An-Najah National University Faculty of Graduate Studies

# Study of Active-Carbon (AC)/Graphene-Nanoplates as Supercapacitor Electrodes Using H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and KOH Aqueous Electrolytes

By

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This Thesis is Submitted in Partial Fulfillment of Requirements for the Degree of Master of Physics, Faculty of Graduate Studies, An- Najah National University, Nablus - Palestine. Study of Active-Carbon (AC)/Graphene-Nanoplates as Supercapacitor Electrodes Using H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and KOH Aqueous Electrolytes

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## iii **Dedication**

I am dedicating this thesis for people who mean so much to me. First and formost, my father and mother whom overcome difficulties and taught me the value of hard work. Next, my dear husband who stood with me in all my hard times. My two beloved little girls Hala and Rahaf. Also, this thesis is dedicated to my brothers, sister and thier families.

Last but not least I am dedicating this thesis for everyone who supported, helped and stood by me, starting with my friends especially Sabrin and Thara and my working colleagues.

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أنا للموقعة أدناه، مقدّمة الرسالة التي تحمل العنوان:

# Study of Active-Carbon (AC)/Graphene-Nanoplates as Supercapacitor Electrodes Using H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and KOH Aqueous Electrolytes

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## Declaration

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No. Content Pages Dedication Iii Acknowledgment Iv V Declaration List of Tables Viii List of Figures Ix Xi Abbreviations Abstract Xiii 1 **Chapter One: Introduction** 1.1 Supercapacitor 1 1.2 **Previous studies** 5 1.3 8 Supercapacitor components 1.4 9 Supercapacitor types and principle 1.4.1 Electrical double layer capacitors (EDLC) 9 1.4.2 11 **Pseudocapacitors** 1.4.3 Hybrid capacitors 11 Supercapacitor materials 1.5 12 1.5.1 **Electrodes** materials 13 1.5.2 Electrolyte materials 19 1.5.3 20 Separator materials 1.6 Motivation and main objectives of this research 21 **Chapter Two: Theoretical Background** 23 Introduction 2.1 23 2.2 Electrochemical characterization 27 2.2.1 27 Cyclic Voltammetry 2.2.2 Galvanostatic Charging Discharging 29 2.2.3 Electronic Impedance Spectroscopy (EIS) 31 2.3 35 Porosity of materials 2.3.1 Specific Surface Area (SSA) 37 2.3.2 39 Pore Size Distribution (PSD) 2.3.3 t-plot method 41 2.3.4 Specific pore volume and area 42 **Chapter Three: Experimental Work** 46 3.1 Materials 46 3.2 Equipments and devices 47 3.3 49 Preparation of electrodes pallets

List of Contents

	vii	
3.4	Preparation of electrolyte solutions	51
3.5	Electrochemical methods	51
3.6	Electrode Surface Morphology	54
3.7	Porosity measurements	55
	<b>Chapter Four: Results and discussion</b>	56
4.1	Electrochemical Characterization	56
4.1.1	Cyclic Voltammetry (CV)	56
4.1.2	Galvanostatic charge-discharge (GCD)	61
4.1.3	Electrochemical Impedance Spectroscopy (EIS)	68
4.2	Surface Morphology	76
4.3	Porosity measurements	77
4.4	Total specific surface area (SBET)	79
4.4.1	Pore Size Distribution (PSD)	80
4.4.2	Brunauer-Joyner-Halenda (BJH) method	80
4.5	Harkins-Jura (HJ) t-plot method	82
	Chapter Five: Conclusion	86
	References	88
	الملخص	ب

No.	Tittle	Page
4.1	The specific capacitance at all scan rates for the three examined electrodes	59
4.2	Ions radii for all used electrolytes	59
4.3	Specific capacitance at each current density $(I/m)$ using GCD for different electrolytes	63
4.4	Voltage drop at different current density $(I/m)$ values for AC/GNPs electrodes using different electrolytes	65
4.5	ESR values for AC/GNPs electrodes tested by GCD method under dif- ferent electrolytes	65
4.6	Power and Energy densities for AC/GNPs electrodes using $H_2SO_4$ elec- trolyte	66
4.7	EIS method values of specific capacitance, equivalent series resistance, solution resistance and charge transfer resistance values for AC/GNPs composite electrodes using different electrolytes	70
4.8	Electrolytic conductivity of $KOH$ , $H_2SO_4$ and $Na_2SO_4$ electrolytes	71
4.9	Size of hydrated ions and their conductivity	71
4.10	Knee frequency, $f_0$ , of AC/GNPs composite electrodes using different electrolytes	73
4.11	Time constant, $\tau$ , and relaxation time, $\tau_0$ , for AC/GNPs composite electrodes using different electrolytes	74
4.12	Specific surface area and total volume using BET analysis	80
4.13	Mesopores and macropores volumes and surface areas with their per- centage contribution	82
4.14	AC/GNPs composite material porosity deduced using HJ t- plot method	84
4.15	AC/GNPs composite material acceptable pores volumes and surface areas results with their percentage contribution for deduced from BJH method and HJ t-plot method	85

viii List of Tables

ix List of Figures

No.	Tittle	Page
1.1	Ragone plot for various energy storage and conversion devices [5].	3
1.2	Supercapacitor Components [17].	8
1.3	Supercapacitor Types [11].	9
1.4	Charging Process in EDLC [3].	10
1.5	Supercapacitor types: (a) EDLC, (b) Pseudocapacitors and	12
16	C) Hybrid capacitors principles [0]. Pores size definition according to IUPAC [18]	15
1.0	Fabrication of active carbon material [9]	17
1.7	Physical and chemical activation of carbon materials [11]	17
1.0	Graphene-based Materials [13]	18
2.1	Schematic of (a) uncharged and (b) charged EDLC [29]	24
2.2	Schematic of EDLC showing the IHP and OHP [32].	25
2.3	Schematic of voltage distribution inside EDLC and its	26
2.4	simplified equiv- alent circuit. Typical CV characteristics of an electrochemical EDLC	28
2.1	(after [35]).	20
2.5	Galvanostatic charging discharging curve for resistive EDLC [36].	30
2.6	Schematic for Nyquist plot for practical EDLC.	34
2.7	Sorption isotherms according to IUPAC classification [43].	37
2.8	Hysteresis loops characteristics according to IUPAC [43].	38
2.9	Schematic of BET plot.	39
2.10	t-Plots of nonporous, mesoporous, microporous and micro- and meso- porous solids [after 49].	42
2.11	t-plot of materials with different micropore-mesopore ratio [after 48].	44
3.1	Equipments used at An-Najah National University: a) PGZ402 Poten- tiostat, b) Swagelok cell, c) Magnetic stirrer, d) Electronic balance, e) Agate mortar, f) Ultrasonic path, g) Oven and h) Hydraulic press.	48
3.2	Equipments used at Barcelona University: a) Jeol J-7100 SEM and b) TriStar 3000 BET.	49
3.3	Electrodes pellets (disks)	50
3.4	Glass fiber separator	52
3.5	Assembling electrodes disks and the glass fiber separator into the Swagelok cell.	52
3.6	Swagelok connected to computerized PGZ 402 potentiostat.	54

	Х	
4.1	Cyclic voltammetry curves for $AC/GNP_s$ supercapacitor using: (a) $H_2SO_4$ , (b) $Na_2SO_4$ , (c) $KOH$ electrolytes and (d) comparison at scan rate = 100 mV/s	58
4.2	Specific capacitance vs. scan rate for three samples	59
4.2	Specific capacitance vs. scal fact for three samples. Cyclic voltammetry using $KOH$ electrolyte for: (a) AC [34]	<u> </u>
4.5	and (b) GNPs.	00
4.4	Cyclic stability at scan rate =100 mV for $AC/GNP_s$ supercapacitor for the first 100 cycle using: (a) $H_2SO_4$ , (b) $Na_2SO_4$ and (c) $KOH$ electrolytes.	61
4.5	Galvanostatic charge-discharge curves for $AC/GNP_s$	62
	supercapacitor us- ing: (a) $H_2SO_4$ , (b) $Na_2SO_4$ , (c) $KOH$ electrolytes and (d) Comparison at current I = 50mA.	
4.6	Variation of (a) specific capacitance and (b) voltage drop with current density for AC/GNPs electrodes for different electrolytes.	64
4.7	Energy density and power density relation for the three samples.	67
4.8	Cyclic stability for AC/GNPs electrodes using different electrolytes at current = 100mA.	67
4.9	Nyquist plot from electrochemical impedance spectroscopy for $H_2SO_4$ , <i>KOH</i> and $Na_2SO_4$ .	69
4.10	Specific capacitance relation with frequency for all used electrolytes.	70
4.11	Nyquist plot from EIS method using KOH electrolyte for: (a) AC [after 34] and (b) GNPs.	73
4.12	Relation between frequency and: (a) real part of impedance $(Z_r)$ and (b) imaginary part of impedance $(Z_i)$ for all samples.	75
4.13	Relation between imaginary part of the specific capacitance with fre- quency.	76
4.14	SEM micrographs for AC/GNPs composite materials with different magnifications: (a) X400, (b) X900, (c) X3300 and (d) X8000.	77
4.15	Adsorption desorption isotherm for AC/GNPs composite electrode supercapacitor.	78
4.16	BET plot for AC/GNPs composite electrode material.	79
4.17	<ul><li>(a) incremental pore volume, (b) differential pore volume,</li><li>(c) cumulative pore vol- ume and (d) cumulative surface area.</li></ul>	81
4.18	Harkins Jura $N_2$ adsorption t-plot for AC/GNPs composite material.	83

# xi List of Abbreviations

SC	Supercapacitor
AC	Active Carbon
$CNT_s$	Carbon Nanotubes
<i>CNF</i> <sub>s</sub>	Carbon Nanofibers
ESR	Equivalent Series Resistance
EDLC	Electrical Double Layer Capacitor
IUPAC	International Union of Pure and Applied Chemistry
GNPs	Graphene Nanoplates
MWCNTs	Multi-Walled Carbon Nanotubes
CV	Cyclic Voltammetry
GCD	Galvanostatic Charge/Discharge
EIS	Electrochemical Impedance Spectroscopy
SEM	Scanning Electronic Microscopy
TEM	Tunneling Electronic Microscopy
BET	Brunauer-Emmett-Teller
BJH	Brunauer-Joyner-Halenda
HJ	Harkins-Jura
$C_s$	Specific Capacitance
S	Scan Rate
SSA	Specific Serface Area
PVDF	Polyvinylidene Flouride
PVA	Polyvinyl Alcohol
STP	Standard Temperature and Pressure
$V_{drop}$	Voltage Drop
$E_d$	Energy Density
$P_d$	Power Density
$R_s$	Solution Resistance
$R_{ct}$	Charge Transfer Resistance
τ	Time Constant
$ au_0$	Relaxation time

xii		
$f_0$	Knee frequency	
Z'	Real Part of the Impedance	
$Z^{\prime\prime}$	Imaginary Part of the Impedance	
$ q_c $	Cathode Charge	
$q_a$	Anode Charge	
S <sub>meso</sub>	Mesopores Area	
Smacro	Macropores Area	
$Q_m$	Adsorbed Quantity	
$S_t$	Total Surface Area	
$V_{tot}$	Total Volume	
$V_{mac}$	Macropores Volume	
$V_{mes}$	Mesopores Volume	
$V_{mic}$	Micropores Volume	
$S_{ext}$	External Area	
$S_{open}$	Meso and External Surface Area	
С′′	Imaginary part of the capacitance	

# Study of Active-Carbon (AC)/Graphene-Nanoplates as Supercapacitor Electrodes Using H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and KOH Aqueous Electrolytes By

Fatima Nabil Mohammed Shahrouj Supervisors Dr. Allan Daraghmeh Dr. Iyad Saadeddin Abstract

This thesis discuss the effect of changing the electrolyte material on activecarbon/graphene-nanoplates supercapacitor. Active-carbon/ graphene-anoplates elec-trode pellets were prepared and examined using KOH,  $H_2SO_4$  and  $Na_2SO_4$  electrolytes. The electrochemical characteristics (cyclic voltammetry, galvanostatic charge- discharge and electronic impedance spectroscopy) of supercapacitor were studied using a universal potentiostat/galvanostat. The specific surface area of the electrode was  $951.01m^2/g$ . This study showed that the specific capacitance achieved.

a highest values of 320.3 F/g using  $H_2SO_4$  electrolyte solution when measured by cyclic voltammetry method at scan rate of 5mV/s. Also, using  $H_2SO_4$  electrolyte, it was found to have the lowest equivalent series resistance of 0.311  $\Omega$  using electrochemical impedance spectroscopy method. Consequently, the electrode measured using  $H_2SO_4$  electrolyte has the highest specific energy and specific power of 14.82 Wh/kg and 4177.8 W/Kg, respectively. The specific energy and power were calculated using charge-discharge method. In addition, this sample was observed to have a very good cyclic stability and efficincy when examined for a thousand cycles. Also, surface characteristics and pore size distribution were studied

xiii

by brunauer- emmett- teller, brunauer-joyner-halenda and harkins-jura. Results show that active- carbon/graphene-nanoplates electrodes have a proper pore size distribution that is consistant with the ions size of  $H_2SO_4$ , so that this solution gives the highest specific capacitance.

## **Chapter One**

# Introduction

### **1.1 Supercapacitor**

Recently, many energy problems took attention such as depleting fossil fuel reserves, rising prices, increasing human pollution and  $CO_2$  emission. This lead, to increase the devoted efforts for developing new efficient, clean and renewable energy storage devices to decrease  $CO_2$ gas emission and develop energy storage and conversion devices [1-3]. One of the most important energy storage devices that attracted much attention are supercapacitors (SCs) or electrochemical capacitors. SCs are electrical components that store and accommodate certain amounts of energy because they have thin dielectric layer and high surface area in its electrodes. They are based on the formation of an electric double layer at the interface between an electonically conductive material and an electrolyte solution, so they exhibit capacitances that are much larger than the traditional capacitors [4-7].

These days, SCs are used in many important electronic devices, such as renewable power supplies, military devices and volatile memory backups in computers. They are also used in energy harvesting systems, where SCs play a supplementary role next to batteries. In addition, they are used in electric vehicles, fuel cell vehicles, trains and trolleybuses. Moreover, they are used to increase the efficiency of hybrid vehicles, they use SCs at the moments when the power demand is high, such as starting a car, to decrease the overall consumption from batteries. Hybrid vehicles turn off the engine completely when the car stops, then they start it again using the stored energy in SCs [5, 8].

Compared to conventional capacitors, SCs have many intrinsic properties such as high power density, high energy density, long cycle life and wide operating temperature range [1, 4]. SCs have high power density and can release a huge amount of energy in a short period of time and they have excellent cyclability and very good power performance. So, they are suitable to be employed in a variety of energy storage devices either independently or in combination with batteries or fuel cells. SCs have low energy performance in comparison to batteries, as shown in the Ragone plot (fig. 1.1 [5]), that limits their range of applications in different devices. Hence, they need to improve their energy performance to a level comparable to batteries to meet the requirements of future energy storage devices. SCs are being increasingly popular for their ability to be used with batteries due to their rapid charge-discharge rate. So, they can be coupled with batteries for applications that need an energy supply for long period of time [2, 6, 9, 10].

#### • Ragone Plot



Figure 1.1: Ragone plot for various energy storage and conversion devices [5].

The Ragone Plot is a method to represent the energy storage performance of various energy storage devices. In this energy-power relation, the energy density is plotted versus power density to compare different electrochemical power sources. As shown from Ragone plot, supercpacitors fill the gap between conventional capacitors and conventional batteries among different energy storage devices. This property is important from the application point of view. Supercapacitors have much higher power density than batteries and much larger energy density compared with conventional capacitors, the typical supercapacitor has an energy density in the range of  $(5 - 10Whkg^-1)$ , which is much higher than conventional dielectric capacitors, but significantly lower than conventional batteries. Additionally, in comparison to batteries SCs have higher current that they can operate with. Recently, a great efforts and studies have been done to develop a high performance batteries, but the poor power capability and high maintenance cost of them kept them away from many applications. Batteries and fuel cells can store more energy, but this have a poor dynamic performance. On the other hand, conventional capacitors generally have a high power because they can release the stored charge fast, but can't store much energy. Supercapacitors store more power than batteries and more energy than conventional capacitors. It means that supercapacitor can be charged or discharged very fast and obtain a relatively high specific energy (energy stored per unit mass) [3, 5, 8, 11].

Increasing the capacitance of SCs is related to the number of stored ions in the interface region between the electrode and electrolyte surfaces. In order to have a large number of stored ions, the SC electrode need to have a large specific surface area; the specific surface area is the capacity to accumulate electric charges on that surface. Also, to increase the energy density, it is important to notice that the energy is directly proportional to the capacitance and the square of the operational potential window. So, researchers are now focusing on the development of nanostructured material electrodes with tailored surface area and porosity, such as carbon materials. Also, the use of pseudocapacitance materials such as transition metal oxides and metal sulfides, allow a large increase in the specific capacitance of SCs [1, 4, 12].

4

It is also found that the development of both electrode material and the electrolyte solution in the supercapacitor are essential to decrease the equivalent series resistance (ESR) of  $SC_s$  to enhance its total performance. ESR is inversely proportional to the power density. Hence, decreasing ESR increases the power density of supercapacitor electrode. The ESR comes from various resistances associated with *SC* components, such as electrolyte solution resistance, charge transfer resistance of the ions in the electrode and contact resistance between the current collector and the electrode. Hence, a high-performance super capacitor must simultaneously satisfy the requirements of large capacitance value, high operating cell voltage, and minimum ESR.

The main materials used in SCs are: firstly, carbon materials such as Active Carbon (AC), Carbon nanotubes (CNTs), graphene-based materials. Because they use double layer capacitance mechanism, they stores charges electrostatically using reversible adsorption of electrolyte ions onto electrode active materials that are elec-trochemically stable and have high accessible area. Secondly, redox-based materials that used transition metal oxides such as  $MnO_2$  and  $RuO_2$ . They stores energy by fast and reversible redox reactions at the surface of the electrode active materials[2, 13].

### **1.2 Previous studies**

The experiments to develop SCs are started in the 50s of the last century. First experiments were conducted by US companies, General Electric (GE) and Standard Oil of Ohio (SOHIO). Their first electrochemical SCs reached

5

a capacity of 1F. The first commercial SC named Gold Cap was released to the market in 1982 by Panasonic, but is had a high ESR. The first electric double layer capacitor (EDLC) that had low ESR was developed for military purposes in 1982 by the Pinnacle Research [5]. Here are some results that researchers got to develop supercapacitors:

- Allan Daraghmeh et al have fabricated a symmetric supercapacitors by carbon nanofibers and activated carbon (AC) using similar proportions of 7 wt% polyvinylidene fluoride (PVDF) polymer binder in an aqueous electrolyte. The results showed that AC provided higher specific capacitance retention up to very fast scan rate of 500 mV/s. AC carbon had a specific capacitance of 334 F/g, and CNFs had 52 F/g at scan rate 5 mV/s. Also, the measured equivalent series resistance (ESR) showed a very small value for CNFs (0.28) in comparison to AC that has an ESR resistance of (3.72) [14].
- M. A. Hashim et al, have fabricated a Supercapacitor using activated carbon electrodes and combinations of two electrolytes solutions; polymer electrolyte polyvinyl alcohol (PVA) and Phosphoric acid (*H*<sub>3</sub>*PO*<sub>4</sub>). The result indicates a relatively high efficiency of about 90% and also exhibited long cyclability (life time) under different voltage windows [19].
- Xianzhong Sun et al, have prepared activated carbon-based symmetric supercapacitor using  $Li_2SO_4$  and KOH electrolytes. The results indicate that in the case of  $Li_2SO_4$ , the AC electrode can deliver a specific

capacitance and energy density higher than that in the case of KOH [69].

- Allan Daraghmeh et al, have synthesized a new nanocomposites based on a mixture of ACs and CNFs using a simple powder processing and evaluated their electrochemical behavior as electrode materials in symmetric EDLC. The EDLC, with 10 wt. % CNFs in AC/CNFs as the electrodes have showed a high conductivity and surface area. The highest value of specific capacitance estimated is around 207 F g-1 at 5 mV s1 and the highest specific energy is 13.2 Wh kg1 at 1 A g1 for the 10 wt.% CNFs in AC/CNFs [16].
- Thierry Brousse et al, have assembled AC MnO<sub>2</sub> hybrid supercapacitor with K<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. A laboratory cell achieved 195,000 cycles with stable performance. The maximal cell voltage was 2V associated with 212 Fg<sup>-1</sup> and equivalent series resistance below 1.3Ω [70].
- Ahmed A. Moosa et al, have studied the mechanical and thermal properties of graphene nanoplates and functionalized carbon-nanotubes hybrid epoxy nanocomposites (FMWNTs). The best improvements in mechanical properties was found at two mixing ratios of GNPs: FMWNTs (5:5) and (9:1) [15].
- Majid Beidaghi et al, have studied the electrostatic spray deposition of graphene nanoplatelets for high-power thin-film supercapacitor electrodes. It was found that Cyclic voltammetry measurements

of  $1\mu m$  thick electrodes yield near rectangular curves even at a very high scan rate of 20 V/s. Thin-film electrodes ( $1\mu m$  thickness) show specific power and energy of about 75.46 kW/kg and 2.93 Wh/kg, respectively, at a 5 V/s scan rate [20].

## **1.3 Supercapacitor components**

Supercapacitor structure is similar to that of a battery which consists of two electrodes in contact with an electrolyte solution and separated by a porous separator that is sandwiched between the electrodes [7, 13, 17]. Supercapacitors consists of two electrodes separated from any electrical contact by a semipermeable membrane separator that is immersed in an electrolyte solution (fig. 1.2). This membrane allows the movement of ions and charges from electrolyte material to the electrode/electrolyte interface area. Hence, the membrane allows the flow of ionic current between electrodes and prevents the electronic current from discharging the supercapacitor. The two electrodes are connected to current collectors that conduct electrical current from the electrodes [6, 17, 21].



Figure 1.2: Supercapacitor Components [17].

9

## **1.4** Supercapacitor types and principle

Conventional electrostatic capacitors can store a little amount of energy due to their limited surface area and geometrical issues such as the small separation distance be- tween the two charged plates. On the other hand, supercapacitors can store much more energy because of the large electrode/electrolyte interface area that is access- able for ions, and the very small (nano-scale) charge-electrodes separation distances. Supercapacitors are classified into three types according to the energy storage mechanism of the capacitor (fig. 1.3). These types are the electrical double layer capacitor (EDLC) that stores energy from pure electrostatic charge accumulation, pseudocapacitor that stores energy due to fast and reversible surface redox reactions and hybrid capacitor that stores energy by combination of EDLC and pseudocapacitor mechanisms [6, 8, 11, 13].



Figure 1.3: Supercapacitor Types [11].

## **1.4.1 Electrical double layer capacitors (EDLC)**

In EDLC, the energy storage and release mechanism is nonfaradic and no redox reactions occurs. It is based on the separation between charges and the interface region between electrode and electrolyte surfaces as shown in figures 1.4 and 1.5.a. The behavior at the electrode surface depends on the applied electrical field across the electrode, intrinsic properties of electrode, electrolyte and chemical affinity between the electrolyte material ions and the electrode surface. Electrical double layer capacitors use electrostatic interaction to store energy in the interface double layer at the electrodeelectrolyte surfaces. There is no electron exchange occurs, and the doublelayer capacitance is arising from potential dependence of the surface energy stored electrostatically at the interface of capacitor electrodes. EDLCs have long cycling life because only a physical charge transferring occurs and no electron exchange occurs. In fact, to increase the EDLC capacitance, the electrode material should have large surface area in order to store high amounts of charges inside electrodes pores. In addition, EDLCs have a low equivalent series resistance (ESR) value comparing with the conventional capacitors. This is very important property because it make  $SC_s$  maintain a very high power density which is a desirable feature for supercapacitors designing and studying [3, 5, 6, 8].



#### **1.4.2 Pseudocapacitors**

Pseudocapacitors also called faradic capacitors, and they are used less frequently than EDLC. They are based on faradic oxidation reduction reactions that comes from the bonds in the compounds. According to their operation principle they are closer to conventional batteries. The pseudo-capacitance arises at the electrode surface where faradic reaction occurs, it is responsible of the electron transfer and redox reactions. The reactions involving the passage of energy across the double layer as shown in figure 1.5.b. The energy in pseudocapacitors is not stored in the dielectric layer as in the electric double layer capacitors, but it represented by the energy of molecule bonds. This type has many disadvantages such as shorter cycling lives, lower stability and longer time response than electric double layer capacitors. Additionally, during charging and discharging processes, the electrodes are stressed and degrade faster compared to the electrostatic storage principle, and this is leads to increase the internal resistance of the supercapacitor [5-7].

## **1.4.3 Hybrid capacitors**

Hybrid capacitors are the newest and the most advanced supercapacitors that com- bine both types, EDLCs and pseudocapacitors as shown in figure 1.5.c in order to improve supercapacitor performance. Because of the interaction that occurs between charge carriers from electrolyte materials and electrode surface, they can deliver high currents. In the negative electrode where a faradic reaction occurs, it possess higher energy density. While positive electrode mainly made from active carbon, it stores energy electrostatically in the double layer on the electrode surface. Till now, no commercial hybrid supercapacitors available in the markets [5, 6].



Figure 1.5: Supercapacitor types: (a) EDLC, (b) Pseudocapacitors and (c) Hybrid capacitors principles [6].

## **1.5** Supercapacitor materials

The capacitance of the cell depends mainly on the specific capacitance of electrode material that is represented in (F/g). While the resistance is affected mainly by the electrolyte material, and the cell voltage is limited by the thermodynamic stability of the electrolyte material. Depending on the energy storage type of the supercapacitor and the desired capacitance range, SCs can be manufactured from different materials.

The developing of nano-structured materials is considered now as the major factor for developing and enhancing supercapacitor devices. This is because of its high surface area and high capacitive performance [6, 13, 21].

## **1.5.1 Electrodes materials**

Supercapacitor electrode performance depends mainly on the material used. It must have high surface area with proper pore size that fit with the electrolyte ions sizes in order to store the largest possible number of ions inside electrode pores. The electrode material should be electrically conductive with a good stability after relatively high number of cycles. Using suitable porous material with suitable pore size distribution matching the ions size leads to improve the capacitance of the supercapacitor. Additionally, it is important to design high performance energy and power by using the suitable electrode material. Also, in some cases a binder such as Polyvinylidene Fluoride (PVDF) and Polyvinyl Alcohol (PVA) polymers is used in the supercapacitor electrode. Their main job is to join the particles together and provide enough strength during the formation of electrodes. However, some pores of the active material are blocked when using binders which closes some ions Fluoride paths and then decrease the surface area accessible for ions storage [13, 21, 22]. The main supercapacitors materials are listed hereafter:

#### • Carbon-based materials

Porous carbon materials are the most attractive choice as supercapacitor electrode material because of their important characteristics such as low cost, large interface area, good electronic conductivity, good chemical stability, non-toxicity, high temperature stability and easy processing. To have high performance of carbon material, many factors must be taken into account such as structure, texture and its form. Carbon materials exist in many forms like Active Carbon (AC), Graphene, Carbon Nanotubes ( $CNT_s$ ) and Carbon Nanofibers ( $CNF_s$ ). Other important parameters, that make carbon materials to be the most electrode materials used in the electric double layer capacitors, is their diverse pore structure. It was noticed that the specific capacitance of the supercapacitor increases with increasing specific surface area of the electrode material, so carbon material characteristics including pore shape must be taken into account. Hence, the energy stored in carbonbased materials is also depends on the specific surface area and pore structure of electrodes [8, 9, 11, 13].

Note that the pores structure was defined by the International Union of Pure and Applied Chemistry (IUPAC) according to their size into three types (fig. 1.6): Macropores for pores structure of size greater than 50 nm, mesopores for pores size ranges from 2 to 50 nm and micropores for those of size less than 2 nm [11, 18].



Figure 1.6: Pores size definition according to IUPAC [18].

It was also found that the performance of carbon materials is greatly affected by the source of carbon material and the synthesis method. They can determine the pore characteristics, chemical property and electrical conductivity. For example, carbon derived from coal could include impurities, and carbon derived from polymers has low specific surface area [7, 9, 11, 20]. In this thesis, the carbon material selected to be part of our composite SC electrode is active carbon.

## Active carbon (AC)

Active carbon is studied widely for supercapacitor applications. This is beacause it is cheap, has high surface area, wide distribution of pore sizes, easy to process, has high electrical conductivity, has high chemical and electrical stability and it can be synthesized from many available sources. AC is cheaper than other carbon materials and known for its large surface area, which is due to their high porous structure. Although AC has a high specific surface area, it has low electrical conductivity that limits its applications. High porosity can cause some problems, such as the existence of pores that may be smaller than the electrolyte ions size, that will not contribute to charge storage. Also, porosity can lead to the limiting of power density because of the poor electrical conductivity. AC is composed of small hexagonal rings organized in graphene sheets, or discrete fragments of curved graphene sheets. It is fabricated in two steps (fig. 1.7) [9], firstly is carbonization, in which the carbon-rich organic material undergoes heat treatment to remove non-carbon elements. Secondly is the activation of carbon material, to improve the performance and increase surface area of carbon material.

This is done by several treatments methods such as the use of *KOH* or  $CO_2$ . Physical activation is done by using  $CO_2$  and chemical activation is done using *KOH*. This treatment open pores that are closed or obstructed, which leads to increase the surface area available for storing charges. Activation methods are shown in figure 1.8 [6, 11, 13].

## • Graphene-based materials

Graphene-based materials have a special importance because of its electrical and mechanical properties and structure. They are classified according to their dimensions into four main types, zero-dimensional fullerenes, one-dimensional carbon nanotubes, two-dimensional graphene and three-dimensional graphite. Graphene is composed of one layer of carbon atoms packed into a two dimensional honeycomb  $sp^2$  lattice. It has some important properties, such as light weight, strong mechanical strength and chemical stability. It is considered as a vital building block for electrodes, because it can provide a good medium



Figure 1.7: Fabrication of active carbon material [9].



Figure 1.8: Physical and chemical activation of carbon materials [11].

to transfer hydrate ions in aqueous electrolytes, that will increase the capacitance of the supercapacitor. It is also exhibits a good mechanical, thermal and electrical properties and has higher specific surface area than other materials. So, graphene and graphene-based materials are considered as a promising electrode materials for high performance electronic and energy devices including energy generation and storage. Also, the combination of these important physical, mechanical and chemical properties make graphene-based material more suitable for electrochemical and sustainable energy generation devices, such as Li-ion batteries, fuel cells, SCs, and solar cells. This two dimensional material is considered as the source of all graphitic materials, and it becomes one of the most important research topics in the last few years. The fullerene, CNT and graphite can be formed by wrapping, rolling and



Figure 1.9: Graphene-based Materials [13].

stacking of a graphene sheet, respectively as shown in figure 1.9. Each one of these materials exists as a different structure with different electrochemical properties [1, 2, 11, 13, 15]. In this thesis, graphene nanoplates has been used with activated carbon to form a nanocomposite electrode for EDLC.

#### • Graphene nanoplates (GNPs)

Graphene nanoplates  $GNP_s$  are the thinnest material discovered and the strongest material ever measured in the universe till now. They have attained prominence due to their high surface area, high electronic conductivity and chemical stability. GNPs tend to form graphite due to their strong interacion and large van der waals bonds, so the applications of GNPs/polymer still limited. The major challenge now is to get homogeneous dispersion of GNPs when mixed with polymer. On the other hand, hybrid nanocomposites have attracted more attention because it can decrease GNPs restacking. As a result, the surface area of GNPs increased. This is done by using many materials, for example mixing multi-walled carbon nanotubes (MWCNTs) with GNPs can bridge adjacent GNPs and prevent their restacking [4, 15].

#### **1.5.2 Electrolyte materials**

The choice of electrolyte material is very important because the supercapacitor is greatly affected by electrolyte material properties. The cell potential window depends on the electrolyte break down voltage, hence the energy density that depends on the voltage window will be limited. Additionally, the power density depends on the equivalent series resistance of the cell, which is dependent on the conductivity of electrolyte material. Electrolytes are devided into two groups according to their solvent material, protic and aprotic electrolytes. Protic or aqueous electrolytes, that based on water, are more environmentally friendly, cheap, offer higher conductivity, which leads to higher power density, and can be easily processed and treated in the laboratory without having dangerous issues. On the other hand, they have narrower working potential window because it is limited by the thermodynamic potential window of water which is approximately 1.2V. The aqueous electrolytes can be divided into three groups, alkaline, acid, and neutral solutions. The most widely protic electrolytes used are ( $H_2SO_4$ ), ( $Na_2SO_4$ ) and (KOH). Aprotic or non-aqueous electrolytes are most commonly used in commercial devices because they produce a higher energy density, due to their higher working voltage window (2.8 up to 4V) than protic electrolyte. However, the resistivity of organic electrolytes is higher than aqueous electrolytes, thus limiting the cell power range, they have lower ionic conductivity and high viscosity compared to protic electrolytes. The most widely aprotic electrolytes used are lithium salts. The ability to store charges in the electrodes of the supercapacitor depends on both electrode and electrolyte materials. This is because the ability to store charged ions in the electrode material depend on ions sizes of the electrolyte and electrode pores sizes [4, 5, 11, 13, 23].

## **1.5.3 Separator materials**

It is very important to save the supercapacitor from fire dangerous and prevent the damage of the capacitor devices by separating the two electrodes from each other by a membrane separator. This separator membrane prevent short circuit in the supercapacitor. There is many important parameters of a membrane separator, such as thickness, permeability, absorbance, chemical stability, pore sizes, tensile strength and thermal properties. Membrane separator should be porous and has a good permeability to enable transferring of electrolyte ions to be stored into the electrode pores. Also, a very good permeability of the membrane decreases the resistance of the supercapacitor, and hence ions can move easily through it to reach the electrodes surface. Also, separator membrane should have good chemical stability in different electrolytes, cycling stability under high potential and good absorbency in order to decrease the internal resistance. This is because absorbency is the ability to absorb electrolyte material which reveal the wetting ability of the membrane to the electrolyte [11].

### **1.6** Motivation and main objectives of this re- search

The performance of a supercapacitor is obtained according to many important parameters: power density must be greater than batteries with acceptably high energy densities (>  $10Whkg^{-1}$ ), a very good cyclic stability after high number of cycles, fast charge-discharge processes (within seconds), low self-discharging, safe operation and low cost. The time constant  $\tau$  is another important property for the supercapacitor, it is expressed as resistance (R) times capacitor. All these parameters can be adjusted by the proper use of electrode and electrolyte materials as mentioned before [13].

The main objectives of this research is to test supercapacitor electrodes made from carbon nonacomposite materials (GNPs and AC) with different electrolytes ( $1MH_2SO_4$ ,  $1MNa_2SO_4$ , 6MKOH) and study their electrical and surface properties to determine the best electrolyte materials for SCs manufacturing. This is done by the following steps:

- 1. Learning deeply about supercapacitors; types and principle.
- 2. Preparing electrodes from AC/GNPs mixture.
- 3. Studying the effect of changing the electrolyte solution on the supercapacitor.
- 4. Studying the electrochemical properties using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electronic impedance spectroscopy (EIS) methods.
- 5. Testing the cyclic impedance stability of the supercapacitor electrodes.
- 6. Studying the structure of the AC/GNPs electrodes.
- 7. Calculating the specific surface area and pore size distribution of the sample.
- 8. Comparing the results and determine the best sample with high specific capacitance, low equivalent series resistance (ESR), high power and energy densities.
# Chapter Two Theoretical Background

#### **2.1 Introduction**

Today, huge amount of energy is required to meet the demand for society requirements of energy. Due to this efficient energy storage systems are needed in parallel with sustainable clean energy sources. Supercapacitor (SC) is considered to be one of high performance energy storing devices needed for high power sources applications. Conventional capacitor stores energy on its metallic plates electrostatically. The capacitance (C in Farad, F) is defined as the amount of charges (q in coulomb, C) stored in correspondence with the potential change (V in volts, V) across the capacitor. Mathematically, the capacitance is given by [24, 25]:

$$C = \frac{q}{v} \tag{2.1}$$

Considering a parallel plate capacitor, the capacitance is then can be given as:

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \tag{2.2}$$

Where  $\varepsilon_r$  is the dielectric constant of the dielectric material between the parallel plates,  $\varepsilon_0$  is the permittivity of the free space (8.854 \* 10<sup>-12</sup> F/ m), A is the area ( $m^2$ ) and d is the thickness of the dielectric material (m). The energy stored (E in joules, J) can be found from the area under the q-V graph of equation 2.1, and it is given by [24-26]:

$$E = \frac{1}{2} CV^2 \tag{2.3}$$

24

Supercapacitors or electrochemical capacitors are divided into three different types. These types are Electric Double Layer Capacitors (EDLCs), pseudocapacitors and hybrid capacitors [6, 11, 8, 13]. In this study, EDLC is studied with double electrodes of AC/GNPs nanocomposites. EDLCs employ only electrostatic separation between charges. In EDLC, the energy storage takes place at the interface between the electrolyte and the surface of electrode [27, 28]. EDLCs consist of two electrodes and a separator that separate between them. The separator be an insulator and permeable for ions. The gap between the electrodes is filled with electrolyte interface of the two electrodes, forming double layers of charges as shown in figure 2.1.



Figure 2.1: Schematic of (a) uncharged and (b) charged EDLC [29].

According to the Grahame and Bockris-Devanathan-Mller model [30], inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) are formed by charge layer in the electrolyte. These layers are referred to the monolayer of solvent molecules polarized just near the electrode surface (Fig. 2.2) [31].



Figure 2.2: Schematic of EDLC showing the IHP and OHP [32].

To estimate the capacitance of the EDLC, equations (2.1) and (2.2) can be used since the accumulated charges are electrostatically separated at the electrode- electrolyte interface is analogous to parallel plate capacitor. For supercapacitor, q represents the accumulated charge density at the electrode-electrolyte interface region, V is the operating voltage of SC, A is the specific surface area of the electrodes,  $\varepsilon_r$  is the electrolyte permittivity and d is the distance between the center of ions (OHP) and electrode pore surface. Hence, to get supercapacitor (EDLC) with higher specific capacitance (capacitance per unit mass), the specific surface area of the electrode have to be as large as possible and the distance between ions center and pores should be as small as possible [12, 22, 24]. Figure 2.3 shows the equivalent circuit of an EDLC. It shows two capacitors in series addition to the resistance of electrode material ( $R_E$ ) and the electrolyte-separator resistance ( $R_s$ ) [11, 24, 33].

Hence, EDLC composed of two capacitors ( $C_+$  and  $C_-$ ), one for each electrode-electrolyte interface of the supercapacitor cell. The equivalent capacitance (C) of these two series connected capacitors is:

$$C = \frac{C_{+}C_{-}}{C_{+}+C_{-}}$$
(2.4)

In our present work, both electrodes are made from the same material and they have same dimensions. Hence we have what is called symmetric electrodes supercapacitor. Thus the equivalent capacitance is equal one half of one electrode capacitance



Figure 2.3: Schematic of voltage distribution inside EDLC and its simplified equiv- alent circuit.

$$C = \frac{C_+}{2} = \frac{C_-}{2} \tag{2.5}$$

27

The equivalent capacitance can be found experimentally using different electrochemical characterization methods. This includes cyclic voltammetry (CV), galvanostatic charge discharge (GCD), and electrochemical impedance spectroscopy (EIS).

#### 2.2 Electrochemical characterization

A two electrode Swagelok cell and PGZ402 potentiostat were used to study the electrochemical properties of AC/GNPs nanocomposite electrodes using  $1MH_2SO_4$ ,  $1MNa_2SO_4$  and 6MKOH electrolytes. The electrochemical methods (CV, GCD, and EIS) are used to evaluate the electrochemical performance of supercapacitors. The results obtained from these methods are used to calculate the specific capacitance (capacitance per unit mass,  $C_s$ in F/g), energy density (energy per unit mass,  $E_d$  in Wh/Kg), power density (power per unit mass,  $P_d$  in W/Kg) and the equivalent series resistance (ESR) [3, 8, 11, 18].

#### 2.2.1 Cyclic Voltammetry

CV is a screening technique used to identify materials. In this method, the potential (V) sweeps linearly between two specific values (voltage window) at a constant scan rate (s = dv/dt). The current response (I(t)) is recorded against the sweeping potential to produce cyclic voltammetry (CV) curve. In this work, the potential was allowed to sweep between the two values (0 -1 volts) at different scan rates. By analyzing the CV curve (Fig. 2.4),

the information of the supercapacitor such as voltage window, capacitance and cycle life can be obtained. Perfect rectangular curve indicates ideal capacitive behavior, semi-rectangular curve indicate a practical capacitive behavior, while the existence of peaks in the curve indicate the existence of pseudocapacitance [3, 8, 11, 18, 34].



Figure 2.4: Typical CV characteristics of an electrochemical EDLC (after [35]).

Equivalent capacitance, C, of EDLC cell can be found experimentally from CV graph using charge stored in the two electrodes according to:

$$C = \frac{q_a + |q_c|}{V} \tag{2.6}$$

Where  $q_a$  is the anode charge,  $|q_c|$  is the cathode charge and V is the CV voltage window (V).  $q_a$  and  $|q_c|$  are extracted from the area under current-time graph according to [11, 12, 23, 33].

$$\int q = \int I dt \tag{2.7}$$

The equivalent capacitance, C, is used to calculate the specific capacitance,  $C_s$ , of an electrode. It can be calculated by dividing the capacitance of one electrode ( $C_+$  or  $C_-$ ) on its active material mass, m (g), as follows:

$$C_s = \frac{C_+}{m} = \frac{2C}{m} \tag{2.8}$$

Once  $C_s$  is calculated, the energy density of the electrode can be calculated from equation 2.3.

#### 2.2.2 Galvanostatic Charging Discharging

GCD is another method to study the electrochemical performance of supercapacitor. A constant current is applied to the two electrodes terminals of the supercapacitor using the potentiostat and the response potential is measured as a function of time. For charging and discharging of a supercapacitor, different two values of constant current is applied and the resulting galvanostatic charge discharge curve is obtained as shown in figure 2.5.

The relation between discharge current, I, and the slope the linear part of discharging curve, dV/dt is investigated by [36, 37]:

$$I = \frac{dq}{dt} = \frac{dq}{dV}\frac{dV}{dt} = C\frac{dV}{dt}$$
(2.9)

Substituting C in term of  $C_s$  (from equation (2.8)) and rearrange, then  $C_s$  can be given as:



Figure 2.5: Galvanostatic charging discharging curve for resistive EDLC [36].

$$C_s = \frac{2I}{(\frac{dV}{dt})m}$$
(2.10)

The voltage drop ( $V_{drop}$ ) observed in figure 2.3 when switching current from charging current (+I) to discharging current (-I) is due to the equivalent series resistance (ESR) of the EDLC. Hence ESR can be found from  $V_{drop}$  using ohms law according to:

$$ESR = \frac{V_{drop}}{2I} \tag{2.11}$$

In addition, from GCD method (Fig. 2.5), energy density,  $E_d$  (in Wh/kg), and power density,  $P_d$  (in W/kg), can be calculated using the equations [10, 38]:

$$E_d = \frac{C_s dV^2}{2 \times 3.6} \tag{2.12}$$

and

$$P_d = \frac{E_d \times 3600}{dt} \tag{2.13}$$

where  $C_s$  is the specific capacitance of one electrode, dV (in V) is the discharge voltage change (excluding  $V_{drop}$ ) and dt (in sec) is the discharge time.

Ragone plot, which represents the energy-power relationship, can be found by plotting the energy density,  $E_d$ , versus the power density,  $P_d$ . Ragone plot is a method to determine the position of a specific energy source device among other energy sources.

#### 2.2.3 Electronic Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is an important tool to investigate the behavior of supercapacitor under frequency range and to find its ESR. EIS measurement is done by applying a small-amplitude AC signal over a wide range of frequency. The potential V, with amplitude  $V_0$ and radial frequency ( $\omega = 2\pi f$ ), changes with time according to:

$$V = V_0 sin(\omega t) = V_0 e^{j\omega t}$$
(2.14)

Since supercapacitor equivalent circuit contains both resistance and capacitance (Fig. 2.3), the current *I* of the input signal will have a phase shift ( $\phi$ ) and is given by:

$$I = I_0 sin(\omega t + \phi) = I_0 e^{j\omega t - \phi}$$
(2.15)

Where  $I_0$  is the amplitude of the signal.

The total impedance Z of the supercapacitor is then can be given by:

$$Z = \frac{V}{I} = \frac{V_0 e^{j\omega t}}{I_0 e^{j\omega t - \phi}} = Z_0(\cos\phi + j\sin\phi) = Z' + jZ''$$
(2.16)

where Z' and Z'' represent the real part and imaginary part of the impedance, respectively [8, 39].

When the imaginary part of the impedance (Z'') is plotted against the real part of the impedance (Z'), for the all applied frequency range, a plot called "Nyquist plot" obtained.

Nyquist plot (Fig. 2.6), also called impedance plot, study the behavior of supercapacitor with varying frequency, f. It is divided into three regions according to the frequency range; high frequency, low frequency and Warburg regions [40, 41]. At high frequency, the capacitive reactance  $(1/\omega C)$  is very small and hence the supercapacitor have a resistive behavior in this region. In this region, x-axis intercept,  $R_s$ , represents the current collector resistance, electrode resistance and the ionic electrolyte resistance. In the addition, the semicircle observed at high frequency represents the charge transfer resistance,  $R_{CT}$ , which is the resistance between electrolyte/electrode surface. At low frequency region, the capacitive reactance of the supercapacitor is very high (almost vertical line is observed)

and hence the imaginary part of the impedance (Z'') highly increase compared to impedance real part (Z'). This reveals the dominant capacitive behavior of the supercapacitor in this range of frequency. The transition region between high frequency and low frequency regions (Warburg region), which is the straight line observed at 45°, represent the ion diffusion resistance,  $R_W$ . The frequency associated with 45° point is called the knee frequency ( $f_0$ ) at which the supercapacitor turns from resistive behavior at high frequency region to capacitive behavior at low frequency region.

The specific capacitance  $(C_s)$  of one electrode (of mass m) can be calculated from Nyquist plot at very low frequency by using Z'' in the following equation [22, 42]:

$$C_s = 4(\frac{-1}{2\pi f z'' m})$$
 (2.17)

 $R_s$  and  $R_{CT}$  observed in Nyquist plot are used to find the ESR ( $\Omega$ ) according to [3, 11]:

$$ESR = R_s + R_{ct} \tag{2.18}$$



Figure 2.6: Schematic for Nyquist plot for practical EDLC.

Other property which is very important in supercapacitors is the time constant ( $\tau$ ). It demonstrate the charging response of the supercapacitor; small  $\tau$  signifies fast response.  $\tau$  depends on resistance and capacitance of the supercapacitor, and can be calculated using two ways as shown in the following equation [3, 11, 22, 33]:

$$\tau = RC = (ESR)C \tag{2.19}$$

where

$$C_{s} = 4\left(\frac{-1}{2\pi f z'' m}\right)$$

is the capacitance of the supercapacitor.

The time needed for transition of supercapacitor from resistive to capacitive behavior is called relaxation time which is equal to [2]:

$$\tau_0 = \frac{1}{f_0}$$

where  $f_0$  is knee frequency.

#### 2.3 Porosity of materials

Porosity is one of the major factors that affects the solids physical interactions and chemical reactivity of material with liquids and gases. Porous materials is extensively used in many industrial application that include active components in supercapacitors, batteries and fuel cells electrodes, membranes, catalysts, construction materials, pharmaceutical products, ceramics, pigments, sensors, and etc. According to pore size distributed into porous materials, the International Union of Pure and Applied Chemistry (IUPAC) define pore size into three types, macropores (50 nm and above), mesopores (between 2 and 50 nm) and micropores (less than 2 nm). For porous electrodes used in supercapacitor manufacturing, the specific surface area (SSA) of the pores, total pore volume and pore size distribution (PSD) are studied by gas adsorption/desorption using different techniques. These techniques includes Brunauer-Emmett-Teller (BET) to study the SSA and Brunauer-Joyner-Halenda (BJH) method to investigate PSD. BET and BJH methods are based on isothermal multilayer adsorption/desorption of nitrogen  $(N_2)$  gas. In these methods, the amount of adsorbed and extracted  $N_2$  gas at different relative pressure is measured at certain constant temperature  $(77^{\circ}K)$  [3, 8, 11, 18, 43, 44]. The plot between adsorbed/desorbed gas quantity against relative pressure (adsorption isotherm) differ from a material to another, because the plot type depends on the

(2.20)

porosity type and its distribution within material. According to IUPAC, adsorption isotherms are categorized into six types (Fig. 2.7) [43]. Type I reversible isotherm is usually obtained for microporous materials with almost no external surface area. Very high adsorption is observed at very low  $P/P_0$  (<0.01) before reaching a plateau. Sorption isotherms of type II are obtained for macroporous or nonporous materials. Point B observed in type II is called the inflection point or the isotherm knee, which indicate the beginning of multilayer adsorption after the monolayer is completed. Isotherms of type III are not common, the isotherm is convex to the relative pressure ( $P/P_0$ ) indicating a relatively weak attractive interactions between the adsorbate and the adsorbent.

Mesoporous materials are characterized by type IV isotherms. The hysteresis loop occurs in this isotherm is due to capillary condensation and evaporation that takes place within the mesopores. At high range of  $P/P_0$ , the plateau observed in the isotherm indicates a complete filling of the pores and hence the adsorbate uptake is limited. In type IV isotherms, depending on mesopore shape, mesopores hysteresis loop may have four types (H1-H4) as shown in figure 2.8. Tubular or cylindrical mesopores are characterized by H1 hysteresis loop. H2 isotherms is for interconnected complex pore structure with narrow pore openings. Platy particles materials with slit-shaped pores are characterized by H3 hysteresis loop. As seen in type II, an inflection point B is observed at the initial part of type IV, which is attributed to monolayer-multilayer adsorption. In type V

isotherms, hysteresis due to condensation is shown. However, the beginning of this isotherm is convex to  $P/P_0$  similar to that in type III isotherm, which indicate a relatively weak adsorbent- adsorbate attractive interactions. Type VI isotherm represents multilayer adsorption occurs in steps on a uniform, non-porous surface.



Figure 2.7: Sorption isotherms according to IUPAC classification [43].

### 2.3.1 Specific Surface Area (SSA)

The specific surface area (SSA) of a solid porous material is the total area contributed by all open pores. Specific surface area is determined from Brunauer-Emmett.



Figure 2.8: Hysteresis loops characteristics according to IUPAC [43].

Teller (BET) analysis that is based on the amount of adsorption/desorption of N<sub>2</sub> gas molecules. The relation between the relative pressure,  $P/P_0$ , and the amount of adsorbed  $N_2$  gas,  $Q(\frac{P_0}{p} - 1)$ , is represented by the BET equation [8, 43, 44]:

$$\frac{1}{Q(\frac{P_0}{P}-1)} = \frac{1}{Q_m c} + \frac{C-1}{Q_m c} \left(\frac{P}{P_0}\right)$$
(2.21)

where C is BET constant,  $Q_m$  is the adsorbed monolayer of  $N_2$ , P is the pressure and  $P_0$  is the saturation presure.

Plotting  $\frac{1}{Q(\frac{P_0}{P}-1)}$  versus P/P<sub>0</sub>, observed in BET equation (2.21), gives a straight line with slope  $s = \frac{C-1}{Q_m C}$  and intercept line  $i = \frac{1}{Q_m C}$  as shown in figure 2.9. Using *s* and *i*, the quantity of absorbed  $N_2$  monolayer ( $Q_m$ ) can be calculated according to:

$$Q_m = \frac{1}{s+i} \tag{2.22}$$

and the total surface area  $(S_t)$  then can be obtained using:

$$S_t = \frac{Q_m N A_{cs}}{V} \tag{2.23}$$

Where  $A_{cs}$  is the cross sectional area of  $N_2$  molecule (0.162  $nm^2$ ), N is avgadro's number (6.023 \* 10<sup>23</sup>) and V is molar volume (22411  $cm^3/mole$ ) of  $N_2$  gas at STP.



Figure 2.9: Schematic of BET plot.

The specific surface area SSA  $(m^2/g)$  can then be obtained by:

$$SSA = \frac{S_t}{m} \tag{2.24}$$

where m is the total mass of the solid porous material.

## 2.3.2 Pore Size Distribution (PSD)

BJH method is used to determine the total pore volume ( $V_{tot}$ ) of mesopores and macropores in addition to their surface areas. However, micropores are undistinguishable by this method. To investigate micropores, mesopores and material external area, Harkins-Jura isotherm model plot (t-plot method) is usually used [23, 45]. In BJH method, the gas is allowed to condense into liquid (capillary condensation) inside the pores at relative pressure less than saturation pressure. Pores surface area, volume and their distribution can be found with the help of Kelvin equation (2.25), which explain the desorption branch equilibrium phase transition [3, 11, 18,43].

$$\ln(\frac{P}{P_0}) = -\frac{2}{r_k} \frac{\gamma \overline{V}}{RT}$$
(2.25)

where  $\gamma$  is the surface tension, *V* is the molar volume of liquid, *R* is the universal gas constant, *T* is the temperature in *K*, and  $r_k$  is the Kelvin radius pore radius. For  $N_2$  adsorption at 77.35 *K*,  $\gamma = 8.85$  *dyne/cm*, V = 34.71  $cm^3/mol$  and R = 8.314107 *dyne.cm/K.mol*. Substitute these values in equation (2.25) and rearrange you get the Kelvin radius:

$$r_k = -\frac{0.955339}{\ln(\frac{P}{P_0})} \ [nm] \tag{2.26}$$

The pore radius  $(r_p)$  and pore diameter  $(d_p)$  then can be calculated to be equal to:

$$d_p = 2r_p \tag{2.27}$$

$$r_p = r_k + t \tag{2.28}$$

where *t* is the thickness of the adsorbed gas layer at corresponding  $P/P_0$ . t value (in angstrom Å) can be calculated from Hasley equation (2.29) (used in our calculations for PSD) [46]:

$$t = 3.54 \left(\frac{-5}{\ln\frac{P}{P_0}}\right)^{1/3} \tag{2.29}$$

Assuming pores of cylindrical shape for mesopores and macropores, then

$$\frac{V}{S} = \frac{\pi r_p^2 h}{2\pi r_p h} = \frac{r}{2}$$
(2.30)

Where *V* is pore volume, *S* is the pore surface area, *h* is the pore depth and *r* is the pore radius  $r_p = \frac{d_p}{2}$ . So, the average pore diameter is related to *V* and *S* by:

$$d_p = 2r_p = \frac{4V}{S} \tag{2.31}$$

Hence the incremental gas volume  $\Delta V$  (absorbed quantity by pores volume) for each increment in relative pressure  $P/P_0$  is related to the incremental surface area  $\Delta S$  by

$$d_p = 2r_p = \frac{4\Delta V}{\Delta S} \tag{2.32}$$

Then the cumulative pore volume and cumulative pore surface area can be calculated by addition of all incremental values of pore volume and pore surface area.

## 2.3.3 t-plot method

BJH method is valid only for mesopores and macropores. However, for micropores, t-plot method is usually used. t-plot [47] is a technique to approximate the specific micropore volume and the open specific surface area (mesopores ( $S_{meso}$ ) and external specific surface area ( $S_{ext}$ )). In this method, the  $N_2$  adsorbed quantity ( $V_{ads}$  in  $cm^3/g$  STP) is plotted against the statistical

thickness (t) of adsorbate  $N_2$  layer at corresponding  $P/P_0$ . The equations that is used in this thesis to calculate the t values in angstrom (Å) for  $N_2$  adsorbate is Harkins and Jura equation:

$$t = \left(\frac{13.99}{0.034 - \log\frac{P}{P_0}}\right)^{0.5} \tag{2.33}$$

Figure 2.10 shows t-plot ideal examples of for different porosity materials referring to nonporous material.  $V_{ads}$  vs. t-plot of nonporous solid gives up a straight line that passes very close or through the origin. Vertical deviation of isotherm from straight line indicates capillary condensation in mesopores. While horizontal deviation is due to microporous solid. Extrapolation of the linear region to the  $V_{ads}$  axis gives the specific micropore volume ( $V_{mic}$ ) and the slope of the linear fit gives the open specific surface area ( $S_{open} = S_{meso+ext}$ ) [48].



**Figure 2.10:** t-Plots of nonporous, mesoporous, microporous and micro- and meso- porous solids [after 49].

#### 2.3.4 Specific pore volume and area

The total specific pore volume  $(V_{tot} \text{ in } cm^3/g)$  for all pore types exist into the solid material can be determined by the number of adsorbed  $N_2$  liquid volume adsorbed at maximum relative pressure  $(P/P_0 \approx 0.99)$  of adsorption/desorption isotherm. In isotherms, the quantity absorbed is usually given by the quantity of  $N_2$  gas absorbed at standard temperature pressure (STP). In order to convert the gas volume to liquid volume, the quantity of adsorbed gas needs to be multiplied by a factor 0.001547, which is the ration between  $N_2$  gas density at STP (0.00125 g/cm<sup>3</sup>) to  $N_2$  liquid density at 77K (0.808 g/cm<sup>3</sup>) [50, 51].

The total  $N_2$  liquid adsorbed represents the liquid absorbed by all types of pores exist into the solid. Hence the total specific volume ( $V_{tot}$ ) will be equal to:

$$V_{tot} = V_{mic} + V_{mes} + V_{mac} \tag{2.34}$$

For solid material containing micropores and mesopores, t-plot, in the relative pressure range  $0.009 < P/P_0 < 0.8$ , is considered be good method to determine the specific volume of micropores ( $V_{mic}$ ) and mesopores ( $V_{mes}$ ). In addition, the specific surface area of mesopores ( $S_{mes}$ ) and external specific surface area ( $S_{ext}$ ) can be demonstrated. Figure 2.11 illustrates the t-plot as a function of absorbed quantity of  $N_2$  gas volume at STP for solid material containing micropores and mesopores [48].



Figure 2.11: t-plot of materials with different micropore-mesopore ratio [after 48].

As shown in the figure (Fig. 2.11), the intercept of the first linear fit (done at t for low  $P/P_0$ ) represents the micropore specific volume ( $V_{mic}$ ), and its slope corresponds to the open specific surface area ( $S_{mes+ext}$ ). On the other hand, the slope of the second linear fit (done at t corresponds to high  $P/P_0$ ) represents the external specific surface area ( $S_{ext}$ ). The mesopore specific volume ( $V_{mes}$ ) is obtained when the t-plot points just start to be lower than the second fit.

Hence from SBET and t-plot method, the specific surface area of each pores types into solid material can be determined from:

$$S_{BET} = S_{mic} + S_{mes} + S_{ext}$$
(2.35)

then micropores specific surface area  $(S_{mic})$  will be equal to:

$$S_{mic} = S_{BET} - S_{mes+ext} \tag{2.36}$$

and

$$S_{mes} = S_{mes+ext} - S_{ext} \tag{2.37}$$

Alternatively, specific volume and area for all pore types of are related to each other by relation [52, 53]:

$$V = St \tag{2.38}$$

# Chapter Three Experimental Work

In this research, supercapacitor electrode using activated carbon and graphene nanoplates (AC/GNPs) composite had been prepared to be investigated in a two terminal Swagelok cell. The effect of electrolyte solution ( $H_2SO_4$ ,  $Na_2SO_4$  and KOH) on the electrode electrochemical properties have been studied to optimize the electrolyte solution that gives the highest specific capacitance, power density, energy density and cycling stability. For this purpose, different electrochemical methods were applied using a universal potentiostate/galvanostate. In addition, surface and internal morphological and structural properties have been performed using Scanning Electronic Microscopy (SEM). Moreover, porosity analysis of the electrode material have been studied by adsorption/desorption of  $N_2$  gas. In order to make this study, many materials, equipments and experimental procedures had been performed to facilitate research on this subject.

#### 3.1 Materials

The Materials that been used in this research are:

- 1. Locally self-backed de-ionized water  $H_2O$ .
- 2. Locally self-backed Acetone  $C_3H_6O$ .
- Commercial Active Carbon AC (purchased from Donau Carbon supplied by Quimics Dalmau (reference Carbopal CCP80).
- 4. Commercial Graphene Nanoplates GNP<sub>s</sub> (from Grupo Antolin).

- 5. Glass fiber separator *M* 5*V* 5 (from Alter-Lab).
- 6. Sulfuric acid  $H_2SO_4$  (98 % from Merck).
- 7. Locally self-backed sodium sulfate  $Na_2SO_4$ .
- 8. Potassium hydroxide *KOH* (from Frutarom).

#### **3.2 Equipments and devices**

The first part of the practical work in this thesis was preparing the supercapacitor electrodes, electrolytes and study the electrochemical properties of the electrodes under different electrolyte solutions. This was done at Advanced Material Science Laboratory in Physics Department and Heavy Instrumental Laboratory in Chemistry Department at An-Najah National University. The second part of experimental work is performing the surface morphology, inner morphology and structure and porosity of the electrodes. This part was done at Barcelona University laboratories.

Equipments and devices used at An-Najah National University laboratories are listed below and shown in figure 3.1:

- 1. PGZ402 Potentiostat (figure 3.1.(a))
- 2. Swagelok cell (figure 3.1.(b))
- 3. Magnetic stirrer (figure 3.1.(c))
- 4. Electronic balance (figure 3.1.(d))
- 5. Agate mortat (figure 3.1.(e))

- 6. Ultrasonic path (figure 3.1.(f))
- 7. Oven (figure 3.1.(g))
- 8. Hydraulic press (figure 3.1.(h))



**Figure 3.1**: Equipments used at An-Najah National University: a) PGZ402 Poten- tiostat, b) Swagelok cell, c) Magnetic stirrer, d) Electronic balance, e) Agate mortar, f) Ultrasonic path, g) Oven and h) Hydraulic press.

Equipments and devices used at Barcelona University laboratories are listed below and shown in figure 3.2:

- 1. Scanning Electronic Microscope (SEM, Jeol J-7100), (figure 3.2.(a)).
- Brunauer-Emmett-Teller analyzer (BET, TriStar 3000 V6.04A), (figure 3.2.(b)).



**Figure 3.2:** Equipments used at Barcelona University: a) Jeol J-7100 SEM and b) TriStar 3000 BET.

## **3.3 Preparation of electrodes pallets**

AC/GNPs composite electrode pellets to be used in two terminal Swagelok supercapacitor cell. They were prepared following the steps below:

- 1. Milling of AC (60 wt%) and GNPs (40 wt%) using agate mortar.
- 2. Mixing AC/GNPs with 10 ml acetone in a beaker using magnetic stirrer to make a slurry.
- 3. The slurry was agitated ultrasonically into the ultrasonic bath for 20 minutes at 35°C.

- 4. The slurry was dried in an oven for 90 minutes at  $70^{\circ}$  C.
- 5. The dried slurry was milled again using agate mortar to make a powder.
- 6. The powder was used to make circular electrode disks (pellets shown in Fig. 3.3) using a mold and a hydraulically pressed at 6 tons.
- 7. The mass of each electrode was weighted by electronic balance.
- 8. The calculated mass of the electrodes ranged between 0.06 and 0.07 g with 13 mm diameter (area of about 13.3  $cm^2$ )



Figure 3.3: Electrodes pellets (disks)

#### **3.4** Preparation of electrolyte solutions

Three electrolyte materials ( $H_2SO_4$ ,  $Na_2SO_4$  and KOH) were used to make  $1MH_2SO_4$ ,  $1MNa_2SO_4$  and 6MKOH aqueous electrolytes. These electrolytes are used to examine supercapacitor different electrochemical properties. To make 100 ml solution of each material, 10.66 ml of liquid  $H_2SO_4$ , 14.204 g of solid  $Na_2SO_4$  and 33.66 g of solid KOH were dissolved into 100 ml distilled water. The mixture then was put in the magnetic stirrer for 30 minutes at room temperature.

#### **3.5 Electrochemical methods**

Electrochemical properties of AC/CNFs composite electrode have been performed using different electrochemical methods (CV, GCD and EIS). The three different electrolyte solutions supercapacitors are firstly assembled in the Swagelok as follows:

- 1. A disk of glass fiber separator was cut as shown in figure 3.4.
- 2. The glass fiber separator is immersed into the selected electrolyte solution for 5 minutes.
- 3. The glass fiber soaked with electrolyte solution was sandwiched between the electrodes as shown in figure 3.5.
- 4. The Swagelok cell is closed tightly to prevent the existence of any space between electrodes and any movement of the electrodes and separator.



Figure 3.4: Glass fiber separator



Figure 3.5: Assembling electrodes disks and the glass fiber separator into the Swagelok cell.

After assembling the Swagelok cell, it was connected and tested using the PGZ 402 potentiostat. The Swagelok cell was connected to the potentiostat using two terminal mode as shown in figure 3.6. Work and sense leads of the potentiostat were connected together to one terminal (Anode) of Swagelok cell, while auxiliary and reference leads were connected the other terminal (cathode) of the cell. The data were collected using the potentiostat software (VoltaMaster 4 program). The electrochemical experiments performed are:

- Cyclic Voltammetry (CV) method was done using a potential linearly changes from 0 to 1 V at different scan rates (5, 10, 20, 50, 80 and 100 mV/s). 100 CV cycles were performed for the three supercapacitor cells of different electrolyte solution.
- 2. Galvanostatic Charge Discharge (GCD) method was done at different current values (50, 80, 100, 120, 150 and 200 mA). Each current value alters between positive and negative for respectively charging and discharging the supercapacitor. The response voltage during charging and discharging was allowed to vary between 0 and 1 V. For each cell of different electrolyte, few cycles of charging-discharging was performed in order to study the electrochemical properties deduced from GCD method.
- 3. Electrochemical Impedance Spectroscopy (EIS) technique was used to study the impedance of the supercapacitor cell under applied AC signal of different input frequency. For each cell of different electrolyte, 20 mV amplitude AC sine wave was applied to the cell with frequency ranges from 100 kHz to 10 mHz.
- 4. Cyclic stability was tested for 100 cycles by CV method and 1000 cycles by GCD for all prepared supercapacitor cells with different electrolytes, in order to test the cyclic stability and reversibility of each cell.
- 5. Finally, the collected data by all methods were analyzed using OriginPro8.5 program.



Figure 3.6: Swagelok connected to computerized PGZ 402 potentiostat.

#### **3.6 Electrode Surface Morphology**

The surface morphology of AC/GNPs electrodes in this research were studied by SEM. Electron backscatter diffraction is usually used in SEM study crystal structure and specific morphology of solid materials. This is done by firing a beam of accelerated electrons to the sample to get an interference pattern. Surface shape and properties are studied using scanning electronic microscopy (Fig. 3.2.(a)). SEM image is done by scanning the sample with the excited electron beam. Electron beam size is controlled by an aperture to fit the sample surface. The electron beam interact with surface atoms of the sample emitting a secondary electrons from the surface. These electrons are detected and studied to give information about surface characteristics and electrical conductivity of the material[11].

#### **3.7** Porosity measurements

Porosity of AC/GNPs composite electrode was studied by  $N_2$  gas adsorption/desorption at liquid nitrogen boiling temperature (77.3 K).  $N_2$  is used because it has a very well-known molecular size. Hence, the surface area and volume of pores is calculated easily. Also, nitrogen is inert gas and hence does not react with the material surface during measurements. Porosity measurements was conducted using BET analyzer (TriStar 3000 V6.04A) shown in figure 3.2.(b). The quantity of absorbed  $N_2$  gas at STP is measured as a function of relative applied pressure ( $P/P_0$ ). The relative pressure in this method varies from 0 to  $\approx 0.999$  which allow to have all pores into the material to be almost completely filled with condensed liquid  $N_2$ . collected data are analyzed by Brunauer-Emmett-Teller (BET) method in order to determine the total specific surface area ( $S_{BET}$ ). Pore size distribution, pores specific volumes and pores specific areas are determined using Brunauer-Joyner-Halenda (BJH) and Harkins-Jura (HJ).

# **Chapter Four**

# **Results and Discussion**

For the AC/GNFs composite supercapacitor electrode, different experiments have been performed in order to investigate different properties of this electrode under different electrolyte solutions ( $H_2SO_4$ ,  $Na_2SO_4$  and KOH). These experiments includes electrochemical methods (CV, GCD, and EIS) to investigate electrochemical properties, SEM to study surface and internal morphology and structure, and finally porosity study to study physical interactions of the material.

### 4.1 Electrochemical Characterization

The electrochemical properties of  $AC/GNP_s$  supercapacitor electrodes were studied using two electrode Swagelok cell and PGZ 402 potentiostat. Various electrolytes ( $H_2SO_4$ ,  $Na_2SO_4$  and KOH) were used to test the supercapacitor. To examine the supercapacitor performance, the specific capacitance were calculated by CV, GCD and EIS methods. Note that the working principle of each method is different from another.

### 4.1.1 Cyclic Voltammetry (CV)

The cyclic voltammetry analysis is done using a potential range (0 - 1V) and a potential scan rate ranges (5 - 100mV/s). Each supercapacitor electrode is studied using different electrolytes with a composite of 60wt.% of AC and 40wt.% of GNPs. The CV results for each electrolyte and a comparison between them are shown below in figure 4.1.(a-d). At low scan

rates (5-20 mV/s) we have semi-rectangular shape of CV curves. This is an indication of electric double layer capacitor type, and hence high capacitive characteristics of the supercapacitor with fast current response to the potential change [54, 55]. On the other hand, a distortion from rectangular shape was observed at higher scan rates (50-100 mV/s). At higher scan rate, the current density increase due to an increase in the mobility of ions and hence the ions accumulates at the pore surface into the diffusion layer which cause a difficulty for ions to enter deeply in the vacant pores or it may even not enter the pores (specially small size pores). This will decrease the area exposed to ions and consequently, decrease the specific capacitance of the supercapacitor electrode [56-58].

Figure 4.1.(d) shows a comparison between three samples at scan rate = 100 mV/s. Higher area inside the CV curve was observed for electrodes with  $H_2SO_4$  electrolyte, indicating higher stored charges and hence, higher specific capacitance ( $C_s$ ). The specific capacitance was calculated for each sample at different scan rates using equations 2.6 to 2.8 and tabulated in table 4.1 and drawn in figure 4.2.  $C_s$  were found to have highest values, at all scan rates, for sample examined using  $H_2SO_4$  electrolyte, with highest specific capacitance (320.3 F/g) at scan rate 5 mV/s. Less  $C_s$  values were observed for  $Na_2SO_4$  electrolyte, and the least values of  $C_s$  were observed for samples when using *KOH* electrolyte. This evolution of specific capacitance is due to the variation of ionic radius for ions ( $H^+$ ,  $K^+$ ,  $Na^+$ ,  $OH^-$  and  $SO_4^{-2}$ ), see table 4.2. As the ionic radius of the ion decrease, it will go deeply within the pores of the electrodes. This will increase the specific

surface area and hence increase the specific capacitance,  $C_s$ . On the other hand, decreasing the mass of ion will increase the mobility of ions and hence higher current density at given potential (see figure 4.1.(d)) and consequently higher charge density will be stored leading to higher  $C_s$ . The tendency of specific capacitance with electrolyte type is in full agreement with this discussion. The  $H^+$  ion is smaller and lighter than other ions. Hence, the specific capacitance for  $H_2SO_4$  is the highest and lowest for *KOH* because K+ is the heaviest ion. Also, figure (4.2) shows that the specific capacitance decrease with increasing the scan rate. This occurred because the ions have enough time to occupy and diffuse into vacant pores. Thus higher specific surface area is contributed to the capacitance, and hence Cs increased [8, 11, ,23, 59].



**Figure 4.1:** Cyclic voltammetry curves for  $AC/GNP_s$  supercapacitor using: (a)  $H_2SO_4$ , (b)  $Na_2SO_4$ , (c) *KOH* electrolytes and (d) comparison at scan rate = 100 mV/s.
Scan rate (mV/s)	Cs (F/gm)		
	$H_2SO_4$	$Na_2SO_4$	КОН
5	320.3	124.3	128.8
10	243.7	117.5	104
20	201.7	105.8	78.2
50	146.45	79.9	47.4
80	116.7	63	34.9
100	103.713	55.5	30.1

 Table 4.2: Ions radii for all used electrolytes.

ion	Radius (Å)	Reference
$H^+$	0.38	[59]
$Na_2^+$	1.02	[59]
<i>K</i> <sup>+</sup>	1.38	[59]
$OH^-$	1.41	[60]
$SO_4^-$	2.30	[60]



Figure 4.2: Specific capacitance vs. scan rate for three samples.

Obtained CV results showed an improvement of the specific capacitance for AC/GNPs composite supercapacitor electrode compared with GNPs alone (examined separately by CV method in this thesis using KOH electrolyte and shown in figure 4.3.(b)). AC/GNPs composite electrode using KOH electrolyte have a specific capacitance  $C_s = 128.8$  F/g at scan rate 5 mV/s, while for GNPs electrode alone the specific capacitance was found to be 32.5 F/g at the same scan rate. Comparing with AC supercapacitor electrode [34],  $C_s$  for AC (334 F/g using 6MKOH electrolyte scanned at 5 mV/s) was found to have higher value than AC/GNPs electrode. This could be explained by higher specific surface area for AC and higher molar concentration of the electrolyte ions. On the other hand, the shape of CV curves for AC/GNPs composite electrodes is more rectangular than AC supercapacitor alone (figure 4.3.(a)). This indicated that AC/GNPs supercapacitor has faster current response than AC supercapacitor and hence better capacitive characteristics of the EDLC supercapacitor [11, 14, 61].



Figure 4.3: Cyclic voltammetry using KOH electrolyte for: (a) AC [34] and (b) GNPs.

Finally, the cyclic stability for AC/GNPs composite electrode was tested for all used electrolytes due to its importance in practical applications. All samples have a very good cyclic stability, figure 4.4.(a-c) shows cyclic stability from first to 100th cycles for  $H_2SO_4$ ,  $Na_2SO_4$ , and *KOH* electrolytes, respectively. The 100th cycle for all electrolytes has the same shape of the first cycle, that indicates a high reversibility and very good stability for the three electrolytes [14].



**Figure 4.4:** Cyclic stability at scan rate =100 mV for  $AC/GNP_s$  supercapacitor for the first 100 cycle using: (a)  $H_2SO_4$ , (b)  $Na_2SO_4$  and (c) *KOH* electrolytes.

## **4.1.2** Galvanostatic charge-discharge (GCD)

GCD analysis were done using a range of currents between 50 and 200 mA. Many important relations were studied from GCD curves. The specific capacitance were calculated for each value of the current density which represents the current per unit mass of electrode I (A/g). Figure 4.5.(a-c) shows the relation between the potential and the time required for charging and discharging processes for the three used electrolytes, and figure 4.5.(d) shows a comparative study between the three samples at current = 50 mA. The specific capacitance was calculated at each current density according to equation (2.10) and the results were tabulated in table 4.3 and drawn in figure 4.6.(a). As noticed in table 4.3 and figure 4.6.(a), the specific capacitance decreasing with increasing current density, and this is usually happened because of the limitation of ions diffusion inside electrodes pores due to increasing ions mobility at higher currents [3, 8, 11]. Also indicates that the capacitor with  $H_2SO_4$ 



**Figure 4.5:** Galvanostatic charge-discharge curves for  $AC/GNP_s$  supercapacitor us- ing: (a)  $H_2SO_4$ , (b)  $Na_2SO_4$ , (c) KOH electrolytes and (d) Comparison at current I = 50mA.

electrolyte has the highest specific capacitance at all current densities compared to those with  $Na_2SO_4$  and KOH electrolytes. The least specific capacitance at all discharge currents were observed for supercapacitor with KOH electrolyte. This result confirms the results observed for same samples when examined using CV measurements. As mentioned before, the highest specific capacitance is observed for ionic liquid with least ion radius and mass ( $H^+$  in this case). As ionic radius decreases, it penetrate the electrode pores deeply, and hence higher specific surface area is maintained and as ion mass decrease, higher current density is obtained at given potential [11, 23, 14, 59].

The voltage drop (Table 4.4 and Figure 4.6.(b)), that is due to potential loss through the equivalent series resistance (ESR) of the AC/GNPs composite electrode, was deduced for all electrodes at each current density from figure 4.5. An increasing voltage drop with increasing current density was observed for all electrodes with different electrolytes.

$H_2SO_4$		$Na_2SO_4$		KOH	
<i>I/m</i> (A/g)	Cs (F/g)	<i>I/m</i> (A/g)	Cs (F/g)	<i>I/m</i> (A/g)	Cs (F/g)
0.83	138.9	0.83	61.3	0.7	60.3
1.33	130.1	1.33	56.9	1.14	52.7
1.67	124.4	1.67	53.5	1.4	44.2
2	118.3	2	49.7	1.9	32.8
2.5	114.4	2.5	43.1	2.1	20.8
3.33	103.2	3.33	31.5	2.9	7.6

Table 4.3: Specific capacitance at each current density $(I/m)$ using GC	<b>D</b>
for different electrolytes.	



**Figure 4.6:** Variation of (a) specific capacitance and (b) voltage drop with current density for AC/GNPs electrodes for different electrolytes.

This is due to the increase in ions mobility and decrease in their conductivity though the electrolyte. Consequently, the specific capacitance decrease with increasing current density [8, 11, 22]. AC/GNPs electrode using  $H_2SO_4$  electrolyte gives lower voltage drop values for all current densities (table 4.4). In addition, higher symmetry charge discharge curve (Fig. 4.5.(a)) than other electrodes with other electrolytes. This indicate that this electrode have lowest ESR, highest conductivity and excellent electrochemical reversibility than other electrodes [14, 41].

ESR for all prepared electrodes was calculated from the slope of voltage drop versus current density graph (figure 4.6.(b)) according to equation (2.11) and their values are listed in table 4.5.

$H_2$	$SO_4$	Na <sub>2</sub>	$2SO_4$	КОН	
<i>I/m</i> (A/g)	$V_{drop}\left(\mathrm{V} ight)$	<i>l/m</i> (A/g)	$V_{drop}\left(\mathrm{V} ight)$	<i>I/m</i> (A/g)	$V_{drop}\left(\mathrm{V} ight)$
0.83	0.12	0.83	0.091	0.71	0.24
1.33	0.15	1.33	0.169	1.14	0.37
1.67	0.16	1.67	0.186	1.43	0.47
2	0.16	2	0.23	1.86	0.53
2.5	0.2	2.5	0.28	2.14	0.57
3.33	0.26	3.33	0.38	2.86	0.65

Table 4.4: Voltage drop at different current density (I/m) values for AC/GNPs electrodes using different electrolytes.

As expected, supercapacitor electrode examined using  $H_2SO_4$  electrolyte was found to has the lowest ESR compared with those of  $Na_2SO_4$  and KOH, that is because  $H^+$  ions have the highest conductivity into the  $H_2SO_4$  electrolyte than other ions in the other electrolytes [23].

 Table 4.5: ESR values for AC/GNPs electrodes tested by GCD method

 under dif- ferent electrolytes.

Sample	ESR (ohm)
$H_2SO_4$	0.449
$Na_2SO_4$	0.928
КОН	1.35

Energy density ( $E_d$ ) and power density ( $P_d$ ) of the prepared electrodes were calculated using equations 2.12 and 2.13, respectively, during discharging process of supercapacitor. Table 4.6 present the values of  $E_d$  and  $P_d$  at different discharge currents for  $H_2SO_4$ ,  $Na_2SO_4$  and KOH. To compare between different prepared supercapacitor electrodes, Ragone plot (relation between  $P_d$  and  $E_d$ ) for AC/GNPs composite electrode using the three different electrolytes is represented in figure 4.7. AC/GNPs composite electrode using  $H_2SO_4$  electrolyte was found to have highest power and energy densities. It has power density increasing from 1024.5 to 4177.8 [W/Kg] with decreasing energy density from 14.82 to 7.8 [Wh/Kg].

This was expected because sample with  $H_2SO_4$  electrolyte have highest specific capacitance and lowest ESR value. On the other hand, since sample with KOH electrolyte have lowest specific capacitance and highest ESR, it was found to have lowest value of power and energy densities. Also, the observed increasing in energy density with decreasing power density is normal behavior because decreasing the power density increase the time needed to deliver the energy density stored into the device [8, 9, 18, 23].

Table 4.6: Power and Energy densities for AC/GNPs electrodes using  $H_2SO_4$  elec- trolyte.

Current (A)	<u>H</u> <sub>2</sub>	<u>SO4</u>	<u> </u>	$Va_2SO_4$	<u>K</u> <u>H</u>	<u>0</u> <u>1</u>
	E <sub>d</sub> (Wh/Kg)	$P_d$ (W/Kg)	E <sub>d</sub> (Wh/Kg)	$\begin{array}{c} P_d \\ (W/Kg) \end{array}$	$E_d$ (Wh/Kg)	$P_d$ (W/Kg)
0.05	14.82	1024.5	7.03	899.38	4.88	714.24
0.08	13.1	1589.1	5.72	1484.3	2.9	1147.6
0.1	12.3	2060.8	4.95	1936.9	1.76	1174.9
0.12	11.5	2514.3	4.13	2313.4	1.01	1630.49
0.15	10.1	3161.3	3.09	2931.7	0.54	1779.17
0.2	7.8	4177.8	1.73	3461.8	0.132	1993.14

Finally, the cyclic satiability (1000 cycle plotted in figure 4.8) was performed for all prepared electrodes using GCD method at current value = 100 mA. As shown in figure 4.8, for the first 200 cycles,  $C_s$  decreases to 95%, 98% and 83% for supercapacitor electrodes with  $H_2SO_4$ ,  $Na_2SO_4$  and KOH, respectively. In the range above 200 cycle, all the electrodes show a high stability with cycle number. This high stability indicates that these electrodes are suitable to be used as supercapacitors with long cycling life.



Figure 4.7: Energy density and power density relation for the three samples.



**Figure 4.8:** Cyclic stability for AC/GNPs electrodes using different electrolytes at current = 100mA.

#### **4.1.3 Electrochemical Impedance Spectroscopy (EIS)**

Electrochemical impedance spectroscopy gives an important information about capacitive and resistive behavior of the supercapacitor. Nyquist plot schematic (figure 2.6) is obtained using electrochemical impedance spectroscopy, which study the relation between real and imaginary parts of the supercapacitor impedance at extended frequency range. At low frequency range the specific capacitance can be calculated from the imaginary part of the impedance using equation (2.17). At high frequency region, from semicircle intercept on the real part of the impedance, the solution resistance,  $R_s$ , charge transfer resistance,  $R_{ct}$  and hence the equivalent series resistance, ESR can be determined [3, 11, 24]. Figure 4.9 represent the Nyquist plot (at frequency range 10mHz - 100KHz) for AC/GNPs supercapacitor electrodes examined using  $H_2SO_4$ ,  $Na_2SO_4$  and KOH electrolytes. As expected, all samples show a decrease in imaginary part of impedance with increasing signal frequency. The calculated specific capacitance,  $C_s$ , for all samples in chosen frequency range is presented in figure 4.10. The figure shows that all samples exhibited capacitive behavior ( $C_s$  increase) at low frequency range (below 10 Hz). This can be explained by the frequency dispersion phenomena; the high frequency voltage signal is hard to penetrate inside the narrow pores while the low frequency signal can be easily penetrates in the electrode porous structure. Also, as shown in figure 4.9 in the low frequency range, samples examined using  $H_2SO_4$  electrolytes has specific capacitance, in the low frequency range, higher than those studied using  $Na_2SO_4$  and KOH. Again, this is due to lowest ionic radius for  $H^+$  ion in the  $H_2SO_4$  electrolyte [23,

59, 62]. The recorded specific capacitance at 10 mHz frequency for the three electrodes using different electrolytes are presented in table 4.7.

Semicircle observed in Nyquist plot, at high frequency range, was found to begin at lowest value of impedance real point and has lowest radius for supercapacitor with  $H_2SO_4$  electrolyte. This indicate that solution resistance  $R_s$  and charge transfer resistance  $R_{ct}$  for  $H_2SO_4$  are lowest than other two electrolytes. Hence it has highest conductivity and consequently lowest equivalent series resistance ESR.  $R_s$ ,  $R_{ct}$  and ESR for all investigated electrolytes are also in table 4.7 [11, 23, 24].



**Figure 4.9:** Nyquist plot from electrochemical impedance spectroscopy for  $H_2SO_4$ , *KOH* and  $Na_2SO_4$ .

Table 4.7: EIS method values of specific capacitance, equivalent series resistance, solution resistance and charge transfer resistance values for AC/GNPs composite electrodes using different electrolytes.

Sample	$C_s$ (F/g)	ESR (ohm)	Rs (ohm)	$R_{ct}$ (ohm)
$H_2SO_4$	387.5	0.31	0.303	0.008
$Na_2SO_4$	227.0	0.51	0.43	0.08
KOH	103.8	1.81	1.67	0.14



Figure 4.10: Specific capacitance relation with frequency for all used electrolytes.

The aqueous  $H_2SO_4$  electrolytes exhibit higher conductivity (table 4.8) than  $Na_2SO_4$  and KOH. This explains the lowest  $R_s$  for electrodes with  $H_2SO_4$  electrolyte. In addition, electrodes with  $H_2SO_4$  electrolyte has the highest ion conductivity (table 4.8) which leads to lowest  $R_{ct}$ . Combining these with the lowest hydrated  $H^+$  ion size (table 4.9), the observed highest  $C_s$  and lowest ESR can be understood for AC/GNPs composite supercapacitor electrode [23, 59].

Table 4.8: Electrolytic conductivity of KOH,  $H_2SO_4$  and  $Na_2SO_4$  electrolytes.

Electrolyte solution	Conductivity (mS/cm)
Aqueous $H_2SO_4$	750
Aqueous $Na_2SO_4$	91.1
Aqueous KOH	220

According to these results,  $H_2SO_4$  is the most frequently used aqueous electrolyte in supercapacitors because of its high conductivity. The dependence of the ionic conductivity on the molar concentration of the electrolyte is another important parameter, the ionic conductivity can be quickly decreased when the concentration becomes extremely low or high. For high concentrations, supercapacitor will have low specific capacitance due to many reasons. Mainly the decrease in the hydration of the electrolyte solution and consequently decreasing the mobility of ions. Also,

 Table 4.9: Size of hydrated ions and their conductivity.

Ion	Size of hydrated ion (Å)	Ion conductivity (Scm <sup>2</sup> /mol)
$H^+$	2.8	350.1
Na <sup>+</sup>	3.58	50.11
<i>K</i> <sup>+</sup>	3.31	73.5
$SO_4^{-2}$	3.79	160
$OH^-$	3.0	198

the electrolyte material could be dissolved into distilled water to a certain amount, then the solution will be saturated and an excess amount of the material is not dissolved that will obstruct the dissolved ion path. So, molar concentrations have already been tested to give higher ionic conductivity of a given electrolyte. The greater number of research studies uses  $1MH_2SO_4$ solution, especially for carbon- based supercapacitors [11, 23, 59]. Comparing Nyquist plot for AC/GNPs composite supercapacitor electrode using *KOH* electrolyte with those for AC (previously reported in [14] and shown in figure 4.11.(a)) and GNPs (examined separately by EIS method in this thesis using 1*MKOH* electrolyte and shown in figure 4.11.(b)); in the high-frequency region, the ESR for AC and GNPs was found to be 3.72  $\Omega$ and 8.92  $\Omega$ , respectively. While for AC/GNPs composite electrode, the ESR was found to be 1.81  $\Omega$ .  $R_s$  and  $R_{ct}$  were also obtained from Nyquist plots (Fig. 4.11) for AC ( $R_s = 0.16 \Omega$  and  $R_{ct} = 3.56 \Omega$ ) and for GNPs ( $R_s$ =2.96  $\Omega$  and  $R_{ct} = 5.96 \Omega$ ). These resistances values are much lower than those for AC/GNPs ( $R_s = 1.67 \Omega$  and  $R_{ct} = 0.14 \Omega$ ). The calculated specific capacitance (by EIS method at f= 0.01 Hz) of AC/GNPs composite electrode, using *KOH* electrolyte, was equal to 103.8 F/g. It showed a high increase in value compared with GNPs (31.47 F/g), and lower value than AC alone (284 F/g using 6*MKOH*) [3, 14]. This result confirmed the result obtained in CV method.

The knee frequency  $f_0$  (table 4.10) represents the maximum frequency where the capacitive behavior is dominant in the supercapacitor. So, for  $f < f_0$  the supercapacitor behave as a pure capacitor, while for  $f > f_0$  the supercapacitor behave as a resistor. The knee frequency  $f_0$  was found for all AC/GNPs electrodes at a point where the imaginary part of the impedance rapidly increase (immediately



**Figure 4.11:** Nyquist plot from EIS method using KOH electrolyte for: (a) AC [after 34] and (b) GNPs.

after Warburg region) in the Nyquist plot (Fig. 4.9). The highest  $f_0$  (79 mHz) was found for electrode with *KOH* electrolyte followed by that with  $H_2SO_4$  electrolyte ( $f_0 = 56$  mHz), while the lowest ( $f_0 = 36$  mHz) is for electrode with  $Na_2SO_4$  electrolyte. The highest knee frequency is desirable for the supercapacitor because it indicates the high transfer rate from resistor to capacitor behavior. For practical applications,  $f_0$  sets the limit on the maximum operating frequency when ideal capacitance is required in supercapacitor applications [3, 8, 11].

Table 4.10: Knee frequency,  $f_0$ , of AC/GNPs composite electrodes using different electrolytes.

Sample	$f_0(\mathrm{mHz})$
$H_2SO_4$	56
$Na_2SO4$	36
KOH	79

The time constant  $\tau$  for each sample was obtained from equation (2.19) at lowest frequency value (0.01 Hz) and results are given in table 4.11. Supercapacitor with low time constant have a high response rate.  $H_2SO_4$  and  $Na_2SO_4$  samples with relatively small time constants comparing to KOH sample. This means that charging of AC/GNPs supercapacitor electrodes used with  $H_2SO_4$  and  $Na_2SO_4$  electrolytes will be about two times faster than those with KOH electrolytes. This could be explained by faster ion diffusion for  $H^+$  and  $Na^+$  into electrolytes due to their lighter ion mass than  $K^+$  ion. The relaxation time,  $\tau_0$ , which represent the transition of electrochemical capacitor from resistive to capacitive behavior, is calculated from knee frequency  $(\tau_0 = \frac{1}{f_0})$ , for the prepared electrodes using different electrolytes, and the results are presented in table 4.11. Lowest value of relaxation time was observed for KOH ( $\tau_0 = 12.7$  s) and the highest for  $Na_2SO_4$  ( $\tau_0 = 27.8$  s). Low values of  $\tau_0$  are desirable to have efficient power transfer in power application devices [3, 8, 11, 16]. This is because  $\tau_0$ represents the minimum time needed to discharge the stored energy to greater than 50% of its maximum value [63].

Table 4.11: Time constant,  $\tau$ , and relaxation time,  $\tau_0$ , for AC/GNPs composite electrodes using different electrolytes.

Sample	$\tau$ (s)	$\tau_0$ (s)
$H_2SO_4$	3.5	17.9
$Na_2SO4$	3.4	27.8
KOH	6.54	12.7

The relation between the real part of the impedance  $Z_r$  and the frequency (Fig. 4.12.(a)) for the prepared AC/GNPs electrodes gives us information about the sum of electrolyte resistance and charge transfer resistance (ESR). While the relation between the imaginary part of the impedance  $Z_i$  and the frequency (Fig. 4.12.(b)) gives us information about the boundary region at which the supercapacitor turn from resistor to capacitor [11]. As expected,  $Z_i$  value decrease and approaches zero with increasing frequency above  $f_0$ . In the same range of frequency ( $f > f_0$ ),  $Z_r$  dominate and becomes almost constant with increasing frequency. This reveals the resistive behavior of the supercapacitor above knee frequency,  $f_0$ . On the other hand,  $Z_i$  value highly increased below  $f_0$  indicating the capacitive behavior for the supercapacitor electrode.

In addition, the relation between the imaginary part of the capacitance with the frequency (figure 4.13) to obtain important parameters, such as the relaxation time. Imaginary part value of the capacitance (C'') can be found according to [10, 16]:



**Figure 4.12:** Relation between frequency and: (a) real part of impedance  $(Z_r)$  and (b) imaginary part of impedance  $(Z_i)$  for all samples.

$$C'' = \frac{z'}{2\pi f |Z|^2} \tag{4.1}$$

where |Z| is the magnitude of the total impedance for equivalent series RC circuit electrode and is given by:

$$|Z| = \sqrt{Z_r^2 + Z_i^2} \tag{4.2}$$

Figure 4.13 clearly indicate the capacitive behavior if the electrode below knee frequency.



Figure 4.13: Relation between imaginary part of the specific capacitance with fre- quency.

#### 4.2 Surface Morphology

Surface morphology of AC/GNPs electrodes were studied by Scanning Electron Microscope (SEM). Figures 4.14 present SEM images for  $AC/GNP_s$  composite electrode material. It shows that the electrode material surface had non-uniform and porous structure with particle size of various grain size. Two types of gains are observed in SEM micrographs correspond to GNPs sheets dispersed on AC particles [4, 11, 14].



**Figure 4.14:** SEM micrographs for AC/GNPs composite materials with different magnifications: (a) X400, (b) X900, (c) X3300 and (d) X8000.

# **4.3 Porosity measurements**

Different techniques were used to analyze and determine porosity of the AC/GNPs composite electrode material. The porosity of material includes measurement of specific surface area (SSA), pore size distribution (PSD) and total specific pore volume. porosity measurements was conducted by  $N_2$  adsorption/desorption isotherm using BET analyzer (TriStar 3000 V6.04 A) at relative pressure  $P/P_0$  of about 1.  $N_2$  adsorption/desorption isotherm for AC/GNPs composite electrode is presented by figure 4.15. As shown in figure, increasing the relative pressure increases the quantity absorbed of

the gas into pores until all pores of material are filled at a relative maximum pressure of 0.9934. The quantity absorbed, Q, (555.85  $cm^3/gSTP$ ) at this relative maximum pressure gives the total specific pore volume,  $V_{tot}$  (0.8600  $cm^3/g$  - presented in table 4.12) of the electrode material. The type of pores can be observed from the isotherm profile. Very high absorption is observed at very low relative pressure ( $P/P_0 < 0.01$ ) indicating the existence of micropores into the material. In addition, a hysteresis loop at high relative pressure ( $P/P_0 > 0.4$ ) due to capillary condensation within the mesopores. Analyzing the observed isotherm (Fig. 4.15) according to IUPAC classification (Fig. 2.7 and 2.8). It can be classified as type IV-H4 isotherm. This indicate that AC/GNPs composite material contains Slitshaped mesopores associated with micropores. Indeed, this type was expected because the composite contains both AC and GNPs [14, 64].



Figure 4.15: Adsorption desorption isotherm for AC/GNPs composite electrode supercapacitor.

#### 4.4 Total specific surface area $(S_{BET})$

Brunauer-Emmett-Teller (BET) analysis was used to investigate  $S_{BET}$ . AC/GNPs composite material isotherm (Fig. 4.15) was used in relative pressure the range of 0.004 to 0.150.  $S_{BET}$ , that is accessible for electrolyte ions, was extracted from the linear BET plot (Fig. 4.16) between  $\frac{1}{Q(\frac{P_0}{p}-1)}$ 

and  $P/P_0$  according to equation (2.21).

The results from BET plot and given data and are presented in table 4.12. High specific surface area (951.01  $m^2/g$ ), calculated using equations (2.22 - 2.24), was observed compared with low total specific pore volume (0.8600  $cm^3/g$ ). This high specific surface area allows this material to have high specific capacitance as observed when used with  $H_2SO_4$  electrolyte ( $C_s \approx$ 388.F/g using EIS method). This indicate that the material prepared (AC/GNPs composite) is highly porous and a promising candidate for supercapacitor applications.



Figure 4.16: BET plot for AC/GNPs composite electrode material.

Slope, $(g/cm^3 \text{ STP})$	intercept, $(g/cm^3 \text{ STP})$	$Q_m \qquad (g/cm^3 \ { m STP})$	Sample mass (g)	$\frac{SBET}{(m^2/g)}$	$V_{total}$ ( $cm^3/g$ )
0.004565	0.000013	218.4333	0.4382	951.01	0.8600

Table 4.12: Specific surface area and total volume using BET analysis.

The average pore diameter,  $\overline{d_p}$ , for AC/GNPs composite material, calculated from equation (2.31), was found to be equal to 36.4 Å.

## **4.5** Pore Size Distribution (PSD)

### 4.5.1 Brunauer-Joyner-Halenda (BJH) method

The first method to study the pore size distribution is the Brunauer-Joyner-Halenda (BJH) method. It is suitable to make analysis for mesopores and macropores in diameter range (17 - 3000 Å). From desorption isotherm, at each gas relative pressure ( $P/P_0$ ) value, the corresponding pore diameter is calculated through equations (2.26- 2.29). For each average pore diameter, the incremental values of pore volume are obtained from the difference in absorbed gas quantity between two successive  $P/P_0$  values, while the cumulative pore volume are obtained by addition of their incremental values. The corresponding incremental values of pore surface area are calculated from equation (2.32) and the cumulative values are also done by addition of the incremental ones. The results obtained for pore size analysis of AC/GNPs composite material using BJH method are presented in figure 4.17.



**Figure 4.17:** Pore size analysis for AC/GNPs composite material using BJH method: (a) incremental pore volume, (b) differential pore volume, (c) cumulative pore vol- ume and (d) cumulative surface area.

As observed in figure 4.17.(a), the absorbed value of the gas increased with decreasing pore size of material, with highest absorption values below pore size (diameter) of 500 Å. This indicate that small pore size (< 50nm) are dominant in our material. This results are confirmed from pore size distribution (differential pore volume) observed in figure 4.17.(b). The peaks observed are distributed in a pore size ranges from 50.9 nm to 1.97 nm with maximum absorption at 1.97 nm. This indicate that the dominant pore size in this material is of the type mesopores with highest absorption for low diameter mesopores. Only small part is for macropores. BJH cumulative volume (Fig. 4.17.(c)) for both presented meso and macropores, reached a value of 0.6832  $cm^3/g$  with 0.5872  $cm^3/g$  for mesopores ( $V_{mes}$ ) and 0.174

 $cm^3/g$  for macro ( $V_{mac}$ ). The cumulative surface area (Fig. 4.17.(d))was found to reach a value of 569.95  $m^2/g$  with 564.57 m<sup>2</sup>/g for mesopores and 5.38  $m^2/g$  for macropores. Table 4.13 summarize the results of pore volumes and pore surface area with their percentage contribution relative to total volume ( $V_{tot}$ ) and total surface area ( $S_{BET}$ ). BJH method showed that mesopores and macropores volume in the AC/GNPs composite material represents 68.3% and 20.2%, respectively, of the total measured pore volume. Also, as a result of this method, the surface area of mesopores and macropores represents 59.37% and 0.566%, respectively, of the total measured surface area. The rest of pores volume and surface area percentage contribution for the material should be then for micropores and those external to pores. t-plot method could be used in order to calculate micropores and mesopores volumes and surface areas.

 Table 4.13: Mesopores and macropores volumes and surface areas with

 their per- centage contribution.

$V_{mac}$	V <sub>mac</sub>	$V_{mes}$	Vmes	$S_{mac}$	S <sub>mac</sub>	$S_{mes}$	S <sub>mes</sub>
$(cm^3/g)$	(%)	$(cm^3/g)$	(%)	$(m^2/g)$	(%)	$(m^2/g)$	(%)
0.174	20.2	0.5872	68.3	5.38	0.57	564.57	59.37

## 4.5.2 Harkins-Jura (HJ) t-plot method

This method used to perform analysis for micropores and mesopores volumes and surface areas.  $N_2$  adsorption quantity, for  $P/P_0$  data range, was plotted against thickness t (Fig. 4.18) in order to analyze micro and meso porosity of AC/GNPs composite material. From the first intercept, the micropore volume is determined and mesopore volume is deduced from the second intercept. Also, first slope gives us the mesopore and external

surface areas, while second slope gives the external surface area. Table 4.14 summarize the HJ t-plot results and the percentage contribution with respect to total volume ( $V_{tot}$ ) and total surface area ( $S_{BET}$ ). In this method, micropores and mesopores volume had a contribution of 14.36% and 57.36%, respectively, of total pore volume. While for surface area the contributions were 30.33% and 48.35% for micropores and mesopores, respectively.



**Figure 4.18:** Harkins Jura  $N_2$  adsorption t-plot for AC/GNPs composite material. Table 4.14: AC/GNPs composite material porosity deduced using HJt-plot method.

Intercept1	V <sub>mic</sub>	Vmic	Slope1	S <sub>mes+ext</sub>	S <sub>mes+ext</sub>	$S_{mic}$	$S_{mic}$
$(cm^3/g)$	$(cm^3/g)$	(%)	$(cm^3/g.\text{\AA}$	$(m^2/g)$	(%)	$(m^2/g)$	(%)
STP)			STP)				
79.8612	0.1235	14.36	42.828	662.55	69.67	288.46	30.33
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Intercept2	Vmes	Vmes	Slope2	Sext	$S_{ext}$ (%)	$S_{mes}$	Smes
( <i>cm³/g</i>	$(cm^3/g)$	(%)	(cm³/g.Å	$(m^2/g)$		$(m^2/g)$	(%)
STP)			STP)				
318.86	0.4933	57.36	13.104	202.72	21.32	459.83	48.35

 Table 4.14: AC/GNPs composite material porosity deduced using HJ t 

 plot method.

Again HJ t-plot results (table 4.14) confirms the dominance of mesopores within AC/GNPs composite material. Also micropores has high contribution to porosity of material (30.33% for pore surface area and 14.36% for pore volume). Comparing between BJH method and HJ t-plot method,  $S_{mes}$  in HJ method it is 459.83  $m^2/g$  which is lower than that measured using BJH method (564.57  $m^2/g$ ). Also  $V_{mes}$  was observed to be lower when using HJ method (0.4933  $cm^3/g$ ) than that observed in BJH method (0.5872  $cm^3/g$ ). This difference is expected because HJ t-plot is usually used for micro porosity analysis, especially when the micropores has a high contribution into studied material [48]. Hence in this study, final results (table 4.15) for mesopores and macropores analysis were taken from BJH method, while results for micropores were taken from HJ-t-plot method.

Table 4.15: AC/GNPs composite material acceptable pores volumesand surface areas results with their percentage contribution for deducedfrom BJH method and HJ t-plot method.

Smac (BJH) (m <sup>2</sup> /g)	Smac (%)	$S_{mes}$ (BJH) $(m^2/g)$	Smes (%)	$S_{mic}$ (HJ) $(m^2/g)$	Smic (%)	$S_{ext}$ $(m^2/g)$	Sext (%)	$\frac{SBET}{(m^2/g)}$	SBET (%)
5.38	0.57	564.57	59.37	288.46	30.33	92.60	9.73	951.01	100
Vmac	Vmac	Vmes	Vmes	Vmic	Vmic			V <sub>tot</sub>	V <sub>tot</sub>
(BJH)	(%)	(BJH)	(%)	(HJ)	(%)			$(m^2/g)$	(%)
$(cm^3/g)$		$(cm^3/g)$		$(cm^3/g)$					
0.174	20.2	0.5872	68.3	0.1235	14.36			0.8600	100

Between the three different electrolytes used ( $H_2SO_4$ ,  $Na_2SO_4$ , and KOH),  $H_2SO_4$  was found to have the highest specific capacitance  $C_s$  (  $\approx 388F/g$ using EIS method). The radius of hydrated  $H^+$  ion (table 4.9) is the smallest between different ions used in the different other electrolytes. Hence it can penetrates deeper than other ions into pores, specially into the micropores exist in AC/GNPs electrode material. This will allow higher surface area to be active in storing charges and hence higher  $C_s$ . In addition, as quoted before  $H^+$ hydrated have the highest conductivity, which another factor that allows  $H_2SO_4$  electrolyte to have highest Cs and lowest charge transfer resistance,  $R_{ct}$ , and hence the lowest ESR [23, 59].

# Chapter Five Conclusion

Active carbon (AC)/graphene nanoplates (GNPs) electrodes have been prepared in the laboratory and compared as symmetric supercapacitor using aqueous electrolyte solution. The performance of Active Carbon/Graphene nanoplates supercapacitor electrodes was investigated using different electrolytes ( $H_2SO_4$ ,  $Na_2SO_4$  and KOH) and different measurements techniques (cyclic voltammetry, galvanostatic charge- discharge and electronic impedance spectroscopy). It was found that the specific capacitance of supercapacitor examined with  $H_2SO_4$  electrolyte has the highest value with different measurement techniques. Also, supercapacitor examined with  $H_2SO_4$  electrolyte has a long and very good cyclic stability after its thousand cycle using galvanostatic charging discharging method at a current equal to 100 mA, that indicates high performance of supercapacitor with final specific capacitance equal to 95% of its initial value. In addition, it was noticed that the supercapacitor using  $H_2SO_4$  has the lowest equivalent series resistance due to the higher conductivity of  $H^+$  ions in  $H_2SO_4$  solution. The specific power and specific energy also have their highest values using  $H_2SO_4$  electrolyte at all currents values, the highest values were at current equal 0.2 A (4177.8 W/Kg and 7.8 Wh/Kg, respectively). The key factors which help to get the highest possible specific capacitance are surface area and the presence of higher number of suitable pores in the electrodes material that fit with the ions sizes. Porosity measurements and pore size distribution analysis results show that AC/GNPs electrodes contains a dominant mesoporous structure and have a total specific surface area of (951.01  $m^2/g$ ). In addition, the highest value of specific capacitance for  $H_2SO_4$  solution is due to the smaller size and higher conductivity of  $H^+$  ions in the electrolyte solution, hence, higher number of pores have been filled.

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جامعة النجاح الوطنية

كلية الدراسات العليا

## دراسة الكربون النشط/ صفيحات الجرافين النانوية كأقطاب كهربائية للمكثف الفائق باستخدام H<sub>2</sub>SO<sub>4</sub> وNa<sub>2</sub>SO وKOH وKOH كمحاليل كهرلية

إعداد

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قدّمت هذه الأطروحة إستكمالاً لمتطلبات الحصول على درجة الماجستير في الفيزياء، في كلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس – فلسطين. دراسة الكربون النشط/ صفيحات الجرافين النانوية كأقطاب كهربائية للمكثف الفائق باستخدام

## و $Na_2SO_4$ و $H_2SO_4$ و $H_2SO_4$

تناقش هذه الأطروحة تأثير تغيير المحاليل الكهرلية على المكثف الفائق باستخدام لكربون النشط صفيحات الجرافين النانوية كأقطاب للمكثف الفائق. تم تحضير صفيحات الأقطاب للمكثف الفائق بعد خلط كل من الكربون النشط وصفيحات الجرافين النانوية وفحصها باستخدام (KOH، H2SO4 وNa2SO4) كمحاليل كهرلية.

تمت دراسة الخصائص الكهروكيميائية (قياس الجهد الدوري، طريقة الشحن والتفريغ والتحليل الطيفي للمقاومة الإلكترونية) للمكثف الفائق باستخدام جهاز الجلفانوستات العالمي. كانت مساحة السطح للمكثف الفائق التي تم قياسها باستخدام مجهر المسح الالكتروني تساوي 951.01 م<sup>2</sup>/غم.

أظهرت هذه الدراسة أن السعة النوعية التي تم قياسها حققت أعلى قيمة (20.3 فاراد/غم) باستخدام المحلول الكهرلي  $H_2SO_4$  عند فحصه بواسطة طريقة قياس الجهد الدوري بمعدل مسح يبلغ 5 ميللي فولت/ث. أيضًا، باستخدام المحلول الكهرلي  $H_2SO_4$ ، وجد أن أقل مقاومة مكافئة تبلغ 5 ميللي فولت/ث. أيضًا، باستخدام المحلول الكهرلي  $H_2SO_4$ ، وجد أن أقل مقاومة مكافئة تبلغ 5 ميللي فولت/ث. أيضًا، باستخدام المحلول الكهرلي  $H_2SO_4$ ، وجد أن أقل مقاومة مكافئة البلغ 5 ميللي فولت/ث. أيضًا، باستخدام المحلول الكهرلي  $H_2SO_4$ ، وجد أن أقل مقاومة مكافئة الملغ 5 ميللي فولت/ث. أيضًا، باستخدام المحلول الكهرلي  $H_2SO_4$ ، وجد أن أقل مقاومة مكافئة الملغ 5 ميللي فولت/ث. أيضًا، باستخدام المحلول الكهرلي  $H_2SO_4$ ، وجد أن أقل مقاومة مكافئة النا 10.0  $\Omega$  باستخدام طريقة التحليل الطيفي للمقاومة الألكترونية. وبالتالي، فإن المكثف الفائق الذي تم فحصه باستخدام المحلول الكهرلي  $H_2SO_4$  يمتلك أعلى طاقة نوعية وقدرة نوعية الفائق الذي تم فحصه باستخدام المحلول الكهرلي  $H_2SO_4$ ، عدل ألكترونية. وبالتالي، فإن المكثف الفائق الذي تم فحصه باستخدام المحلول الكهرلي  $H_2SO_4$  يمتلك أعلى طاقة نوعية وقدرة نوعية الفائق الذي تم فحصه باستخدام المحلول الكهرلي  $H_2SO_4$ ، عدل ألكترونية، وبالتالي، فإن المكثف الفائق الذي تم فحصه باستخدام المحلول الكهرلي  $H_2SO_4$  يمتلك أعلى طاقة نوعية وقدرة نوعية الفائق الذي تم فحصه باستخدام المحلول الكهرلي  $H_2SO_4$ ، على التوالي، حيث تم حسابهما بطريقة الشحن والتفريغ. بالإضافة إلى ذلك، لوحظ أن هذه العينة تتمتع باستقرار وفعالية دورية جيدة جدًا مند فحصها لألف دورة باستخدام طريقة الشحن والتفريغ.

كما تمت دراسة خصائص السطح وتوزيع حجم المسام بواسطة الطرق التالية: (برونر – ايميت – تيللر، برونر –جوينر –هالندا وهاركنز جورا). أظهرت النتائج أن الأقطاب الكهربائية التي تم تحضيرها من الكربون النشط وصفيحات الجرافين النانوية تحتوي على توزيع مناسب لأحجام المسامات بما يتوافق مع أحجام أيونات المحلول الكهرلي H<sub>2</sub>SO<sub>4</sub> بحيث أعطى هذا المحلول أعلى سعة نوعية.

