Republic of Iraq
Ministry of Higher Education
& Scientific Research
University of Babylon
College of Education for Pure Sciences
Department of Physics

Preparation of $ZnFe_2O_4$ Nanoparticles as Electrodes Used for advanced Energy Storage Applications

A Thesis

Submitted to Council of College of Education
for Pure Sciences University of Babylon in Partial
Fulfillment of Requirement for Higher
Diploma Education/ Physics of Materials and its Applications

By

Liqaa Abbas Hameed Omran

B.Sc. in physics
University of Babylon (2002)

Supervised by

Asst. Prof. Shaymaa Hadi khudhair,(Ph.D.)

2021 A.D **1443A.H**

بسم الله الرحمن الرحيم

صدق الله العظيم

سورة هود (الآية 88)

Supervisor's certificate

I certify that this thesis entitled **"Preparation of $ZnFe_2O_4$ Nanoparticles as Electrodes Used for Advanced Energy Storage Applications**" is prepared by the student **(Liqaa Abbas Hameed Omran)** under my supervision at the College of Education for Pure Sciences, University of Babylon as partial fulfillment of the requirement for the Degree for Higher Diploma Education/ Physics of Materials and its Applications

.

Signature:

Name: Dr.Shaymaa Hadi Khudhair

Title: Assistant Professor

(Supervisor)

Date: / / 2021

Head of the Department Certificate

In view of the available recommendations, I forward this thesis for debate by the examining committee.

Signature :

Name : Dr. Khalid Haneen Abass

Title : Professor

(Head of Physics Department)

Date : / / 2021

Dedication

To who gave me the endurance to complete my work, my family

To the best woman in the universe, my mother

To my brothers and sisters…

To my Supervisor

To My country with honour and dignity…

and

Every one who has helped me …

Acknowledgments

First of all thanks to Allah for helping me to complete this thesis, then,I wish to express my thanks to my supervisors **Dr. Shaymaa Hadi Khudhair** for suggesting this Topic, guidance, support and encouragement through the research work.

The equipment (TEM and SEM) used in the present study was funded by Australian Research Council (ARC) grant LE0237478 and is located at the UOW Electron Microscopy Centre. We would also like to acknowledge the Wollongong Isotope Geochronology Laboratory, University of Wollongong for the BET analysis. The Cooperative Research Centre for Advanced Automotive Technology, Department of Industry and Science of the Australian Government, is also gratefully acknowledged for financial support (Project code: Auto CRC 1-111). Many thanks and appreciations are expressed to **Dr. Ranjusha Rajagopalan** from university of Wollongong (ISEM)- Australia , for helping me in the applications my researches. I'd like to thank Prof.**Dr. Amar Hadee Jareeze** and the University Of Technology's Nanotechnology and Advanced Materials Research Center in particular for their generosity and support.

Many thanks and appreciations are expressed to my father and my mother for their patience and help during this work. Finally, I would like to express my thanks to all the people who helped me to complete this study.

Liqaa

Abstract

Supercapacitors, which are also known as electro-double-layer capacitors or electrochemical capacitors, are promising energy storage devices due to their obvious advantages such as high energy density and long life and the advantages of supercapacitors have made them the most promising candidates to be the next generation of energy storage technology. High including energy density, power density, material stability, long life and short charging time. Moreover, as a required sustainable development strategy, it is also necessary to consider environmentally friendly materials, low cost and natural vitality when designing supercapacitive electrode materials. So a new electrode material of super capacitors was synthesized and investigated to solve common problems facing current energy storage technologies. It is used in medical earphones and tactical communications for police and military. Carbon substrate with $ZnFe_2O_4$ has been studied for use as super capacitor electrode material, providing energy density High and energy density. And it is proved to be a suitable potential $ZnFe_2O_4$ electrode material for super capacitors due to its high theoretical capacitance, low cost, non-toxicity and large confinement in nature. Due to the unique design, a specific capacitance of 1118 F/g with good capacitance rate and high stability has been achieved. Electrochemical properties performed at a current density of 2 A/g showed that 90% of the initial amplitude was retained after more than 10,000 cycles as the structure analysis was performed using X-ray diffraction patternand scanning electron microscopy (SEM) . Therefore, this study identifies $ZnFe_2O_4$ on a cheap, abundant, environmentally friendly and non-toxic natural, used for various energy storage, environmental and biomedical applications.

Contents

List of Symbols

Symbol	Physical Meanings	Unites
C	The electric double layer capacitance	**Farad**
ε	The electrolyte dielectric constant	**-**
D	The thickness of electric double layer	**nm**
ε_r	The dielectric constant	**-**
ε_0	The dielectric constant of vacuum	**-**
A	The surface area of the electrode	**m^2/g**
E	Energy density	**Wh/kg**
V	Potential window of the capacitor	**V**
P	Power of super capacitor	**w/kg**
Rs	Equivalent series resistance	**Ω**
W	Weight of the electrode	**G**
B	Radius of the pores	**nm**
I	The current	**A**
m	Mass of the electrode material	**G**
F	Farad	**F**

List of Abbreviations

Abbreviations	Physical Meanings	Unites
LIBs	Lithium-ion batteries	-
EC	Ethylene carbonate	-
DMC	Dimethyl carbonate	
NEC	Japanese company	
SCs	Supercapacitor	-
AC	Activited carbon	-
FDK	Company	-
SHE	Standard Hydrogen Electrode	-
EDLC	Electrode double layer capacitors	-
SSA	Specific surface area	-
BET	Bruauer –Emmett –Teller	-
CNTs	electrical double-layer	-
PANI	Polyaniline	-
PPy	Polypyrrole	-
PTh	Polythiophene	-
TMOs	Transition metal oxides	-
STH	Solar –to-Hydrogen	-
CNTs	Carbon nanotubes	-
MWNT	Multi –walled carbon nanotube	-
SPEEK	Solfonated poly(ether etherketone)	-
PTFE	Polytetrafluoroethylene	-
PMMA	Poly(methylmethacrylate)	-
EC	Ethylene carbonate	-
PC	Propylene carbonate	-
PEG	Polyethylene glycol	-
PEO	Polyethylene oxide	-
XRD	X-RAY Diffraction	-
SEM	Scanning Electron Microscopy	
CHI660B	Potentionstat (CH Instrument)	

List of Figures

List of Tables

Chapter One

Introduction and

Literature Review

Chapter One

Introduction and Literature Review

1.1 Introduction

The ever-growing concerns about fossil fuel crisis and ecological deterioration have attracted attention to the utilization of renewable energies such as tidal, solar and wind. However, these energies are produced intermittently, therefore energy storage, especially electrical energy storage, has become one of the essential issues which lead to better utilization of sustainable energies in the future. Among various energy storage technologies, lithium-ion batteries (LIBs) and super capacitors hold great promise in broad applications such as portable electronics, smart grids and electrical vehicles. LIBs, as a kind of secondary batteries, have been prevalently used in people's daily lives since they were first commercialized by Sony Company in 1991. LIBs have high energy density, around 150 ~ 200 Wh/kg, which enables it to store electrical energy in lightweight devices. Therefore, LIBs are widely used not only in portable electronics, but also in aircrafts and automotive vehicles, which are commonly powered by fossil fuel. Besides, compared to conventional secondary batteries, which suffer from memory effect, LIBs can be charged at any time even after being only partially discharged. However, there are still some technical challenges posed by LIBs. First, the electrolyte containing flammable organic solvents such as ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate are highly hazardous in the case of short circuit. The explosion of LIBs is usually able to cause extremely serious safety issues even death. The second concerns are related to the battery life. Based on manufacturers' information, the capacity of LIBs drops linearly to 80% after 500 cycles indicating batteries of phones that are used daily can barely last for more than three years. In addition, for rechargeable batteries, a

short recharge time is significant, especially for electric cars. For example, a Tesla electric car can charge at the rate of 92 km of range per hour with a wall connector and dual chargers, which is less convenient for long distance travelling than traditional cars; however when a single charger and mobile connector are utilized the charge rate is even lower. Therefore, the widespread adoption of environmental friendly electrical vehicles is still hampered by the long charge time of LIBs. At last, LIBs are extremely hard to compare with fossil fuels in terms of power density, which are at least two magnitudes lower than that of fossil fuel. As a result, to replace fuels with LIBs, a large quantity of LIBs is needed, thus leading to a sharp increase in the mass of products. Thus,supercapacitors SCs seem to be a promising technology for the next-generation energy storage devices due to their safety, long cycling life, short charge duration and high power [1].

1.2 The Development Electrochemical Capacitors

The growing crisis of fossil fuels and the severe environmental pollution resulting from exhaust gas of internal combustion engine have made researchers focus on developing new energy storage devices to replace conventional engines. Great effort has already been made towards developing hybrid powers, fuel cells, and chemical cells. However, due to their short service life, high cost and low temperature performance, it is hard to solve all the problems at the same time. The emergence of super capacitors which have outstanding features such as long cycling life, high temperature performance and environmental benignity, has opened a way to solve almost all the problems that are faced by current energy storage technologies. Because of the advantages of super capacitors, they can replace conventional batteries or even novel energy storage devices utilized in electrical vehicles. Moreover, super capacitors have more widespread applications than traditional batteries. Therefore, many researchers are sparing no efforts to study the electrode materials of super capacitors.

The discovery of electrolytic capacitors was a coincidence when researchers were conducting experiments for fuel cells and secondary batteries using porous carbon as the electrode in early 1950s. Researchers found that porous activated carbon (AC) with high specific surface area could be used for energy storage. Although the mechanism of electric double layer had not been thoroughly studied, the first “Low voltage electrolytic capacitor with porous carbon electrode” was still reported in 1957 by H.I. Becker [1].

Electrolytic capacitors are energy storage devices with a special metal and electrolyte as anode and cathode materials, respectively. The metal which is used in the electrolytic capacitor is easy to form a layer of metal oxide as the dielectric of the capacitors. Three family members of electrolytic capacitors are aluminum electrolytic capacitors, tantalum electrolytic capacitors and niobium

electrolytic capacitors [2] .Since the first report of electrolytic capacitors, hundreds of patents and articles related to various aspects of this field were subsequently written by developers. However, electrolytic capacitors only have limited capacitance [3] . Researchers were not able to achieve a breakthrough until the emergence of electrochemical capacitors.

In the early stage, electrodes of electrochemical capacitors were usually made of activated carbon coating on aluminum foil and the electrodes were soaked in liquid or solid electrolyte with a porous separator between them. This mechanical design established the prototype of electrochemical capacitors, which greatly increased the capacitance to the order of 1 farad. In 1971, this invention was successfully commercialized as “super capacitors” by the Japanese company, NEC Corporation. At that time, SCs only had limited applications and were mainly used as back-up power supplies for volatile clock chips or computer memories [4] . The capacitance of first generation SCs was mainly hampered by large internal equivalent series resistance (ESR), owing to the low conductivity of electrodes and electrolytes used during that time. These problems were basically solved with improved electrode materials and electrolyte by the 1980s; when large amount of SCs were marketed, most of them were applied in the military due to their high cost. From 1975 to 1980, Brain Evan Conway, a researcher form the University of Ottawa, conducted a large number of experiments using ruthenium oxide as SCs electrode material [5].This special material not only can store electrostatic charges by electrical double layer, but also generate a kind of “pseudo capacitance” resulting from faradaic reaction or under potential deposition on the surface of electrode. Based on his research, the concept of SCs has been extended, and B.E. Conway explained the difference between batteries and super capacitors in his report in 1991 [6] .

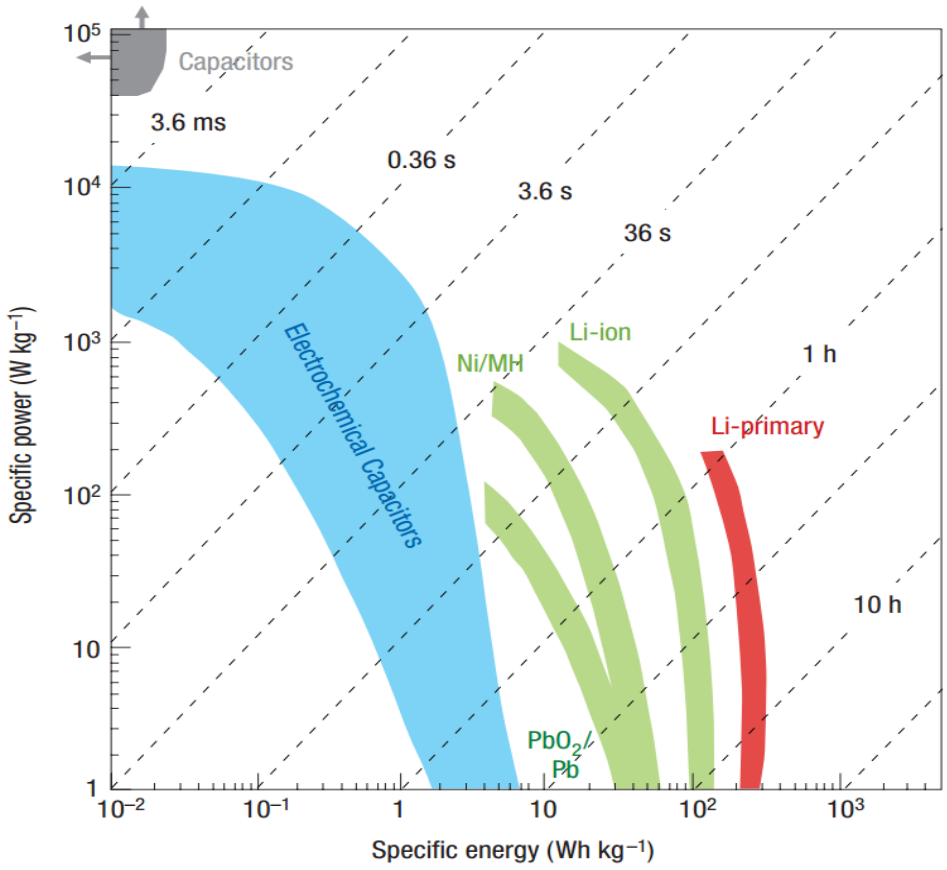


Figure 1.1: A diagram of gravimetric energy density and specific power density of different energy storage technologies such as electrochemical capacitors, PbO_2/Pb batteries, Ni/MH batteries, Lithium-ion Batteries and Li-primary batteries [6].

Recently, in order to combine the high power density of SCs and the high energy density of LIBs, hybrid capacitors have been popular in the research which are also known as lithium-ion capacitors [7-9]**.** This technology was first reported by FDK company who used carbon and pre-doped lithium-ion as the electrode materials in 2007. The pre-intercalation of lithium ions is capable of lowering the potential of anode electrodes leading to higher a potential widow and a higher energy density of Capacitors. For example, the initial potential of carbonaceous electrodes are approximately(-0.1 V) versus Standard Hydrogen Electrode (SHE). After doping of lithium ions, the electrode potential can be reduced to(-2.8V). As can be seen in Figure(1.1) lithium-ion capacitors have at least one magnitude higher energy density than electrode double layer

capacitors (EDLC). However, the power density of lithium-ion capacitors are comparable with EDLCs. But, the organic solvent containing in the lithium-ion capacitor electrolyte has potential risk of explosion when a short circuit occurs. In order to avoid the safety issue that exists in lithium-ion capacitors, many other scenarios of improving energy density of super capacitors are being studied. Compared with dangerous organic electrolytes, aqueous super capacitors hold more promise. But at the same time, novel electrode materials are highly demanded for aqueous super capacitors to increase the capacitance.

1.3 Physical Model of Supercapacitors

A typical structure of a super capacitor involves two polarized electrodes connected with current collectors. Power source is able to be applied on the current collectors to polarize the electrodes to charge the device. A separator which is located between two electrodes is ion-permeable but can prevent electrons from passing through. Both electrodes and the separator is immersed into electrolyte, which contains positive and negative ions. When a voltage is applied, the ions with opposite polarity to the electrode will be absorbed onto the corresponding electrode, forming an electric double layer on the interface between the electrode and the electrolyte. The electric double layer model was firstly proposed by Helmholtz in 1853 [10]. Helmholtz model can be simply described as a capacitor since he supposed that only a single layer of ions is absorbed on the surface. The electric double layer capacitance calculated by this model is indicated as:

$$C = \frac{\varepsilon}{d} \qquad \text{.....(1.1)}$$

Where: ε is the electrolyte dielectric constant, which is also known as permittivity of the electrolyte, and d is the thickness of electric double layer. However, the Helmholtz model is not accurate enough to show the relation between capacitance and voltage, because Helmholtz failed to a consider the

resistance in the electrolyte which can lead to a different distribution of charges.

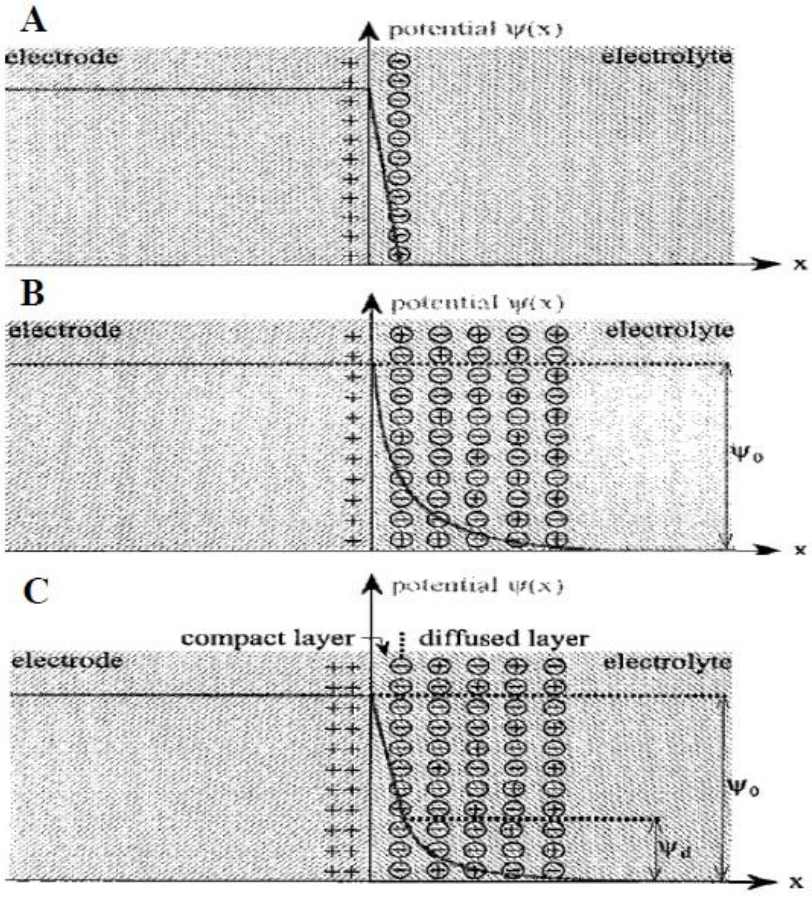


Figure 1.2: The relation of potential with distance away from interfacial layer between electrode and electrolyte in three models: Helmholtz's model (A), Gouy and Chapman's model (B), and Stern's model C [10].

The Helmholtz model was later modified by Gouy and Chapman who proposed the existence of a diffuse layer of ions which leads to an exponentially decrease of the electric potential from the electrode surface to the bulk of electrolyte. As Gouy and Chapman did not involve the dimension of ions and molecules in their model, the relationship between surface capacitance versus surface potential cannot be described correctly especially at high surface potential. To solve this problem, Sterrn established a new model by combining theories of Helmholtz and Gouy and Chapman, which separates the space of

charges into two parts: the compact, formed by absorption of electrolyte ions and diffused layer, explained by Gouy and Chapman [11-12]. Thus, the total specific capacitance C depends on the surface capacitance of the compact layer Cc and the diffused layer Cd:

$$\frac{1}{C} = \frac{1}{C_C} + \frac{1}{C_d} \qquad \text{…….. (1.2)}$$

For a conventional capacitors or parallel electrode capacitors, their capacitance can be determined by the following equation:

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d} \quad \text{……} \qquad (1.3)$$

Where: εr is the dielectric constant, $\varepsilon 0$ is the dielectric constant of vacuum, d is the distance between separated charges, and A is the surface area of the electrode [13]. According to electric double layer theory, if larger surface area of an electrode can contact with the electrolyte and if more charges can be absorbed onto the electrode, a super capacitor can have higher capacitance. Therefore, porous materials (e.g. activated carbon), which have large specific surface area (SSA) and are highly conductive, are ideal super capacitors electrode materials. It is possible to imagine that each pore in the porous electrode works as a conventional parallel electrode capacitor. Thus, as shown in Figure 1.3, a super capacitor is composed of billions of small electric double layer capacitors. When a super capacitor is converted to a circuit model, it is necessary to involve the resistance of each pore, the external resistance and the membrane resistance [14].

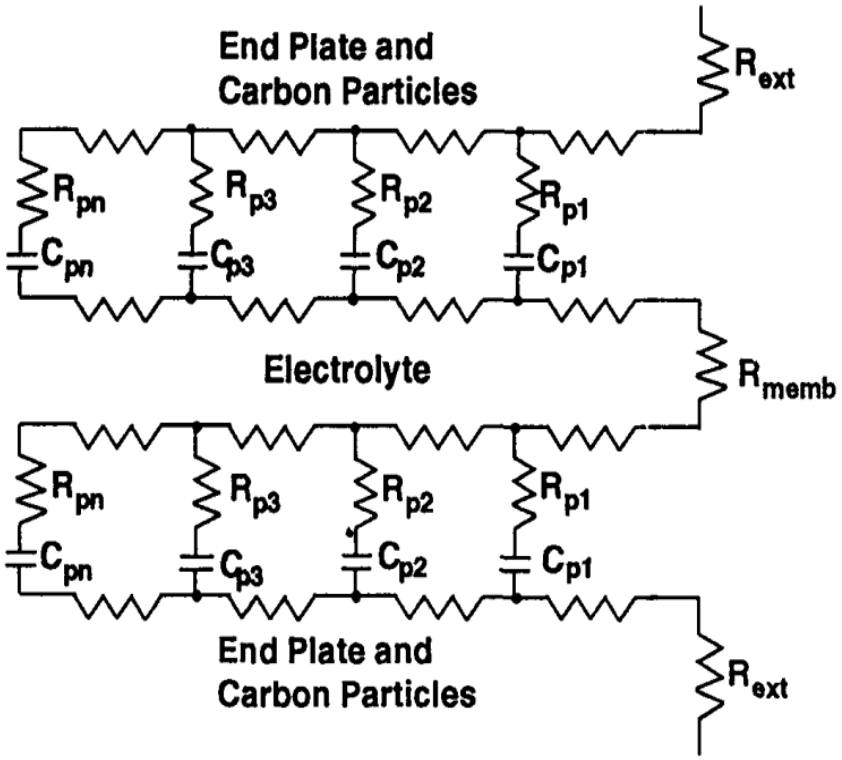


Figure 1.3 Circuit model of a supercapacitor which includes capacitance and resistance in each small pores as well as the external and membrane resistance [10].

1.4 Operation Principle of Supercapacitors

Unlike traditional capacitors whose energy is stored on the two metal electrodes separated by a dielectric media, Super capacitors can store energy by forming electric double layers between the electrode and the electrolyte. Depending on whether a faradaic reaction occurs in an energy storage process, the capacitance of super capacitor is classified into electric double layer capacitance and pseudo capacitance. The capacitor which has electric double layer capacitance is called electric double layer capacitor because it stores energy in an electrostatic way by separating electrons and electrolytic ions in the electric double layer. The capacitor which has pesudocapacitance is called electrochemical capacitor since it stores energy in an electrochemical way by having fast faradaic redox reaction on the surface of electrodes.

1.4.1 Mechanism of Electric Double Layer Capacitors

In an electric double layer capacitor, there is no faradaic reaction involved in the energy storage process leading to the major difference from batteries whose electrodes have redox reaction during charging and discharging. On the electrodes of electric double layer capacitor, there are only absorption and desorption of ions when external voltage is applied. Thus, the electrode polarization of electric double layer capacitor is much faster than batteries due to the absence of limitation of chemical reaction kinetics. The fast charge and discharge features of super capacitors can lead to better power performance than that of batteries. From the Rag one Plot shown in Figure (1.4), double layer capacitors have one magnitude higher power density than LIBs, solar batteries and fuel cells. In addition, faradaic reactions that occur in active materials on the electrodes may result in the swell or dissolve of active materials during charge and discharge. For example, the dendritic Li growth on the electrode during charge and discharge may penetrate the separator between two electrodes and causes a short circuit or even explosion [15]. Similar phenomena also present in silicon based anode of LIBs. Insertion and extraction of lithium ions can cause large volume and morphology change of silicon based electrode. This drawback is the main reason for degradation of electrode materials and inferior cycling stability of silicon based LIBs [16]. Lithium sulfur batteries also suffer from the loss of active electrode materials because sulfur can convert to dissolvable products during charge and discharge, which is well known as the “shuttle effect” [17]. However, electric double layer capacitors take the advantage of absence of faradaic reaction, so generally, double layer capacitors can maintain over 100,000 cycles. Compared with SCs, batteries can only survive thousands of cycles. Besides, double layer capacitors have more choices in terms of the electrolyte. Unlike batteries, the reactions of electrodes and electrolytes are

fixed, double layer capacitors can adopt various electrolyte to satisfy different functions.

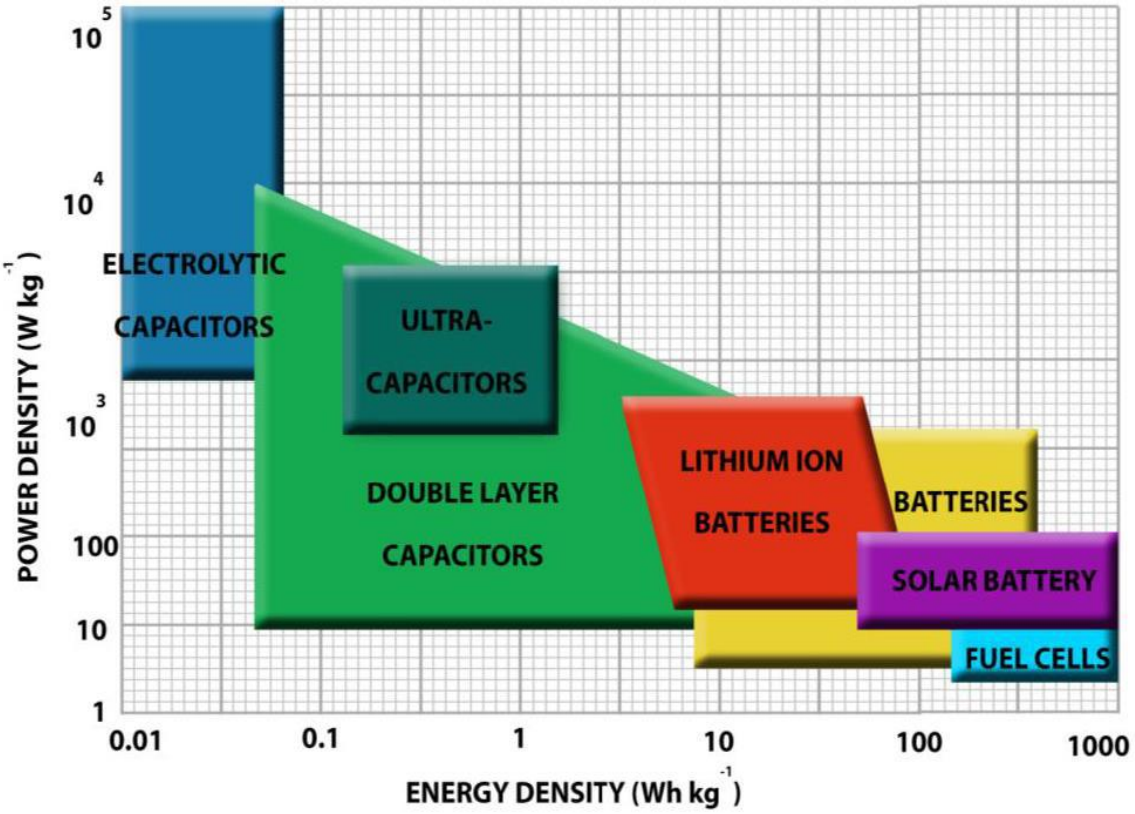


Figure 1.4: Ragone Plot showing energy density versus power density of common electrical energy storage devices [18].

1.4.2 Mechanism of Electrochemical Capacitors

Electrochemical capacitors are designed by using the active materials which can have fast and reversible reaction on the surface of electrodes. Due to the presence of faradaic reactions, electrochemical capacitors are similar to batteries. Thus, electrochemical capacitors are also called pseudo-capacitors, and the capacitance of electrochemical capacitors is defined as pseudo capacitance. When a voltage is applied on the two electrodes of electrochemical capacitors, faradaic redox reaction occurs on the surface of the electrode to transfer charges between electrodes and the electrolyte, generating circuit in the electrochemical capacitors system. Transition metal

oxides such as MnO_2, [19] RuO_2, [20] NiO, [21] Co_3O_4, [22] and V_2O_5 [23] are common active materials of electrochemical capacitors. In addition to conventional transition metal oxides, materials that possess pseudo capacitance also include: ternary metal oxides and metal hydroxides such as $NiCo_2O_4$, [24]$ZnCo_2O_4$,[25] $Ni(OH)_2$,[26] and $Co(OH)_2$;[27] metal sulfides; and conductive polymers such as polypyrrole, polyaniline, and polythiophene.[28]. Generally, pseudocapacitance is higher than electric double layer capacitance because electrochemical capacitors not only store electrical energy on electrode surface but also store energy in the bulk of the electrode near the surface. The average specific capacitance of AC is only 150 F/g whereas specific capacitance of some pseudo-capacitors can reach over 1000 F/g [29]. Therefore, electrochemical capacitors are able to provide higher energy density than electric double layer capacitance according to the equation (1.4).

$$E = \frac{1}{2CV^2} \qquad \text{……..} \qquad (1.4)$$

Where: E refers to energy, C is the capacitance, and V is the potential window of the capacitor.

Some electrochemical processes can even increase the working potential window to further enhance the energy density. However, the rate of electrochemical processes is limited by chemical kinetics, resulting in the sacrifice of the power density. Moreover, electrochemical capacitors also suffer from poor cycle life due to the presence of reversible redox reaction, which can lead to loss of active materials.

1.5 SCs Capacitance, Energy Density and Power Density

In the structure of a super capacitor, the two electrodes are able to be treated as two capacitors in series. Thus, the total capacitance of a super capacitor can be described using the following equation:

$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.5)$$

Or $$C_T = \frac{C_1 C_2}{C_1 + C_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.6)$$

Herein, C_T is the total capacitance and C_1, C_2 are individual capacitance of each electrode. When the materials of two electrodes are same, C_1 is equal to C_2. According to equation (1.6), the total capacitance is half of individual capacitance of one electrode. This type of SCs is called symmetric super capacitors. On the other hand, if C_1 is not equal to C_2, which illustrates the materials of two electrodes are different, the corresponding super capacitors are named asymmetric super capacitors. Based on equation (1.6), the total capacitance of asymmetric super capacitors is mainly determined by the electrode which has lower capacitance. Depending on the total capacitance and the operational voltage of the super capacitor, it is possible to evaluate the total energy that can be stored in this device by equation (1.4). In addition, the power of a super capacitor is given by the following equation:

$$P = \frac{V^2}{4Rs} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.7)$$

Where: Rs represents the equivalent series resistance (ESR) of a super capacitor. ESR generally derives from the intrinsic resistance of electrode materials and electrolyte, transfer resistance of the diffusion of ions from electrolyte to the surface of the electrode as well as the resistance between electrodes and current collectors due to poor contact.

Hence, in order to achieve a high power, it is necessary to reduce the inner resistance of a super capacitor. On the other hand, since the value of power is proportional to the square of voltage, extending the potential window of a super capacitor is a more effective way to increase the power. Basically,

the potential window is associated with the intrinsic property, structure of the electrode materials and the stability of the electrolyte. With regard to energy density, it can be determined by equation (1.4). In addition to increasing the potential window, enhancing the specific capacitance of a super capacitor is also beneficial for its energy density. The specific capacitance is defined as the amount of capacitance possessed by unit mass of a material. The relationship of specific capacitance and mass is indicated by the following equation:

$$Cs = \frac{C_T}{W} \qquad \text{……..} \quad (1.8)$$

Where: Cs is the specific capacitance whose unit is F/g, C_T is the total capacitance of an electrode whose unit is Farad (F), and W is the weight of the electrode whose unit is gram (g). However, although some materials have extremely high theoretical specific capacitance, they may be unable to exert their capacitance completely in practical operation because of the low utility ratio of electrodes. On one hand, the utility ratio is hampered by the bad diffusion of electrolyte ions, which makes the ions fail to arrive at the whole surface of the electrode. On the other hand, poor conductivity of the electrode materials can also reduce the utility ratio of an electrode by impeding the formation of an electric double layer or by retarding the reversible redox reactions. Thus, to boost the utility ratio of an electrode, it is essential to build a rational electrode structure with effective electrons and ions transition channels.

1.6 Carbon Materials for EDLC

Carbon materials are found to be suitable materials for super capacitors electrodes in early stage due to their large reservation in nature, low cost, environmental benignity, facile processing procedure, controllable pore size, high specific surface area, high electrical conductivity, good chemical stability and stable performance in wide range of temperature. Carbon materials are basically utilized in electric double layer capacitors. Due to the stability of

carbon materials in electrolyte, it can hardly be used as electrochemical capacitors electrodes which store electrical energy by fast reversible reaction. As shown in Figure 1.5, the cyclic voltammetry of carbon materials are approximately rectangular without any redox peaks. With regard to the galvanostatic charge-discharge curves, the charge curves and corresponding discharge curves are basically symmetrical, indicating the high columbic utility ratio of electrostatic energy method.

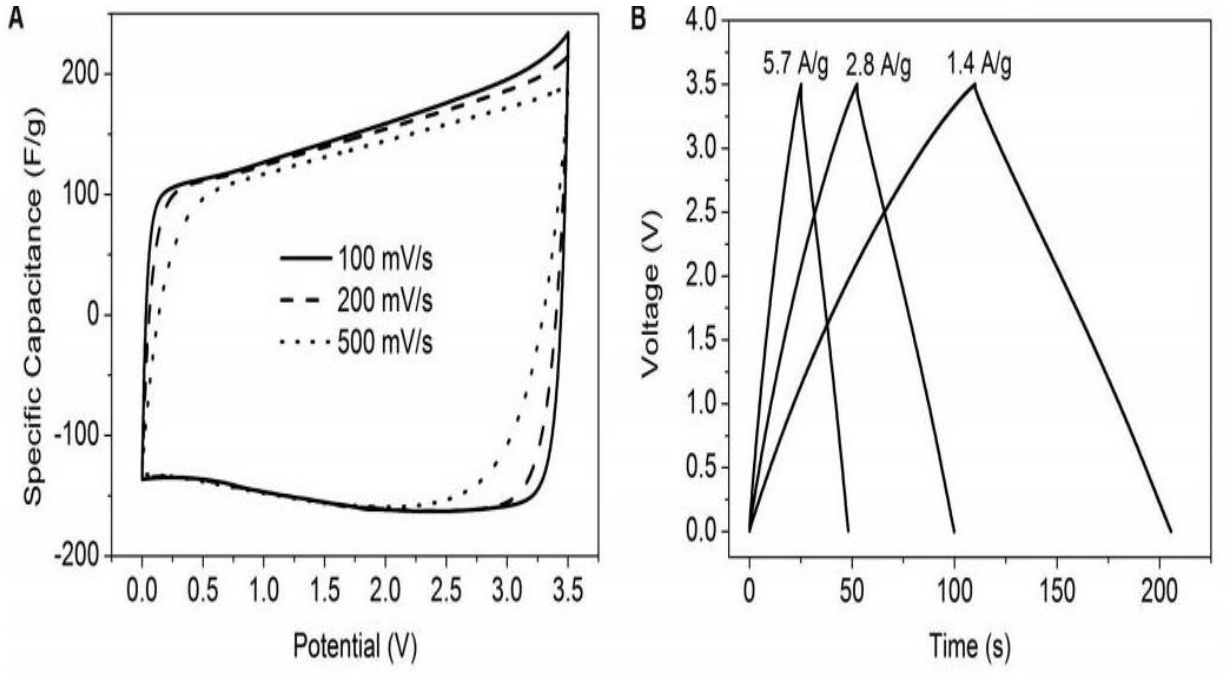


Figure 1.5: (A) Cyclic voltammetry curves of microwave exfoliation/reduction of GO electrode at different scan rate of 100 mV/s, 200 mV/s and 500 mV/s. (B) Galvan static charge-discharge curves of microwave exfoliation/reduction of GO electrode under different current density [30].

Since carbon materials are only able to store electrical energy on the surface of the electrode, the capacitance of carbon materials is mainly associated with the characteristics of electrode surface such as specific surface area, pore volume, pore shape, pore size distribution, and conductivity. As reported by Jiujun Zhang, [31] among all the factors mentioned above, the performance of carbon materials are dominantly influenced by specific surface

area and pore size distribution. Currently many carbon materials with high surface area have been reported such as AC [32], templated porous carbon[33], carbon aerogels[34], carbon nanotubes (CNTs), [35] and graphene [36].

High specific surface area plays an essential role in super capacitor electrode materials. Since carbonaceous materials only store energy on the interface between electrode and electrolyte by the absorption and desorption of charges, higher specific surface area can allow the electrode to accumulate more charges in unit mass materials. Based on Brunauer–Emmett–Teller (BET) theory, the specific surface areas (SSA) of different carbonaceous materials are studied. SSA of commercial AC is between 500-1700 m^2/g [37] .The SSA of activated carbon fiber varies with the processing techniques. The highest SSA of AC can be more than 3000 m^2/g. [38-39] SSA of templated porous carbons is mainly associated with the property of templates. Some templated porous carbons can achieve as high as 4000 m^2/g [40-43] .In addition to specific surface area, pore size also has significantly effect on specific capacitance. But the mechanism of this effect is still not quite clear. A theoretical formula is reported by Huang et al [44] **.** In case of mesoporous carbon whose pore size is larger than 2 nm and smaller than 100 nm, the model showing the relation of pore size and specific capacitance with fixed SSA can be described in the following equation:

$$\frac{C}{A} = \frac{\varepsilon_r \varepsilon_0}{b \ln(\frac{b}{b-d})} \qquad \ldots\ldots\ldots\ldots \quad (1.9)$$

Where: b is the radius of the pores, d is the distance between electrolyte ions and carbon surface. Recent study shows that when the pore size is below 1 nm, the capacitance increases sharply and reaches the maximum value when the pore size is the same as that of ions, indicating the highest capacitance is achieved when a single ion is in one pore. Further research was carried out to

demonstrate that it is necessary for ions to remove the solvation shells when they enter into pores.

1.6.1 Activated Carbon

Activated carbon materials not only have the general characteristics of carbonaceous materials such as benign conductivity, chemical stability, and application in a wide temperature range, but also have high SSA, making it preferred materials for super capacitors. AC is enormously popular due to the low cost and facile processing techniques. Many carbonaceous materials, such as coke wood, and charcoal, can be used as precursors of AC. Materials with low degree of porosity are able to be processed to AC by suitable activation including chemical activation, physical activation, and hybrid activation [45]**.** Carbonization is usually applied to synthesize AC, since most of other elements such as hydrogen, oxygen, and nitrogen are removed by the heat treatment in the inert atmosphere. After calcination, the carbonized materials only generate a little porosity. In order to largely increase the SSA of carbonized product, further activation is necessary.

Basically two scenarios: chemical activation and physical activation, are able to be adopted. In chemical activation procedures, some activation agents such as $ZnCl_2$, H_3PO4, KOH, K2S and KCNS are added and are subsequently removed by washing to obtain pores. Physical activation is also known as partial gasification which uses steam, carbon dioxide, and air as the activation agents. Following reactions may happen during the physical activation such as endothermic reaction of carbon with steam:

$$C + H_2O \rightarrow CO + H_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (1.10)$$

reaction of carbon with carbon dioxide:

$$C + CO_2 \rightarrow 2CO \qquad \ldots\ldots\ldots\ldots\ldots\ldots \qquad (1.11)$$

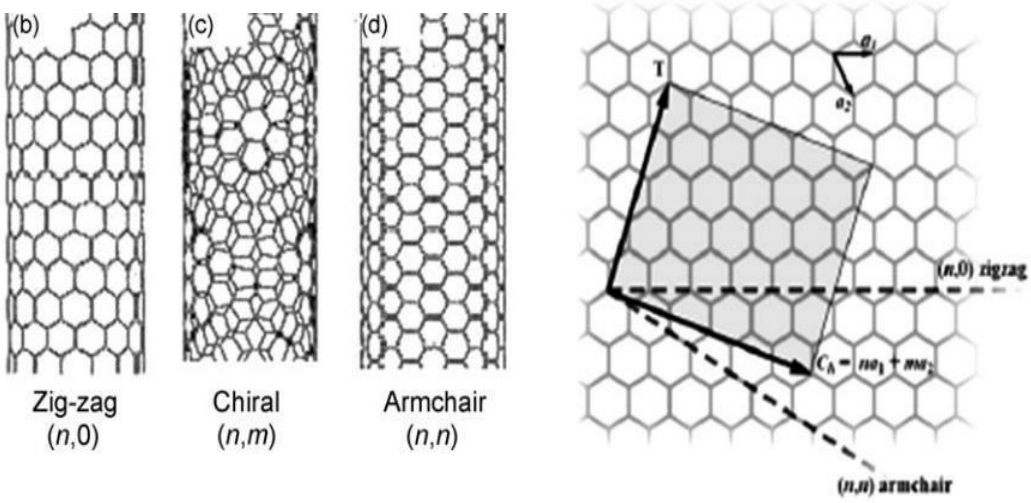
reaction of vapor with carbon oxide:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{……..} \qquad (1.12)$$

The performance of super capacitors using activated carbon electrodes is not only related to the surface area but also to the pore size distribution. It is reported that an activated carbon based super capacitor with up to 3000 m^2/g specific surface area only has the specific capacitance less than 10 $\mu F/cm^2$, which is smaller than theoretical capacitance. Thus, the utility ratio of high specific surface area is also essential to the behavior of super capacitors [46] **.** To increase the efficiency of surface area, it is necessary to adjust the pore shape, pore size distribution, and the pore structure. Generally, the capacitance of AC in aqueous electrolyte is from 100 F/g to 300 F/g.[47] However, in organic electrolyte, the capacitance is relative smaller (approximately 150 F/g). This is mainly because the ions in organic electrolyte are larger than the ions in aqueous solvent, making some small pores in the AC unable to store charges any more.

1.6.2 Carbon Nanotubes

Carbon nanotubes are advanced carbon materials due to their superior properties such as high conductivity, good mechanical property, benign chemical and thermal stability, as well as the unique porosity. Based on directions of rolling a graphene sheet, carbon nanotubes are categorized as Zig-zag.



(a) **(b)**

Figure 1.6: (a) Different atomic structures corresponding to the directions of rolling a graphene sheet. Atomic structure of Zig-zag CNTs (b), atomic structure of Chiral CNTs (c), and atomic structure of Armchair CNTs (d) from [48].

CNTs are preferred electrode materials for high power density devices owing to their low resistance. As mentioned above that the power is determined by equation (1.7) which shows that a low resistance value can lead to high power density. Besides, the small resistance in CNTs is also able to show good rate capability. In addition to the good conductivity, the unique structure and mechanical stability has made CNTs good substrates for other active materials. Combination of CNTs and faradaic materials such as TiO_2, [49] MnO_2, [50] and V_2O_5[28], are widely studied. The composites take advantage of the high power density of CNTs and high energy density of faradaic materials.

1.6.3 Templated Porous Carbon

Owing to overwhelming advantages of porous carbon in the area of super capacitors, active carbon cannot meet the requirements of high-performance super capacitors. The templating methods are very effective to synthesize carbon materials with high specific surface area, interconnected pore structure,

and proper pore size, which are essential factors for advanced super capacitor electrodes [51]. Basically, the process of templating techniques includes the preparation of carbon precursors, introduce of the carbon precursors into the template, and removal of the template.

To synthesize porous carbon materials with different pore shape, pore order, and pore size, various templates have been used to fabricate specific porous carbon. Silica spheres are one of very common templates. Since the presence of silica spheres with different sizes, it is possible to produce high ordered porous carbon with micropores, mesopores, and macropores. A mesoporous carbon spheres with silica spheres as the templates have been studied and achieved 159 F/g at (0.5 A/g) [52]. Other types of hard templates are also studied such as SBA-15 ordered mesoporous silica[53], MCM-41 mesostructured silica[54], and zeolites[55]. In addition to hard templates, soft templates (surfactant templates) such as Pluronic P-123 and F-127 are also common templates for synthesizing porous carbon [56-57]. A three-dimensional ordered mesoporous carbon sphere electrode was synthesized by using Pluronic P-123 as the template. The mesoporous carbon sphere electrode can achieve a specific capacitance of (14 $\mu F/cm^2$) with specific surface area of (601 m^2/g) and pore volume of (1.70 cm^3/g).

1.6.4 Graphene

Graphene is a two-dimensional carbon sheet forming by sp2-hybridized. This specific honeycomb structure is possible to be built into many other allotropes of carbon such as CNTs, graphite, and fullerenes. Graphene was discovered during the study of graphite when people tried to utilize fewer layers. Finally, a single layer of graphite was exfoliated in Manchester University in 2004 by Geim and his colleagues [58] .

Basically, a single layer graphene is composed of hexagonal sp2 carbon atoms. The specific structure exhibits high mechanical stability, thermal

stability, and great electrical property. In addition, graphene also has extraordinary high specific surface area (2675 m^2/g) which especially benefits for the performance of electric double layer capacitors. If the large specific surface area can be fully utilized, the specific capacitance of an EDLC is able to reach 550 F/g, proving that graphene is a promising materials for supercapaictor electrodes.

Many graphene-based electrode materials of supercapacitors have been studied both in aqueous and organic electrolytes. Among the synthesis of these electrode materials, different methods have been adopted such as chemical modification, microwave irradiation, thermal treatment of graphene oxide at high temperature, and at low temperature but in vacuum circumstance. Normally, the capacitance of aqueous super capacitors with graphene electrodes is between 130 F/g and 200 F/g, [59] and the capacitors tested in organic electrolyte show lower capacitance from (100 F/g to 150 F/g). The reason that the specific capacitance of practical graphene-based super capacitors cannot reach theoretical specific capacitance of (550 F/g) is mainly because that graphene sheet has high possibility of restacking during the preparation, leading to the lack of sufficient utilization of surface area in graphene.

Due to the high conductivity and mechanical stability, graphene is also suitable for using as the substrate for active materials like faradaic materials with pseudo capacitance. A 3D macroporous graphene frameworks combined with thin layer of MnO_2 have been reported for super capacitor electrodes. The porous graphene frameworks successfully offer high surface area, interconnected channels for electrolyte ions, and conductive channels for electrons. A thin layer of MnO_2 is essential for the high specific capacitance of 389 F/g at a current density of (1 A/g) owing to its high pseudo capacitance [60] **.** The contribution of faradaic materials strongly depends on their effective surface being used and their uniform coating on the carbon substrates. Although pure carbon materials are hard to achieve high energy

density and power density for super capacitors, they still play an important role in obtaining high-performance super capacitors owing to their high surface area and superior conductivity. Currently, one strategy of developing super capacitors with high power density and energy density is to uniformly coat a thin layer of faradaic materials on carbon materials. With the help of high-surface-area and conductive carbon materials, active materials are able to exert high pseudo capacitance and greatly contribute to the energy density.

1.7 Faradaic Materials

Unlike carbon materials, which store charges in the Helmholtz Double layer, faradaic materials store charges with fast redox reactions on the surface or in the bulk of the electrode near the surface. Basically, the specific capacitance of carbon-based materials is from 10 $\mu F/cm^2$ to 50 $\mu F/cm^2$. However, the specific pseudo capacitance is approximately10-100 times higher than carbon materials, which is very attractive. Therefore, pseudo capacitive materials are widely studied in recent years in order to develop advanced electrode materials for the next generation of super capacitors. Typically, the pseudo capacitive materials are able to be divided into two categories: conductive polymers and transition metal oxides [61].

1.7.1 Conductive Polymers

Conductive polymers are generally low-cost, environmental friendly, and their source is extensive. Besides conductive polymers have high conductivity, wide potential widow, and high porosity, making them promising candidates for super capacitor electrode materials. During charging and discharging process, redox reactions occur not only on the surface of the conductive materials but also in the bulk.

When oxidation reaction occurs, ions are attracted from the electrolyte to the polymers, and released to the electrolyte during reduction. The redox reactions are highly reversible, since there is no phase

transition, making conductive polymers competent for long cycle life. The conductive behavior of conductive polymers is mainly because conductive polymers are positively or negatively charged by oxidation or reduction processes. These specific oxidation and reduction processes are generally named as doping. Conductive polymers only have conductive property at a doped state.

There are three types of conductive polymers commonly used as electrode materials for super capacitors: polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and their derivative materials. Since conductive polymers are active and can work well only under certain conditions, it is important to use them in the right electrolyte and right potential ranges. For example, the negative doping potentials of PANI and PPy are usually lower than the reduction potential of electrolyte, therefore they can only be positively doped and better to be used as the cathode electrode materials. In addition, PANI performs better in acidic electrolyte, where contains the necessary protons for PANI during its charging and discharging [61] .The working potential window is also essential for conductive polymers. Under an improper potential, conductive polymers may be degraded or lose the conductivity. Thus, the potential range plays a key role in the performance of conductive polymer based super capacitors.

1.7.2 Transition Metal Oxides

Transition metal oxides (TMOs) are widely studied as the electrode materials for super capacitors because of their high pseudo capacitance and better cycle stability compared to conductive polymers. As faradaic materials, TMOs have two or more oxidation states in the same phases. When charging and discharging take place, TMOS are able to convert between different oxidation states and protons can insert into and extract from the oxide lattice during reduction and oxidation. The redox reactions are fast and reversible,

since no phase changing occurs in the process. Several TMOs such as RuO_2, [62] MnO_2, [63] V_2O_5, [64] NiO, [65] and Co_3O_4 [66], have been found to have the above properties and been tested as super capacitor electrode materials.

RuO_2 is one of extensively studied TMOs for the electrode of super capacitors, which exhibits high conductivity, long cycle life, high capacitance, and high rate capability. In addition, RuO_2 can have high potential window, thus facilitating the energy density of RuO_2-based electrodes. Three oxidation states are accessible for RuO_2 at the voltage of (1.2 V) to attract and release ions during charging and Discharging. Electric double layer mechanism also presents in RuO_2 electrodes; however, up to 90 % of the total capacitance is contributed by pseudo capacitance. The pseucapacitance of RuO_2 is widely studied in both acidic and alkaline electrolyte, and it is reported that RuO_2 can exhibit different faradaic behaviors with distinct reversible redox reaction mechanisms. [67]. In an acidic solvent, the rapid redox reaction can be described as the following chemical equation:

$$RuO_2 + xH^- + xe^- \leftrightarrow RuO_2 - X(OH)X \quad \ldots\ldots\ldots \quad (1.13)$$

Where: protons are absorbed to the surface of RuO_2 and the RuO_2 can convert from oxidation states Ru(II) to Ru (IV). However, the conversion of oxidation state is different in alkaline environment. When discharge occurs, RuO_2 will be oxidized to higher valence state compounds in alkaline electrolyte. Generally, RuO_2 based electrode materials can achieve high capacitance and moderate rate capability. A RuO_2/CNT nanocomposite has been reported with a specific capacitance up to 953 F/g, which is approximately 10 times higher than the specific capacitance of normal carbon materials [68]. Although RuO_2 is very attractive due to the high pseudo capacitance, it is still hindered by the high cost and limited reservation in nature for extensively application.

Therefore, transition metal oxides with low cost, extensive source in nature and high theoretical specific capacitance are highly demanded for the next generation super capacitors. Many transition metal oxides have been explored as super capacitors electrode materials such as the oxides of nickel, cobalt, iron, and vanadium. However, among all the transition metal oxides, manganese dioxide holds the brightest promise in pseudo capacitive super capacitor electrode materials and has been most widely investigated because of the low cost, large natural reservation, high theoretical capacitance (1370 F/g), and nontoxicity [69].

1.8 ($ZnFe_2O_4$) as electrode material for super capacitor

Regardless of the environmental pressure to reduce energy consumption, global power demand is growing—and one of the ways to solve this "looming energy crisis" is through the exploration of novel earth-abundant energy materials [70]. Further, the pace of technological change is getting faster, thus the miniaturization of electronic devices is also key [71]. These demands can be met by realizing an efficient oxide energy material at the nanoscale by controlling their complex crystal structure with many degrees of freedom (i.e., charge, spin, and orbital) [72]. Oxide materials usually possess high density, display robust physical properties, and show great flexibility to tune their optical, electrical, and magnetic properties, with subtle changes such as elemental substitutions, defect, and strain engineering [73]. Among the oxides, earth-abundant Zn-ferrite can be the potential alternative energy material. Zn-ferrites exhibit a unique set of functional properties [74]; it possesses a normal spinel structure ($ZnFe_2O_4$) in the bulk form at room temperature, whereas inverted spinel structure has been observed at the nanoscale. The electronic band structure calculations predict the insulating character of $ZnFe_2O_4$ [75].

The reported room temperature resistivity value of $ZnFe_2O_4$ is $r = 2 * 10^2$ (Ω.cm), which is two to three orders of magnitude lower than other spinel ferrites [76]. The optical band gap energy [77], with values of 2.02 eV and 2.33 eV for the indirect and direct transition near the maxima of UV-Visible absorption curves is suitable for energy harvesting with sufficient amounts of electron-hole pair generation from the solar spectrum, and suitable to drive redox reactions with proper band positions [78]. Appropriate doping of Zn in Fe_3O_4 [79], i.e., a good control of the $Zn_yFe_{3-y}O_4$ stoichiometry, is one way to tune electric, magnetic, and optical properties which provides a versatile playground to build $ZnFe_2O_4$ based sensors, solid-state energy conversion devices, and solar cells. The nanostructuration of $ZnFe_2O_4$ is a second lever of action which enables external tuning competence of the properties by inducing the cation inversion [80]. The cation inversion, an interchange of Zn and Fe atomic positions in the spinel $ZnFe_2O_4$ strongly depends upon the size of nanostructures produced by different growth methods [81]; varying the extent of cation-inversion in spinel structures allows tuning their electronic and spin structure, which eventually can be used to design various spintronic, microwave, and photoelectrochemical (PEC) functionalities. The most important cost factor in energy storage applications is light-absorbing material's efficiency. In the case of $ZnFe_2O_4$, the theoretical solar-to-hydrogen (STH) conversion efficiency is estimated to be 17.9% for PEC water splitting [82]. Furthermore, the morphology and size of $ZnFe_2O_4$ as electrode material are crucial factors in supercapacitors and lithium-ion batteries, wherein theoretical capacity for supercapacitor (2600 F/g) and Li-ion battery (1072 $mAhg^{-1}$) are higher than when using other ferrites. The synergies between Zn and Fe ions in Fe-based binary oxides with large surface area offers higher electrochemical kinetics, active sites, and delivers superior capacitance [83]. Thus, the ability to strongly tune the overall properties of nanostructured

$ZnFe_2O_4$ material demonstrates its pertinence in synergist energy storage applications .

1.9 Literature Review

1. **Bresser *et al.*, (2012) [84],** presented the preparation and electrochemical characterization of a new material consisting of carbon coated ZnFe2O4 nanoparticles. This material is capable of hosting up to nine equivalents of lithium per unit formula, corresponding to an exceptional specific capacity, higher than 1000 mAh g^{-1}. Composite electrodes of such a material, prepared using environmentally friendly sodium carboxymethyl cellulose as binder, showed the highest, ever reported, specific capacity and high rate performance upon long-term testing.

2. **Bourrioux *et al.*, (2017) [85],**studied the electrochemical performances of $ZnFe_2O_4/\gamma\text{-}Fe_2O_3$ nanoparticles prepared by laser pyrolysis was Evaluat. A $ZnFe_2O_4/\gamma\text{-}Fe_2O_3$ nanocomposite was successfully synthesized by laser pyrolysis, a very attractive nanosynthesis technique characterized by high versatility and flexibility. The $ZnFe_2O_4/Fe_2O_3$ nanocomposite was tested as negative electrode material for lithium-ion batteries, showing significantly improved lithium storage properties with a high reversible capacity and rate capability compared to pure $ZnFe_2O_4$ electrode. A capacity exceeding 1200 F g-1 is sustained after 100 cycles at 100 mA/g, with a gradual increase of the capacity during cycling. At 500 mA/g current rate, a reversible and stable capacity of 360 F g-1 is observed after 300 cycles. Electrochemical measurements with several electrolytes and electrode formulations were also conducted in order to explore the origin of the extra capacity and its increase with cycling.

3. **Yao *et al.*, (2018) [86],** $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$ nanocomposites From Sulfuric Acid Leaching Liquor of Jarosite Residue and the preparation of $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$ nanocomposites from the leaching liquor of jarosite residue by a facile chemical coprecipitation method followed by heat treatment at 800°C in air. When evaluated as anode material for Li-ion batteries, the $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$ nanocomposites exhibits high lithium storage activity, superior cyclic stability, and good high rate capability. The synthesis of $ZnFe_2O_4/\alpha\text{-}Fe_2O_3$ nanocomposites from the leaching liquor of jarosite residue and its successful application in lithium-ion batteries open up new avenues in the fields of healthy and sustainable development of industries.

4. **Saraf *et al.*, (2019) [87**], employed a facile solvothermal technique to produce $ZnFe_2O_4$ microspheres. The obtained noticeable specific capacitance (175 F g^{-1} at a current density of 5 A g^{-1}) and rate performance with good cycling stability were assigned to the large surface area and unique porosity of $ZnFe_2O_4$ microspheres.The work opens up an avenue to consider crystalline, porous and high surface area enabled hetero-metallic oxides to be promising candidates for high-performing supercapacitors.

5. **Maksoud *et al.*, (2020) [88],** comparesed the following materials used to fabricate supercapacitors: spinel ferrites, e.g., MFe_2O_4, $MMoO_4$ and MCo_2O_4 where M denotes a transition metal ion; perovskite oxides; transition metals sulfdes; carbon materials; and conducting polymers. The application window of perovskite can be controlled by cations in sublattice sites. Cations increase the specifc capacitance because cations possess large orbital valence electrons which grow the oxygen vacancies. Electrodes made of transition metal sulfdes, e.g., $ZnCo_2S_4$, display a high

specifc capacitance of 1269 F g^{-1}, which is four times higher than those of transition metals oxides, e.g., Zn–Co ferrite, of 296 F g^{-1}. This is explained by the low charge-transfer resistance and the high ion difusion rate of transition metals sulfdes.

6. **Bohra *et al.*, (2021) [89],** studied the properties, such as chemical and thermal stability and the reduced toxicity of Zn over other metals, can be easily tuned was reviewed in various $ZnFe_2O_4$ nanostructures depending on the choice, amount, and oxidation state of metal ions, the specific features of cation arrangement in the crystal lattice and the processing route used for the fabrication. Furthermore, the remarkable cation inversion behavior in nanostructured $ZnFe_2O_4$ extensively cast-off in the high-density magnetic data storage, energy storage devices like Li-ion batteries, supercapacitors, and water splitting for hydrogen production.

1.10. Aim of the Study

1- Preparing the $ZnFe_2O_4$ nanoparticles as electrode for advanced energy storage applications such as medical ear stethoscope used for children ,elderly and police communications system.

2-The remarkable cation inversion behavior in nanostructured $ZnFe_2O_4$ extensively cast-off in the high-density magnetic data storage

3- Exploring the new electrode materials for supercapacitors as a solution to the ever-rising demands for better performing devices exhibiting longer cycle life and improved safety.

Chapter two

Theoretical Background

Chapter Two

Theoretical Background

2.1 Introduction

This chapter includes a general description of the theoretical Background that relates to this study such as the development of supercapacitors,electrolyte of supercapacitors and electrochemical characterization techniques. It will help to understand the enhance the electrochemical properties by altering the components.

2.2 Supercapacitor Technology

Supercapacitor is an advanced energy storage device of higher energy density and higher cycle stability than battery or traditional capacitors. However, its energy density is smaller than that of lithium-based or lead-acid batteries. The development of supercapacitors proceeded very quickly, and they are of particular interest in automotive applications for hybrid vehicles and as supplementary energy storage for battery electric devices. As a result, extensive going work has been undertaken to increase the energy density of the supercapacitors.

2.2.1 double - layer capacitors

Activated carbon-based super capacitors materials applied in Super capacitors. The advantages of activated carbons are due to their low cost, large capacitance, and good cycling stability, which make them the most highly developed technology. In these devices the charge storage is electrostatic, and the electrolyte ions are reversibly adsorbed in the electrochemical double-layer of the porous carbon electrode structure [90].

As carbon nanotubes (CNTs) have special internal structures, high surface area remarkable chemical stability, and electronic conductivity, they have been considered and demonstrated to be excellent new material for

electrodes in electrochemical energy storage and conversion devices, including super capacitor electrodes.

C.Du et.al published a paper in 2006, reporting the fabrication of multi-walled carbon nanotube (MWNT) thin films by an electrophoretic deposition technique [91]. The most important finding in their research is that the super capacitors built from such thin film electrodes presented a superior frequency response, with afrequency "knee" at about 7560 Hz, 70 times higher compared to any "knee" frequency (100 Hz), which has so far been reported.

Other researchers have reported on the electrochemical and cycling characterization of an activated carbon super capacitor cell [92]. This cell contained micro porous activated carbon as the active material and Wbutyl-Wmethylpyrrolidinium bis (trifluoromethanesulfonyl) imide (PYR14TFSI) ionic liquid as the electrolyte. (60 F g^{-1} capacit was exhibited at a 20-mV s^{-1} scan rate, with a maximum operating potential range of 4.5 V at 60 °C in CV measurements in their research. This capacitor maintained high cycling stability for 40,000 cycles without any change in the cell resistance (9 Ω cm^2) and a voltage up to 3.5 V at 60 °C, when assembled in a coin cell. Such high performance makes these sorts of capacitors suitable candidates for potential high temperature applications (>60 °C).

2.2.2 Solid-State Supercapacitors

Most of the redox supercapacitors reported [93] are based on liquid electrolytes. These supercapacitors with liquid electrolytes have the major disadvantages of corrosion, self discharge, bulky design, and low energy density, similar to the case of liquid electrolyte batteries. To avoid these shortcomings, major attention has been recently devoted to the fabrication of so-called solid-state capacitors, which apply solid polymer or gel as electrolytes. This kind of electrolyte is selected to provide high ionic conductivity and advantageous mechanical properties, including flexibility for

proper electrode—electrolyte interactions and the ability to form thin films of desirable area. The solid-state redox supercapacitors are the new generation of supercapacitors and have not been widely reported. A few studies have recently investigated different polymer or gel electrolytes, such as poly(methylmethacrylate) (PMMA)-ethylene carbonate (EC)-propylene carbonate (PC)- [94] etc.

2.3 Key Design and Cost Issues

In the past ten years of research and development of supercapacitors, significant progress has been made, but so far no device is available to meet all the requirements in both the technical and the economic aspects. In vehicle applications for example, it is required for a device to have high energy density (>5 Wh kg^{-1}), high power density (low resistance long cycle and shelf life, and reasonably low cost (<US $2-3/Wh). There are several design issues to be considered, e.g. electrode thickness and material properties, contact resistance between material particles/fibers, bonding of the active materials to a current collector, electrolyte resistivity, cell/stack configuration, packaging, electrode material and electrolyte purity, quality and uniformity of fabrication, cost of materials, and so forth. Batteries, fuel cells and capacitors are the three main types of energy storage devices that are widely used around the world. Supercapacitors have many advantages and fill the gap between batteries and regular capacitors. The most important characteristic of supercapacitors, unlike other types of capacitors, is their “super” high energy density. Several materials, such as activated carbon, transition metal oxides, and conducting polymers, are suitable candidates for supercapacitor electrode materials. Solid-state supercapacitors have been recently developed with solid-state electrolytes, which show advantageous features compared to normal liquid electrolytes. Although different energy storage mechanisms are applied for each type of device, the supercapacitors have promising applications, especially in vehicles [95].

2.4 Supercapacitor Electrochemical Characterization Techniques

Electrochemical characterization techniques are very crucial for the evaluation of the electrochemical performance of electrode materials. Typically, a high-performance supercapacitor electrode material has many necessary properties such as good rate capability, high capacitance, high columbic efficiency, and low electrical resistance. Basic electrochemical characterization techniques involved in supercapacitor evaluation are galvanostatic charge discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS).

In order to characterize the electrode material, an active electrode can be tested in a three electrode system, which is common for testing half cells. In a three electrode system, there are three components, working electrode, counter electrode, and reference electrode, where the active electrode is used as the working electrode. To record the potential of this working electrode, a reference electrode whose potential is almost a constant in a narrow potential range is used. In addition, a counter electrode which is usually a platinum wire, is also necessary to carry the current coming across from the working electrode, which can prevent the reference electrode from carrying current, leading to potential change of the reference electrode.

Full cell test, which usually takes place in a two electrode system, can show more practical performance of active materials than half cell, because full cell test works similar to a practical supercapacitor which has a positive electrode and a negative electrode. In a full cell system, both electrodes are assembled with active materials. According to if the active materials in the two electrodes are same or not, the supercapacitor can be divided into symmetric and asymmetric supercapacitor respectively.The working electrode is assembled by drop casting the electrode slurry directly onto a current collector made from nickel foam. In addition to active electrode materials, 10 wt% of conductive carbon black and 10 wt% of polyvinylidene fluoride (PVDF) are

utilized as conductive additive and binder material respectively. The electrode slurry should be well dispersed onto the current collector to enhance the utilization efficiency of the active material. Wet electrodes need to be dried in a vacuum oven and pressed at 2.0 MPa to enhance the contact between active materials and current collectors. After these procedures, electrodes are able to be characterized by different techniques in a three electrode system or in a full cell.

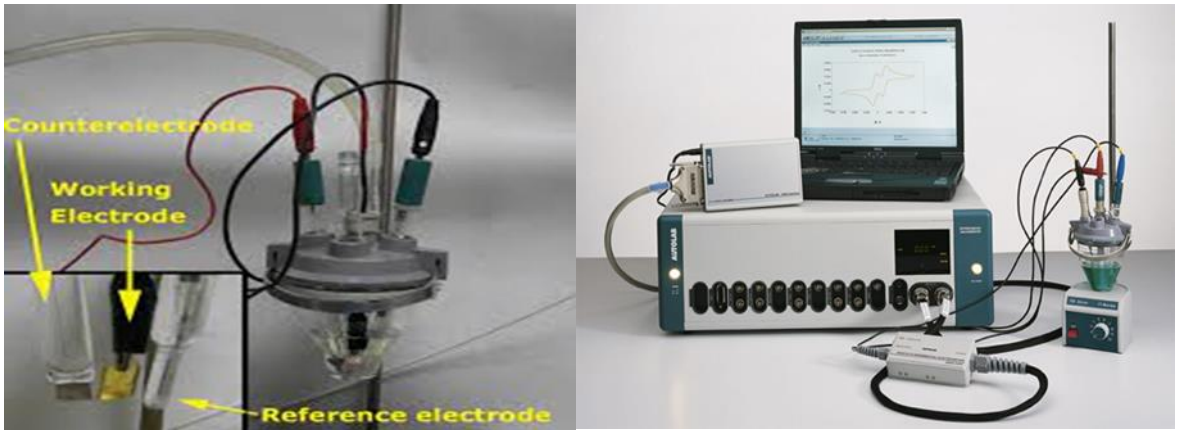


Figure 2.1: Schematic Diagram of the Three Electrode Configuration Set up for the Electrochemical Measurements.

2.4.1 Cyclic Voltammetry

Cyclic voltammetry is a common electrochemical characterization technique to study the electrochemical property of a material. A potential on the working electrode ramps linearly with time from the open circuit potential to a set potential. Then the potential returns to the other set potential in the same way. Both the scan rate and cycles can be controlled. Basically, the redox potential of the active material should be contained within the potential window of CV to analyze the electrochemical property of the material. A typical cyclic voltammogram is shown in Figure(2.2). The corresponding current is a function of the scanning potential. From a cyclic voltammogram, researchers can obtain a large amount of qualitative information with regards to the active material

such as the capacitance, conductivity, polarization, reversibility and the position of reduction and oxidation peaks.

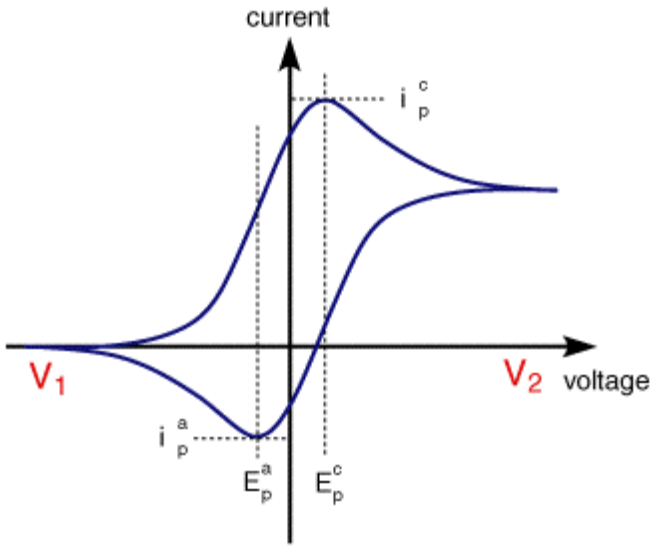


Figure 2.2: a schematic view of cyclic voltammogram.

From the area of a CV curve, the specific capacitance of the active material can be calculated with the following equation:

$$C = \frac{1}{2}\frac{\int Idv}{mvV} \qquad (2\text{-}1)$$

where C is the specific capacitance, m is the mass of active material, V is the potential window, v is the scan rate, and $\int Idv$ is the area of the CV curve. Since a cycle contains both charging and discharging processes, the entire area should be divided by two to obtain the specific capacitance.

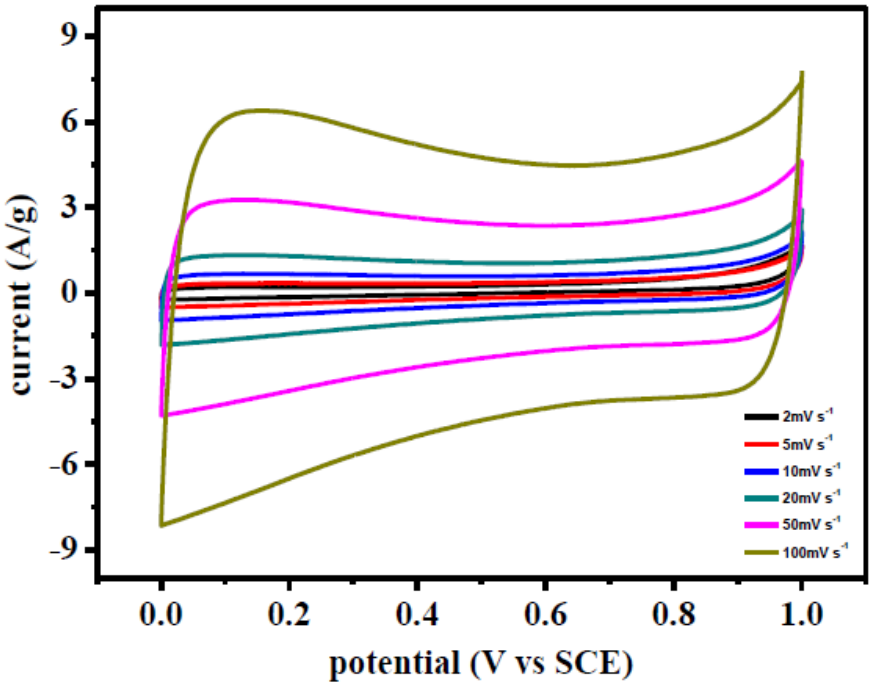


Figure 2.3: Cyclic voltammogram of as synthesized partially graphitized hierarchical porous carbon spheres at various scan rates, which are tested in 1 mol/L sodium sulphate solution with three electrode system.

An example is shown in Figure (2.3); the CV curve of carbon materials with electric double layer capacitance is similar to rectangular with no redox peaks. With the increase of scan rate, the area of CV curves becomes larger and larger. However, due to the growing resistance at high scan rate, the specific capacitance will slightly decrease. Thus, it is significant to reduce the resistance at high scan rate by developing a rational structure for supercapacitor electrode materials.

2.4.2 Galvanostatic Charge and Discharge

Galvanostatic charge and discharge is a more accurate technique to evaluate the specific capacitance of active materials than CV method. Positive and negative constant currents come across the working electrode to charge and discharge the electrode in a set voltage range with recording the time. A typical GCD curve is shown in Figure 2.3, in which the voltage is drawn as a function

of the time. Then, the specific capacitance can be determined by the potential window, current density and discharge time with the following equation: 36

$$C = \frac{I\Delta t}{mV} \qquad (2\text{-}2)$$

where I is the current, Δt is the discharge time, m is the mass of electrode material, and V is the potential window.

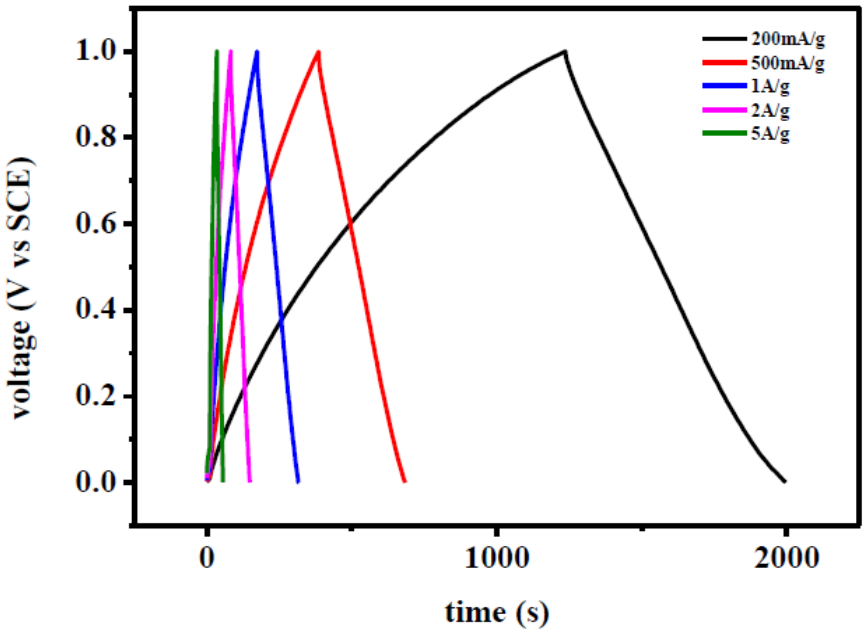


Figure 2.4: Galvanostatic charge-discharge profile of $ZnFe_2O_4$ and porous carbon nanocomposite with the voltage range from 0.0 V to 1.0 V vs. at different current densities

2.4.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy is a powerful tool to analyze the impedance of an electrochemical system, wherein an alternating potential with changing frequency is applied onto an electrochemical system to test the ratio of alternating potential to the corresponding current signal as a function of sinusoidal wave frequency. The Impedance resulting from the quotient of potential divided by current is a complex number. To use the real part as X axis and the imaginary part as Y axis, it is able to obtain a Nyquist plot, which is

important in the analysis of electrochemical impedance. Generally a Nyquist plot consists of a semicircle followed by a 45° straight line. In practice, at high frequency region, the intercept on X axis represents the series resistance of the electrode. The semicircle region mainly reflects charge transfer resistance which is related to reactive kinetics. At low frequency .region, the 45° straight line which is known as Warburg diffusion regime, is attribute to the diffusion transmission resistance in the electrode. However, for some complex EIS curves, the electrochemical system should be studied by representing the system with an equivalent circuit which consists of resistance, capacitance, and inductance etc. basic electrical elements, and analyzed by circuit modelling software.

Electrode impedance checking may be carried out in potentiosatic mode (PEIS) by applying a sine wave around a potential E. The value shall be set as a constant value or a value associated with the equilibrium potential of the working electrode within a range of frequencies [94]. The impedance spectrum generally consists of a high frequency semi-circle corresponding to the kinetic processes and a low frequency tail associated with the diffusion processes, as shown in figure (2.5), where R_e, R_{ct}, C_{dl} and W represent the uncompensated resistance, the resistance to the transfer of charges, the constant angle of phase element Galvanostatic mode is somewhat similar to PEIS mode, except that current replaces of potential mode [96].

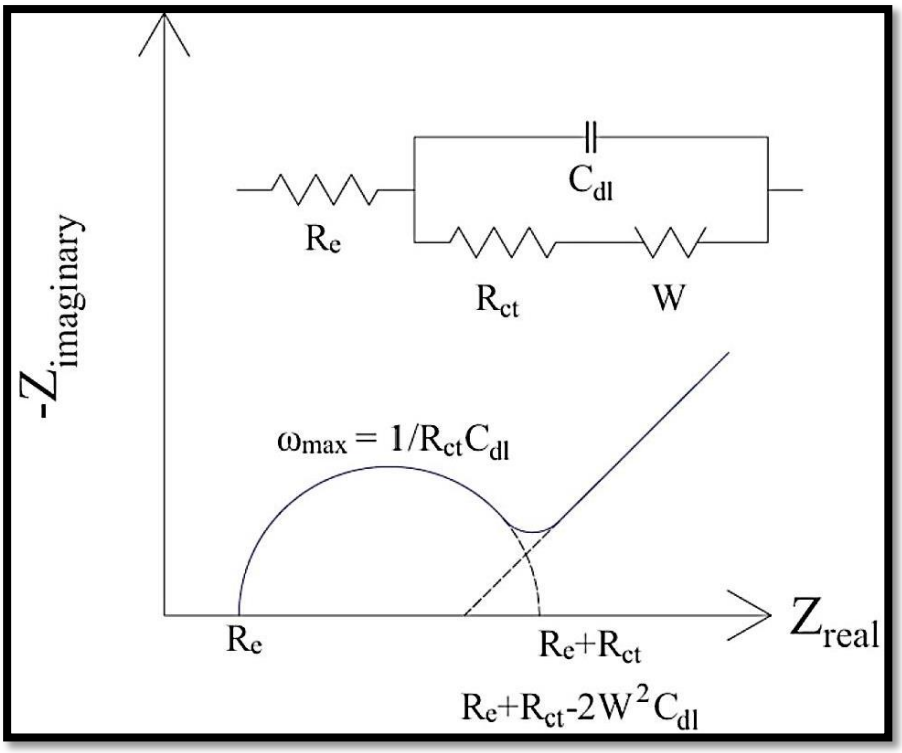


Figure (2.5): Typical Schematic Illustrations of EIS Spectrum and the Equivalent Circuit Used to Interpret the Data for Supercapacitors (Inset) [94].

For this work, EIS data was collected on a (CHI660B) of electrochemical impedance spectroscopy (EIS) was conducted using an AC voltage of (5 mV) in amplitude over a frequency ranged from (0.01 to 100 kHz) at open circuit potential.

2.5 Applications of Supercapacitors

Rather than replacing a battery, supercapacitors due to its unique properties like ultra-fast charging and discharging of high current, are more commonly used as memory standby/backup to bridge short power xinterruptions. In such application, supercapacitors will supply the necessary power to the system when there are energy bursts, at the same point the main batteries can supply the necessary energy since they can store and deliver the required amount of energy over a longer and slower period of time. Another application is improving the current handling of a the battery and hence to

improve the life cycle of battery. Supercapacitors can also do current boosting on high load demand by placing it in parallel to the battery terminal [70].

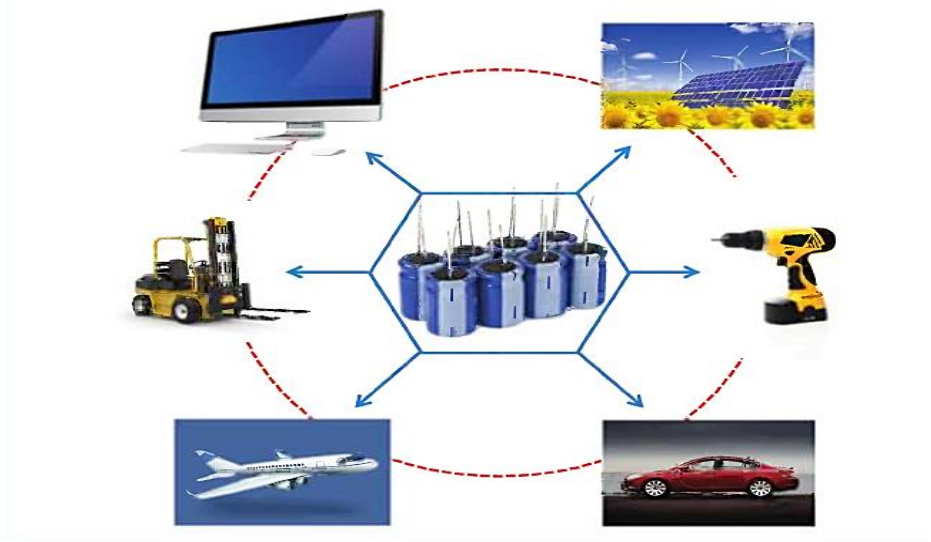


Figure 2.6: Applications of Supercapacitors [71]

Another important application of supercapacitor is to improve the peak load performance of portable fuel cell. The applications of supercapacitors never restricted to electric and hybrid vehicles; they also have a role in the emergency window of A 380 flight for the sudden opening of emergency doors and in cranes to lift heavy loads as shown in Figure (2.6) [71].

Chapter Three

Experimental part

3.1 Introduction

In this study, experimental work was performed in the laboratory of Nanotechnology Institute / University of Technology/Baghdad. The overall experimental procedures for designing electrode materials are shown in Figure (3.1). This chapter refers to the preparation of materials followed by characterization of the prepared materials and evaluation of their electrochemical properties for supercapacitors.

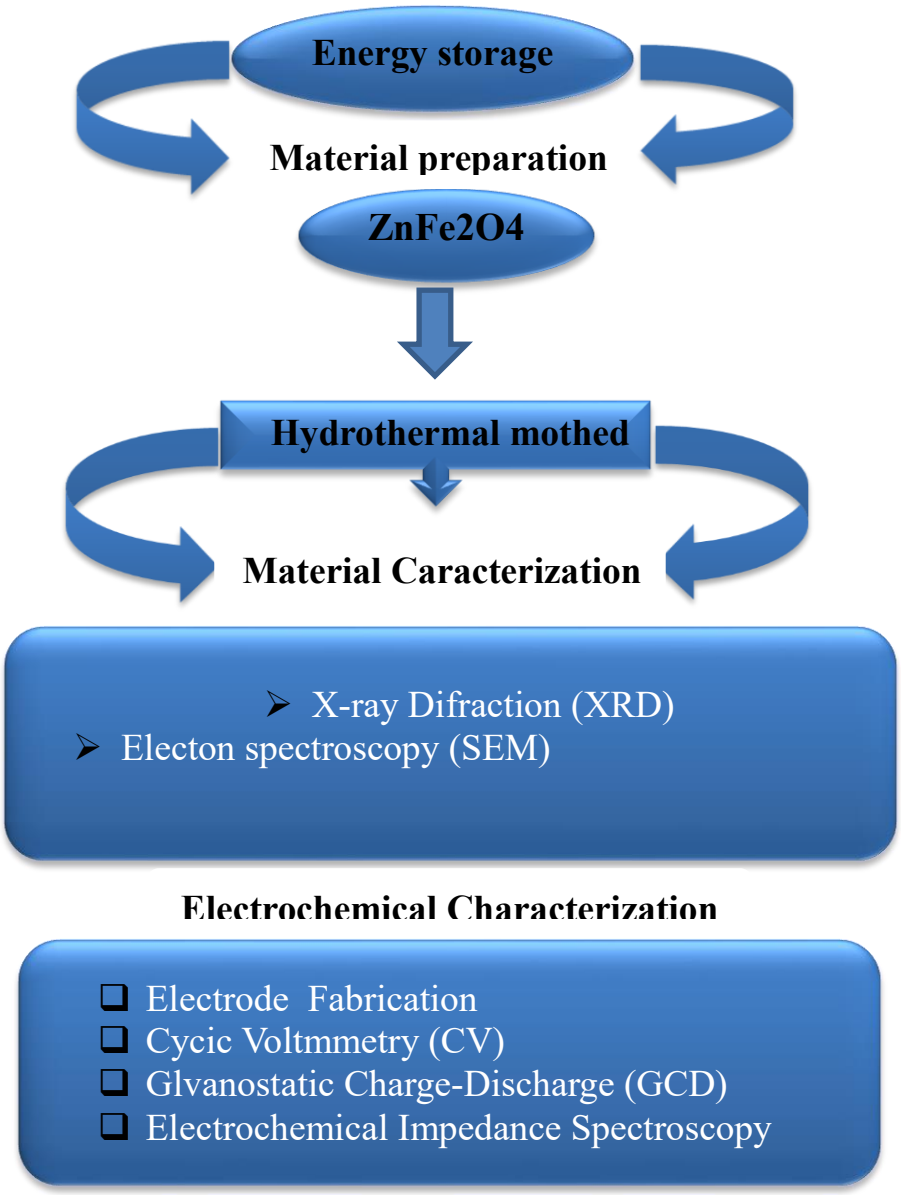


Figure 3.1: Schematic illustration of the overall experimental procedure.

3.2 Materials and Chemicals

A list of materials and chemicals used in this research are presented in Table 3.1.

Table 3.1 Materials and chemicals.

Materials/Chemicals	Formula	Purity	Supplier
N-methyl-2-pyrrolidinone	C_5H_9NO	98%	**Sigma-Aldrich**
Isopropanol	$(CH_3)_2CHOH$	99.7%+	**Sigma-Aldrich**
N,N-dimethyl acetamide	$CH_3CON(CH_3)_2$	99%	**Sigma-Aldrich**
Dimethyl formamide	$HCON(CH_3)_2$	99%	**Sigma-Aldrich**
Ethanol	C_2H_5OH	Reagents	**Q-Store Australia**
1,2-propanediol	$CH_3CH(OH)CH_2OH$	99%	**Sigma/Aldrich**
Carbon black	C	Super P	**Timcal Belgium**
Graphite	**C**	**n/a**	**Fluka**

3.3 Materials Synthesis Techniques

3.3.1 Spray Pyrolysis

Spray pyrolysis is a powerful synthesis technique that can be used to produce a wide variety of chemically homogenous ceramic powders with high purity. Oxide powders with homogenous particle sizes and crystallite sizes less than 100 nm may be prepared by this method. Spray pyrolysis synthesis is simple and time-efficient, allowing for continuous operation. With the addition of a carbon source, oxide/carbon composites can be generated, giving extra benefits for electrochemical performance. The morphology of the particles produced by spray pyrolysis can (to some degree) be controlled by the choice

of precursors, the concentration of the precursor solution, the size of the spray droplets, and the retention time in the furnace.

Figure (3.2) presents a schematic of the spray pyrolysis system for the preparation of nanosized powders [95]. The working procedures are as follows. An initially prepared water-based precursor solution is fed through a nozzle into a rotating furnace, which has been preheated to the predetermined temperature. In the hot-zone, the atomized solution is dried and the metal salts decompose at a high temperature, forming an intimate metal oxide mixture. The spray pyrolysed powders are collected in a cyclone at the bottom of the furnace and are then subjected to further treatment or characterizations.

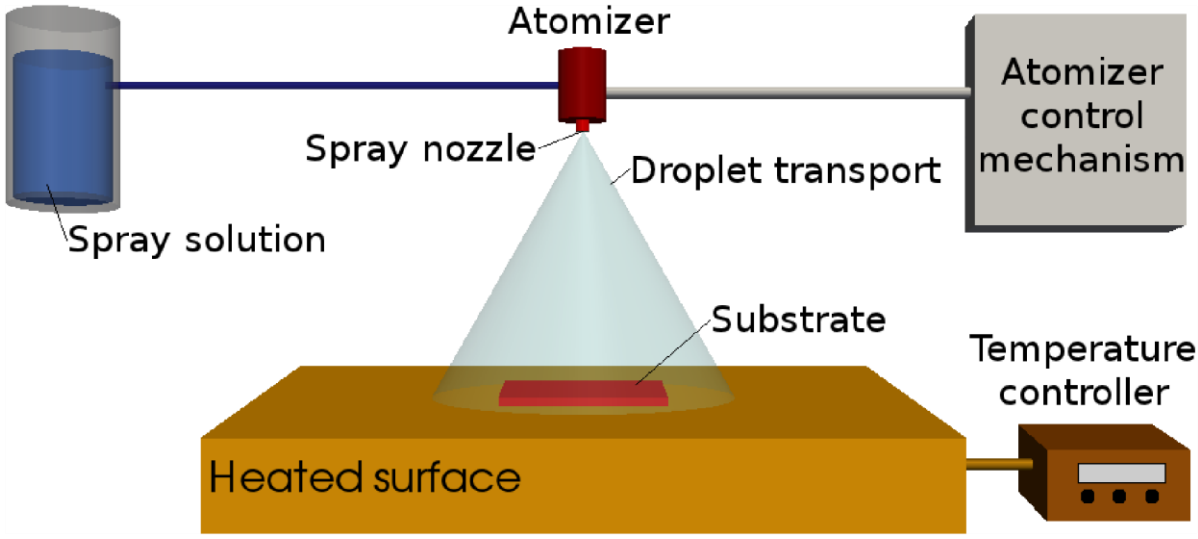


Figure 3.2. Experimental setup for preparing metal oxides by the spray pyrolysis technique [95].

3.3.2 Hydrothermal Synthesis

Hydrothermal synthesis is a method used to synthesize single crystals. The crystal is grown in hot water under high pressure, depending on the solubility of the precursors. The synthesis is performed in an apparatus called

an autoclave, in which the (Nutrient5) solution containing precursors for crystal growth is supplied along with water. A gradient of temperature is maintained at opposite ends of the growth chamber, so that the hotter end dissolves the nutrient and the cooler end facilitates growth of the crystal seeds. A typical Teflon-lined autoclave is shown in Figure (3.3) (left). Precursor solution would be initially prepared and filled into the autoclave. Then this autoclave is to be sealed in a stainless steel container Figure(3.3) (right) and maintained at the aim temperature in an oven [95].

Figure 3.3. Experimental setup for hydrothermal synthesis: a Teflon – lined autoclave (left), and a stainless steel container (right).

There are several advantages of the hydrothermal method over other types of crystal growth. One is that crystalline phases which are not stable at the melting point can be created. Moreover, the growth of materials with a high vapour pressure near their melting points can be performed. Also, it is particularly suitable in that large good-quality crystals can be grown by the hydrothermal method while maintenance of composition control is needed. Possible disadvantages include the need for expensive autoclaves and good

quality seeds of a fair size, and the impossibility of observing the crystal as it grows.

3.4 Materials Characterizations

3.4.1 X-ray Diffraction (XRD)

X-ray diffraction is a non-destructive analytical characterization technique to determine the crystal phase and structure. It produces a beam of X-ray which hitting a specimen as an incident function and scattered angle and polarization in addition to energy. A given specimen contains a specific arrangement through the unit cell which refer to a special relative intensity of diffraction peaks recorded when hitting of x-ray. Thus, the unit cell size and geometry of the angular positions can be resolved for the X-ray diffraction findings. The resulting diffraction lines with clear peaks both are named the pattern of XRD. The X-ray wavelength can be compared to the atom size, it is suitable for investigating the structural arrangement of atoms and molecules in a broad domain of alloys and metals. Every crystal has its own unique properties in a pattern of X-ray diffraction which obey Bragg's law :

$$n\lambda = 2d \sin\theta \qquad (3.1)$$

where d, θ, n and λ, are interplanar spacing, Bragg angle, reflection order and X-ray irradiation wavelength respectively [96] .

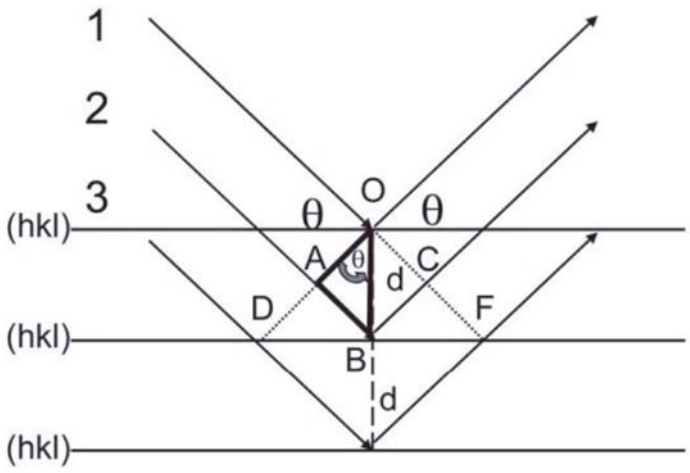


Figure (3.4): Bragg's law can be derived from the geometrical relation between the interplanar spacing d and the diffraction angle [96].

3.4.2 Scanning Electron Microscopy (SEM) & Transmission Electron Microscopy (TEM)

Electron diffraction is a technique used to study matter. When electrons are fired at a sample, the resulting interference pattern can be observed. This is due to the wave-particle duality, meaning that an electron can be regarded as a wave. This technique is similar to X-ray diffraction and neutron diffraction. The a scanning electron microscope (SEM) as electron backscatter diffraction, to study the crystal structure of solids. At first, the electrons are accelerated by an electrostatic potential. This will result in the desired energy and wavelength for the electrons before they interact with the sample to be studied. The periodic structure of a crystalline solid acts as a diffraction

grating, scattering the electrons in a predictable manner. It may be possible to deduce the structure of the crystal from the observed diffraction pattern. However, the technique is limited by the phase problem.

Compared with other types of radiation used in diffraction studies of materials, such as X-rays, the main difference lies in the fact that electrons are charged particles and interact with matter via the Coulomb forces. This means

that the incident electrons feel the influence of both the positively charged atomic nuclei and the surrounding electrons. In comparison, X-rays interact with the spatial distribution of the valence electrons. Because of these different forms of interaction, the two types of radiation are suitable for different studies. Electron diffraction will give high resolution at the nanometer scale, while X-ray diffraction is of relatively low resolution. As mentioned above, the wavelength of electrons accelerated in a TEM is much smaller than that of the radiation usually used for X-ray diffraction experiments. A consequence of this is that the radius of the Ewald sphere is much larger in electron diffraction experiments than in X-ray diffraction. This allows the diffraction experiment to reveal more of the two dimensional distribution of reciprocal lattice points.

3.4.3 Brunauer-Emmett-Teller (BET) Technique and Pore Size Distribution

The Langmuir isotherm will not be valid when molecules form multilayers. To take this possibility into account, in 1938, Stephan Brunauer, Paul Emmett, and Edward Teller developed a model isotherm. The theory is called BET Theory, from the initials of their last names. The BET theory is used to calculate the specific surface area ($m2g^{-1}$) of the materials from N2 adsorption isotherms. The pore size distribution, on the other hand, applies the gas adsorption isotherms to describe the distribution of pore volume with respect to pore size; alternatively, it may be defined by the related distribution of pore area with respect to pore size [96].

3.5 Electrochemical Testing

3.5.1 Preparation of $ZnFe_2O_4$ nanoparticles

A hydrothermal method is used for synthesizing the $ZnFe_2O_4$on nickel foam. Several steps is involved in the synthesis: In a typical experiment, the substrate of the substrate (1x2 cm) degreased by using acetone. Then, the substrate was cleaned and etched by using (4 M) HCL in an ultrasound for (20 minutes) in order to remove the surface layer of NiO and then rinsed by DI and absolute ethanol for (30 minutes), respectively. For the hydrothermal method, $Zn(NO_3)_2 \cdot 6H_2O$ (0.597 g) and $Fe(NO_3)_2 \cdot 6H_2O$ (1.162 g) were melted (dissolved) discretely in 30 mL of DI along with magnetic stirring. Simultaneously, $Co(NH_2)_2$ (0.7 g) were dissolved in mixture contains 20 mL for both of ethanol and ID with magnetic stirring. The stirring process lasted for 30 minutes. Then, a solution of zinc nitrate was added slowly to the solution of cobalt nitrate. Next, the mixture of urea and ammonium fluoride added to cobalt nitrate and zinc nitrate mixture along with magnetic stirring at room temperature (RT) for (30 minutes). Then, the resulted mixture was places in a Teflon-lined autoclave manufactured from stainless steel of (100 mL) in volume. The reaction was accomplished for 24 hours at 120 ºC. as soon as the reaction completed, the autoclave allowed to be cooled to room temperature. DI was used to wash the resulted product for several times followed by ethanol as well. After that, the product was dried in a vacuum at (80 ºC) and lasted for (8 h). The Ni foam coated with a pink product was taken out from the autoclave and washed several times with distilled water and absolute alcohol in an ultrasound to remove the residual nanoparticles and then dried for (12 h) in an oven at (60 °C). The resulted product was calcined for (2 h) at (400 ºC) under Air atmosphere with (2 ºC min^{-1}) as the ramping rate by using a programmable and controllable furnace to get the final product of the composite $ZnFe_2O_4$.The original (pistine) $ZnFe_2O_4$ was produced similarly .

However hydrothermal treatment followed by calcination yielded the crystallite growth of $ZnFe_2O_4$ nanoparticles.

3.5.2 Electrochemical measurements

Electrochemical tests of $ZnFe_2O_4$nanoparticles were first performed utilizing system of three electrode in 2M potassium hydroxide as electrolyte. Pt mesh and Mercury/Mercury oxide electrodes have been utilized as the counter electrode and reference electrode, respectively. The working electrodes were created by mixing the active substance $ZnFe_2O_4$ nanoparticles . 80%), black acetylene (10%), and polyvinylidene

Fluoride (PVDF) (10%) in an N-methyl-2-pyrrolidinone (NMP) solvent. Stirred the mixture overnight, and loaded slurry onto the nickel foam (1.0cm× 2.0cm in area) and use vacuum at 120 ˚C for 10 h for dried. The electrode was compressed under 4 MPa and dried overnight. The mass loading of the efficient substance was obtained by evaluation nickel foaming before and after plating with the material, utilizing a balance with a precision of 0.01 mg. The electrically active material reinforced with nickel foam (area 1 cm^2) was used directly as the working electrode. The $ZnFe_2O_4$ nanoparticles mass load on nickel foam was calculated to be 0.9-1.5 mg cm2. Periodic voltmeter (CV) calculations were conducted on an electrochemical workstation (CHI660B, Chenhua, Shanghai) in the potential range 0 to 0.45 V (Mercury/Mercury oxide) at scan rates variations. Galvanic charge and discharge investigations were conducted on a examine system controlled by LAND battery software. Electrochemical impedance spectroscopy (EIS) measurements (CHI660B) were conducted through using an AC voltage of 5 mV in amplitude over a frequency extent from 0.01 Hz to 100 kHz when open circuit is possible.

3.6 The Evaluation of Electrochemical Capacitors

Generally, there are several evaluation parameters for electrochemical capacitors, including specific capacitance, energy density, and power density.

The electrode's specific capacitance (C) in (Fg^{-1}) from the CV, was calculated as per equation (3.2).

$$C = \frac{\int Idv}{mv\Delta V} \qquad (3.2)$$

Where *m* denotes to the active material mass (g), *I* denotes to the voltametric current (A), ΔV denotes to the CV potential window (V), and ν is the rate of scan.

The specific capacitance values of the single electrode or the cell could be expressed by Equation (3.3):

$$C = \frac{I\Delta t}{m\Delta V} \qquad (3.3)$$

In Equation (3.3), I represents the discharging current (A), Δt represents the discharging time (s), m represents the mass of the active material (m), and ΔV represents the voltage during discharging (V) [70].

The energy density Energy stored per unit of mass ($Wh{\cdot}kg^{-1}$) or volume ($Wh\ L^{-1}$) is another term which is widely used to assess the performance of a supercapacitor device could be expressed by Equation (3.4):

$$E = \frac{0.5C(\Delta V)^2}{3.6} \qquad (3.4)$$

In Equation (3.4), E ($Wh\ kg^{-1}$) represents the energy density of the cell, C represents the total capacitance ($F\ g^{-1}$) of the cell, and V represents the

operating voltage (V) of the cell. Clearly, if the operating voltage is increased, the energy density will be greatly increased [71].

The power density of a supercapacitor device shows the capability of the device to transfer the specific energy (Wh kg^{-1}) or (Wh L^{-1}) in a given unit of time (h). Power density is usually reported per unit of mass (W kg^{-1}) or volume (W L^{-1}) following Equation (3.5):

$$P = \frac{E3600}{\Delta t} \qquad (3.5)$$

In Equation (3.5), P represents the power density (W kg^{-1}) of the cell, E represents the energy density (Wh kg^{-1}) of the cell, and t represents the discharging time (s) [72].

Cycle life is another important criterion which differentiates supercapacitors from batteries. The cycle life shows the number of charge-discharge cycles an electrical capacitor (EC) can be subjected to before it experiences a serious decline in measured capacitance [96].

Chapter Four

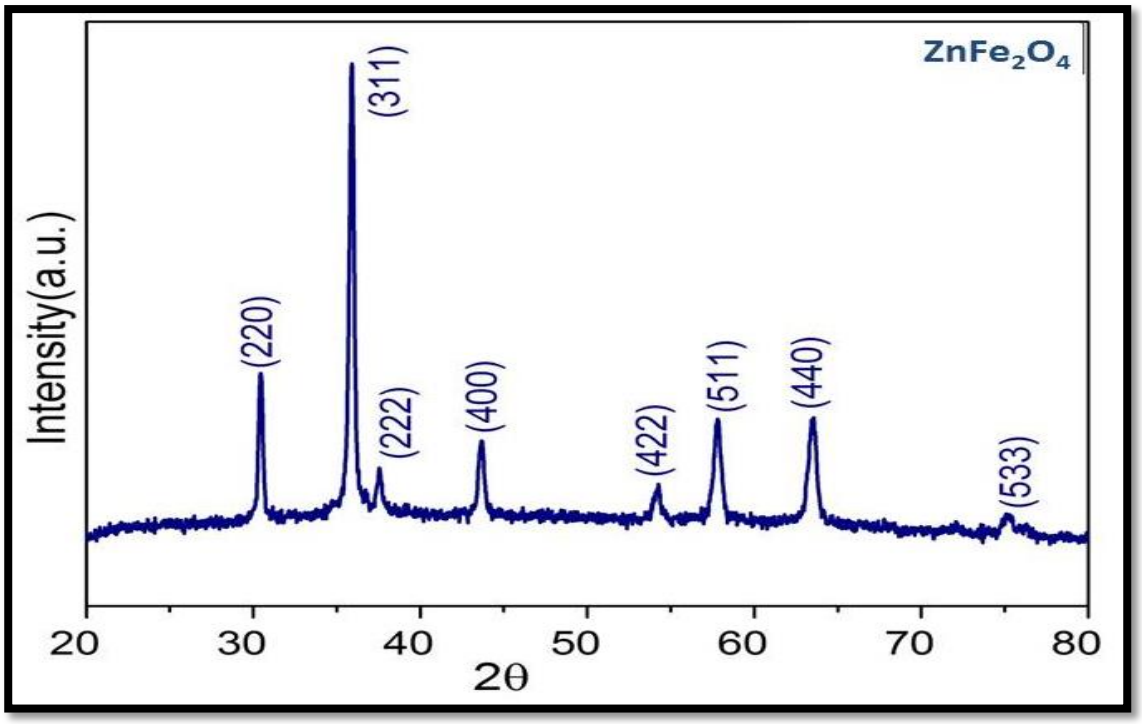
Results & Discussion

4.1 Introduction

This chapter present the results and discussion for the structure , morphology, Electrochemical properties of $ZnFe_2O_4$ nanoparticles decorated on nickel foam. The structural, preparation morphological, and electrochemical properties of pure $ZnFe_2O_4$ by employing the hydrothermal method for preparing electrode materials as $ZnFe_2O_4$ are shown and discussed in this chapter. Schematic illustration for the synthesis of $ZnFe_2o_4$ nanostructure on nickel foam substrate.

4.2 Results and discussion

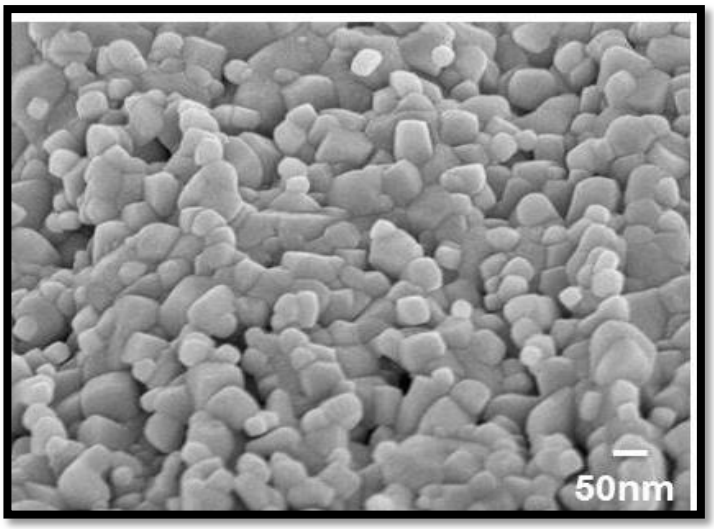
Figure(4.1) shows the XRD pattern of novel synthesized $ZnFe_2O_4$ nanomaterials. All the peaks of the XRD pattern can be easily indexed to cubically shaped spinel type $ZnFe_2O_4$ structure (JCPDS No. 82-1042). The peaks at 2θ values of 35.23°, 42.81°, 56.60° and 62.14° can be assigned to the consideration of (311), (400), (422), (511) and (440) planes of spinel $ZnFe_2O_4$ nanomaterials [15]. The intense and sharp peaks elucidate that the products are well crystallized.



Figure(4. 1) XRD patterns of $ZnFe_2O_4$ ternery oxide

The surface morphology of the synthesized product was identified by FE-SEM measurements. Figure 4.2 show the FE-SEM images of $ZnFe_2O_4$ flaky structure. The particles are uniformly distributed. The sizes of the particles are in few hundred nm and some of the particles sizes are in the range from 10 nm to 50 nm .

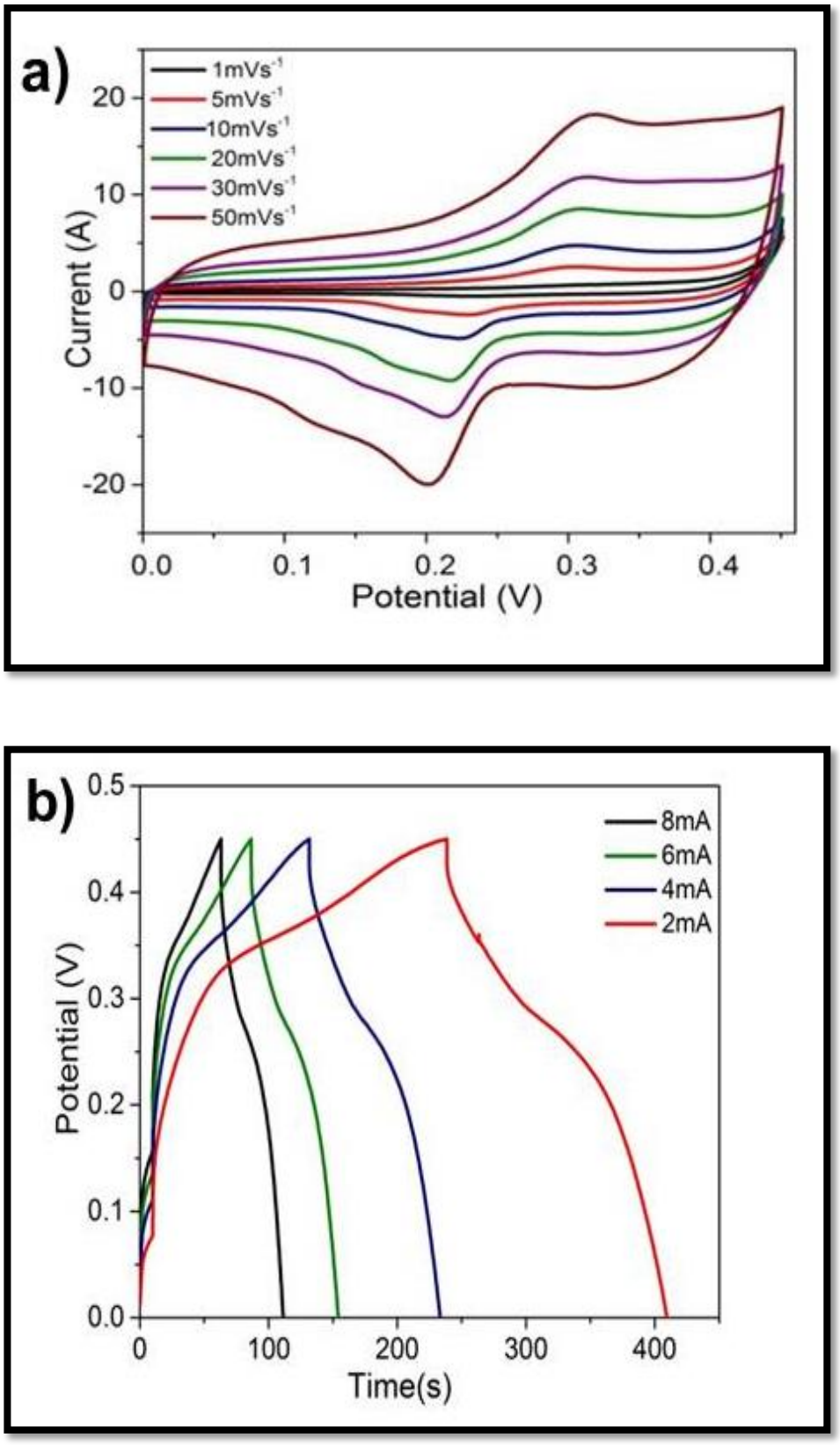
.



Figure(4.2) High magnification - FESEM images of $ZnFe_2O_4$ nanoparticles

Recent studies have found that porous structures could act as an electrolyte ion reservoir, which could be formed within the pores of the electrode materials. This provides spatial confinement of the electrolyte and ensures close contact between the electrode material and the electrolyte, as well as a stable supply of electrolyte ions [47]. Thus, the porous structure could provide better electrode/ electrolyte interaction, facilitating the electrochemical reactions.

The supercapacitors was investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge techniques in a three-electrode system. the $ZnFe_2O_4$ electrodes were subjected to different electrochemical characterizations to evaluate their performance. the $ZnFe_2O_4$ electrode showed superior electrochemical performance as compared to other electrode systems Figure(4.3). [48]. The Table (4.1)Show specific capacitance values of $ZnFe_2O_4$ at current density and Table (4.2) :The specific capacitances of $ZnFe_2O_4$ at various Scanning rates.



Figure(4.3) (a) CV curves at different scan rates of the$ZnFe_2O_4$ (b)charge/discharge curves at different currents of the $ZnFe_2O_4$ nanoparticles.

Table (4.1): The specific capacitance values of $ZnFe_2O_4$ nanoparticles at different current density

Current density ($A.g^{-1}$)	Specific capacitances of $ZnFe_2O_4$ ($F \cdot g^{-1}$)
1	**1010**
5	**1000**
10	**966**
20	**832**
50	**718**

Table (4.2) : The specific capacitances of $ZnFe_2O_4$ at various Scanning rates.

Scanning rates ($mV.s^{-1}$)	Specific capacitances of $ZnFe_2O_4$ ($F \cdot g^{-1}$)
2	**1002**
4	**960**
6	**894**
8	**710**

Figure(4.3) (a) were also carried out to find the best performing electrode system. the $ZnFe_2O_4$ system was observed to be the best performing electrode, by taking all the $ZnFe_2O_4$ electrochemical characterizations into consideration. Thus, further electrochemical performance evaluations were carried out using the the $ZnFe_2O_4$ sample and keeping the $ZnFe_2O_4$ as the standard. The CV curves of the electrodes made from all the $ZnFe_2O_4$ nanoparticles at different scan rates in the potential range of 0.0 to 0.45 V (vs. Hg/HgO) are displayed in Figure(4.3) (a,b). The CV curves of the $ZnFe_2O_4$ electrode show much larger integrated areas and specific current. This suggests that the $ZnFe_2O_4$ has higher electrochemical activity and a faster activation process. As seen in Figure(4.4)(a,b) the Nyquist plots for both electrodes consist of a semicircle representing the charge-transfer resistance (R_{ct}) at the electrode interface, while

the inclined line (W: Warburg impedance) in the low-frequency region is attributed to ion diffusion in the electrolyte to the electrode interface. The first intercept on the x-axis represents the solution resistance (R_s). The nonlinearity in the charge-discharge curves indicates pseudocapacitance behaviour owing to Faradaic reactions occurring at the electrode/electrolyte interface. Overall, the $ZnFe_2O_4$ electrode exhibits high specific capacitance and rate capability, along with superior cycling performance. Such impressive electrochemical properties can be attributed to (i) the presence of in the $ZnFe_2O_4$ system, which enhances the effective specific surface area and shortens the diffusion and migration paths for electrolyte ions; (ii) the intact contact the $ZnFe_2O_4$, which promotes the electronic conductivity of the composite electrode; and (iii) the effective action of the $ZnFe_2O_4$ during charge/discharge process .

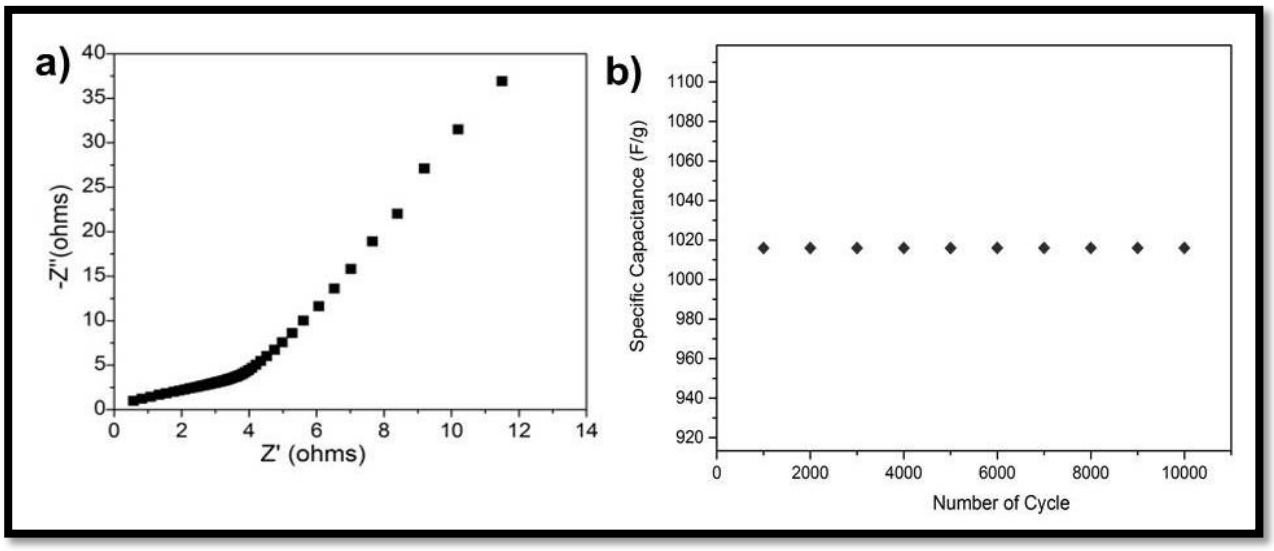


Figure (4.4 a) Nyquist plots recorded between 1 Hz and 100 kHz, and b) cycling performance of the $ZnFe_2O_4$ nanoparticles.

4.3 Conclusions:

1. The results showed the electrode $ZnFe_2O_4$ that fabricated have high electrochemical properties.
2. The prepared $ZnFe_2O_4$ rate had the ability to attain 1118 F g^{-1} as the highest mean specific capacitance at 2 A g^{-1} of current density and capacitance after 10000 cycles of charging/discharging process.
3. The used method offered an easy and effective way for combining the conducting metal oxide composites with porous structures. With its outstanding electrochemical efficiency, the $ZnFe_2O_4$would, without any doubt, make it an attractive option for producing electrode materials with highly performance for potential energy storage applications such as medical ear stethoscope used for children ,elderly and police communications system.

4.4 Suggestions and Future Work

For further studies, the followings are suggested:

1- Developing of new methods for dispersion, electrophoretic deposition and co-deposition of MWCNT,graphene and $ZnFe_2O_4$

2- Investigating of the effect of using different conducting polymers treatment such as polyacetylene, polypyrrole, and polyaniline on metal oxide in supercapacitor applications.

3- Determining of the different electrolyte impression for capacitance behavior.

4- Fabrication and testing of symmetric and asymmetric devices, investigation of capacitance, impedance, power-energy characteristics, capacitance retention at different charge-discharge rates and cyclic stability.

5-Analysis and optimization of microstructure of new materials such as $MnCO_2O_4$,$CrCO_2O_4$ and $FeCO_2O_4$ for battery and supercapacitor.

References

References

1. A brief history of supercapacitors batteries and energy storage technology, (AUTUMN 2007).
2. Maruyama, T., Ikeda Y., and Kuroki N., "Aluminum electrolytic capacitor",(2001).
3. Fishler, M.G., "Electrolytic capacitor with multiple independent anodes", (1999).
4. Pandolfo, A. and Hollenkamp A., "Carbon properties and their role in supercapacitors". Journal of power sources,.157(1): p.11-27, (2006).
5. Conway, B.E., "Electrochemical supercapacitors: scientific fundamentals and technological applications".Springer Science & Business Media, (2013).
6. Conway, B.E., Transition from “Supercapacitor” to “Battery” Behavior in Electrochemical Energy Storage. Journal of The Electrochemical Society. 138(6): p. 1539-1548, (1991).
7. Zhao, X., C. Johnston, and Grant P.S., "A novel hybrid supercapacitor with a carbon nanotube cathode and an iron oxide/carbon nanotube composite anode". Journal of Materials Chemistry, 19(46): p. 8755-8760, (2009).
8. Singh, S., Alok C. Rastogi , Fredrick Omenya , M Stanley Whittingham , Archit Lal, Shailesh Upreti. "Electrochemical Performance of Lithium-Ion Hybrid Supercapacitors based on Activated Carbon and Nanoplatelet Li 4 Ti 5 O 12 Insertion Electrode Synthesized by Nanoscission Technique". in MRS Proceedings. Cambridge Univ Press, (2015).

9. Luo Jia, Yan Jin, Long Liu, PingHe Yong,YaoXia. "A novel LiTi 2 (PO 4) 3/MnO 2 hybrid supercapacitor in lithium sulfate aqueous electrolyte. Electrochimica Acta". 53(28): p. 8128-8133, (2008).

10. Belhachemi, F., Rael S., and Dava B.t. "A physical based model of power electric double-layer supercapacitors". in Industry Applications Conference. Conference Record of the 2000 IEEE, (2000).

11. Conway, B., "Electrochemical supercapacitors: scientific fundamentals and technological applications", Kluwer Academic/Plenum Publishers, New York, (1999).

12. Ohshima, H. and Furusawa K. "Electrical Phenomena at Interfaces: Fundamentals: Measurements, and Applications". 76. CRC Press, (1998).

13. Halper, M.S. and Ellenbogen J.C. "Supercapacitors: A brief overview". The MITRE Corporation, McLean, Virginia, USA, p. 1-34, (2006)

14. Okamura, M.," A basic study on power storage capacitor systems". Electrical engineering in Japan. 116(3): p. 40-51, (1996).

15. Rosso, M., Claire Brissot, Anna Teyssot, Mickaël Dollé, Lucas Sannier, Jean Marie Tarascon, Renaud Bouchet, Stéphane Lascaud. "Dendrite short-circuit and fuse effect on Li/polymer/Li cells". Electrochimica Acta. 51(25): p. 5334-5340. 70, (2006).

16. Hwang, T.H., Yong Min Lee, Byung-Seon Kong, Jin-Seok Seo, Jang Wook Choi "Electrospun core–shell fibers for robust silicon nanoparticle-based lithium ion battery anodes". Nano letters. 12(2): p. 802-807, (2012).

17. Seh, Z.W., Weiyang Li, Judy Cha J. Guangyuan Zheng, Yuan Yang, Matthew T. McDowell, Po-Chun Hsu,Yi Cui. "Sulphur–TiO2 yolk–shell nanoarchitecture with internal void space for long-cycle lithium–sulphur batteries". Nature communications. 4: p. 1331, (2013).

18. Holmberg, S., Alexandra Perebikovsky, Lawrence Kulinsky, Marc Madou. "3-D Micro and Nano Technologies for Improvements in Electrochemical Power Devices". Micromachines. 5(2): p. 171-203, (2014).

19. Peng, L., Xu Peng, Borui Liu, Changzheng Wu, Yi Xie, Guihua Yu. "Ultrathin two-dimensional MnO2/graphene hybrid nanostructures for high-performance, flexible planar supercapacitors". Nano letters. 13(5): p. 2151-2157, (2013).

20. Chen, P., Haitian Chen, Jing Qiu, Chongwu Zhou "Inkjet printing of single-walled carbon nanotube/RuO2 nanowire supercapacitors on cloth fabrics and flexible substrates". Nano Research. 3(8): p. 594-603, (2010).

21. Wang, B., Jun Song Chen, Zhiyu Wang, Srinivasan Madhavi, Xiong Wen (David) Lou. "Green synthesis of NiO nanobelts with exceptional pseudo-capacitive properties". Advanced Energy Materials. 2(10): p. 1188-1192, (2012).

22. Feng, C., Jinfeng Zhang, Yu He, Cheng Zhong, Wenbin Hu, Lei Liu, Yida Deng. "Sub-3 nm Co3O4 Nanofilms with

Enhanced Supercapacitor Properties". ACS nano. 9(2): p. 1730-1739, (2015).

23. Foo, C.Y., Afriyanti Sumboja, Daniel Jia Hong Tan, Jiangxin Wang, Pooi See Lee. "Flexible and Highly Scalable V2O5-rGO Electrodes in an Organic Electrolyte for Supercapacitor Devices". Advanced Energy Materials. 4(12), (2014).

24. Chu, Q., Wei Wang, Xiaofeng Wang, Bin Yang, Xiaoyang Liu, Jiuhua Chen "Hierarchical NiCo 2 O 4@ nickel-sulfide nanoplate arrays for high-performance supercapacitors". Journal of Power Sources. 276: p. 19-25, (2015).

25. Huang, Y., Yue-E. Miao, Hengyi Lu, Tianxi Liu. "Hierarchical ZnCo2O4@ NiCo2O4 Core–Sheath Nanowires: Bifunctionality towards High-Performance Supercapacitors and the Oxygen Reduction Reaction". Chemistry-A European Journal, (2015).

26. Zhou, W., Xiehong Cao, Zhiyuan Zeng, Wenhui Shi, Yuanyuan Zhu, Qingyu Yan, Hong Liu, Jiyang Wang, Hua Zhang. "One-step synthesis of Ni 3 S 2 nanorod@ Ni (OH) 2 nanosheet core–shell nanostructures on a three-dimensional graphene network for high-performance supercapacitors". Energy & Environmental Science. 6(7): p. 2216-2221, (2013).

27. Jagadale, A., Kumbhar V.S., Dhawale D.S, Lokhande C.D. "Performance evaluation of symmetric supercapacitor based on cobalt hydroxide [Co (OH) 2] thin film electrodes". Electrochimica Acta. 98: p. 32-38, (2013).

28. Hou, Y., Luyang Chen, Ling Zhang, Jianli Kang, Tianjin Polyte. "Ultrahigh capacitance of nanoporous metal enhanced

conductive polymer pseudocapacitors". Journal of Power Sources. 225: p. 304-310, (2013).

29. Maiti, S., Pramanik A., and Mahanty S. "Extraordinarily high pseudocapacitance of metal organic framework derived nanostructured cerium oxide". Chemical Communications. 50(79): p. 11717-11720, (2014).

30. Zhu, Y., hanthi Murali, Meryl D. Stoller, Ganesh K.J., Weiwei Cai, Paulo J. Ferreira, Ada. "Carbon-based supercapacitors produced by activation of grapheme". Science. 332(6037): p. 1537-1541, (2011).

31. Wang, G., Zhang L., and Zhang J. "A review of electrode materials for electrochemical supercapacitors". Chemical Society Reviews. 41(2): p. 797-828, (2012).

32. Fan, Jun Yan, Tong Wei, Linjie Zhi, Guoqing Ning, Tianyou Li, Fei Wei. "Asymmetric supercapacitors based on graphene/MnO2 and activated carbon nanofiber electrodes with high power and energy density". Advanced Functional Materials. 21(12): p. 2366-2375, (2011).

33. Chen, L.-F., Xu-Dong Zhang, Hai-Wei Liang, Mingguang Kong, Qing-Fang Guan, Ping Chen, Zhen-Yu Wu, Shu-Hong Yu. "Synthesis of nitrogen-doped porous carbon nanofibers as an efficient electrode material for supercapacitors". ACS nano. 6(8): p. 7092-7102, (2012).

34. Al-Rubaye S., "Nanostructure electrodes based on spinel oxide composites for next generation energy storage devices" university of Wollongong ,thesis, (2018).

35. Weidenthaler C. Pitfalls in the characteraization of nanoporous and nanosized materials. Nanoscale 3, 792, (2011).

36. Zhao, Y., Jia Liu, Yue Hu, Huhu Cheng, Chuangang Hu, Changcheng Jiang, Lan Jiang, Anyuan Cao, Liangti Qu. "Highly Compression-Tolerant Supercapacitor Based on Polypyrrole-mediated Graphene Foam Electrodes". Advanced materials. 25(4): p. 591-595. 73, (2013).

37. Yang, H., Yoshio M., Isono K., Kuramoto R. "Improvement of commercial activated carbon and its application in electric double layer capacitors". Electrochemical and solid-state letters. 5(6): p. A141-A144, (2002).

38. Kim Y.J., Yusuke Abe, Takashi Yanagiura, Ki Chul Park, Makoto Shimizu, Tomoya Iwazaki, Shin Nakagawa, Morinobu Endo, Mildred S. Dresselhaus "Easy preparation of nitrogen-enriched carbon materials from peptides of silk fibroins and their use to produce a high volumetric energy density in supercapacitors". Carbon. 45(10): p. 2116-2125, (2007).

39. Nakagawa, H., Shudo A., and Miura K. "High Capacity Electric Double Layer Capacitor with High Density Activated Carbon Fiber Electrodes". Journal of the Electrochemical Society. 147(1): p. 38-42, (2000).

40. Kyotani, T., Takayuki Nagai, Sanjuro Inoue, Akira Tomita "Formation of new type of porous carbon by carbonization in zeolite nanochannels". Chemistry of materials. 9(2): p. 609-615, (1997).

41. Koichi Matsuoka, Yasushi Yamagishi, Toshiaki Yamazaki, Norihiko Setoyama, Akira Tomita, Takashi Kyotani.

"Extremely high microporosity and sharp pore size distribution of a large surface area carbon prepared in the nanochannels of zeolite Y". Carbon. 43(4): p. 876-879, (2005).

42. Hou, P.-X., Hironori Orikasa, Toshiaki Yamazaki, Koichi Matsuoka, Akira Tomita, Norihiko Setoyama, Yoshiaki Fukushima, Takashi Kyotani. "Synthesis of nitrogen-containing microporous carbon with a highly ordered structure and effect of nitrogen doping on H2O adsorption". Chemistry of materials. 17(20): p. 5187-5193, (2005).

43. Nishihara H., Hiroyuki Itoi, Taichi Kogure, Peng-Xiang Hou, Hidekazu Touhara, Fujio Okino, Takashi Kyotani "Investigation of the Ion Storage/Transfer Behavior in an Electrical Double Layer Capacitor by Using Ordered Microporous Carbons as Model Materials". Chemistry-A European Journal. 15(21): p. 5355-5363, (2009).

44. Huang, J., Sumpter B.G., and Meunier V., "Theoretical model for nanoporous carbon supercapacitors". Angewandte Chemie International Edition. 47(3): p. 520-524, (2008).

45. Wigmans, T., "Industrial aspects of production and use of activated carbons". Carbon. 27(1): p. 13-22, (1989).

46. Kierzek, K., Frackowiak E., Lota G.,Gryglewicz G., Machnikowski J. "Electrochemical capacitors based on highly porous carbons prepared by KOH activation". Electrochimica Acta. 49(4): p. 515-523, (2004).

47. Redondo, E., Javier Carretero-González, Eider Goikolea, JulieSégalini, Roman Mysyk. "Effect of pore texture on performance of activated carbon supercapacitor electrodes

derived from olive pits". Electrochimica Acta. 160: p. 178-184, (2015).

48. Zhang, L.L. and Zhao X, "Carbon-based materials as supercapacitor electrodes". Chemical Society Reviews. 38(9): p. 2520-2531, (2009).

49. Wang, Q., Wen Z., and Li J. "A hybrid supercapacitor fabricated with a carbon nanotube cathode and a TiO2–B nanowire anode". Advanced Functional Materials. 16(16): p. 2141-2146, (2006).

50. Salunkhe, R.R., Heejoon Ahn, Jung Ho Kim, Yusuke Yamauchi. "Rational design of coaxial structured carbon nanotube–manganese oxide (CNT–MnO2) for energy storage application". Nanotechnology. 26(20): p. 204004, (2015).

51. Zhao X. S., Fabing Su, Qingfeng Yan, Wanping Guo, Xiao Ying Bao, Lu Lv, Zuocheng Zhou . "Templating methods for preparation of porous structures". Journal of Materials Chemistry. 16(7): p. 637-648, (2006).

52. Li, W., Dehong Chen, Dehong Chen, Zishuo Li, Yifeng Shi. "Nitrogen-containing carbon spheres with very large uniform mesopores: the superior electrode materials for EDLC in organic electrolyte". Carbon. 45(9): p. 1757-1763, (2007).

53. Wang, D., FengLI, MinLIU, Hui-ming CHENG. "Improved capacitance of SBA-15 templated mesoporous carbons after modification with nitric acid oxidation". New Carbon Materials. 22(4): p. 307-314, (2007).

54. Feng, X., Zhenzhen Yan, Ningna Chen, Yu Zhang, Xingfen Liu, Yanwen Ma, Xiaoyan Yang Wenhua Hou. "Synthesis of

a graphene/polyaniline/MCM-41 nanocomposite and its application as a supercapacitor". New Journal of Chemistry. 37(7): p. 2203-2209, (2013).

55. Ania, C.O., Khomenko V., Raymundo-Piñero E., Parra J.B., Béguin F. "The large electrochemical capacitance of microporous doped carbon obtained by using a zeolite template". Advanced Functional Materials. 17(11): p. 1828-1836, (2007).

56. Roberts, A.D., Li X., and Zhang H. "Porous carbon spheres and monoliths: morphology control, pore size tuning and their applications as Li-ion battery anode materials". Chemical Society Reviews. 43(13): p. 4341-4356, (2014).

57. Liang, J., Xin Du, Christopher Gibson, Xi Wen Du, Shi Zhang Qiao. "NDoped Graphene Natively Grown on Hierarchical Ordered Porous Carbon for Enhanced Oxygen Reduction". Advanced materials. 25(43): p. 6226-6231, (2013).

58. Novoselov, K.S., Geim A.K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V., Firsov A. A."Electric field effect in atomically thin carbon films". science. 306(5696): p. 666-669, (2004).

59. Le L.T., Matthew H.Ervin, HongweiQiu, Brian E.Fuchs, Woo Y.Lee. "Graphene supercapacitor electrodes fabricated by inkjet printing and thermal reduction of graphene oxide". Electrochemistry Communications. 13(4): p. 355-358, (2011).

60. Zhao, X., Lili Zhang, Shanthi Murali, Meryl D. Stoller, Qinghua Zhang,Yanwu Zhu, Rodney S. Ruoff. "Incorporation of manganese dioxide within ultraporous activated graphene for

high-performance electrochemical capacitors". ACS nano. 6(6): p. 5404-5412, (2012).

61. Zhong, M., Yan Song, Yongfeng Li, Chang Ma, "Effect of reduced graphene oxide on the properties of an activated carbon cloth/polyaniline flexible electrode for supercapacitor application". Journal of Power Sources. 217: p. 6-12, (2012).

62. Long, J.W., Karen E. Swider, Celia I. Merzbacher, Debra R. Rolison. "Voltammetric characterization of ruthenium oxide-based aerogels and other RuO2 solids: the nature of capacitance in nanostructured materials". Langmuir. 15(3): p. 780-785, (1999).

63. Juan, L., Qingwen L., and Xi X. "Synthesis of Nanosize MnO2 by Solid State Reaction and Its Electrochemical Property". Synthesis and Performance of MnO2 [J]. Chinese Journal of Applied Chemistry, 3, (1999).

64. Lee, H.Y. and Goodenough J. "Ideal supercapacitor behavior of amorphous V 2 O 5• nH 2 O in potassium chloride (KCl) aqueous solution". Journal of Solid State Chemistry. 148(1): p. 81-84. 75, (1999).

65. Nam, K.-W. and Kim K.-B. "A study of the preparation of NiO x electrode via electrochemical route for supercapacitor applications and their charge storage mechanism". Journal of the Electrochemical Society. 149(3): p. A346-A354, (2002).

66. Wang, Y., Ying Lei, Jing Li, Li Gu, Hongyan Yuan, Dan Xiao. "Synthesis of 3D-nanonet hollow structured Co3O4 for high capacity supercapacitor". ACS applied materials & interfaces. 6(9): p. 6739-6747, (2014).

67. Zheng, J., Cygan P., and Jow T. "Hydrous ruthenium oxide as an electrode material for electrochemical capacitors". Journal of the Electrochemical Society. 142(8): p. 2699-2703, (1995).

68. Bi, R.-R., Xing-Long Wu, Fei-Fei Cao, Ling-Yan Jiang, Yu-Guo Guo, Li-Jun Wan. "Highly dispersed RuO_2 nanoparticles on carbon nanotubes: facile synthesis and enhanced supercapacitance performance". The Journal of Physical Chemistry C. 114(6): p. 2448-2451, (2010).

69. Zhang, Z., Xiao F., and Wang S. "Hierarchically structured MnO $_2$/graphene/carbon fiber and porous graphene hydrogel wrapped copper wire for fiber-based flexible all-solid-state asymmetric supercapacitors". Journal of Materials Chemistry A, (2015).

70. Dusastre, V.; "Martiradonna, L. Materials for sustainable energy". Nat. Mater, 16, 15, (2017).

71. Dalapati, G.K.; Chua, C.S.; Kushwaha, A.; Liew, S.L.; Suresh, V.; Chi, D. "All earth abundant materials for low cost solar-driven hydrogen production". Mater. Lett, 183, 183–186, (2016).

72. Jang, J.-W.; Du, C.; Ye, Y.; Lin, Y.; Yao, X.; Thorne, J.; Liu, E.; McMahon, G.; Zhu, J.; Javey, A.; et al. "Enabling unassisted solar water.splitting by iron oxide and silicon". Nat. Commun, 6, 7447–7452, (2015).

73. Abdel Maksoud, M.I.A.; Fahim, R.A.; Shalan, A.E.; Abd Elkodous, M.; Olojede, S.O.; Osman, A.I.; Farrell, C.; Al-Muhtaseb, A.H.; Awed, A.S.; Ashour, A.H."Advanced materials and technologies for supercapacitors used in energy

conversion and storage": A review. Environ. Chem. Lett, 19, 375–439, (2012).

74. Wong, H.; Iwai, H. "The road to miniaturization". Phys. World, 18, 40–44, (2005).

75. Lorenz, M.; Rao, M.S.R.; Venkatesan, T.; Fortunato, E.; Barquinha, P.; Branquinho, R.; Salgueiro, D.; Martins, R.; Carlos, E.; Liu, A. "The 2016 oxide electronic materials and oxide interfaces roadmap". J. Phys. D Appl. Phys, 49, 433001, (2016).

76. Coll, M.; Fontcuberta, J.; Althammer, M.; Bibes, M.; Boschker, H.; Calleja, A.; Cheng, G.; Cuoco, M.; Dittmann, R.; Dkhil, B. "Towards oxide electronics: A roadmap". Appl. Surf. Sci, 482, 1–93, (2019).

77. Giustino, F.; Lee, J.H.; Trier, F.; Bibes, M.; Winter, S.M.; Valentí, R.; Son, Y.-W.; Taillefer, L.; Heil, C.; Figueroa, A.I. "The 2021 quantum materials roadmap". J. Phys. Mater, 3, 042006, (2020).

78. Fritsch, D. "Electronic and optical properties of spinel zinc ferrite: Ab initio hybrid functional calculations". J. Phys. Condens. Matter, 30, 095502, (2018).

79. Heda, N.L.; Panwar, K.; Kumar, K.; Ahuja, B.L. "Performance of hybrid functional in linear combination of atomic orbitals scheme in predicting electronic response in spinel ferrites ZnFe2O4 and CdFe2O4". J. Mater. Sci., 55, 3912–3925, (2020).

80. Ulpe A.C.; Bauerfeind K.C.; Bredow T." Influence of spin state and cation distribution on stability and electronic properties of ternary transition-metal oxides". ACS Omega, 4, 4138–4146, (2019).

81. Ulpe, A.C.; Bredow, T. "GW-BSE calculations of electronic band gap and optical spectrum of ZnFe2O4: Effect of cation distribution and spin configuration". Chem. Phys. Chem., 21, 546–551, (2020).

82. Harris, V.G. "Modern Microwave Ferrites". IEEE Trans. Magn., 48, 1075–1104, (2012).

83. Lišková-Jakubisová, E.; Viš ˇnovský, Š.; Široký, P.; Hrabovský, D.; Pištora, J.; Sahoo, S.C.; Prasad, S.; Venkataramani, N.; Bohra, M.; Krishnan, R. "Nanocrystalline zinc ferrite films studied by magneto-optical spectroscopy". J. Appl. Phys., 117, 17B726, (2015).

84. Bresser Dominic , Elie Paillard, Richard Kloepsch, Steffen Krueger, Martin Fiedler, René Schmitz, Dietmar Baither, Martin Winter, Stefano Passerini. Carbon Coated $ZnFe_2O_4$ Nanoparticles for Advanced Lithium-Ion Anodes (2012)

85. Bourrioux Samantha, Luyuan Paul Wang , Youri Rousseau , Pardis Simon , Aurélie Habert , Yann Leconte , Moulay Tahar Sougrati , Lorenzo Stievano , Laure Monconduit , Zhichuan J. Xu, Madhavi Srinivasan , Alain Pasturel. Evaluation of electrochemical performances of $ZnFe_2O_4/\gamma$-Fe_2O_3 nanoparticles prepared by laser pyrolysis, New Journal of Chemistry, Royal Society of Chemistry , 41 (17), pp.9236-9243, (2017).

86. Jinhuan Yao, Jing Yan, Yu Huang, Yanwei Li, Shunhua Xiao and Jianrong Xiao. Preparation of $ZnFe_2O_4$/α-Fe_2O_3 Nanocomposites From Sulfuric Acid Leaching Liquor of Jarosite Residue and Their Application in Lithium-Ion Batteries. Front. Chem (2018).

87. Saraf Mohit, Kaushik Natarajan, Anoop K Gupta, Pawan Kumar, Richa Rajak and Shaikh M Mobin Electrochemical energy storage properties of solvothermally driven $ZnFe_2O_4$ microspheres, Materials Research Express, Volume 6, Number 9, (2019).

88. Maksoud Abdel M. I. A., Fahim R. A., Shalan A. E., Elkodous M. A., Olojede S. O., Osman Ahmed A. O., Farrell C., Al Muhtaseb A. H., Awed A. S., Ashour A. H., & Rooney D. Advanced materials and technologies for supercapacitors used in energy conversion and storage: a review. Environmental Chemistry letter (2020).

89. Bohra Murtaza, Vidya Alman, Rémi Arras. Nanostructured $ZnFe_2O_4$: An Exotic Energy Material. Nanomaterials, 11, 1286, (2021).

90. Conway B.E., "Electrochemical Capacitor, Scientific Fundamentals and Technological Application", Plenum Press, New York, (1999).

91. Du C S, Pan J. "Power Sources", 160,1487—1494, (2006).

92. Balducci A, Dugas R., Tabema PL., Simon P, Plee D., Mastragostino M., Passenni S. "Power Sources", 165, 922-927, (2007).

93. Naoi, S. Suematsue, Hanada M., Takenouchi H., Electrochem J. Soc. 149, A427, (2002).

94. Hashmi S.A., Upadhyaya H.M. Solid State Ionics 152-153, 883, (2002).

95. Lao Z.J., "Metal Oxides as Electrode Materials for Electrochemical Capacitors", Master Thesis, University of Wollongong, . (2006).

96. William C. "Materials Science and Engineering": An Introduction, John Wiley & Sons, Inc., USA, (200

الخلاصة

تعتبر المكثفات الفائقة ، والتي تُعرف أيضًا باسم المكثفات الكهربائية مزدوجة الطبقة أو المكثفات الكهروكيميائية ، أجهزة تخزين طاقة واعدة نظرًا لمزاياها الواضحة مثل كثافة الطاقة العالية والعمرالطويل وجعلت مزايا المكثفات الفائقة منهم المرشحين الواعدين ليكونوا بمثابة الجيل التالي من تكنولوجيا تخزين الطاقة.لذلك فإن المكثفات الفائقة ذات الأداء العالي بما في ذلك كثافة الطاقة ، وكثافة القدرة ، واستقرار المادة ، ومدة الادامة الطويلة ووقت الشحن القصير. علاوة على ذلك ،تعتبر كإستراتيجية تنمية مستدامة مطلوبة ، من الضروري أيضًا مراعاة المواد الصديقة للبيئة والتكلفة المنخفضة والحيوية الطبيعية عند تصميم مواد القطب الفائق المكثف. لذلك تم تصنيع مادة إلكترود جديدة من المكثفات الفائقة لحل المشكلات الشائعة التي تواجه تقنيات تخزين الطاقة الحالية ولدعم الاقتصاد الوطني حيث تستخدم في سماعات الاذن الطبية ووسائل التواصل التكتيكي للشرطة والجيش .حيث تم دراسة $ZnFe_2O_4$ لاستخدامها كمواد كهربائية ذات مكثف فائق ، مما يوفر كثافة طاقة عالية وكثافة قدرة. وثبت أنه مادة إلكترود $ZnFe_2O_4$محتملة مناسبة للمكثفات الفائقة بسبب السعة النظرية العالية ، والتكلفة المنخفضة ، وعدم السمية ، والحجز الكبير في الطبيعة.ونظرًا للتصميم الفريد ، فقد تم تحقيق سعة محددة تبلغ 1118 فاراد / جم مع معدل قدرة جيدة واستقرارية العالية. وأظهرت الخواص الكتروكيميائية الذي تم إجراؤه بالكثافة الحالية البالغة 2 A / g أنه تم الاحتفاظ بـ 90 ٪ من السعة الأولية بعد أكثر من 10000 دورة حيث تم إجراء تحليل الهيكل باستخدام نمط حيود الأشعة السينية والفحص المجهري الإلكتروني .(SEM) لذلك فان الدراسة $ZnFe_2O_4$ كمواد نانوية صديقة للبيئة وغير سامة لذلك تستخدم في تخزين الطاقة المختلفة ، والتطبيقات البيئية والطبية الحيوية.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بابل
كلية التربية للعلوم الصرفة
قسم الفيزياء

تحضير جسيمات نانوية من $ZnFe_2O_4$ كقطب كهربائي يستخدم في تطبيقات تخزين الطاقة المتقدمة

رسالة مقدمة

الى مجلس كلية التربية للعلوم الصرفة في جامعة بابل
وهي جزء من متطلبات نيل درجة الدبلوم العالي
تربية / فيزياء المواد وتطبيقاتها

من قبل الطالب

لقاء عباس حميد عمران

بكالوريوس علوم فيزياء
جامعةبابل 2002 م

بأشراف

أ.م. د. شيماء هادي خضير

1443هـ 2021 م