodeposition for Realizing High Capacitance, Rate Capability and Bifunctional Electrocatalytic Behavior for Overall Water Splitting Combining HER and OER" (under review scientific journal: Advanced Functional Materials).

Awards:

- Best poster presentation award at Material Research Society of India Symposium 2018 on 'Advances in Functional and Exotic Materials' at Bharathidasan University, Tiruchirappalli.
- Best poster presentation award at International Workshop on Advanced Nanoscience and Engineering, 2017 at IIT Indore.

Table of Contents

List of Figures	XI
List of Tables	XII
Acronyms	XIII

Chapter 1: Introduction 1

1.1 Nanotechnology	6
1.2 Electrodeposition	7
1.3 Transition Metal Sulphide Based Electrode	9

Chapter 2: Material Synthesis & Characterization

Techniques	11
2.1 Treatment of Ni foam	11
2.2 Compound Synthesis	11
2.3 Characterization Techniques	14
2.3.1 X-ray diffraction	14
2.3.2 FE-SEM	16
2.3.3 TEM	19
2.3.4 Cyclic Voltammetry	20
2.3.5 Electrochemical Impedance Spectroscopy	23
2.3.6 Galvanostatic Charging Discharging	25
Chapter 3: Results & Discussion	27
3.1 XRD Analysis	27

5.1 /MCD / Midry 515	21
3.2 FE-SEM Analysis	29
3.3 TEM Analysis	30
3.4 Electrochemical Analysis	31
3.4.1 CV Analysis	31

3.4.2 GCD Analysis	34
3.4.3 Stability Analysis	35
3.4.4 EIS Analysis	36
3.4.5 Energy density & Power density	38
Chapter 4: Conclusion and Scope for Future Work	41
Chapter 4: Conclusion and Scope for Future Work 4.1 Conclusion	41 41

List of Figures

Fig.1.1	Schematic diagram of types of supercapacitors	5
Fig.1.2	Charging and discharging of electric double layer supercapacitor (EDLCs)	6
Fig.1.3	Simple electrodeposition using 2-electrode system	9
Fig.2.1	Schematic of the electrodeposition setup	12
Fig.2.2	Steps involved in the synthesis process	13
Fig.2.3	Characteristic X-ray generation	14
Fig.2.4	Bragg's diffraction	15
Fig.2.5	Schematic working diagram of FE-SEM	17
Fig.2.6	FE-SEM instrument setup at SIC, IIT Indore	18
Fig.2.7	Schematic diagram of TEM	19
Fig.2.8	Schematic view of three electrodes	21
Fig.2.9	Electrochemical measurement setup	23
Fig.2.10	Sinusoidal Current Response in a Linear System	24
Fig.3.1	XRD pattern of NiCoMnS	28
Fig.3.2	FE-SEM micrographs of NiCoMnS at different magnifications	29
Fig.3.3	TEM micrographs of NiCoMnS at different	
	magnifications	31
Fig.3.4	CV curve showing of NiCoMnS at different scan rates.	32
Fig.3.5	Variation of specific capacitance with scan rate	33

Fig.3.6	GCD curve at different current densities	34
Fig.3.7	Variation of specific capacitance with current	
	densities	35
Fig.3.8	Stability curve of NiCoMnS showing the variation of efficiency with number of charging discharging cycles	36
Fig.3.9	Nyquist plot showing the variation of imaginary impedance value with real impedance value	37
Fig.3.10	Ragone plot of NiCoMnS	38

List of Table

Table 1.1	Approximate evaluation between supercapacitors,	
	capacitors and batteries	4

Acronyms

Acronym	Meaning			
NiCoMnS	Nickel Cobalt Manganese Sulphide			
EDLC's	Electric Double Layer Capacitors			
β	Beta			
α	Alpha			
XRD	X-Ray Diffraction			
Cu	Copper			
BSE	Back Scattered Electron			
Ni	Nickel			
WE	Working Electrode			
CE	Counter Electrode			
RE	Reference Electrode			
CV	Cyclic Voltammetry			
DC	Direct Current			
AC	Alternating Current			
EIS	Electrochemical Impedance Spectroscopy			
HIN	Hierarchical Interconnected Nano-sheets			
GCD	Galvanostatic Charging Discharging			
TEM	Transmission electron microscopy			

Chapter 1

Introduction

The global increase in demand for energy has led to shortage of traditional energy resources (like; fossil fuels, coal, non-renewable source of energy). In response to this change in global landscape, energy has become a primary focus of the major world powers and scientific community. Overconsumption, wars, market manipulation, poor infrastructure and unexplored renewable energy options, *etc.* leads us to marching toward energy crisis. This energy resources to an economy. Conventional energy resources are limited, so energy savings and efficiency are highly promoted by authorities and governments. These governments and authorities are promoting sustainable and renewable energies as an alternative to the limited conventional energy resources.

Therefore, the possible options are solar (photovoltaic or thermal), wind, water *etc.* is a subject of extensive research and interest. As these sources cannot provide a continuous energy throughout the day, therefore energy storage devices come into play which can store energy during peak hours and can be utilized during off hours. Generation discontinuity and the fact that its energy production is not controlled by the system operator makes it difficult to link these plants with an economy. Energy storage is employed to reduce the rate of mismatch between energy supply and energy demand, moreover, energy storage can also play the role of a major stakeholder in energy conservation. A renewable energy generation plant inbuilt with corresponding energy storage system can behave as a constant power generation plant.

Currently, the three major commercialized energy storage devices are batteries, capacitors and supercapacitor.

Energy storage batteries were looked upon as hopeful alternative energy storage devices however, they suffer from the limiting mark pertaining to low power density, low cycle stability, slow charging rate, and safety.

To dissipate these challenges, researchers drifted their focus towards the evolution of high-performance capacitors ^[1-3]. To decode the advantage of supercapacitor, it's mechanism of charge storage, structure, and performance with its counterpart are argued in the following sections of this chapter.

Batteries:

A battery is a device that converts stored chemical energy into electrical energy through a redox reaction. It consists of one or more electrochemical cells with external connections provided to power electrical devices. Batteries are one of the most common source power source for various applications in consumer electronics and industries.

All batteries are made up of three basic components: an anode, cathode, and electrolyte (a substance that chemically reacts with the anode and cathode).

Generally, batteries are enabled by a redox reaction with an oxidation of anions at the anode and a reduction of cations at the cathode. Based on their charging ability, batteries can be divided into two types: rechargeable batteries and disposable batteries.

Currently lithium-ion batteries represent the best energy storage cells with moderate weight and a high energy density of approx. 140-170 Wh/kg. Despite their high energy density, these batteries and their substitutes are suffering from slow charging time and low power density. The lithium ion is highly reactive and can react with water in the electrolyte forming lithium hydroxide and hydrogen gas. Thus, a well-sealed packaging system and organic electrolytes are engaged in lithium ion batteries to attenuate the possibility of dangerous reactions.

Capacitors:

A capacitor is a passive electrical device, which stores electrical energy in the form of static charges in the electrical field between two conducting plates called electrodes. Conventional capacitors, also known as electrostatic capacitors, consist of two conducting electrodes separated by an insulating material called a dielectric.

Charge storage property measured in terms of capacitance which is directly proportional to dielectric material between the plates, surface area of plates and inversely proportional to the separation between the plates. Generally, conventional capacitors have high power density of approx. 5000 W/kg, but low energy density in the somewhere range of 0.01-0.05 Wh/kg. Compared to batteries and fuel cells, capacitors can be charged & discharged sharply, but cannot store a large amount of energy.

Supercapacitors:

Supercapacitor is a high performance capacitor possessing high power and energy density. Considering the low power density of batteries and low energy density of capacitors, the urgent needs for high power energy storage system is appraised, thus more and more attention has been given to supercapacitors.

As a part of a significant field of electrochemical energy storage devices, they bridge the gap between conventional capacitors and batteries in different aspects. These supercapacitors are used in numerous applications. Their very high charge storage and the high current capability enable them to be ideally suited for a number of instances. The supercapacitor, battery and capacitor technologies compete for some applications. It is worth looking at the comparison between a typical supercapacitor, capacitor and a Lithium Ion high capacity battery technology used today. Below *table 1.1* shows

approximate	evaluation	between	supercapacitor,	capacitor	and
batteries.					

Parameters	Capacitors	Batteries	Supercapacitors
Power density (W/kg)	>5,000	100-3,000	5,000-10,000
Energy density (Wh/kg)	0.01-0.3	30-265	0.5-20
Life cycle	>1 million	150-2,000	up to 1 million
(number of			
cycles)			
Charge/discharge time	1 ps-1 ms	1-10 hrs	1 ms-1 s
Operating voltage range (V)	6-800	1.2-4.2	1.0-4.5
Operating temperature range(°C)	-20 to +100	-20 to +65	-40 to +85
Cost per Wh	0.10-1.00	1-2	10-20

Table 1.1 Approximate evaluation between supercapacitors, capacitors and batteries.

Generally, supercapacitor stores energy by two important charge storage mechanisms such as charge separation at electrode/electrolyte interfaces (electrostatically) *i.e.* electric double layer capacitor (EDLCs) and charge storage by Faradic redox reactions (electrochemically) *i.e.* pseudo-capacitors. *Figure 1.1* shows the schematic difference between EDLCs and pseudocapacitors.

EDLCs are based on electrostatic charge diffusion with accumulation at the electrode-electrolyte interface. It contains no conventional dielectric instead an electrolyte (solid or liquid) is filled between two electrodes. In EDLC, an electrical condition called "electrical double layer" which is formed between the electrodes and electrolyte works as the dielectric. Transition metal oxides and electrically conducting polymers are being used as electrodes because of their predominant fast and reversible surface or near-surface reactions for charge storage ^[4].

Whereas, in pseudocapacitors charge storage is achieved by Faradic electron charge transfer with redox reactions taking place. Metal oxides, metal ferrites ^[5-6] and metal sulphides ^[7-8] based Pseudocapacitors have been explored as hopeful energy storage devices. These capacitors suffer with obstacles such as smaller cycle stability and low energy density ^[9]. Thus, it is essential to improve the cycle stability and energy density of these devices by developing new systems of electrodes and electrolytes with improved properties.



Fig. 1.1 Schematic diagram of types of supercapacitor:
(a) Electric Double Layer Capacitor (EDLC)
(b) Pseudo-capacitor.

A capacitor is charged when we supply a voltage with current running through the capacitor, in the process the capacitor accumulates charges and get charged. A charged capacitor can then be discharged by draining the current through its two terminals or connecting some load through its terminals. Charging and discharging mechanism of electric double layer capacitor is shown in *figure 1.2*.



Fig. 1.2 Charging and discharging of electric double layer supercapacitor (EDLCs).

Electrodes are the core of the SCs for their electrochemical performances such as the life cycles, power density, *etc*. To improve electrochemical performances, some strategies can be used by increasing the specific surface area of the working electrode. Most research endeavours so far have been focused on seeking the synthesis of a variety of electrode materials with unique structural morphologies like: as nano-flakes, nano-rods, nano-wire, nanospheres and other unique structural morphologies ^[10-11].

The development of more effective energy-producing, energyabsorbing, high surface area and a high degree of order in smaller and more efficient devices is possible with nanotechnology.

1.1 Nanotechnology

Nanotechnology depends on the fact that it is possible to tailor the structures of materials at extremely small scales to achieve specific properties, thus greatly extending this technology in interdisciplinary toolkit. Using nanotechnology, materials can effectively be made more durable, stronger, lighter, more reactive, better electrical conductors just by limiting the size of constituent particles (approx. order of 10^{-9} m to 10^{-7} m).

Nanostructures can be classified in terms of their structural morphology as; 0-D nanostructures (nanocluster and nanodispersion materials), 1-D nanostructures (nanorods, nanotubes, nanowires), 2-D nanostructures (nanofilms, nanolayers, nanocoating), 3-D nanostructures (bulk nanomaterials).

There are two types of approaches for synthesis of nano-material and fabrication of nano-structure: (i) Bottom-up (ii) Top-down. The bottom-up approach is more advantageous than the top-down approach because the former has a better chance of producing nanostructures with less defects, more homogenous chemical composition, and better short- and long-range ordering.

The dimensionality plays a major role in determining the characteristics of nanomaterials including physical, chemical and biological characteristics. With the decrease in dimensionality, an increase in surface-to-volume ration is observed. This indicate that smaller dimensional nanomaterials have higher surface area. Recently, two dimensional (2D) nanomaterials are extensively investigated for electronics and biosensors applications because electrodes made from Nano-flakes facilitate the charge storage during electrochemical process due to their large surface area.

Thus, nanotechnology can enable in the fabrication of electrode with higher surface area, porosity, varied morphology and dimension which will provide high charge storage and its efficient transport during redox reaction.

1.2 Electrochemical Synthesis

Electrochemical synthesis is a highly efficient method for the fabrication of nanostructured materials. Various nanostructures, such as nanorods, nanowires, nanotubes, nanosheets, dendritic nanostructures, and nano-composite, can be easily fabricated. The electrochemical synthesis and characterization have progressed greatly in the past few decades, allowing an increasing understanding of property and performance relationships ^[12].

• Faraday's laws of electrolysis: Faraday presents 2 laws of electrolysis in 1834 which are as follows;

Faraday's First Law of Electrolysis: According to this law, the chemical deposition due to flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it.

$$Q = Z m/M$$

where; Q: Charge; Z: change in oxidation state; m and M: mass and molar mass.

Faraday's second law of electrolysis: It states that, when the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.

$$\mathbf{Q} = \mathbf{It} = (\mathbf{Z} \ \mathbf{n}) \ \mathbf{F}$$

where; Q: Charge; I: current; t: time duration; Z: change in oxidation state; F: Faraday constant (96 485 C mol⁻¹, the charge of one mole of e^-); n: Amount of substance oxidized or reduce.

Among various synthesis routes such as; hydrothermal synthesis, galvanic replacement reaction, electrospinning, and molten salt method, the electrochemical deposition is a facile and efficient route. It shows additional advantages like low synthesis temperature, low cost, fast and well controlled crystal growth, environmental friendly are among some of the traits. *Figure 1.3* shows the schematics of electrodeposition using simple 2 electrode system.



Fig. 1.3 Simple electrodeposition using 2-electrode system.

Factors Effecting Electrodeposition:

- pH level
- Time
- Current density
- Temperature
- Metal Ions
- Concentration Bath

To achieve the high-quality plating condition these parameters must be studied properly.

1.3 Transition Metal Sulphide Based Electrodes

Transition metal sulphides, oxides and their mixed composites have come out as a unique class of active materials for supercapacitor electrodes. In addition, binary metal sulphides and oxides like; Ni-Co oxide, Ni-Co sulphide and Ni-Co-Mn based mixed sulphides have been introduced as promising electrode materials because of their advanced electrochemical activities like high electric conductivity and low electro-negativity ^[14-16]. These metal oxides/sulphides containing transition metal elements like Ni, Co and Mn, which provide higher redox state than carbonaceous material ^[17-19].

Transition metal sulphides commonly exhibit higher conductivity as compared to their oxide alternatives and it is related to the convenient pathway for electron transport, resulting in higher capacitance values ^[20]. As compared to ternary transition metal oxides, sulphides possess higher electrochemical activity due to the replacement of oxygen with sulphur atoms which possess higher ionic conductivity ^[21], due to their narrow band gap and higher ionic diffusivity due to their large anionic polarizability, which arises from the larger sizes of S⁻² ions ^[22-23].

Form the above literature survey we conclude that compared to the monometallic sulphides (nickel sulphide, cobalt sulphide and manganese sulphide), the electrochemical contributions from nickel, cobalt and manganese ions in the tri-metallic sulphides can deliver comparatively rich redox reactions and enhance the electronic conductivity which in result gives excellent specific capacitance ^[24]. Transition metal based supercapacitors can exhibit high specific capacitance and high energy density at low current densities. Binary transition metal based composite materials possess synergistic enhancements in properties like stability, chemical activity and resistance to electrolyte which are far better than a simple combination of individual composites ^[25].

The above literature survey also provides us an insight to synthesise ternary transition metal sulphide nanocomposite (NiCoMnS) on nickel foam substrate by an intelligible electrodeposition technique. The obtained NiCoMnS nanocomposite are expected to exhibit high specific capacitance, cycling stability and energy density.

10

Chapter 2

Material Synthesis & Characterization Techniques

Sample preparation for nickel cobalt manganese sulphide (NiCoMnS) nanostructure composite was carried out in two step process (i) Cleaning of the nickel foam and (ii) Electrodeposition of NiCoMnS on cleaned nickel foam in the presence of metal sulphide ions based electrolyte.

2.1 Treatment of nickel foam

In order to remove the impurity from the 3-D nickel foam following treatment was carried out:

- Sonicating of nickel foam in HCl (10% dilution) solution for 3-4 min.
- Sonication in acetone for 5-7 min.
- Followed by ethanol for 5-7 min.
- De-ionized water was used to wash the foam several times.

After that, Ni foam was dried at room temperature and weighed using weighing balance.

2.2 NiCoMnS nanostructure synthesis

To carry out electrochemical synthesis, initially the electrolyte was prepared as mentioned below:

(i) Initially 0.001 M nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O),
 0.001 M cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O) and 0.001 M manganese chloride (MnCl₂) were weighted and transferred to a 150 ml beaker with subsequent addition of 20 ml Di-Water. The solution was magnetically stirred at 400 rpm for 30 min.

(ii) Afterward 0.01 M sodium sulphide (Na₂SO₃) and 0.01M potassium chloride (KCl) was added to the above solution and again stirred for 30 minutes.

Electrodeposition was carried out by chronoamperometry in three electrode systems at a potential of -1.1 V for 10 min. at a constant temperature of 80 °C in an electrochemical cell containing above electrolyte, cleaned nickel foam as working electrode, platinum electrode as counter electrode and a saturated Ag/AgCl calomel as reference electrode, the schematic of the 3 electrode electrodeposition setup is show in *figure 2.1*.



Fig. 2.1 The schematics of the electrodeposition set-up.

After deposition nickel foam was washed with deionized water several times to remove loose ions. Deposited nickel foam is dried at 60° C in furnace for 24 hours. Dried nickel foam was hydrostatically pressed at 100 kg cm⁻². The amount of mass deposited on nickel foam was calculated from the difference in weight of nickel foam before and after deposition. The steps involved in sample preparation are as mentioned in *figure 2.2*.



Fig. 2.2 Steps involved in the synthesis process, (a) Ultra-sonication, (b) Magnetic stirring of prepared sample, (c) Electrodeposition synthesis using Autolab instrument (d) Sample placed in furnace to dry.

2.3 Characterization Techniques

2.3.1 X-Ray Diffraction

In 1913 W.H. Bragg and W.L. Bragg ^[26-27] found that the substances whose macroscopic forms are 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, which is a required condition for the diffraction phenomena to occur in crystals.

When high energy electron interacts in-elastically with an atom, the primary electron loses a detectable amount of energy(ΔE). This interaction will give rise to phonon scattering, Plasmon scattering, characteristic X-ray, bremsstrahlung X-ray, auger electron production *etc*. The schematics of characteristics of X-ray generation is shown in *figure 2.3*.



Fig. 2.3 Characteristic X-ray generation.

Principle

Crystalline solids behave as a diffraction grating for X-rays, constructive interference of diffracted monochromatic X-rays give rise to diffraction peaks. The faster be the original electron, the more is its photon energy and greater the number of electron, 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)^[28-29].

When electromagnetic radiation of wavelength ' λ ' comparable to atomic spacing 'd', are incident upon a crystalline sample, then it gets scattered by the atoms in the system and undergo constructive interference in accordance to Bragg's law and represented in *figure* 2.4.



Fig. 2.4 Bragg's diffraction

The total path difference between two rays is:

- = AB + BC
- $= dSin\theta + dSin\theta$
- $= 2dSin\theta$

The two separate waves will arrive at a point with the same phase, and hence undergo constructive interference, if and only if this path difference is equal to any integral value 'n' of wavelength of incident X-rays, i.e.

$2dSin\theta=n\lambda$

'This is Bragg's law of diffraction'.

Instrumentation

A powder X-ray diffractometer consists of 3 parts:

- An X-ray source (usually Cu-Kα radiation)
- A sample stage
- A detector

Sources of X-rays generation are radioisotopes and secondary fluorescence, the most common source of X-rays are copper (Cu-K_{α} of λ =1.5418 Å) and molybdenum. Now these X-rays are directed onto the sample mounted on the sample stage at some angle θ , while the detector opposite to the source detects the intensity of the diffracted X-ray received at an angle 2 θ away from the source path. As the detector is 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.

2.3.2 Field Emission Scanning Electron Microscopy

Field Emission Scanning electron microscope (FE-SEM) is a type of electron microscope that uses a focused beam of high-energy electrons in producing a variety of signals at the surface of a solid specimen. These high energy electrons interact with electron of the samples to produce the secondary electrons and some electrons gets back scattered from sample. The signals produced by these secondary electrons contain useful information such as the surface morphology, chemical composition atomic structure etc.

When an electron beam is incident on the sample surface, it may be reflected, absorbed, or conducted away. The electrons that are absorbed by the sample can interact with atoms of the sample and makes it unstable, forcing it to eject secondary electron. Secondary electrons are most valuable for determining the morphology and topology of the samples and back-scattered electrons are most valuable for getting the chemical composition of multiphase samples. Due to the higher resolution of the SEM, very closely spaced specimens can be magnified to very large extent. This magnification to such a large level is possible due to use of electromagnetic lenses which focus electron precisely on to the sample. All these advantages make the scanning electron microscope one of the most useful instruments in surface morphology characterization. Schematic diagram of field emission scanning electron microscopy is shown in *figure 2.5:*



Fig. 2.5 Schematic working diagram of FE-SEM.

Principle and working:

The process initiates with an electron gun which generates a beam of high energy electrons passing through a series of electromagnetic lenses. These electromagnetic lenses are the tubes, wrapped in coil and referred to as solenoids. These coils focus the incident electron beam on the sample. The electron beam is affected by air and water molecules, so the sample must be placed in a vacuum.

Samples should be conductive for SEM measurement, non-conductive samples are coated with gold/copper in order to preserve the sample and keeping it away from changing or decaying throughout the scanning process. When high energy electron beam is incident on the sample, energetic electrons (secondary and backscattered electrons) are ejected from the surface of sample. These energetic electrons yield information about the size, shape, texture and composition of the sample. X-rays, emitted from depth of the sample surface, can provide element and mineral information. Different detectors are used to detect the different types of scattered electrons, including secondary and backscattered electrons. FE-SEM instrument setup at SIC lab, IIT Indore is shown in *figure 2.6*.



Fig. 2.6 FE-SEM instrument setup at SIC, IIT Indore.

2.3.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. A high energy beam of electrons is incident through a very thin sample, and the interactions between the electrons and the atoms can be used to observe parameters such as particle size, morphology, crystal structure, dislocations and grain boundaries. Chemical analysis can also be performed through EDX. TEM can be used to study the growth of layers, their composition and defects.



Fig. 2.7 Schematic diagram of TEM.

The TEM operates on the same basic principles as the optical microscope but uses electron beam instead of light beam. Since, the wavelength of electron is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from optical microscope. Thus, TEMs can reveal the finest details of internal structure, in some cases as small as individual atoms. The schematic of the TEM is shown above in *figure 2.7*.

TEM usually have emission gun from which electrons are accelerated. TEM with >1000 kV acceleration potential has been developed for obtaining higher resolutions. Owing to their brightness and very fine electron beams, field emission guns are becoming more popular as the electron guns.

2.3.4 Cyclic Voltammetry

Cyclic voltammetry (CV) is a method for investigating the electrochemical behaviour of a system. It was first reported in 1938 and described theoretically by Randies ^[30]. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption process ^[31].

CV is observed by applying a ramped linear potential (i.e. a potential that varies linearly with time) to the working electrode. As the potential is swept back and forth past the formal potential E° , of an analyte, a current flow through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of analyte in the solution, which allows cyclic voltammetry to be used in an analytical determination of concentration.

The instrument required to perform cyclic voltammetry consists of a conventional three-electrode potentiostats connected to three

electrodes (working, reference and counter) immersed in a test electrolyte. The potentiostats applies and maintains the constant potential between the working and reference electrode while at the same time measuring the current between counter and working electrode. A recording device (such as a computer or plotter) is used to record the resulting CV as a graph of current versus potential. The schematic view of 3 electrodes is shown in *figure 2.8*.



Fig. 2.8 Schematic view of 3 electrodes

Working electrode (WE)

It is the electrode in an electrochemical cell on which the reaction of interest occurs. 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. The size and shape of the working electrode also varies, and it depends on application.

Reference Electrode (RE)

It is an electrode which has a stable and well-known electrode potential and it is used as a point of reference in the electrochemical cell for potential control and measurement. It is used as an electrode in a half cell ^[32,33], which allow the potential of another half to be

determined. Standard Hydrogen Electrode (SHE), Standard Calomel electrode (SCE), electrode is generally used as reference electrode as they remain unaffected during the whole electrochemical process. For measurement in aqueous systems, the 'Hg/HgCl' or 'Ag/AgCl' reference is quite popular.

Counter/Auxiliary Electrode (CE)

This auxiliary (or counter) electrode provides a disjunctive path for the current to follow, so that only a very small current flows through the reference electrode. Design choices are usually based on finding a material that is chemically inert in the particular test solution being studied, and it is generally a good idea for the auxiliary electrode to have a large surface area. It is made of an inert material (*e.g.* Pt, Au, graphite, glassy carbon, *etc.*) 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. Electrochemical measurement setup is shown in *figure 2.9*.

Capacitance is given by charge divided by voltage and it is termed to be specific when divided by mass. Charge can be written as a product of current and time.

The Specific capacitance is given by the formula:

$$C = \frac{\int I dV}{m \vartheta \Delta V}$$

where, C is specific capacitance (F/g), m is loaded mass, ϑ is scan rate (V/s), Δ V is potential window (in Volts), and $\int I. dV$ is the area of the I-V graph plotted from the data received.



Fig. 2.9 Electrochemical measurement setup.

3.2.2 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) measures the ability of a circuit element to resist the flow of electrical current. Ohm's law defines resistance in terms of the ratio between voltage, E, and current, I.

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell. It is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoidal at the same frequency but shifted in phase (*figure 2.10*).



Fig. 2.10 Sinusoidal Current Response in a Linear System

The excitation signal, from Euler's relationship,

$$\exp(j \Phi) = \cos \Phi + j \sin \Phi$$

It is possible to express the impedance as a complex function. The potential is described as:

$$E_t = E_o \exp(j\omega t)$$

 ω is angular frequency given as: $\omega = 2\pi f$

and the current response as:

$$I_t = I_0 \exp(j\omega t - \Phi)$$

The impedance (Z) is then represented as a complex number,

$$Z(\omega) = \frac{E}{I} = Z_{o} \exp(j\Phi) = Z_{o} (\cos\Phi + j\sin\Phi)$$

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'. In which the impedance can be represented as a vector of length |Z|. The angle between this vector and the X-axis, commonly called the 'phase angle', is f (=arg Z).

Nyquist Plot has one major shortcoming, by looking at any data point on the plot, one cannot tell what frequency was used to record it.

3.2.3 Galvanostatic Charging Discharging

Galvanostatic charge discharge (GCD) is a reliable method to evaluate performance, cycle-life and the electrochemical capacitance of materials (EDLCs and batteries) under controlled current conditions. A repetitive loop of charging and discharging is called a cycle.

In GCD, a constant current is applied to the working electrode and the resulting potential is measured against a reference electrode as a function of time. At the moment current is applied, the measured potential abruptly changes due to IR (internal resistance) loss and after that, it gradually changes because concentration over-potential is developed across the electrodes, since the concentration of the reactant is exhausted at the electrode surface.

The value of specific capacitance (C) can be calculated with the help of GCD curve using the formula:

$$C = \frac{I\Delta t}{m\Delta V}$$

Where; C is the specific capacitance (F/g), I is the current (A), Δt is discharging time, m is the loaded, ΔV is the potential window.

Chapter 3

Results and Discussion

In this chapter we present the results and discussions of Nickel sulphide, Cobalt sulphide and Manganese Sulphide (NiCoMnS) composite characterized through X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) to study the diffraction planes, phase, surface morphology and particle size, distribution, etc. Electrochemical measurements of NiCoMnS were carried out through cyclic voltammetry (CV), galvanostatic charging-discharging (GCD) and electrochemical impedance spectroscopy (EIS) to study specific behaviour capacitance, material's vs frequency response (degradation). Capacitance stability measurement of NiCoMnS electrode was carried through continuous cycles of GCD. Energy and power density of electrode was calculated and represented in form of Ragone plot.

3.1. Physical Characterization

3.1.1. X-Ray Diffraction

Crystal structure of the as prepared nanocomposite of NiCoMnS was examined by X-Ray diffraction. The XRD patterns were recorded by Rigaku Smart Lab, Automated Multipurpose X-ray diffractometer with Cu K_{α} radiation ($\lambda = 1.5416$ Å) in angle range of 35° to 80°. XRD pattern of NiCoMnS is shown in *figure 3.1*. It can be seen that intensity of diffraction peaks is very high, reflecting high degree of crystallinity of sample. Diffraction peaks corresponding to 2 θ values of 43.86° corresponds to planes (422) of NiS₂ and (221) of MnS₂; 51.06° corresponds to plane (440) of Co₉S₈ and (222) of MnS₂; and 75.78° corresponds to plane (422) of MnS₂. Crystal structure of all these materials are cubic with estimated lattice constants; NiS₂: cubic a=b=c=5.618 Å (JCPDS Card No. 01-080-0375), Co₉S₈: cubic a=b=c= 9.905 Å (JCPDS Card No. 01-075-2023) and MnS₂: cubic a=b=c= 6.107 Å (JCPDS Card No. 01-076-2051). Moreover, Co, Ni, and Mn have a small difference in atomic radii and substitution of one into other with sulphide will have little influence on the crystal structure, therefore the peaks of the sulphides of Co, Ni and Mn are found to be overlapping.



Fig. 3.1 XRD pattern of NiCoMnS composite nanostructure

The above analysis of XRD pattern confirms the presence of NiS_2 , MnS_2 , Co_9S_8 present in the synthesised nanocomposite.

3.1.2 Field Emission Scanning Electron Microscopy

Field emission scanning electron microscopy (FE-SEM) of NiCoMnS nanocomposite electrodeposited on nickel foam was carried out by using Supra 55 Zeiss model.



Fig.3.2 *FE-SEM micrographs of NiCoMnS with scale bar (a)1 µm and* (b) 300 nm.

Surface morphologies of NiCoMnS electrode analysed through SEM micrograph is shown. *Figure 3.2* (*a*) & (*b*) revels the formation of hierarchical interconnected nanosheet (HIN) like structure of NiCoMnS at 1 μ m and 300 nm scale bar. These HIN structures also form a flower-like structure having sheets of 25 nm thickness, with porous architecture, growth of such HIN over and in-plane offer large active surface area, which favours fast electron transfer and more accessible sites to electrolyte species for efficient ion/mass transport.

3.1.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) of as prepared NiCoMnS sample was carried on TECNAI F-20 philips operated at 200 KV. TEM sample was prepared by sonication of electrodeposited NiCoMnS on nickel foam in ethanol for 15 min. in order to obtain the suspended foam of nanocomposite in the solution (ethanol). Drop of this solution was casted on carbon coated copper grid with the help of micropipette, later which was dried at 65 °C for TEM measurement.

TEM micrograph presented in *figure 3.3* (*a*) shows the flake like structure, 3.3(b) represents the nano-porous nature and 3.3(c) shows the selective area electron diffraction pattern with polycrystalline nature. The planes marked (221) and (422) corresponds to NiS₂ and MnS₂ which can further be correlated to XRD results thereby supporting the presence of this crystal structure system. HIN structures play a synergetic effect, favourable environment suggesting high performance of this material in terms of energy storage.



Fig. 3.3 *TEM micrograph of NiCoMnS at (a) 50 nm, (b) 20nm and (c) 10 1/ nm magnifications.*

3.2. Electrochemical Characterization

3.2.1. Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were carried out to study electrochemical redox behaviour of HIN NiCoMnS electrodeposited Ni foam using three electrode arrangement in 2 M KOH electrolyte solution. CV scans were measured by varying scan rates from 1 to 90 mV/s in a fixed potential window of -0.1 to 0.4 V as shown in *figure 3.4*.

CV curve of NiCoMnS electrode possesses a non-rectangular shape having three strong redox peaks representing asymmetric shape indicates its capacitive behaviour is different from electric doublelayer. Oxidation peak, $E_{Pa}=0.23$ V can be related to nickel and similarly reduction peak at $E_{Pc} = 0.16$ V and 0.27 V corresponds to cobalt and nickel. The small difference ΔE_{ac} between anodic and cathodic peaks favours reversibility and pseudocapacitive property of electrode leading to fast reversible redox mechanism. As the scan rate increases, anodic peak (oxidation) in CV curve shifts towards more positive potential *i.e.* from 0.225 to 0.3 V due to redox reaction mechanism governed by charge transfer mechanism whereas cathodic peak (reduction) shows almost no shift, moreover broad nature of these redox peaks can be related to high conductivity and intercalation nature of pseudocapacitive materials which involve faradic mechanism without any phase change.



Fig. 3.4 CV curve of NiCoMnS at different scan rates.

The shape of CV curve remains same with increasing scan rate (1 to 90 mV/s) which shows a fast charge-discharge behaviour of material, whereas an increase in bounded area with increasing scan rate can be related to rapid diffusion of ions in KOH electrolyte.

Variation of specific capacitance with different scan rates is shown in *figure 3.5*, highest value of specific capacitance of 5420.3 F/g is obtained at 1 mV/s which decreases to 1257.5 F/g at 90 mV/s. This high value of specific capacitance can be attributed to ultrathin HIN structure of NiCoMnS electrode which offers large surface area and highly porous structure for the rapid diffusion of electroactive species during charge transport process.



Fig. 3.5 Variation of specific capacitance with scan rate.

Decrease in capacitance with scan rate can be attributed as, 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 decreases.

3.2.2. Galvanostatic Charging-Discharging

Galvanostatic charge-discharge (GCD) measurements of HIN NiCoMnS electrode was carried out in potential window of 0 V-0.37 V at different values of current densities ranging from 5-150 A/g as shown in *figure 3.6*.



Fig. 3.6 GCD curve at different current densities.

Charge-discharge curves of HIN NiCoMnS electrode shows sloped plateau *i.e.* mixed state of regular triangular (EDLCs) and plateau (pseudocapacitor) with long charging/discharging time which can be attributed to pseudocapacitive or battery mimic behaviour of electrode. Highest specific capacitance of 5000.8 F/g was achieved at a current density of 5 A/g (1 mA/cm2), from GCD curve data, this ultra-high value of specific capacitance can be attributed to HIN structure of electrode material, which favours high accessible surface area for diffusion of charges on the surface of HIN nanosheets of NiCoMnS, thereby providing path for rapid transport of electrons/ions by intercalation-deintercalation between sulphide layers.

Rate capability i.e. relationship between calculated specific capacitance and current density of electrode is shown in *figure 3.7*, electrode delivers a high specific capacitance of 5000.8, 3878.7, 2918.9 and 2108 C/g, at current density of 5, 50, 100 and 150 A/g respectively *i.e.* gradual decrease with increasing current density which can be related to incremental voltage drop/less active material taking part in redox process at high current densities. It can also be related to the diffusion and transport of OH- ions within the electrode material at high current density.



Fig. 3.7 Variation of specific capacitance with current densities.

3.2.3 Stability Test

Cyclic stability of NiCoMnS measured at a current density of 100 A/g for 3500 cycles, specific capacitance of NiCoMnS electrode remains about 48% after 3500 cycles, indicating an extraordinary behaviour of electrode material, long-term stability at a high current density of 100

A/g as shown in *figure 3.8*. This high rate capability behaviour can be attributed to diffusion length of ions, time period for such high current densities, reflecting that external surface area of electrode plays a major role in charge storage processes. 45 % retention after 3500 cycles.



Fig. 3.8 Stability curve of the NiCoMnS composite showing variation of efficiency with number of charging discharging cycles.

3.2.3 Electrochemical Impedance Spectroscopy

In order to understand the superior performance of the electrode material, comparative EIS study was performed before and after cyclic stability test in frequency range of 10 mHz to 100 kHz with imposed sinusoidal AC signal of 10mV in an open circuit model. The Nyquist plot of variation of imaginary part of impedance vs real part is shown in *figure 3.9*. In terms of frequency, Nyquist plot can be divided into

three regions; first high frequency region 100 kHz to 0.1169 Hz, from 0.1169 Hz to 0.0131 Hz and later the remaining region.



Fig. 3.9 *Nyquist plot showing the variation of imaginary impedance value with real impedance value.*

Contribution of resistance in electrochemical circuit of above Nyquist plot can be divided into 3 regions as: first due to electrolyte and cell $(Re = 0.314 \ \Omega)$, second region arising from surface film and constant phase element $(R_{sf+b})/C_{sf+b} = 211 \ \Omega \parallel 1.8 \text{ mMho})$ and last due to charge transfer resistance i.e. diffusion process $(R_{ct})/C_{dl} = 180\parallel 6.85$ mMho). Low frequency region i.e. Warburg region with the value of 28.6 mMho, showing an increase of diffusion current component.

Small diameter of EIS semicircle before stability test shows high conductivity of NiCoMnS electrode, circuit elements fitted to above data is shown in EIS curve. A higher value of R_{ct} after cyclic test shows that the material is in a state of degradation.

3.2.4 Energy Density and Power Density

Ragone plot of HIN NiCoMnS electrode shows the variation of Energy density and power density at different current densities, as shown in *figure 3.10* using the formula given below:

Energy density
$$(E) = \frac{C_s V^2}{8}$$

Where; C_s = Specific Capacitance and V = Potential window

Power density
$$(P) = \frac{E}{\Delta t} * 3600$$

Here; E= Energy density and Δt = discharging time



Fig. 3.10 Ragone plot of the NiCoMnS.

Ragone plot shows a superior value of energy density of 38 Wh/Kg and power density of 25 KW/Kg at a constant current of 1mA. Energy density decreases from 85.7 to 36 Wh/kg and the power density increases from 832.5 to 24975 W/kg. This high energy density and power density can be related to high conductivity due to sulphide layers and HIN structure of sample which enables it to store a high amount of charge and its subsequent release at high current densities.

Chapter 4

Conclusion and Scope for future work

To conclude this thesis, Nickel Cobalt Manganese Sulphide was synthesised by electrodeposition technique. The resulted NiCoMnS was confirmed by multiple physical characterization techniques. XRD confirms the pure phase formation of composite and the formation of uniform hierarchical interconnecting flakes like structure was confirmed by FE-SEM. TEM reveals well-ordered nanoflakes at even higher magnification. These interconnecting flakes had enhanced the surface area thus leads to high specific capacitance.

Multiple electrochemical characterizations were carried out in three electrode systems. Cyclic voltammetry shows high specific capacitance of 5420 F/g at 1 mV/s scan rate and galvanostatic charging-discharging shows specific capacitance of 5008 F/g at a current density of 5 A/g. Moreover, excellent energy density of 36 Wh/kg and power density of 24975 W/kg was also investigated. Due to the outstanding physical and chemical properties of NiCoMnS nanocomposite, it plays a smart role as electrode material, and makes it possible to manufacture high-performance supercapacitor. Stability test for charging and discharging cycles shows good retention of 48% even after 3500 cycles.

Although NiCoMnS has been confirmed to be highly effective, the quality of produced nano-composite still can be improved. To instate this, novel synthesis methods can be unearthed such as thermal annealing, plasma treatment, irradiation, chemical activation, and so on. Some biological carbon materials also be worth attention because of their easy access and natural porous structure.

It is highly desirable to find the balance point between performance and cost. As to the supercapacitor research, alternation, improvement in the electrode preparation, electrolyte selection, packaging method and device structure are under research.

In the coming future, it is highly probabilistic that a full cell supercapacitor device with analogous energy density to lithium ion batteries would influence the market. That will bring an energy and technical revolution for the century with its outstanding performance and features in terms of energy storage.

References

- [1] E. Kady, Maher F, Shao, Yuanlong, R. B. Kaner, *Nat. Rev. Mater.*, 1, (2016) 16033-16046.
- [2] G. Nystrom, A. Marais, E. Karabulut, L. Wågberg, Y. Cui, M. M. Hamedi, *Nat. Commun.*, 6, (2015) 7259-7266.
- [3] H. Tang, J. Wang, H. Yin, H. Zhao, D. Wang, Z. Tang, *Adv. Mater.*, 27, (2015) 1117-1123.
- [4] X. Zhao, B. M. Sanchez, P. J. Dobson, P. S. Grant, *Nanoscale*, 3, (2011) 839-855.
- [5] M. M. Vadiyar, S. C. Bhise, S. S. Kolekar, J. Y. Chang, K. S.
 Ghule, A. V. Ghule, *J. Mater. Chem. A*, 4, (2016) 3504-3512.
- [6] M. M. Vadiyar, S. S. Kolekar, N. G. Deshpande, J. Y. Chang,A. A. Kashale, A. V. Ghule, *Ionics*, 23, (2016) 741-749.
- [7] J. Yang, C. Yu, X. Fan, S. Liang, S. Li, H. Huang, Z. Ling, C. Hao, J. Qiu, *Energy Environ. Sci.*, 9, (2016) 1299-1307.
- [8] X. Y. Yu, L. Yu, X. W. Lou, Adv. Energy Mater., 6, (2016), 1333-1346.
- [9] J. Zhu, A. S. Childress, M. Karakaya, S. Dandeliya, A. Srivastava, Y. Lin, A. M. Rao, R. Podila, *Adv. Mater.*, 28, (2016) 7185-7192.
- [10] X. Xiong, B. Zhao, D. Ding, D. Chen, C. Yang, Y. Lei,
 M. Liu, *NPG Asia Mater*, 8, (**2016**) 300-306.
- [11] Y. Jiang, Z. Li, B. Li, J. Zhang, C. Niu, J. Power Sources, 320, (2016) 13-19.
- [12] G. Li, H. Xu, X. Lu, J. Feng, Y. Tong, C. Su, *Nanoscale*, 5, (2013) 4056-69.
- [13] S. Kumar, S. Pande, P. Verma, International Journal of Current Engineering and Technology, 5, (2015) 700-703.
- [14] G.Q. Zhang, H. B. Wu, H.E. Hoster, M.B. Chan-Park, X.W.D.Lou, *Energy Environ. Sci.*, 5, (2012) 9453–9456.

- [15] Y. Zhang, M. Ma, J. Yang, C. Sun, H. Su, W. Huang, X. Dong, *Nanoscale*, 6, (**2014**) 9824–9830.
- [16] L. Liu, *Nanoscale*, 5, (**2013**) 11615–11619.
- [17] X. Huang, X. Qi, F. Boey, H. Zhang, *Chem. Soc. Rev.*, 41, (2012) 666–686.
- [18] G. Xiong, C. Meng, R.G. Reifenberger, P. P. Irazoqui, T. S. Fisher, Adv. Energy Mater., 4, (2014) 1300515.
- [19] K. Krishnamoorthy, G.K. Veerasubramani, S. Radhakrishnan,S.J. Kim, *Chem. Eng. J.*, 251, (2014) 116–122.
- [20] X. Wang, J. Hu, W. Liu, G. Wang, J. An, J. Lian, J. Mater. Chem. A, 3, (2015) 23333–23344.
- [21] S.H. Park, Y.K. Sun, K.S. Park, K.S. Nahm, Y.S. Lee, M. Yoshio, *Electrochim. Acta*, 47, (2002) 1721–1726.
- [22] M. Acerce, D. Voiry, M. Chhowalla, *Nat. Nanotechnol.*, 10, (2015) 313–318.
- [23] G. Gao, H. Bin Wu, S. Ding, L. Liu, X.W.D. Lou, *Small*, 11, (2015) 804–808.
- [24] J. Cheng, H. Yan, Y. Lu, K. Qiu, X. Hou, J. Xu, L. Han, X. Liu, J.-K. Kim, Y. Luo, J. Mater. Chem. A, 3, (2015) 9769–9776.
- [25] H. Wang, Q. Zhao, X. Wang, Y. Zhang, J. Gao, Y. Fu, X. Yang, H. Shu, *RSC Advances*, 4, (2014) 42910.
- [26] M. Jayalakshmi, K. Balasubramanian, International Journal of Electrochemical Sciences, 3, (2008), 1196-1217.
- [27] K. Lota, A. Siercyznska, G. Lota, International Journal of Electrochemistry, (2011), 321473.
- [28] M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff, *Nanoletters*, 8(10), (2008), 3948-3502.
- [29] J.Randles, Trans. Far. Soc, 44, (1948) 327.
- [30] D.B. Hibbert, "Introduction to Electrochemistry" (*Macmillan, London Eds*), **1993**.
- [31] S. Kannappan, K. Kaliyappan, R. Kumar, A. S. Pandian, H. Yang, Y. S. Lee, J. H. Jang, W. Lu, *Journal of Materials Chemistry A*, 2, (2012) 10652.

- [32] L. L. Zhang, R. Zhuo, X. S. Zhao, Journal of Materials Chemistry, 20, (2010), 5983-5992.
- [33] J. P. Renault, A. Bemard, A. Bietsch, B. Michel,
 H.R.Bosshard, E.B.Dalamarche, M.Kleiter, B.Hecht,
 U.P.Wild, *J.Phys.Chem.B.*, 107 (2003) 703.
- [34] E. Gileadi, E. K. Eisner, J. Penciner, "Interfacial Chemistry: An Experimental Approach" (*Addison-Wesley Eds*), **1975**.
- [35] J. Bard, L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications" (*John Wiley and Sons, New York Eds*) 1980.