

**OPTIMIZING THE PERFORMANCE OF POLYANILINE
BASED SUPERCAPACITOR FOR ENERGY STORAGE
APPLICATION**

BY

AHMAD ABBAS DALHATU

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This thesis, written by **AHMAD ABBAS DALHATU** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMISTRY**.

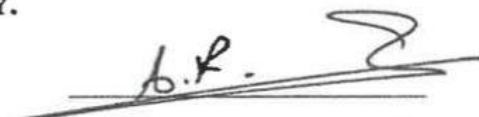


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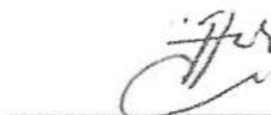
Date _____



Dr. ABDULRAHMAN FAISAL AL-BETAR
(Advisor)



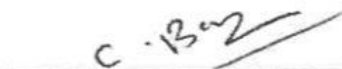
Dr. MD. ABDUL AZIZ
(Co-Advisor)



Dr. MUHAMMAD TAHIR
(Member)



Dr. AHMED ALHARBI
(Member)



Dr. BASHEER CHANBASHA
(Member)

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Dedication

This work is dedicated to everyone who has offered every bit of help from my birth till date.

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TABLE OF CONTENTS

ACKNOWLEDGMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xiv
ABSTRACT.....	xv
ملخص الرسالة.....	xvi
CHAPTER 1 INTRODUCTION.....	1
1.1 Energy	1
1.2 Energy storage	1
1.3 Supercapacitor.....	3
1.4 Characteristics of Supercapacitor	4
1.5 Components of Supercapacitor	5
1.5.1 Electrodes.....	5
1.5.2 Electrolyte	6
1.5.3 Separator	7
1.6 Classification of supercapacitors	8
1.6.1 Electrical Double Layer Capacitors (EDLCs)	8
1.6.2 Pseudocapacitors.....	9
1.6.3 Hybrid supercapacitor	10

1.6.4 Symmetric supercapacitors	11
1.6.5 Asymmetric supercapacitors	11
1.7 Optimization of supercapacitor	12
1.8 Conducting polymers	13
1.9 Steel mesh as current collector	14
CHAPTER 2 LITERATURE REVIEW	15
2.1 Polyaniline	15
2.2 Synthesis of polyaniline	16
2.3 Polyaniline Supercapacitors	17
2.4 Objective of the study	22
CHAPTER 3 EXPERIMENTAL	23
3.1 Materials	23
3.2 Preparation of woven steel mesh substrate	23
3.3 Electropolymerization process	24
3.4 Assessing the impact of deposition cycles on supercapacitor performance	26
3.5 Electrochemical measurements	27
3.6 Characterization Instruments	29
CHAPTER 4 ENHANCING THE PERFORMANCE OF SUPERCAPACITORS THROUGH OPTIMIZED ELECTRODEPOSITION OF POLYANILINE ON VARIOUS SIZE OF WOVEN STEEL MESH SUBSTRATES	30
4.1 Electrochemical evaluation of PANI electrode material in a three-electrode system	30
4.2 Structural and morphological characterization of PANI	32

4.3	Electrochemical evaluation of PANI-coated woven steel meshes in a two-electrode system	37
CHAPTER 5 ENHANCED PERFORMANCE OF SYMMETRIC POLYANILINE-BASED SUPERCAPACITOR USING MIXED-SOLVENT DOPANT		
47		
5.1	Morphology and structure of polyaniline	47
5.1.1	SEM	47
5.1.2	TEM	49
5.1.3	Raman Spectra	50
5.1.4	FTIR Spectra	50
5.2	Electrochemical response test of polyaniline modified electrodes in three-electrode set up	51
5.3	Electrochemical study of the fabricated supercapacitor	53
CHAPTER 6 CONCLUSION AND RECOMMENDATION.....		62
REFERENCES.....		64
VITAE		87

LIST OF TABLES

Table 2.1	Performance evaluation of supercapacitors based on areal capacitance and other parameters.....	19
Table 2.2	Evaluation of supercapacitors based on specific capacitance and other parameters	21

Table 4.1	Comparative workability of PANI-based supercapacitors, offers a side-by-side comparison of the performance characteristics of previously reported PANI based supercapacitors with those developed in this study, highlighting advancements and efficiencies in supercapacitor technology.	45
Table 5.1	Comparing the performance of <i>PANI-SA-PA 3:1</i> based on voltage ranges of 0 to 0.4V and 0 to 0.8V	58
Table 5.2	Comparing the performance of PANI-based supercapacitor developed in this work based on dual doping with other supercapacitors previously reported from literature.	61

LIST OF FIGURES

Figure 1.1	Performance of different electrochemical energy storage and conversion systems shown using Ragone plot.	3
Figure 1.2	Classification of electrolytes for supercapacitor application	7
Figure 1.3	Supercapacitor	8
Figure 1.4	Classification of supercapacitors	12
Figure 2.1	Structure of polyaniline; leucoemeraldine (x=0), emeraldine (x=0.5), penigraniline (x=1)	16

Figure 3.1	An illustrative representation of the process of electrochemically depositing PANI on woven steel meshes of different porosity and the subsequent assembly of a symmetric supercapacitor using the PANI-coated woven steel mesh electrodes.....	26
Figure 4.1	CV curves illustrating the electrochemical deposition of PANI for 35 cycles. (b) Comparative CV curves displaying the electrochemical properties of PANI deposited on four different sizes of woven steel mesh, using a three-electrode system. (c) CV curves showcasing the impact of varying deposition cycles on the electrochemical behavior of PANI coated on a 20 mesh size.....	31
Figure 4.2	(a-e) FESEM images and (f) EDX spectrum of PANI deposited electrochemically for 35 cycles on 20 mesh size steel current collector using CV at 50 mV/s scan rate and voltage window of 0 to 1.3 V obtained at different magnifications, (g-m) elemental mapping of the electrodeposited PANI along with the woven steel mesh current collector.....	33
Figure 4.3	(a-d) TEM, and (e) HRTEM images, and (f) SAED pattern of PANI deposited electrochemically for 35 cycles on 20 mesh size steel current collector using CV at 50 mV/s scan rate and voltage window of 0 to 1.3 V.	35
Figure 4.4	(a) XRD pattern and (b) FTIR spectrum of PANI deposited electrochemically for 35 cycles on 20 mesh size steel current collector using CV at 50 mV/s scan rate and voltage window of 0 to 1.3 V.....	37
Figure 4.5	(a) CV curves of the optimal electrodes, fabricated from 35 cycles of PANI deposition on 20, 50, 100, and 200 mesh sizes at 0 to 1.3 V, measured at a	

scan rate of 50 mV/s and a OVW of 0 to 0.4 V. (b) GCD profiles of the same electrodes, measured at a current density of 1 mA/cm² and a OPW of 0 to 0.4 V. (c) CVs of the electrodes made from 5, 15, 25 and 35 cycles of PANI deposition on 20 mesh size at 0 to 1.3 V, measured at a scan rate of 50 mV/s and a OVW of 0 to 0.4V. (d) GCD profiles of the electrodes made from 5 15, 25 and 35 cycles deposition of PANI on 20 mesh size at 0 to 1.3 V, measured at a current density of 1 mA/cm² and a OVW of 0 to 0.4 V. **39**

Figure 4.6 (a) CV profiles at different scan rates for the optimal electrode (35 cycle deposition on 20 mesh) at a OPW of 0 to 0.4 V. (b) Capacitance vs. scan rate relationship plot derived from CV data across OPWs 0 to 0.4 V, 0 to 0.6 V, and 0 to 0.8 V. (c) GCD profiles at varying current densities for the optimal electrodes at 0 to 0.4 V. (d) Ragone plot illustrating the energy density-power density relationship for the optimum supercapacitor, using GCD data at OPWs 0 to 0.4 V, 0 to 0.6 V, and 0 to 0.8 V. (e) Cyclic stability in terms for capacitance retention for 1000 cycles. **41**

Figure 4.7 (a) EIS Nyquist plot for the optimal supercapacitor with 35 cycle PANI deposition on a 20 mesh electrode, showing impedance characteristics before and after the stability test. (b) Comparative Nyquist plots illustrating impedance variations among supercapacitors with electrodes of different mesh sizes (20, 50, 100, 200 mesh). (c) Nyquist plots contrasting impedance responses of supercapacitors assembled from electrodes with varying PANI deposition cycles on a 20 mesh size stainless steel substrate. **44**

Figure 5.1 FESEM images of PANI-SA (a) and PANI-SA-PA 3:1 (b-d) obtained at different magnifications (e) EDX spectrum of PANI-SA-PA 3:1, (f-m)

	elemental mapping of the electrodeposited PANI-SA-PA 3:1 along with steel mesh current collector.	48
Figure 5.2	(a-c) HRTEM images, and (d) SAED pattern of PANI PANI-SA-PA 3:1	49
Figure 5.3	(a) Raman spectra and (b) FTIR spectra of PANI-SA, PANI-SA-PA 1:1 and PANI-SA-PA 3:1	51
Figure 5.4	(a) CV curves representing 15 cycles of electrochemical deposition of PANI (b) CV curves recorded in three-electrode set up comparing the electrochemical behaviors of PANI deposited based on different ratio of sulfuric acid and phosphoric acid.	53
Figure 5.5	(a) CV curves of the three supercapacitors measured at a scan rate of 50 mV/s over voltage range of 0 to 0.4 V. (b) GCD profiles of the same supercapacitors, measured at a current density of 1 mA/cm ² over a voltage range of 0 to 0.4 V. (c) CV curves of the three supercapacitors measured at a scan rate of 50 mV/s over a voltage range of 0 to 0.8 V. (d) GCD profiles of the same supercapacitors, measured at a current density of 1 mA/cm ² over a voltage range of 0 to 0.8 V.....	55
Figure 5.6	(a) CV curves of PANI-SA-PA 3:1 supercapacitor at different scan rates over a voltage range of 0 to 0.4 V. (b) Capacitance vs. scan rate relationship plot derived from CV data over a voltage range of 0 to 0.4 V (c) GCD profiles of the PANI-SA-PA 3:1 supercapacitor at varying current densities over a voltage range of 0 to 0.4 V.....	57

Figure 5.7 (a) CV curves of PANI-SA-PA 3:1 supercapacitor at different scan rates over a voltage range of 0 to 0.8 V. (b) Capacitance vs. scan rate relationship plot derived from CV data over a voltage range of 0 to 0.8 V (c) GCD profiles of the PANI-SA-PA 3:1 supercapacitor at varying current densities over a voltage range of 0 to 0.8 V..... **58**

Figure 5.8 (a) Ragone plot illustrating the relationship between energy density and power for PANI-SA-PA 3:1 supercapacitor, using GCD data over voltage ranges of 0 to 0.4 V and 0 to 0.8 V. (b) Plot displaying cyclic stability and capacitance retention by PANI-SA-PA 3:1 over 1000 cycles. (c) Nyquist plot comparing the ionic mobility within the electrochemical systems of the three supercapacitors (d) Nyquist plots illustrating impedance for PANI-SA-PA 3:1 supercapacitor showing impedance characteristics before and after the stability test..... **60**

LIST OF ABBREVIATIONS

CV	: Cyclic Voltammetry
EDS	: Energy Dispersive Spectroscopy
EIS	: Electrochemical Impedance Spectroscopy
FESEM	: Field Emission Scanning Electron Microscopy
FTIR	: Fourier Transform Infrared Radiation
GCD	: Galvanostatic Charge Discharge
HRTM	: High Resolution Transmission Electron Microscopy
PA	: Phosphoric Acid
PANI	: Polyaniline
SA	: Sulphuric Acid
SEM	: Scanning Electron Microscopy
TEM	: Transmission Electron Microscopy
XRD	: X-ray Diffraction

ABSTRACT

Full Name : Ahmad Abbas Dalhatu

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Optimization of polyaniline-based supercapacitors to enhance their electrochemical efficacy in terms of energy density has been investigated. First, the effect of porosity of woven steel mesh as current collector on the workability of symmetric supercapacitors was studied. This study was based on electropolymerization of polyaniline on four different pore sizes of steel mesh (20 pores per inch, 50 pores per inch, 100 pores per inch, 200 pores per inch) by optimizing the deposition parameters. The successfully deposited polyaniline films were characterized by SEM, TEM, XRD and FT-IR. Symmetric supercapacitors fabricated from these electrodes were electrochemically tested using CV, GCD and EIS. Notably, 20 mesh size, characterized by the fewest pores per inch, demonstrated superior performance with an optimum capacitance of 4730 mF/cm^2 , an energy density of $317.8 \text{ }\mu\text{Wh/cm}^2$ at a power density of $400 \text{ }\mu\text{W/cm}^2$ at a current density of 1 mA/cm^2 . In the second aspect of this research, double doping of polyaniline using two mineral acid dopants was studied. This is achieved by using three different solutions with varying volumes of sulphuric acid and phosphoric acid with their concentrations at constant aniline concentration. Comparing the electrochemical performance of the mixed-doped PANI with sulphuric acid-doped PANI, improved electrochemical performance has been noticed. Supercapacitor **PANI-SA-PA 3:1** prepared from the mixed-doped PANI exhibits capacitance of 933.8 mF/cm^2 , energy density of $69.0 \text{ }\mu\text{Wh/cm}^2$ at a power density of $405.2 \text{ }\mu\text{W/cm}^2$ while retaining capacitance stability of 91% after 1000 GCD cycles.

ملخص الرسالة

الاسم الكامل : أحمد عباس طلحة

عنوان الرسالة : تحسين أداء المكتف الفائق القائم على البولي أنيلين لتطبيقات تخزين الطاقة

التخصص : كيمياء

تاريخ الدرجة العلمية : مايو ٢٠٢٤ |

تمت دراسة تحسين المكثفات الفائقة القائمة على البولي أنيلين لتعزيز فعاليتها الكهروكيميائية من حيث كثافة الطاقة. أولاً، تمت دراسة تأثير مسامية الشبكة الفولاذية المنسوجة كمجمع تيار على قابلية تشغيل المكثفات الفائقة المتماثلة. اعتمدت هذه الدراسة على البلمرة الكهربية للبولي أنيلين على أربعة أحجام مختلفة المسام من الشبكات الفولاذية (20 مسام في البوصة، 50 مسام في البوصة، 100 مسام في البوصة، 200 مسام في البوصة) من خلال تحسين معاملات الترسيب. تم تشخيص أغشية البولي أنيلين التي تم ترسيبها بنجاح بواسطة FTIR، XRD، TEM، SEM. تم اختبار المكثفات الفائقة المتناظرة المصنعة من هذه الأقطاب الكهربية كهروكيميائياً باستخدام CV و GCD و EIS. على وجه الخصوص، أظهر حجم الشبكة 20، الذي يتميز بأقل عدد من المسام في البوصة، أداءً فائقاً مع سعة مثالية تبلغ 4730 مللي فاراد/سم²، وكثافة طاقة تبلغ 317.8 ميكرووات/سم² عند كثافة طاقة تبلغ 400 ميكرووات/سم² عند كثافة تيار تبلغ 1 مللي أمبير/سم². في الجانب الثاني من هذا البحث تمت دراسة التطعيم المزدوج للبولي أنيلين باستخدام اثنين من المنشطات الحمضية المعدنية. يتم تحقيق ذلك باستخدام ثلاثة محاليل مختلفة بأحجام مختلفة من حمض الكبريتيك وحمض الفوسفوريك مع الحفاظ على ثبات تركيز الأنيلين في كل محلول. بمقارنة الأداء الكهروكيميائي لـ PANI المخدر بشكل مضاعف مع PANI المخدر بحمض الكبريتيك، فإن PANI المخدر بشكل مضاعف يعرض أداءً أفضل. يُظهر المكثف الفائق 3:1 PANI-SA-PA المصنوع من PANI المخدر بشكل مضاعف سعة تبلغ 933.8 مللي فاراد/سم²، وكثافة طاقة تبلغ 69.0 ميكرووات/سم² عند كثافة طاقة تبلغ 405.2 ميكرووات/سم² مع الاحتفاظ بالسعة بنسبة 91% بعد 1000 دورة GCD.

CHAPTER 1

INTRODUCTION

1.1 Energy

The level of environmental pollution has been dramatically rising due to heavy consumption of fossil fuels. The large and increasing global population, urbanization and industrial advances majorly depend on using fossil fuels as their main source of energy and this significantly influences climate changes. It is estimated that the energy demand due to the rising global population can reach up to 36500 Tera Watt hour (TWh) by the year 2040 [1]. This significant reliance on fossil fuels expectedly rises the earth's average temperature making it difficult to maintain environmental sustainability [2]. In order to reduce or even completely replace the usage of fossil fuels and quench this energy demand, the use of natural and renewable energy sources like wind and solar energy has been explored [3], [4]. However, these renewable energy sources are intermittent, and the need for technologies to store the excess energy arises in order to ensure constant supply [5]. Hence, scientists started working on development of extremely efficient energy storage technologies [6].

1.2 Energy storage

Currently, technologies involving energy storage can be categorized based on the type of energy they store, including mechanical, thermal, or electrochemical, which are among the prevalent forms of energy that are being stored.

Focusing on electrochemical energy storage, charges are stored in the form of either chemical reaction or charges separation across dielectric medium. This energy storage system involves the use of anode and cathode as electrodes which are internally set apart by an ionic conductor, membrane, permitting electrons to flow through the external circuit [7]. Electrochemical energy storage technology is made possible by using devices such as Lithium ion batteries [8], fuel cells [9] and supercapacitors, with batteries being at the forefront [10]. Even though batteries are characterized by having high power density, low dissipation of power density has limited their application because their energy storage mechanism suffers from limitation in kinetics as due to chemical changes and rearrangement in their bulk structures [11]. As a result, supercapacitors supplement their application due to the fact that while batteries have higher energy density, supercapacitors have lower energy density [12]. This comparison is shown with a Ragone plot (Fig. 1) which shows specific power versus specific energy. The intensification for the need of supercapacitors for environmental friendly energy storage has been fueled by the investment of some technology businesses such as Tesla [13].

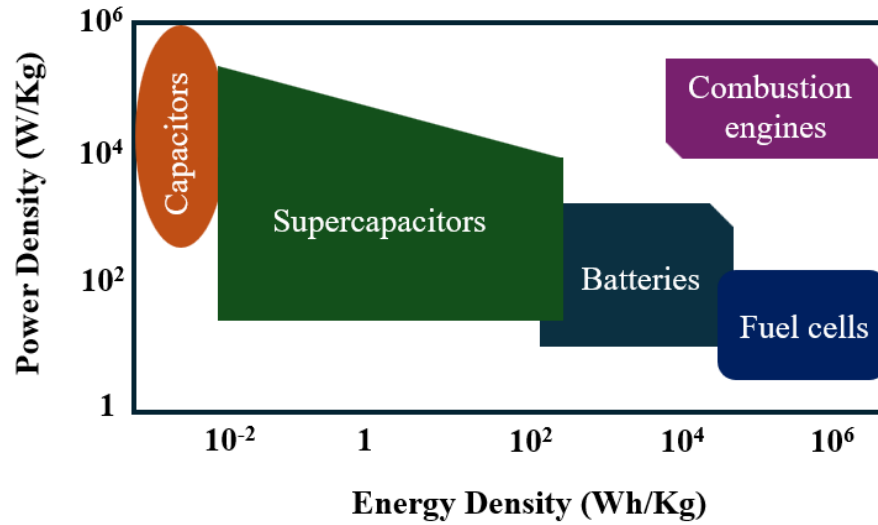


Figure 1.1 Performance of different electrochemical energy storage and conversion systems shown using Ragone plot.

1.3 Supercapacitor

Supercapacitor is an electrochemical storage device fabricated from two electrode which are separated by a membrane that is otherwise submerged in an electrolyte solution [14].

The origin of capacitor technology can be traced back to the invention of the Leyden Jar in the 1740s. This early device consisted of a glass vessel coated with metal foils inside and out of the vessel which acted as electrodes. The glass was serving as the dielectric material, separating the two plates of foil. When the jar was charged, one plate of foil would accumulate positive charges as a negative electrode while the other accumulate negative charges as positive electrode. Connecting the two electrodes would then cause the device to discharge. The main idea of using supercapacitor for energy storage application can be dated back to 1957 when group of engineers from General Electric were running experiments on some devices using activated charcoal as the electrode material. This led

them to inventing the first supercapacitor which was patented as the first electric double-layer capacitor (EDLC) [10].

1.4 Characteristics of Supercapacitor

Substantial power density, quick charging, efficient discharging, extended cycle life, low maintenance requirements, wide range of operating temperature, and most importantly ecological affability are the essential qualities that categorize supercapacitor among devices that efficiently store energy [15]. When correlated with supercapacitors, batteries store energy by both chemical processes and modifications to their internal bulk structures as opposed to supercapacitors which store energy by either electrostatic or electrochemical processes. The kinetic characteristics and cycle life of the batteries are constrained by these processes. They are therefore unsuitable for applications in effective energy storage since they are required to work at many charge/discharge cycles [16]. The main challenge of supercapacitor as compared with batteries is lower energy density. This energy density is related proportionally to the square of its operating voltage as well as capacitance of supercapacitor. Therefore, to bridge this gap of energy density deficiency in supercapacitors, research is ongoing on determining the best out of its components such as electrode material, substrate, electrolyte, and separator. The desired result is either having high capacitance or voltage which will directly raise up the energy density. Electrode material of a supercapacitor should desirably offer higher capacitance. To achieve that, it must be of appropriate morphology that will be able to synergize compatibly with the sizes of electrolytic ions. Electrolytes on the other hand are required to contribute to the wider

operating voltage of supercapacitors. Other important contributions of electrolytes include low resistance, good ionic concentrations, good electrical and thermal stability.

1.5 Components of Supercapacitor

Supercapacitor is composed of electrodes, electrolyte, and membrane or separator [17].

1.5.1 Electrodes

Electrode as one of the key components of supercapacitor is made of two components; electrode material and current collector or substrate on which the electrode material is casted. There are a variety of supercapacitor electrode material depending on its type. Some of these electrode material include but not limited to carbon related substances like activated carbon, carbon nanotubes[18], graphene [19] and carbon sheets [20], oxides of transition metal or their hydroxides such as manganese oxide (MnO_2 and Mn_3O_4) [21], nickel oxide (NiO) [22], iron oxide (Fe_3O_4 , Fe_2O_3) [23] and copper oxide (CuO) [24], [25], [26], metal sulphides such as nickel sulphide (NiS), cobalt sulphide (CoS), nickel cobalt sulphide (NiCoS) [27], MXenes such as $\text{Ti}_3\text{C}_2\text{T}_x$ [28], Metal Nitrides such as TiN and Fe_2N [29], conducting polymers such as polyaniline [30], [31], polypyrrole [32] and PEDOT [33]. Electrode materials of supercapacitor can composed of materials like composites of the conducting polymers such as PEDOT/ WO_3 [34] and PANI/rGO [35]. Many substrates are used in supercapacitor applications. For a substrate to be qualified as a good choice, it must be conductive enough to support the electrode material in conveying and storing electric energy. It should also be able to provide good support for the electrode material to

have a high surface area. Some of the substrates used in supercapacitor application include metal current collectors like aluminium (Al), steel (SS), titanium (Ti), copper (Cu), nickel (Ni). Others include carbon nanoforms and carbon paper, cable-like substrates and synthetic sponges [36]. ITO [37], FTO [38], steel mesh [14] and graphene paper [39] are other forms of substrates used in supercapacitor's application.

1.5.2 Electrolyte

Electrolytes are the second key components without which supercapacitors will not perform. electrolytes majorly facilitate conductivity of ions within the electrochemical system of supercapacitors, thereby compensating the charge on each electrode. For electrolyte to be suitable in supercapacitor's application, many considerations are put in place such as size and type of ion, concentration, voltage range as well as interaction at electrode-electrolyte interface. Electrolytes used in supercapacitors application are generally categorized into three types which include solid state or quasi solid-state electrolytes, liquid electrolytes, and redox-active electrolytes. Liquid electrolytes are of two types which are aqueous electrolytes such as H_2SO_4 , HCl , H_3PO_4 and KOH , and non-aqueous electrolytes such as $\text{TEABF}_4/\text{ACN}$ and $[\text{EMIM}][\text{BF}_4]$. Solid state electrolytes include dried solid polymer electrolyte such as gel polymer electrolyte such as $\text{PVA-H}_2\text{SO}_4$, PEO/LiCl , and inorganic electrolyte such as $\text{Li}_2\text{S-P}_2\text{S}_5$. Redox-active electrolytes include aqueous electrolytes such as KI , organic electrolytes such as $(\text{Et}_4\text{N})_2\text{B}_{12}\text{F}_{11}\text{H/PC}$ and ionic liquids such as $[\text{EMIN}][\text{I}]^+$ $[\text{EMIM}][\text{BF}_4]$ [40].

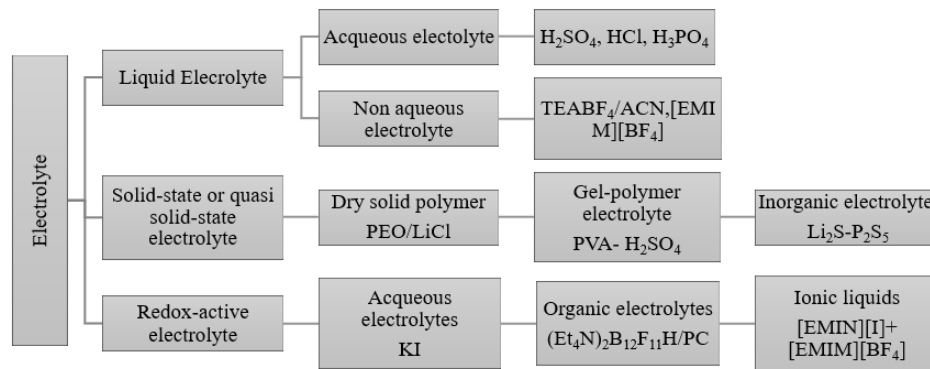


Figure 1.2 Classification of electrolytes for supercapacitor application

1.5.3 Separator

Separator is an insulating material which serves as a carrier of electrolyte in supercapacitors. It is usually saturated with the electrolytic solution and sandwiched in between the electrodes to complete the fabrication of supercapacitor. A good separator should be a good insulator, porous, permeable, light weight and should have good mechanical strength [41]. The main idea behind using separator is to prevent ionic conductivity between the electrodes that will lead to short circuit. The choice of a good separator is key to constructing a supercapacitor with good performance [42]. Some example of materials that can be used as separator for supercapacitor include filter paper [14], cellulose, egg shell [42], polypropylene, polyvinylidene difluoride.

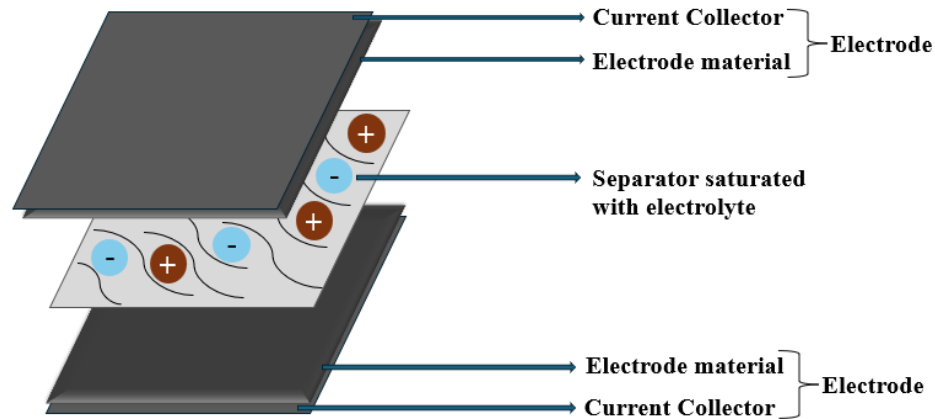


Figure 1.3 Supercapacitor

1.6 Classification of supercapacitors

Supercapacitors can be classified based on the mechanism by which they store energy as well as the configuration of the electrode materials with which they are fabricated.

On the basis of their energy storage mechanisms, supercapacitors are of three categories: Electrochemical Double Layer Supercapacitors EDLC [43], Pseudocapacitors [44], Hybrid Supercapacitors [45].

1.6.1 Electrical Double Layer Capacitors (EDLCs)

EDLCs conserve energy based on electrostatics where ionic species are adsorbed at the surface between the electronic conductor and ionic conductor [43]. The basis of energy storage mechanism in electric double-layer capacitors (EDLCs) is on electrochemical double layer principle. Applying a voltage accumulates charges on the electrode surfaces because of the difference in potential. This causes ions in the electrolyte to diffuse across

the membrane separating the electrodes while adsorbing on the surface of the other electrode that is oppositely charged. To prevent the reconstitution of these ionic substances at the electrode surfaces, a charge is formed based on double layer. This double layer structure, coupled with the expanded particular surface area and the minimized spacing between electrodes, enables Electric Double-Layer Capacitors (EDLCs) to attain a greater energy density relative to conventional capacitors [46].

1.6.2 Pseudocapacitors

Pseudocapacitors store energy based on redox reaction due to quick faradaic process at the interface between electrode and electrolyte [44]. In a pseudocapacitor, when a potential is applied, the electrode material undergoes reduction and oxidation reactions. This procedure entails the movement of charge through the double layer, leading to the circulation of faradic current within the supercapacitor unit. The faradic mechanism in pseudocapacitors permits them to secure elevated levels of specific capacitance and energy densities in contrast to electric double-layer capacitors (EDLCs) [20]. Pseudocapacitors can be fabricated from electrodes made with materials such as oxides of transition metal or their hydroxides such as manganese oxide (MnO_2 and Mn_3O_4) [21], nickel oxide (NiO) [22], iron oxide (Fe_3O_4 , Fe_2O_3) [23] and copper oxide (CuO) [24], [25], [26], nickel sulphide (NiS), cobalt sulphide (CoS), nickel cobalt sulphide (NiCoS) [27], MXenes such as $\text{Ti}_3\text{C}_2\text{T}_x$ [28], titanium nitride TiN and iron nitride Fe_2N [29]. They can also be made of electrodes fabricated with conducting polymers such as polyaniline [30], [31], polypyrrole [32] and PEDOT [33].

1.6.3 Hybrid supercapacitor

A hybrid supercapacitor stores energy through both redox and electrostatic mechanisms taking advantage of EDLCs which offer good power performance and cycling stability and pseudocapacitors which offer high specific capacitance. This is achieved when electrode materials of both EDCL and pseudocapacitor are brought together in one device to have a hybrid supercapacitor configuration. With hybrid supercapacitor, cell voltage, power density, capacitance, energy density can be improved [45]. Electrode from which hybrid supercapacitors are fabricated can be classified into composites and battery-type.

Composite electrodes are made by blending carbon-based substances with either polymers that are conducting or metal oxides and use a single material for electrode. This way, the electrode utilizes both physical and chemical methods of storing charges. The carbon-based materials contribute to high surface area as well as capacitive behavior for double-layer charge storage. This characteristic enhances the interaction between the pseudocapacitive materials and the electrolyte. Pseudocapacitive materials, such as conducting polymers or metal oxides contribute with Faradaic redox reactions. These reactions lead to an increase in the overall capacitance of the composite electrode [47].

There are two primary types of composite electrodes:

Binary composites: These incorporate two distinct electrode materials within a single electrode.

Ternary composites: These encompasses using three materials differently used in a single electrode.

By combining carbon-based materials with pseudocapacitive elements in composite electrodes, a superior level of capacitance and energy storage performance is achieved

compared to using individual components separately [48]. Example of composites materials include PEDOT/WO₃ [34].

A hybrid battery type encompasses two distinct electrodes, like asymmetric hybrids. But in this instance, it involves pairing a supercapacitor electrode with a battery electrode. This arrangement is designed to harness the unique characteristics of both supercapacitors and batteries within a single cell. [48]

Based on the configuration of electrodes from which they are fabricated, we can classify supercapacitors as symmetric and asymmetric.

1.6.4 Symmetric supercapacitors

In symmetric supercapacitors, the two electrodes from which they are fabricated are composed of the same material. Each of the electrodes used in the fabrication process can be either made of EDLC electrode materials where their contribution is purely based on EDLC behavior or can be made of pseudocapacitive materials where their contribution is purely based on pseudocapacitive behavior [14].

1.6.5 Asymmetric supercapacitors

Asymmetric supercapacitors are fabricated using electrodes made up of different materials. Notably, one electrode is made of EDLC materials, contributing to the EDLC behavior of the supercapacitor while the other electrode is made of pseudocapacitive materials, contributing to the pseudocapacitive behavior of the supercapacitor [18].

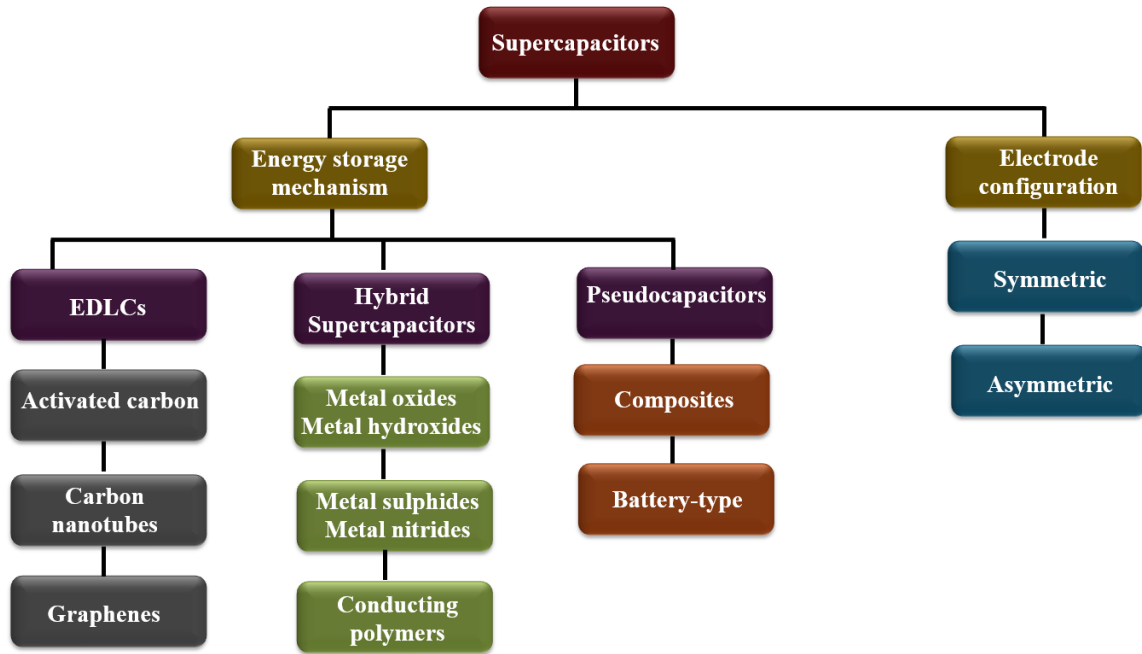


Figure 1.4 Classification of supercapacitors

1.7 Optimization of supercapacitor

Optimization of supercapacitor involves playing with composition of the key components of supercapacitor which are electrode material, current collector, and electrolyte to enhance its performance in better energy storage capability. Usually, low energy density is the major limitation of supercapacitor while working at high power density. To bridge this gap, there is need for high capacitance as well as high cell operating voltage. This is because energy density is related proportionally to the square of the cell voltage and capacitance. While EDLCs are characterized by having low capacitance but high cycling performance, pseudocapacitors are characterized by having higher capacitance but lower cycling performance. Also, pseudocapacitors have lower operating voltage when compared with

EDLCs [49]. Researchers are now taking advantage of both EDLCs and pseudocapacitor electrode materials including other newly invented materials to improve performance of supercapacitors especially boosting the energy density. Various materials as current collectors, electrolytes and dopants were reported in the literature and new ones are now being analyzed to investigate how well they can contribute towards enhancing performance of supercapacitors [50].

1.8 Conducting polymers

Conducting polymers are pseudocapacitive materials which are synthesized from their aromatic monomer such as aniline [30], [31], pyrrole [32] and EDOT [33]. Conducting polymers are used as pseudocapacitive materials due to their ability to partake in doping and de-doping with various dopants such as mineral acids. During the doping process, electron conductivity is facilitated by the delocalization of electrons. These charged particles traverse the conjugated π system and this process is influenced by applied voltage. Owing to their exceptional ability to conduct electricity and the reversible nature of their doping and de-doping processes, these conductive polymers are highly sought after for use as electrodes in pseudocapacitors [51].

Polyaniline is the most widely used conducting polymer because of its enhanced workability due to ease of synthesis, good conductivity, mechanical robustness [52], being able to be doped [53] cheaply available as well as capable of good energy storage [14]. Aniline can be polymerized either by chemical or electrochemical means [54], [55]. Polyaniline is preferably synthesized electrochemically because of the simplicity and swiftness of the approach. This can be achieved by using manageable electrochemical

instruments. There is also an advantage of controlling the thickness of deposition through variation of the deposition parameters. This electrochemical approach is also eco-friendly [56], [57], [58], [59].

1.9 Steel mesh as current collector

To fabricate an effective supercapacitor, excellent current collector is one of the significant components to consider [60], [61]. Various literatures have reported using steel mesh as current collector for supercapacitor application. Steel mesh is of different porosity, and this has become a great advantage to be capitalized on to investigate its contribution towards enhancing the performance of supercapacitors. Some key qualities of steel mesh for being used as a current collector are its resistance to corrosion and its readily availability in the market at cheap price [62], [63].

CHAPTER 2

LITERATURE REVIEW

2.1 Polyaniline

Historically, polyaniline pioneered among the polymers considered as conductive polymers. Since its inception and report in 1886, a lot of progress has been made in terms of its applicability due to its exceptional qualities mentioned in the introductory part of this proposal [52]. In 1968 when conductivity of these conducting polymers was accentuated, the plausibility in terms of application in electrochemistry and electrical conductivity of polyaniline was first reported [64]. Among the polymers with intrinsic conductive properties, polyaniline happens to be the most inexpensive with appreciable thermal stability [65]. As a result, significant research output has been achieved due to utilization of polyaniline in various applications such as in secondary batteries [66], [67], solar cells [68], fuel cells [69], biological or chemical sensors [70], drug deliver and corrosion inhibition [71] as well as electrode material for fabrication of pseudocapacitors. Intrinsically, polyaniline exists in three electrochemical states (scheme 3) namely; leucoemeraldine ($x=0$) which is the fully reduced form, emeraldine ($x=0.5$) which is half oxidized form and penigraniline ($x=1$) which is the fully oxidized form [54]. The emeraldine form of polyaniline exists in two forms namely emeraldine base and emeraldine salt. Emeraldine base is doped by using protonic organic or inorganic acids via electrochemical means or by charge transfer groups via chemical means to convert to the emeraldine salt, which is the conducting form of polyaniline. Numerous studies have been carried out where different inorganic protonic acids have been used to dope polyaniline.

Inorganic protonic acids are recently prioritized for doping polyaniline because when compared with organic protonic acids, their size is somewhat small, which makes possible structure of polyaniline with better pathways for diffusivity [55]. Nanostructures of polyaniline using inorganic protonic acids such as H_3PO_4 , H_2SO_4 , HCl and HBF_4 were studied by Zhang et al. [72]. In their study, it was found out that the nanostructure of polyaniline with morphological size of 150-340 nm as well as the film conductivity of $0.1\text{--}10\text{ S cm}^{-2}$ were solely because of doping with these mineral acids coupled with tuning the condition of the reaction. In another study, morphology, spectroscopy and transport of the doped polyaniline were evaluated using the following acids H_2SO_4 , HCl , HNO_3 , HClO_4 , and H_3PO_4 [73]. The result of this study showed that using HClO_4 as acidic medium the polyaniline structure contained a larger portion of emeraldine salt. Appealingly however, H_3PO_4 doped polyaniline was found to be most stable thermally when compared with the other acids doped polyaniline structures.

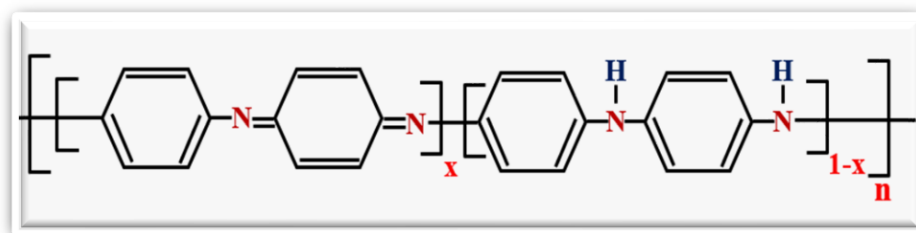


Figure 2.1 Structure of polyaniline; leucoemeraldine ($x=0$), emeraldine ($x=0.5$), penigraniline ($x=1$)

2.2 Synthesis of polyaniline

Polyaniline can be synthesized in two ways namely, chemical oxidation and electrochemical methods. In both cases, utilization of either organic or aqueous inorganic

solvents is done to achieve successful polymerization. However, electrochemical synthesis of polyaniline is preferred over chemical synthetic method. This is due to the facile nature of the electrochemical method. Also, electrodeposition of polyaniline films can be controlled by tuning the deposition parameters such as potential range, current density, pH and concentration of the supporting electrolyte [74], [75], [76], [77], [78], [79]. Chemical synthesis of polyaniline is usually carried out successfully before being applied to a substrate depending on the application [80] while electrochemical synthesis of polyaniline is performed on the substrate before being used for an application [14]. From the literature, various substrates have been reported for successful electrochemical deposition of polyaniline including nickel foam [80], porous carbon [81], carbon fiber, reticulated vitreous carbon [82], tin oxides [83], gold [84], indium-doped tin oxide [85], stainless steel [86] and many other substrates.

2.3 Polyaniline Supercapacitors

One of the most widely present applications of polyaniline is in the field of energy storage, specifically in the fabrication of electrode materials for supercapacitors. Polyaniline based supercapacitors are called pseudocapacitors due to their nature of faradaic charge/discharge mechanism. When compared with EDLCs, Pseudocapacitors can show more charge storage ability and improved rate of performance which could be due to innate nature of the substances utilized for making the electrode materials [87], [88], [89]. Polyaniline alone or with other materials as composite can be used as an electrode material to fabricate a supercapacitor. Generally, the same parameters namely volumetric capacitance, areal capacitance, specific capacitance, energy density, power density, cyclic stability and

impedance are used in evaluation of workability of the assembled supercapacitors irrespective of type and composition of electrodes. Table 3.1 shows some supercapacitors fabricated with electrodes made with polyaniline alone or as a composite along with their performance evaluations based on areal capacitance (F cm^{-2}) while table 2 shows the same data based on specific capacitance (F g^{-1}).

Table 2.1 Performance evaluation of supercapacitors based on areal capacitance and other parameters

Electrode composition	Electrolyte	Current density (mA cm ⁻²)	Capacitance (mF cm ⁻²)	Energy density (μW h cm ⁻²)	Power density (μW cm ⁻²)	Cyclic stability (cycles/%)	Ref
PANI/SME at 0-0.4V	0.1 M H ₂ SO ₄	1	353	26.4	199	-	[14]
PANI/SME at 0-0.8V	0.1 M H ₂ SO ₄	1	297	7.8	400	-	[14]
PNA/G	H ₃ PO ₄ /PVA	0.1	230	37.2	-	8000, 86.9	[90]
PANI/CNTs/G/P ETC	1 M H ₂ SO ₄	1.5	791	-	-	3000, 76	[91]
VACNT/PANI	1 M Na ₂ SO ₄	0.25	16.17	-	-	3000, 52	[92]
fCC/PANI/rGO	1 M H ₂ SO ₄	0.1	197	-	-	7000, 91.3	[93]
CNT/PANI/hydrogel	H ₂ SO ₄ /PVA	1	184.6	-	-	500, -	[94]
CNF/CNT, CNT/PANI	H ₃ PO ₄ /PVA	0.5	67.31	-	-	5000, 90	[95]
PANI/rGO	H ₃ PO ₄ /PVA	0.1	23	-	-	2000, 100	[35]
PANI/Graphene nanosheets	H ₂ SO ₄ /PVA	0.5	355.6	320	54	-	[96]

Considering from literature the important role played by polyaniline in the field of energy storage for the fabrication of various types of supercapacitors, this research is proposed to improve capacitance using low-cost approach of exploring the effects of different sizes of steel mesh as substrates to polyaniline electropolymerization. This approach is considered to improve on the result obtained by previous research for the fabrication of symmetric supercapacitor by preparing polyaniline on various sizes of steel mesh electrodes. The result obtained was a capacitance of 353 m F cm^{-2} at a current density of 1 mA cm^{-2} and there was no significant drop in the capacitance after stability test of 1000 cycles [14].

Table 2.2 Evaluation of supercapacitors based on specific capacitance and other parameters

Electrode composition	Electrolyte	Current density	Capacitance (F g ⁻¹)	Energy density (W h kg ⁻¹)	Power density (KW kg ⁻¹)	Cyclic stability (cycles/%)	Ref
PANI nanowires	1 M H ₂ SO ₄	23 A g ⁻¹	742	68	16	1500, 92	[97]
PANI nanowhiskers	1 M H ₂ SO ₄	1 A g ⁻¹	470	-	-	1000, 90	[98]
De-doped PANI nanofibres	1 M H ₂ SO ₄	2.5 A g ⁻¹	593	-	-	5000, 70	[99]
PANI	H ₃ PO ₄ /PVA	0.5 A g ⁻¹	890	-	-	1000, 89	[100]
PANI	1 M H ₂ SO ₄	1.5 A g ⁻¹	532	-	-	-	[101]
PANI/CNT	0.5 M H ₂ SO ₄	0.5 A g ⁻¹	1065	-	-	1000, 92	[102]
OMC/PANI	1 M H ₂ SO ₄	0.1 A g ⁻¹	517	-	-	1000, 91.5	[103]
C/PANI/G	1 M H ₂ SO ₄	1 A g ⁻¹	1145	25.4	92.2	5000, 94	[93]
CNT/PANI/G	1 M H ₂ SO ₄	1 A g ⁻¹	510	20.5	25	5000, 91	[104]
PANI/Graphene	1 M H ₂ SO ₄	1 A g ⁻¹	808	28	0.25	-	[105]

2.4 Objective of the study

The current study aims at the following objectives:

- I. To prepare environmentally benign polyaniline by electrochemical deposition on four steel mesh substrates of varying porosity.
- II. To make electrochemical co-doping of polyaniline using phosphoric acid in a sulphuric acid medium.
- III. To characterize the as-synthesized polyaniline in both cases using techniques such as SEM, TEM, XRD, Raman and FT-IR.
- IV. To construct symmetric supercapacitors.
- V. To assess the electrochemical performance of the supercapacitors using CV, GCD, and EIS.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

Steel meshes four different porosities, i.e., 20, 50, 100, and 200 pores per inch, were acquired from a local market in Dammam, Eastern Province, Saudi Arabia. Purposely for the first study, these varied mesh sizes were selected to examine their impact on the supercapacitors' performance. For the second study, 100 pores per inch steel mesh was used. Sulfuric acid (95%), Phosphoric acid (85%) and Ethanol, essential for the electropolymerization process and cleaning procedures, were sourced from Fisher Chemical Company. Aniline, used in synthesizing PANI for the electrodes, was procured from Sigma Aldrich with a purity of 99.05%, adhering to American Chemical Society standards. The use of high-purity materials is crucial for ensuring consistent and reliable results in supercapacitor fabrication.

3.2 Preparation of woven steel mesh substrate

Each woven steel mesh, in sizes of 20, 50, 100, and 200 meshes per inch, was cut to 1 cm² dimensions. The substrates were first sonicated in ethanol for 15 minutes to remove surface oil and dirt. After rinsing with deionized water, they were sonicated again in the water for another 15 minutes to ensure thorough cleaning. Finally, the meshes were dried in an oven at 50 °C for an hour to remove any residual moisture, preparing them for the electrodeposition process.

3.3 Electropolymerization process

Electropolymerization of PANI onto the prepared woven steel mesh substrates was conducted using a CHI 760E Potentiostat. Each woven steel mesh, with an area of 1 cm^2 , served as the working electrode in a three-electrode electrochemical cell. For the first study, the electropolymerization solution consisted of 0.5 M aniline prepared in 0.5 M H_2SO_4 . In this setup, a standard Ag/AgCl electrode was used as the reference, and a platinum wire served as the auxiliary electrode. CV was the chosen method for the electrodeposition process. During deposition, a scan rate of 50 mV/s was consistently maintained. To explore the effects of different electrochemical environments on the deposition quality and the resultant supercapacitor performance, three distinct operating voltage windows were employed: 0.0 to 1.0 V, 0.0 to 1.1 V, and 0.0 to 1.3 V. Within each voltage window, varying cycle numbers, 5, 15, 25, and 35 cycles, were investigated to determine the optimal deposition conditions. It was observed that 35 cycles at a voltage window of 0 to 1.3 V yielded the most favorable results in terms of capacitance, energy, and power densities. Post-electropolymerization, the woven steel meshes displayed a characteristic green coating of PANI. To remove any unreacted monomer or by-products, each coated mesh was gently rinsed with deionized water and then air-dried at ambient temperature. The drying step is critical to ensure the stability and integrity of the PANI layer.

For the second study, electrochemical polymerization of PANI was conducted in conventional three-electrode set up using CHI 760E Potentiostat, employing Cyclic Voltammetry over a potential range of 0-1 V at scan rate of 50 mV/s. The prepared steel mesh, Platinum strip and Ag/AgCl served as working, counter, and reference electrodes, respectively. Three different fixed volume solutions with varying volumes of sulphuric

acid and Phosphoric acid were used for the PANI electropolymerization. The concentration of aniline in each solution was maintained to be 0.5 M and each of the acids used was of 1 M concentration. The first solution was composed of 0.5 M aniline in 1:0 volume ratio of H_2SO_4 and H_3PO_4 (**PANI-SA**). The second solution was composed of 0.5 M aniline in 1:1 volume ratio of H_2SO_4 and H_3PO_4 (**PANI-SA-PA 1:1**). The third solution was composed of 0.5 M aniline in 3:1 volume ratio of H_2SO_4 and H_3PO_4 (**PANI-SA-PA 3:1**). After successful electrochemical deposition of the PANI on the electrode, the deposited materials were rinsed with deionized water to wipe the modified surface off any possible electrolytic ions and then dried at ambient temperature.

For the construction of symmetric supercapacitors, pairs of these PANI-coated woven steel meshes were utilized. Each device was assembled by placing two electrodes face-to-face, separated by a filter paper separator soaked in a 0.1 M H_2SO_4 . Fig. 3.1 illustrates the fabrication scheme as per the first study. This simple yet effective assembly method allowed for the straightforward evaluation of the supercapacitors' electrochemical performance, with a particular focus on the influence of woven steel mesh size and electropolymerization parameters in the case of the first study as well as influence of mixed doping on polyaniline in the case of the second study.



Figure 3.1 An illustrative representation of the process of electrochemically depositing PANI on woven steel meshes of different porosity and the subsequent assembly of a symmetric supercapacitor using the PANI-coated woven steel mesh electrodes

3.4 Assessing the impact of deposition cycles on supercapacitor performance

The functionality of a supercapacitor is intricately linked to the fabrication and application of its electrode material, particularly in the context of the electropolymerization processes involved in synthesizing PANI. To evaluate the redox cyclability and supercapacitive properties of the electrodeposited PANI, CV tests were conducted using a three-electrode system in both studies. In this setup, each PANI-coated woven steel mesh, representing the four different mesh sizes, functioned as the working electrode.

In the first study, these electrodes were immersed in an aqueous electrolyte solution of 0.1 M H_2SO_4 . A standard Ag/AgCl electrode and a platinum wire served as the reference and auxiliary electrodes, respectively. The CV tests were carried out under two operating voltage windows (OVWs), i.e., -0.4 V to 0.8 V and -0.4 V to 1.0 V. Throughout these experiments, a consistent scan rate of 50 mV/s was maintained. This methodology aimed

to thoroughly investigate the electrochemical behavior of the PANI layers deposited under different conditions, particularly focusing on how the number of deposition cycles influences the overall performance of the supercapacitors. The choice of OVWs and scan rate was critical to ensuring a comprehensive analysis of the electrochemical characteristics of the PANI-coated substrates, thereby shedding light on the optimization of electrode fabrication for enhanced supercapacitor functionality.

In the second study, the electrochemical response of the deposited film of polyaniline, confirming electrochemistry and PANI deposition for the three types of modified electrodes was studied in a three-electrode system. Cyclic Voltammetry was employed with the three electrodes immersed in an electrolyte solution of 1M H_3PO_4 over a voltage range of -0.4 – 0.8V at scan rate of 50 mV/s [106].

3.5 Electrochemical measurements

Electrochemical performance of the fabricated supercapacitors was rigorously evaluated using a two-electrode system, employing CV, galvanostatic charge discharge (GCD), and electrochemical impedance spectroscopy (EIS) techniques. These assessments were conducted using a CHI 760E Potentiostat in both studies.

In the first study, experiments were conducted across three operating voltage windows of 0 to 0.4 V, 0 to 0.6 V, and 0 to 0.8 V, each applicable for all tests except EIS. In the second study, experiments were conducted over two different voltage ranges of 0 to 0.4V and 0 to 0.8V. The resulting data were utilized to calculate capacitance, energy density, and power density, using the following equations:

For CV measurements, the areal capacitance (C_{ar}) was determined using equation (1) [107], [108], [109], [110].

$$C_{ar} = \frac{\int I \times dV}{A \times v \times \Delta V} \quad (1)$$

Where $\int I \times dV$ represents the integration of the area under the CV curve, A is the area of the electrode material (cm^2), v is the scan rate (mV/s), and ΔV is the operating voltage window (OVW, V).

In the case of GCD measurements, C_{ar} was calculated by using equation (2) [107], [111], [112].

$$C_{ar} = \frac{I \times t}{A \times \Delta V} \quad (2)$$

Where I is the discharging current (A), t is the discharging time (s), A is the area of the electrode material (cm^2), and ΔV is the OVW.

Energy density (E) and power density (P) were derived from the GCD data using the following equations (3) and (4), respectively [113], [114].

$$E = 0.5 \times \frac{C_{ar} \times \Delta V^2}{3.6} \quad (3)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (4)$$

Where E and P are the energy density (Wh/cm^2) and power density (W/cm^2), respectively. C_{ar} is capacitance per unit area (F/cm^2), Δt is the difference between final and initial discharging time (s), and ΔV is the discharge OVW (V).

3.6 Characterization Instruments

To comprehensively characterize the electrochemically deposited PANI and the woven steel mesh substrate, an array of advanced instrumentation was employed. The surface morphology and chemical composition were analyzed using a Thermo Scientific Quattro S field emission scanning electron microscope (ESEM), equipped with an energy dispersive X-ray spectroscopy (EDX) detector. This setup provided detailed insights into the microstructural features of the PANI and the elemental composition of the woven steel mesh. For an in-depth examination of the synthesized nano-sized PANI, a JEOL JEM-2100F transmission electron microscope (TEM) was utilized. This instrument, renowned for its high-resolution imaging capabilities, enabled the visualization of the nanoscale morphology of PANI, offering valuable data on its structural characteristics. The crystalline structure of the synthesized PANI was determined through X-Ray diffraction (XRD) analysis, conducted using 8 X-Ray diffractometer (XRD) Rigaku Ultima IV. This spectroscopy carried out between 3° and 90° utilizing a current of 40 mA at 40 kV voltage, facilitated the identification of crystalline phases and provided insights into the degree of crystallinity of PANI. Furthermore, the Fourier transform infrared spectrometer (FTIR) Nicolet iS10, equipped with a Smart iTR Accessory, was employed to investigate the functional groups and chemical structure of the as-synthesized PANI. The FTIR analysis was instrumental in identifying and confirming the presence of specific functional groups, thereby elucidating the molecular composition of PANI.

CHAPTER 4

ENHANCING THE PERFORMANCE OF SUPERCAPACITORS THROUGH OPTIMIZED ELECTRODEPOSITION OF POLYANILINE ON VARIOUS SIZE OF WOVEN STEEL MESH SUBSTRATES

4.1 Electrochemical evaluation of PANI electrode material in a three-electrode system make font 12

This research primarily focuses on optimizing the capacitive performance of symmetric supercapacitors assembled from electrodes developed using four different sizes of woven steel meshes. To achieve this, PANI was electrochemically deposited on each mesh size through CV, employing three distinct voltage windows: 0.0 to 1.0 V, 0.0 to 1.1 V, 0.0 to 1.3 V, at 50 mV/s scan rate. The deposition process was executed in a 0.5 M aniline and 0.5 M H₂SO₄ solution. Figure 4.1 a illustrates the CV of deposition conducted at the voltage range of 0.0 to 1.3 V (vs. Ag/AgCl) for 35 cycles, which was identified as the optimal condition, particularly on the 20 mesh per inch substrate, yielding the highest capacitance, energy density, and power density. The CV curves of the electrodeposited PANI was recorded in a three-electrode set up, with 0.1 M H₂SO₄ electrolyte, over OVWs of -0.4 to 1.0 V (fig 4.1 b), for all four modified woven steel mesh sizes. In these setups, the PANI-coated meshes acted as working electrodes, while Ag/AgCl and platinum wire were used as the reference and counter electrodes, respectively. Analysis of these voltammograms revealed that the mesh with 20 pores per inch exhibited the highest current density and the largest area under the curve, followed by 50, 100, and 200 pores per inch mesh sizes. This trend suggests that a decrease in the number of pores per inch in the woven steel meshes

leads to an increase in the electroactive surface area, thereby enhancing the capacitive properties [115]. Moreover, when examining the effect of deposition cycles (5, 15, 25, and 35 cycles) on the 20 pores per inch mesh, it was observed that the area under the CV curves increased with the number of cycles. Specifically, the deposition of 35 cycles showed the largest area, indicating an augmentation in capacitance with an increase in deposition cycles (Fig. 4.1 c). However, deposition of higher number of cycles lead to PANI deposition with poor mechanical stability. These findings underscore the importance of mesh size and deposition cycles in the electrochemical performance of PANI-coated woven steel mesh electrodes. They provide crucial insights into the design and optimization of supercapacitors, particularly in terms of maximizing power density and capacitance through strategic selection of electrode material properties and electrochemical deposition parameters.

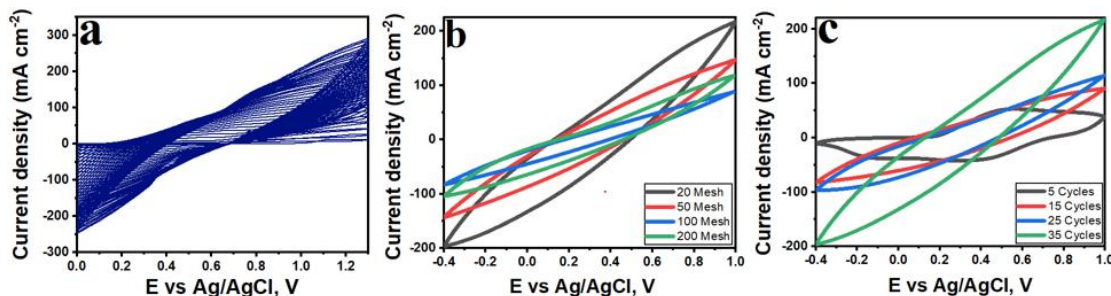


Figure 4.1 CV curves illustrating the electrochemical deposition of PANI for 35 cycles. (b) Comparative CV curves displaying the electrochemical properties of PANI deposited on four different sizes of woven steel mesh, using a three-electrode system. (c) CV curves showcasing the impact of varying deposition cycles on the electrochemical behavior of PANI coated on a 20 mesh size.

4.2 Structural and morphological characterization of PANI

To gain insights into the nanoscopic architecture of electrochemically deposited PANI on woven steel mesh, detailed FESEM studies were conducted. Figure 4.2 a-e display the different magnifications FESEM images of PANI layers, deposited electrochemically for 35 cycles on a 20-mesh size steel current collector, using a CV process with a 50 mV/s scan rate and a voltage window of 0 to 1.3 V, offering a closer examination of its nanostructure. The SEM images, particularly at 100 μm and 50 μm magnifications, reveal a uniform, compact, and porous distribution of PANI on the woven steel mesh. This morphology is noteworthy as it suggests an efficient porosity that is conducive to ion transport, thereby enhancing the conductivity and stabilizing the electrode material. This binder-free deposition process is crucial in maintaining the integrity and functional efficiency of the PANI layers. At higher magnifications of 2 μm and 1 μm , the PANI exhibits a coral-like structure. Such a formation indicates a high surface area, which is beneficial for electrochemical reactions. The most detailed view at 500 nm magnification shows a richly porous and interconnected nanostructure, further emphasizing the potential for excellent electrochemical performance. EDX was employed to ascertain the elemental composition and distribution within the PANI-coated woven steel mesh. The EDX spectrum in Figure 4.2 f identifies the elemental constituents of both the electrodeposited PANI and the woven steel mesh substrate. The detection of carbon and nitrogen predominantly arises from the PANI, while oxygen and sulfur are attributed to the dopant sulfate ions incorporated during the polymerization process. The elements iron, nickel, and chromium are indicative of the woven steel mesh composition. Figure 4.2 g-m provides elemental mapping, confirming the uniform distribution of these elements across the PANI-modified woven steel mesh. This comprehensive FESEM/EDX analysis not only confirms the successful deposition of PANI on the woven steel mesh but also provides valuable information about the nanostructured morphology and elemental composition, which are critical factors in determining the electrochemical properties of the supercapacitor electrodes.

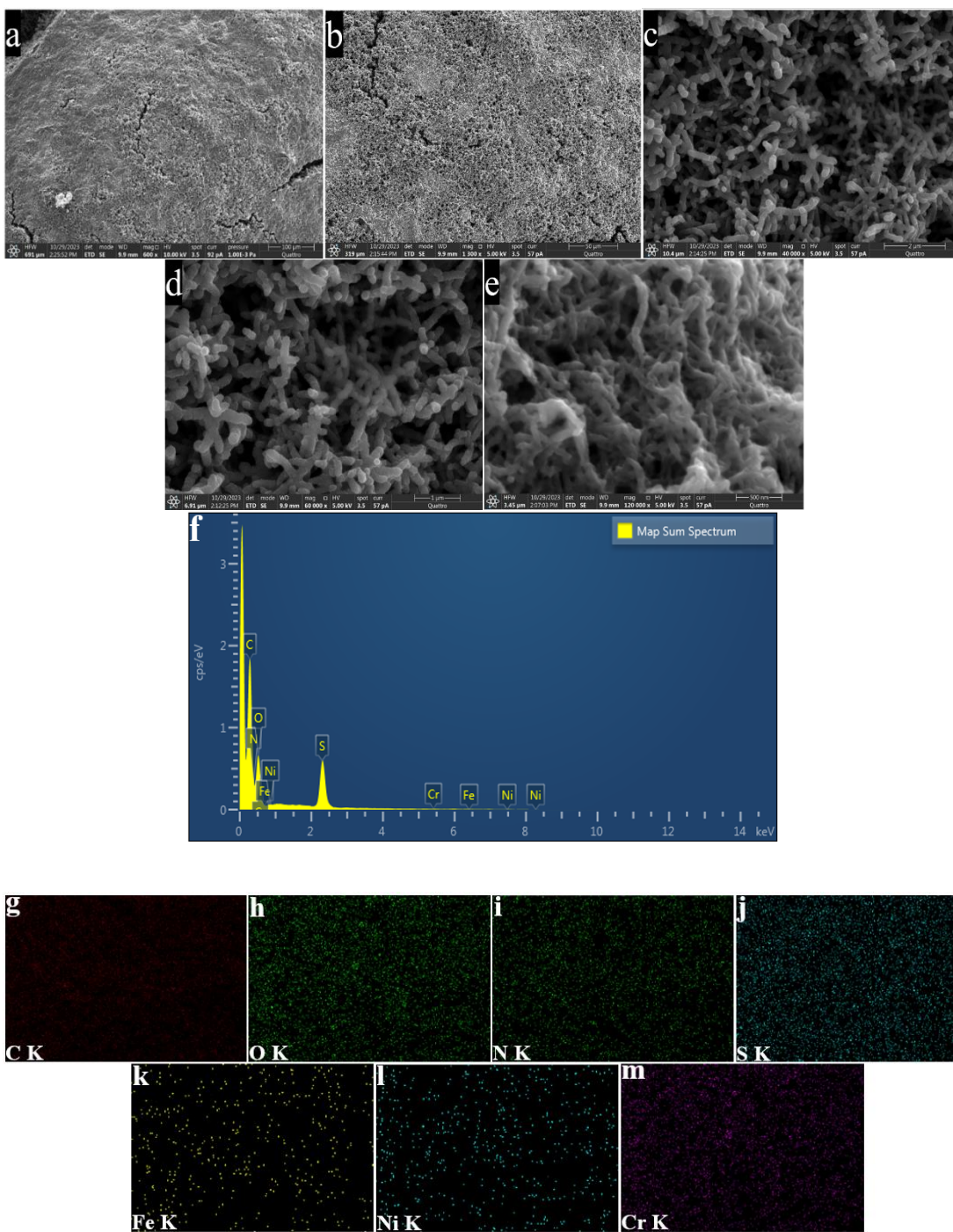


Figure 4.2 (a-e) FESEM images and (f) EDX spectrum of PANI deposited electrochemically for 35 cycles on 20 mesh size steel current collector using CV at 50 mV/s scan rate and voltage window of 0 to 1.3 V obtained at different magnifications, (g-m) elemental mapping of the electrodeposited PANI along with the woven steel mesh current collector.

The nanostructured details of the electropolymerized PANI were meticulously examined using high resolution transmission electron microscopy (HRTEM). Figure 4.3 a-f showcases the TEM images of PANI at various magnifications, with scale bars ranging from 500 nm down to 10 nm. These 2- dimensional images reveal that the rod like PANI which resemble coral as shown by FESEM adopts a sheet-like or film-like morphology. Particularly notable in Figure 4.3 a-d is the way these sheets or films appear to overlap each other, suggesting a layered structure. This overlapping arrangement could be indicative of a high surface area, which is advantageous for electrochemical applications such as supercapacitors. When the magnification is increased to the 10 nm scale, as depicted in Figure 4.3 e, the PANI structure exhibits an amorphous nature. This observation is critical, as amorphous materials often display different electrochemical properties compared to their crystalline counterparts. The amorphous nature of PANI is further corroborated by the selected area electron diffraction (SAED) pattern shown in Figure 4.3 f. The SAED pattern is characterized by highly blurred concentric circles, lacking the distinct crystalline dots typically associated with ordered structures. This detailed TEM analysis provides valuable insights into the microstructural characteristics of electropolymerized PANI. Understanding these features is essential for comprehending and optimizing the material's electrochemical behavior, particularly in applications where surface area and material morphology play pivotal roles in performance.

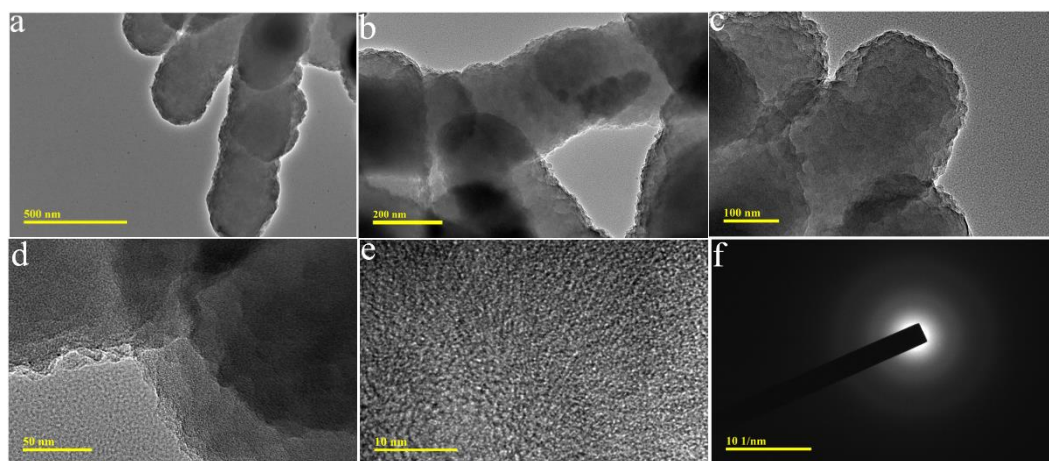


Figure 4.3 (a-d) TEM, and (e) HRTEM images, and (f) SAED pattern of PANI deposited electrochemically for 35 cycles on 20 mesh size steel current collector using CV at 50 mV/s scan rate and voltage window of 0 to 1.3 V.

XRD and FTIR spectroscopy were employed to elucidate the crystal structure and functional group composition of the electrosynthesized PANI. Figure 4.4 illustrates the XRD pattern of the PANI. The XRD analysis revealed three sharp peaks at 2θ values of 20.4° , 25.6° and 43.7° . The reflection peak at 2θ value of 20.4° corresponds to the periodicity that is perpendicular to the chain direction of the polymer. The reflection peak at 2θ value of 25.6° corresponds to the periodicity that runs parallel to the chain direction of the polymer. The reflection peak around 2θ value of 43.7° may be attributed to some scattered planes that run parallel to the direction of the polymer. The single broad peak ranging between 2θ values of 18° and 35° elucidates some amorphous structures in the formed PANI [116], [117]. The presence of some sharp peaks and broad diffraction pattern indicates that some regions within the synthesized PANI possess crystalline structure while some regions possess amorphous structure. Therefore, the analysis that resulted in the finding from SAED showing the amorphous nature of the material would have focused on

the region of the synthesized PANI containing purely the amorphous structure. Figure 4.4 b presents the FTIR spectrum of the electrodeposited PANI, highlighting various absorption bands corresponding to different functional groups and bonding modes in the PANI structure. The peak at 595 cm^{-1} is indicative of the C-N-C bonding mode in the aromatic ring. The absorption at 713 cm^{-1} is attributed to the C-C and C-H bonding in the aromatic ring. Peaks at 861 cm^{-1} and 932 cm^{-1} are characteristic of the out-of-plane C-H bonding in the benzoid ring. The peak at 1166 cm^{-1} suggests the presence of S=O bonding, likely due to sulfate ion doping in the PANI. Stretching vibrations of C-N and C=C in the benzoid ring is represented by peaks at 1293 cm^{-1} and 1433 cm^{-1} , respectively. The peaks at 1547 cm^{-1} and 1692 cm^{-1} are indicative of stretching vibrations of C=C and C=N in the quinoid ring of the PANI structure. The peaks at 2099 cm^{-1} and 2324 cm^{-1} correspond to the vibration bands of methylene $[-(\text{CH}_2)_n-]$ due to symmetric stretch. Lastly, the peak at 3226 cm^{-1} is attributed to the -OH vibration band, which could be a result of residual moisture in the sample [115], [118], [119]. Together, the XRD and FTIR analyses provide a comprehensive understanding of the structural and chemical properties of the electrosynthesized PANI. These insights are crucial for assessing the material's suitability for supercapacitor applications, particularly in terms of its amorphous structure and the specific functional groups that contribute to its electrochemical performance.

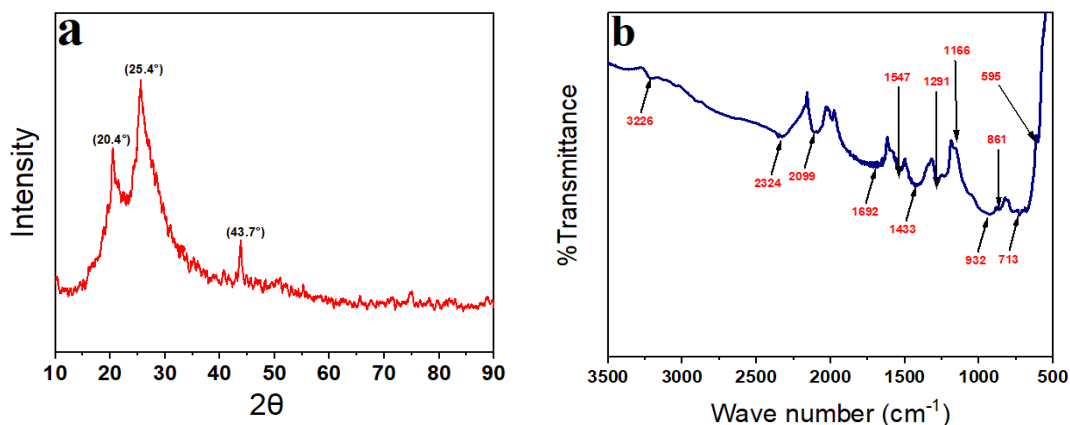


Figure 4.4 (a) XRD pattern and (b) FTIR spectrum of PANI deposited electrochemically for 35 cycles on 20 mesh size steel current collector using CV at 50 mV/s scan rate and voltage window of 0 to 1.3 V.

4.3 Electrochemical evaluation of PANI-coated woven steel meshes in a two-electrode system

To assess the electrochemical efficacy of the fabricated symmetric supercapacitors, a series of tests were conducted in a two-electrode system, utilizing CV, GCD, and EIS techniques. These supercapacitors were composed of electrodes with 35 cycles of PANI deposition, achieved at a voltage window of 0 to 1.3 V. For CV analysis, 50 mV/s was applied to supercapacitors constructed from four different mesh sizes, evaluated over OVWs of 0.0 to 0.4 V, 0.0 to 0.6 V, and 0.0 to 0.8 V. The CV curves recorded over OVW of 0-0.4V (Fig. 4.5 a) reveal that the supercapacitor with 20 mesh size exhibited the highest current response and the largest area under the curve, indicating superior capacitive behavior. Further analysis was conducted using GCD at 1 mA/cm^2 , over the same set of OVWs. GCD profiles recorded over OVW of 0 to 0.4V (Fig. 4.5 b) demonstrate that the discharge time and capacitance increased inversely with the mesh size, with the 20-mesh having the fewest pores per inch. This observation suggests that a larger pore size in the woven steel mesh allows for more uniform deposition of PANI, thereby enhancing the surface area available for electrochemical. This study's comprehensive electrochemical analysis underscores the critical

influence of woven steel mesh pore size on boosting the workability of PANI-based supercapacitors, highlighting the importance of mesh selection and deposition parameters in supercapacitor design. In the study of the electrochemical properties of supercapacitors assembled from 20 mesh size electrodes, CV and GCD measurements were crucial. These tests were performed at three different OVWs (0.0 to 0.4 V, 0.0 to 0.6 V, and 0.0 to 0.8 V) on supercapacitors constructed from electrodes that had undergone varying cycles (5, 15, 25, and 35 cycles) of PANI deposition. The CV results (Fig. 4.5 c) are particularly revealing. They show that the supercapacitor assembled from electrodes modified with 35 cycles of deposition read the highest current density, even though it does not demonstrate the highest area under the CV curve. This highest current measurement is a direct indication of the best delivery of power density, which is the best feature of a supercapacitor [120]. This observation is significant as it directly correlates with enhanced capacitive performance, indicating superior energy storage capability of these electrodes. Similarly, the GCD measurements further validate these findings. As seen in Figure 4.5 d, the supercapacitors with electrodes subjected to 35 deposition cycles exhibit the highest value of capacitance due to the longest discharge time. These results are consistent with the CV findings and reinforce the notion that increased deposition cycles lead to improved supercapacitor performance. These findings highlight a critical aspect of supercapacitor design, the number of deposition cycles in the electrode fabrication process can significantly influence the electrochemical performance of the supercapacitor. The 35-cycle deposition not only enhances the capacitive behavior but also ensures that the supercapacitor can sustain prolonged discharge times, which is pivotal for energy storage applications. This underscores the importance of optimizing electrode fabrication parameters to achieve maximum efficiency and efficacy in supercapacitor performance. In our research on symmetric supercapacitors using PANI deposited on stainless steel with 0.1 M H_2SO_4 electrolyte, an intriguing EDLC-like behavior was observed, contrary to the expected redox activity of PANI. This phenomenon could be attributed to several factors, the interaction between PANI and the woven steel mesh substrate possibly altering redox properties, the influence of PANI layer

thickness on its electrochemical behavior, the specific ionic interaction of the H_2SO_4 electrolyte with PANI, and the surface characteristics of the PANI layer favoring ion adsorption-desorption typical of EDLCs.

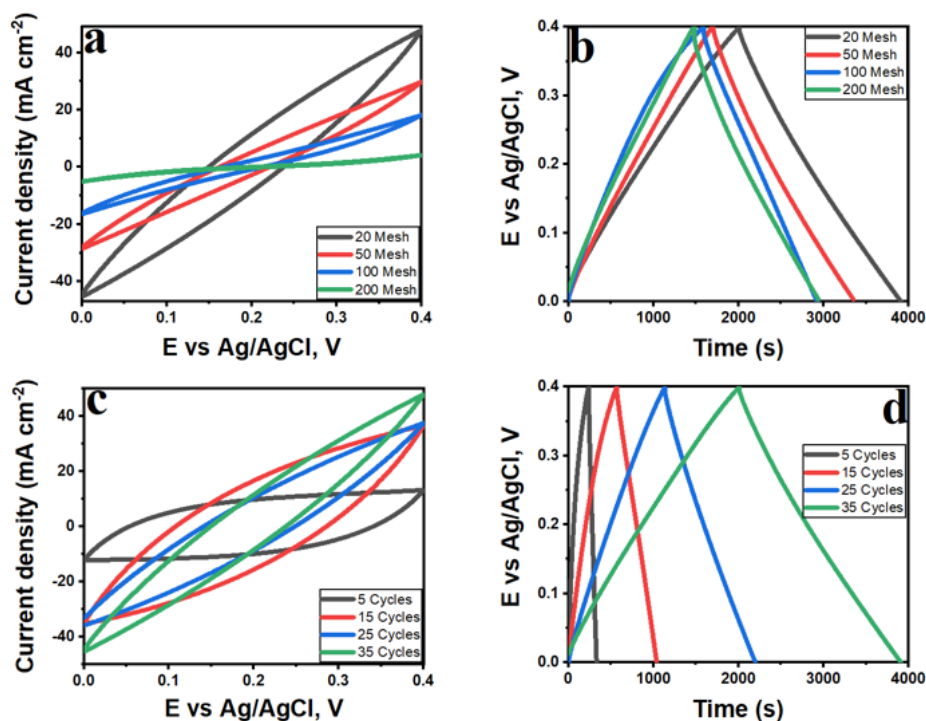


Figure 4.5 (a) CV curves of the optimal electrodes, fabricated from 35 cycles of PANI deposition on 20, 50, 100, and 200 mesh sizes at 0 to 1.3 V, measured at a scan rate of 50 mV/s and a OVW of 0 to 0.4 V. (b) GCD profiles of the same electrodes, measured at a current density of 1 mA/cm² and a OPW of 0 to 0.4 V. (c) CVs of the electrodes made from 5, 15, 25 and 35 cycles of PANI deposition on 20 mesh size at 0 to 1.3 V, measured at a scan rate of 50 mV/s and a OVW of 0 to 0.4V. (d) GCD profiles of the electrodes made from 5 15, 25 and 35 cycles deposition of PANI on 20 mesh size at 0 to 1.3 V, measured at a current density of 1 mA/cm² and a OVW of 0 to 0.4 V.

In-depth electrochemical investigations were carried out on the symmetric supercapacitors assembled from 20 mesh size electrodes, which underwent 35 cycles of PANI deposition at a voltage range of 0.0 to 1.3 V. These analyses were performed using CV and GCD techniques across three OPWs 0.0 to 0.4 V, 0 to 0.6 V, and 0 to 0.8 V. CV measurements were conducted at varied scan rates as 10, 25, 50, 75, and 100 mV/s. The areal capacitance values calculated at the 0.0 to 0.4 V window, using equation (1), for these scan rates were 2502, 1052, 257.5, 245.3, and 163 mF/cm², respectively. At 0.0 to 0.6 V, the values were 3313, 1547, 466.3, 382.4, and 256.8 mF/cm², and at 0.0 to 0.8 V, they were 3237, 1514, 517.5, 377, and 252.9 mF/cm². The CV curves (Fig. 4.6 a) reveal a decrease in the area under the curve as well as decrease in areal capacitance with increasing scan rates (Fig. 4.6 b), which is a typical behavior of supercapacitor [107], [121], [122]. GCD tests were performed at current densities ranging from 1 to 5 mA/cm². The areal capacitance values calculated using equation (2), at 0.0 to 0.4 V were 4730, 3395, 3285, 2860, and 2801.3 mF/cm², respectively. At 0.0 to 0.6 V, the values were 4483.3, 3486.7, 3345, 3233.3, and 3025 mF/cm², while at 0.0 to 0.8V, they were 3575, 3375, 3292.5, 3200, and 3118.8 mF/cm². The GCD curves (Fig. 4.6 c) show a decrease in discharge time with increasing current density, leading to reduced capacitance. This phenomenon is attributed to the limited participation of electrode materials in the redox processes at higher current densities and the insufficient diffusion of electrolyte ions [107], [121], [122]. The equilateral triangular shape of the GCD curves indicates the presence of EDLC in the device [115]. For the optimal supercapacitor (20 mesh, 35 cycle deposition), areal capacitance values at the three OVWs were 4730, 4483, and 3575 mF/cm² for 0 to 0.4 V, 0 to 0.6 V, and 0 to 0.8 V, respectively. Figure 4.6 d displays the Ragone plot indicating

the relation between energy density and power density calculated from GCD data obtained at OPWs of 0.0 to 0.4 V, 0.0 to 0.6 V and 0.0 to 0.8 V. According to the plotted data, as power density increase, energy density decreases [107], [123]. Energy density and power density, calculated using equations (3) and (4), were 105.1, 224.2, and 317.8 $\mu\text{Wh}/\text{cm}^2$ for energy density, and 200, 300, and 400 $\mu\text{W}/\text{cm}^2$ for power density at these OPWs. This comprehensive electrochemical evaluation demonstrates the superior performance of the optimized supercapacitor, highlighting its potential for high-capacity energy storage applications. The decline in capacitance with increasing scan rates and current densities aligns with the fundamental characteristics of supercapacitors, reflecting the intrinsic limitations of the electrode materials and ion diffusion dynamics under varying electrochemical conditions.

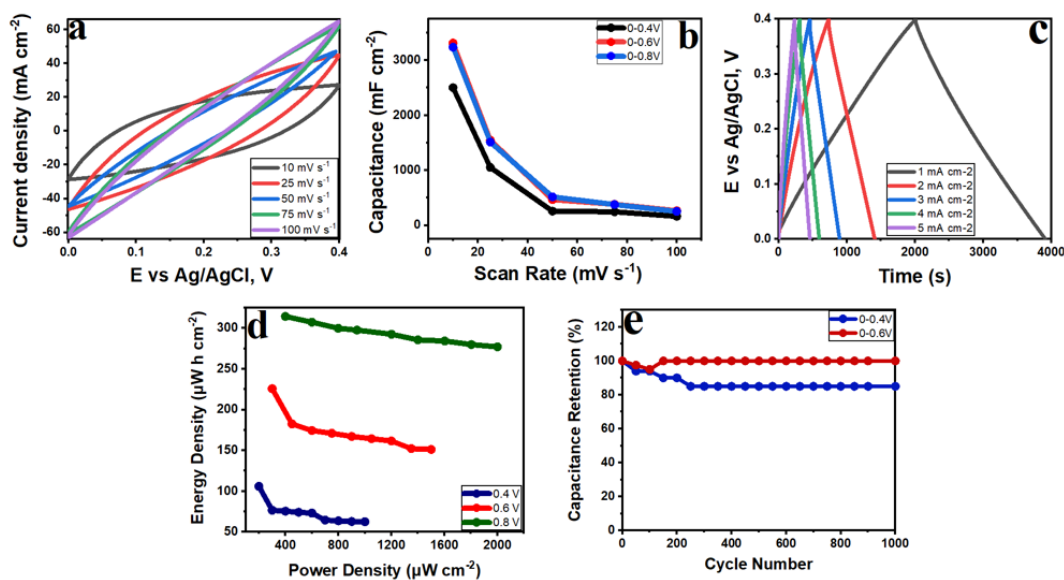


Figure 4.6 (a) CV profiles at different scan rates for the optimal electrode (35 cycle deposition on 20 mesh) at a OPW of 0 to 0.4 V. (b) Capacitance vs. scan rate relationship plot derived from CV data across OPWs 0 to 0.4 V, 0 to 0.6 V, and 0 to 0.8 V. (c) GCD profiles at varying current densities for the optimal electrodes at 0 to 0.4 V. (d) Ragone plot illustrating the energy density-power density relationship for the optimum

supercapacitor, using GCD data at OPWs 0 to 0.4 V, 0 to 0.6 V, and 0 to 0.8 V. (e) Cyclic stability in terms for capacitance retention for 1000 cycles.

The stability of the optimal symmetric supercapacitor, as depicted in (Fig 4.6 e), was rigorously evaluated through a series of extended GCD cycling tests. These tests were conducted over two distinct OPWs, 0.0 to 0.4V and 0.0 to 0.6V, with the device subjected to 1000 GCD cycles at a high current density of 50 mA/cm² to assess its endurance and durability. At the 0.0 to 0.4 V OPW, the supercapacitor exhibited commendable stability, retaining 86% of its initial capacitance after the 1000-cycle test. The initial capacitance measured at this window was 2900 mF/cm², which decreased marginally to 2500 mF/cm² by the end of the test period. This slight decline in capacitance is a normal occurrence in supercapacitor operation due to the gradual degradation of electrode materials and electrolyte under repetitive charging and discharging conditions. Remarkably, at the 0.0 to 0.6 V OPW, the supercapacitor demonstrated exceptional stability, maintaining 100% capacitance retention throughout the test. The initial capacitance at this window was recorded at 3333 mF/cm² and was consistently upheld until the final cycle, indicating no significant loss in storage capability. These results provide compelling evidence of the robustness and reliability of PANI as an electrode material for supercapacitors. The ability of the supercapacitor to sustain its performance over numerous charge-discharge cycles, particularly at higher OPWs, underscores the potential of PANI-based electrodes in long-term energy storage applications. The maintenance of capacitance, especially at the higher OPW of 0.0 to 0.6 V, is a strong indicator of the material's structural integrity and electrochemical stability, key factors for the practical deployment of supercapacitors in various technological domains.

EIS was conducted on the symmetric supercapacitor, optimized with 35 cycles of PANI deposition on a 20-mesh size electrode at a voltage window of 0.0 to 1.3 V. This analysis aimed to elucidate the ionic mobility at the interface between the ionic (electrolyte) and electronic (electrode)

conductors. The Nyquist plot, depicted in (Fig. 4.7 a), illustrates the impedance spectra of the device both before and after the stability test. Measurements spanned a frequency range from 0.01 Hz to 100 kHz, revealing a characteristic semicircle at higher frequencies and a linear response at lower frequencies. The semicircle in the high-frequency region is indicative of the ionic interactions between the electrolyte and the electrodes. In contrast, the straight line in the low-frequency region corresponds to the diffusion of ions within the device. Key parameters extracted from the Nyquist plot include the solution resistance (R_s), charge transfer resistance (R_{CT}), and Warburg impedance (W). R_s , denoted by the initial intersection of the curve with the X-axis, decreased from 2.08 Ω before the stability test to 1.11 Ω after. This reduction suggests enhanced ionic conductivity as a result of repetitive charging and discharging. R_{CT} , represented by the diameter of the high-frequency semicircle, also showed a decrease from 0.42 Ω to 0.24 Ω , indicating improved charge transfer capabilities post-stability test. Conversely, the Warburg Impedance, associated with ion diffusion, increased from 1.66 Ω to 2.00 Ω , reflecting the enhanced ion diffusion into the electrode material after repeated cycling [115]. Figure 4.7 b and c provide comparative Nyquist plots for different supercapacitor configurations. Figure 4.7 b compares the impedance spectra of supercapacitors assembled from various mesh sizes (20, 50, 100, 200 mesh), highlighting the influence of mesh size on impedance characteristics. Figure 4.7 c contrasts the impedance behavior of supercapacitors with different PANI deposition cycles on the optimal 20 mesh size, offering insights into how deposition cycles impact the electrochemical properties of the device. This comprehensive EIS analysis provides critical insights into the electrochemical stability and ion transport mechanisms within the supercapacitor, emphasizing the role of electrode structure and cycling in determining the device's overall performance. Table 4.1 provides a detailed comparison, highlighting how the performance of the PANI-based supercapacitors developed in this study aligns with or surpasses those reported in previous research. This comparison serves to contextualize our advancements within the broader landscape of supercapacitor technology.

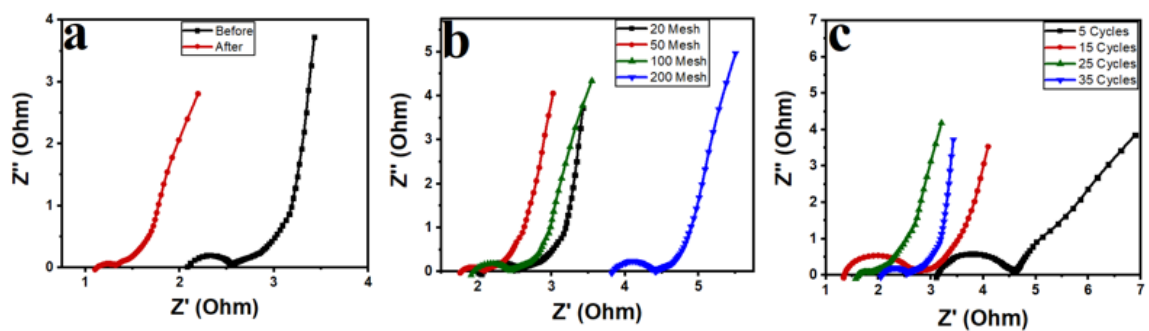


Figure 4.7 (a) EIS Nyquist plot for the optimal supercapacitor with 35 cycle PANI deposition on a 20 mesh electrode, showing impedance characteristics before and after the stability test. (b) Comparative Nyquist plots illustrating impedance variations among supercapacitors with electrodes of different mesh sizes (20, 50, 100, 200 mesh). (c) Nyquist plots contrasting impedance responses of supercapacitors assembled from electrodes with varying PANI deposition cycles on a 20 mesh size stainless steel substrate.

Table 4.1 Comparative workability of PANI-based supercapacitors, offers a side-by-side comparison of the performance characteristics of previously reported PANI based supercapacitors with those developed in this study, highlighting advancements and efficiencies in supercapacitor technology.

Electrode composition	Electrolyte	Current density (mA/cm ²)	Areal capacitance (mF/cm ²)	Energy density (μWh/cm ²)	Power density (μW/cm ²)	Cyclic stability (No. of cycles, %)	Ref.
PANI/SME at 0 to 0.4V	0.1 M H ₂ SO ₄	1	353	26.4	199	...	[115]
PANI/SME at 0 to 0.8V	0.1 M H ₂ SO ₄	1	297	7.8	400	...	[115]
PNA/G	H ₃ PO ₄ /PVA	0.1	230	37.2	...	8000, 86.9	[124]
PANI/CNTs/G/PETC	1 M H ₂ SO ₄	1.5	791	...	...	3000, 76	[125]
VACNT/PANI	1 M Na ₂ SO ₄	0.25	16.17	...	...	3000, 52	[126]
fCC/PANI/rGO	1 M H ₂ SO ₄	0.1	197	...	...	7000, 91.3	[127]
CNT/PANI/hydrogel	H ₂ SO ₄ /PVA	1	184.6	...	...	500, ...	[128]
CNF/CNT, CNT/PANI	H ₃ PO ₄ /PVA	0.5	67.31	...	...	5000, 90	[129]
PANI/rGO	H ₃ PO ₄ /PVA	0.1	23	...	...	2000, 100	[130]
PANI/Graphene nanosheets	H ₂ SO ₄ /PVA	0.5	355.6	320	54	...	[131]
CNFs paper/PANI/rGO	H ₂ SO ₄ /PVA	0.0043	5.86	...	...	1000, 78.3	[132]

PANI/20-mesh stainless steel	0.1 M H ₂ SO ₄	1	4730	317.8	400	1000, 100	This work
PANI/50-mesh stainless steel	0.1 M H ₂ SO ₄	1	4150	271.3	400	...	This work
PANI/100-mesh stainless steel	0.1 M H ₂ SO ₄	1	3885	280	400	...	This work
PANI/200-mesh stainless steel	0.1 M H ₂ SO ₄	1	3768	273.3	400	...	This work

CHAPTER 5

ENHANCED PERFORMANCE OF SYMMETRIC POLYANILINE-BASED SUPERCAPACITOR USING MIXED- SOLVENT DOPANT

5.1 Morphology and structure of polyaniline

5.1.1 SEM

Analysis of Scanning Electron Microscopy of polyaniline was carried out on the as-prepared **PANI-SA** figure 1a and **PANI-SA-PA 3:1** figure (b-d). The morphology between these two prepared PANI are different, depending on the solution in which the polymerization takes place. **PANI-SA** shows an interconnected porous network, resembling coral structure whereas the morphology of **PANI-SA-PA 3:1** indicates that addition of phosphoric acid influenced the surface, transforming it into an agglomeration of nanotubes, forming a noticeable dense structure which explains the higher performance. This higher performance could be attributed to the enhanced nanotube structure as it provides shorter ions diffusion path along with high electrode-electrolyte contact area thereby enhancing accessibility of ions. [133], [134]. EDX analysis was carried out to ascertain the composition of elements comprising the electrodeposited co-doped PANI. As can be seen on the spectrum Figure 1e and elemental mappings figure 1(e-m), the presence of carbon and nitrogen, oxygen, sulfur and phosphorus confirm the formation of PANI, sulphate ion dopant and phosphate ion dopant respectively. The presence of iron, chromium and nickel confirms the elements forming the substrate steel mesh.

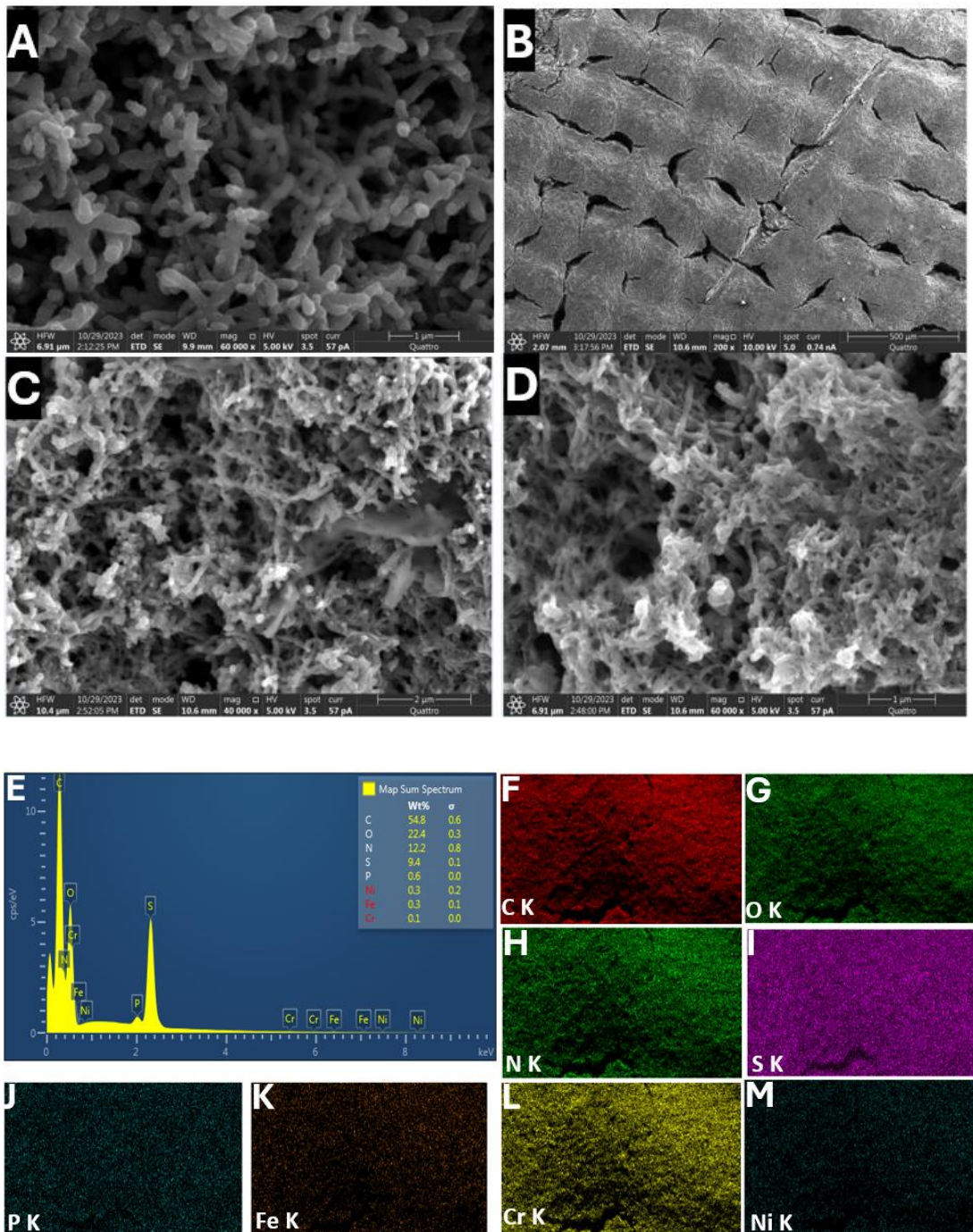


Figure 5.1 FESEM images of PANI-SA (a) and PANI-SA-PA 3:1 (b-d) obtained at different magnifications (e) EDX spectrum of PANI-SA-PA 3:1, (f-m) elemental mapping of the electrodeposited PANI-SA-PA 3:1 along with steel mesh current collector.

5.1.2 TEM

Figure 2(a-c) showcases the HRTEM images of **PANI-SA-PA 3:1** at various magnifications. The structure of the as-prepared **PANI-SA-PA 3:1** resembles film-like morphology, notably appearing to overlap with each other, suggesting a layered structure. This overlapping arrangement could be indicative of a high surface area, which is advantageous for electrochemical applications such as supercapacitors. Selected Area Electron Diffraction (SAED) pattern shown in Figure 2d shows that the electrodeposited PANI is amorphous in nature. The SAED pattern is characterized by highly blurred concentric circles, lacking the distinct crystalline dots typically associated with crystalline structures. This detailed TEM analysis provides valuable insights into the microstructural characteristics of electropolymerized **PANI-SA-PA 3:1**.

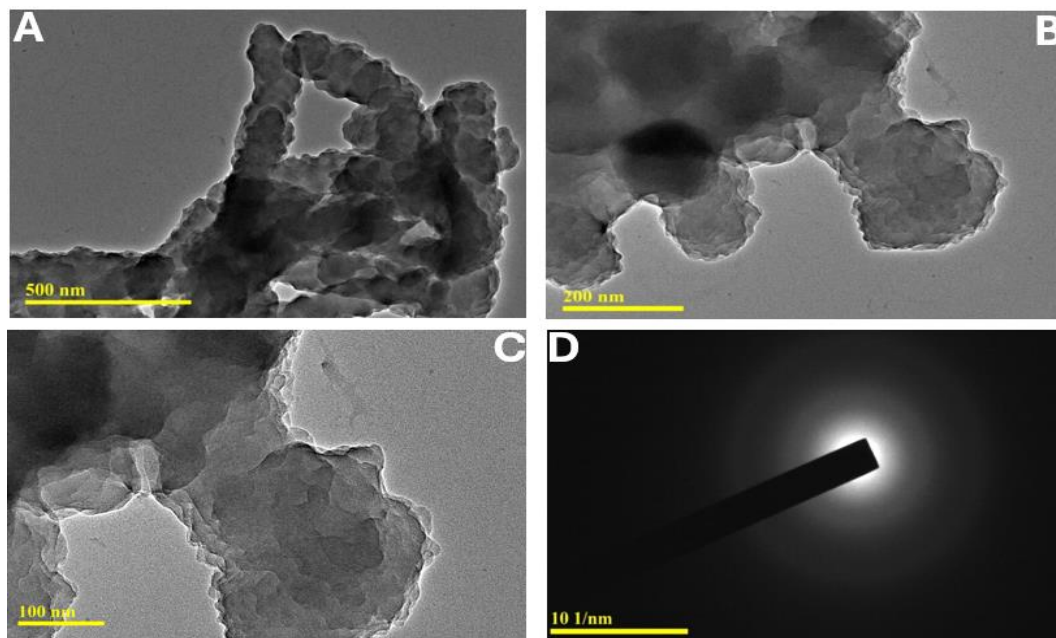


Figure 5.2 (a-c) HRTEM images, and (d) SAED pattern of PANI PANI-SA-PA 3:1

5.1.3 Raman Spectra

The chemical structures of the as-electrodeposited **PANI-SA**, **PANI-SA-PA 1:1** and **PANI-SA-PA 3:1** was analyzed using Raman spectroscopy. The results of the three samples show similar peaks with slight shift and intensity as shown in Figure 3a. The band around 1600 cm^{-1} can be assigned to the C-C stretching vibration of the benzenoid ring [135], [136]. The peak at 1350 is indicative of the $\text{CN}^+\bullet$ vibrations, the bonds associated with the delocalized polaronic structure in the polymer chain [137]. This vibration is a characteristic of the polaronic structure within the polymer, which is essential for its conductivity. The intensity at this band indicates the degree to which the chain was protonated [138]. The peaks at 1490 cm^{-1} and 1260 cm^{-1} can be attributed to C=N stretching vibrations in quinoid and benzene-ring deformation vibrations, respectively. From the peak intensities, it can be inferred that the quinoid-benzenoid existence is of close ratios, except for **PANI-SA-PA 1:1** in which benzenoid seems to predominate. The band around 1175 cm^{-1} can be assigned to the C-H bending vibrations of the semi-quinonoid rings. The band around 420 cm^{-1} corresponds to the out-of-plane deformations of the benzene ring [137], [139].merge [39, 41]

5.1.4 FTIR Spectra

Further analysis was carried out through FTIR technique Figure 3b. There are noticeable differences among spectra of the samples. The peak around 2900 cm^{-1} is more pronounced with **PANI-SA-PA 3:1** sample and can be attributed to the symmetric stretch vibration band of methylene $[-(\text{CH}_2)_n-]$ and methyl $-(\text{CH}_3)$ [14], [140]. The peak around 1490 cm^{-1} and 1294 cm^{-1} are indicative of C-N stretching of benzenoid ring [14], [137]. The peak

around 856 cm^{-1} can be assigned to C–H out of plane bonding in benzenoid ring [140]. The peak around 728 cm^{-1} indicates C–C, C–H bonding mode of aromatic ring [14], [140]. The weak peak around 3225 cm^{-1} more pronounced with **PANI-SA-PA 3:1** can be attributed to hydrogen bonding between amine groups [139], [141]. This shows that **PANI-SA-PA 3:1** has a higher protonation level, which suggests higher electrical performance.

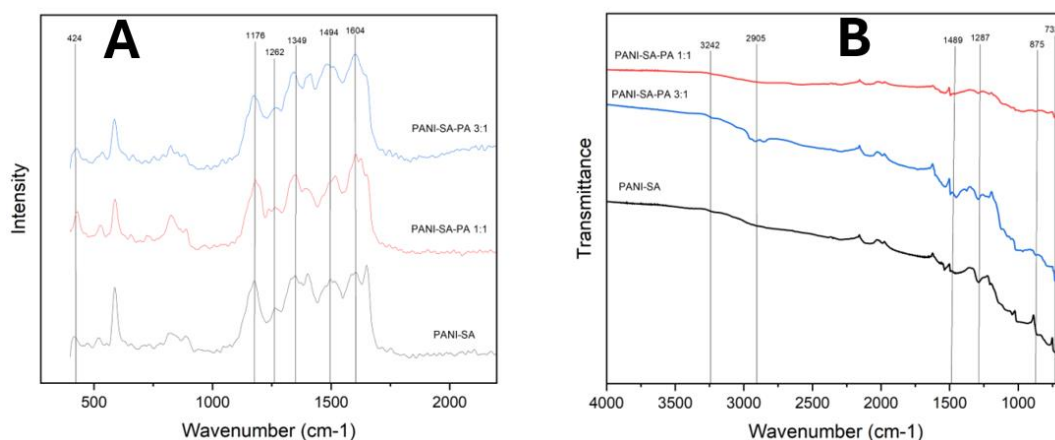


Figure 5.3 (a) Raman spectra and (b) FTIR spectra of PANI-SA, PANI-SA-PA 1:1 and PANI-SA-PA 3:1

5.2 Electrochemical response test of polyaniline modified electrodes in three-electrode set up

The focus of this research is to fabricate a supercapacitor with enhanced performance based on PANI-SM electrodes developed by doubly doping PANI with two mineral acid dopants in an appropriate acidic volume ratio. The aim is to have capacitive improvement in terms of capacitance, energy density and power density through utilization of phosphoric acid as co-dopant along with sulfuric acid dopant. To achieve this aim, PANI was electrodeposited on clean and prepared steel mesh substrate through cyclic voltammetry over a voltage range of 0 to 1V at scan rate of 50 mV/s. This deposition was carried out using three different

aqueous electrodeposition solutions of varying volumes of sulfuric acid and phosphoric acid as highlighted above. Figure 4a shows cyclic voltammograms showing PANI deposition of **PANI-SA-PA 3:1** as the optimum electrode. It can be seen from the curve that current increased with cycling, indicating successful polymerization of active PANI films. The redox peaks that can be seen indicate the electroactivity of PANI [142]. Electrochemical response of the deposited film of polyaniline, confirming electrochemistry and PANI deposition for the three types of modified electrodes was studied using Cyclic Voltammetry in an electrolyte solution of 1M H_3PO_4 over a voltage range of -0.4 V– 0.8 V at scan rate of 50 mV/s [106]. Figure 4b displays the result of the analysis. Looking at voltammograms of **PANI-SA-PA 1:1** and **PANI-SA-PA 3:1**, two oxidation peaks indicating transition from leucoemeraldine to emeraldine forms of the polyaniline and the reduction peaks indicating the reverse process are clearly seen [143], [144]. In terms of **PANI-SA**, the electrochemistry is less pronounced, probably because there is no presence of any trace of H_3PO_4 in the deposition solution, yet redox reversibility is confirmed. It can be deduced that **PANI-SA-PA 3:1** shows the highest response of current density, indicating that it has the tendency of dissipating highest power density, a typical nature of a supercapacitor [120]. It is noteworthy that even though phosphate ions are larger than sulfate ions, using less volume of H_3PO_4 entails presence of smaller number of phosphate ions in the electrodeposition solution. Consequently, H_3PO_4 as co-dopant plays a role in enhancing the morphology, increasing the surface area of PANI, thereby paving a way for higher penetration of electrolytic ions into the system [145].

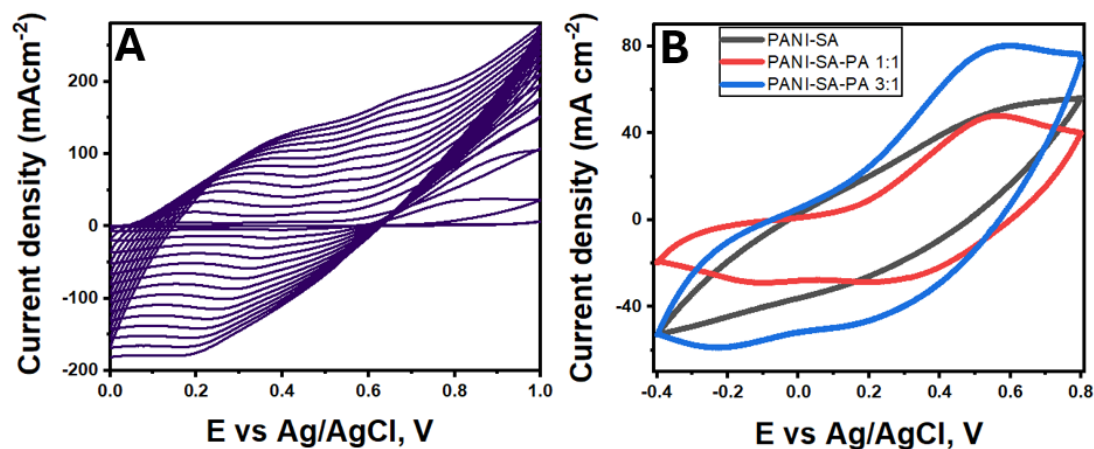


Figure 5.4 (a) CV curves representing 15 cycles of electrochemical deposition of PANI (b) CV curves recorded in three-electrode set up comparing the electrochemical behaviors of PANI deposited based on different ratio of sulfuric acid and phosphoric acid.

5.3 Electrochemical study of the fabricated supercapacitor

Electrochemical performance of the assembled symmetric supercapacitors was studied in a two-electrode set up employing electrochemical techniques of CV, GCD and EIS. CV and GCD were operated over two different voltage ranges of 0 – 0.4V and 0 – 0.8 V. Amplitude voltage of 0.2 V and frequency range of 0.1 Hz to 100 KHz were utilized in EIS measurement. Figure 5a shows CV measurements on the three fabricated supercapacitors recorded at a scan rate of 50 mV/s over a voltage range of 0 to 0.4V. Each of these curves displays EDLC supercapacitive behavior by exhibiting quasi-rectangular shape. Among them, **PANI-SA-PA 3:1** shows the highest area and current response which is confirmation of it having the best performance. Figure 5b shows the GCD profiles of the three fabricated supercapacitors recorded over this voltage range of 0 V to 0.4 V at a current density of 1 mA/cm². **PANI-SA-PA 3:1** displays the longest discharging time, confirming its best

supercapacitive performance. Areal capacitance of these supercapacitors was calculated from GCD data using **Equation 2**, valuing 775.5 mF/cm² for **PANI-SA** supercapacitor, 443.3 mF/cm² for **PANI-SA-PA 1:1** supercapacitor and 933.8 mF/cm² for **PANI-SA-PA 3:1** supercapacitor. Energy density and power density calculated using **Equations 3 and 4** are 17.2 $\mu\text{Wh}/\text{cm}^2$ and 200 $\mu\text{W}/\text{cm}^2$, respectively for **PANI-SA** supercapacitor, 9.9 $\mu\text{Wh}/\text{cm}^2$ and 200 $\mu\text{W}/\text{cm}^2$ respectively for **PANI-SA-PA 1:1** supercapacitor and 20.8 $\mu\text{Wh}/\text{cm}^2$ and 200 $\mu\text{W}/\text{cm}^2$ respectively for **PANI-SA-PA 3:1** supercapacitor. At voltage range of 0 V to 0.8V, the same scan rate of 50 mV/s was maintained for CV measurements and current density of 1 mA/cm² for GCD measurements were maintained. The same trend of performance is followed by the three supercapacitors as seen in both the CV curves Figure 5c and the GCD profiles Figure 5d. In both cases **PANI-SA-PA 3:1** displays the best supercapacitive performance. However, the CV curves show that these supercapacitors undergo pseudocapacitive behavior due to changing shape from quasi-rectangular to a squeezed form, portraying the true nature of PANI as electrode material for Pseudocapacitors [2]. In the same way, areal capacitance of these supercapacitors was calculated from GCD data using **Equation 2** which values at 554.5 mF/cm² for **PANI-SA** supercapacitor, 351.8 mF/cm² for **PANI-SA-PA 1:1** supercapacitor and 766.5 mF/cm² for **PANI-SA-PA 3:1** supercapacitor. Energy density and power density calculated using **Equations 3 and 4** are 49.3 $\mu\text{Wh}/\text{cm}^2$ and 400 $\mu\text{W}/\text{cm}^2$ respectively for **PANI-SA** supercapacitor, 31.3 $\mu\text{Wh}/\text{cm}^2$ and 399.9 $\mu\text{W}/\text{cm}^2$ respectively for **PANI-SA-PA 1:1** supercapacitor and 69.0 $\mu\text{Wh}/\text{cm}^2$ and 405.2 $\mu\text{W}/\text{cm}^2$ respectively for **PANI-SA-PA 3:1** supercapacitor. From the results above, it can be clearly seen that the synergy between sulfuric acid and phosphoric acid with a volumetric ratio of 3:1 is the best towards

enhancing the supercapacitive performance of PANI by showing the highest areal capacitance, energy density and power density.

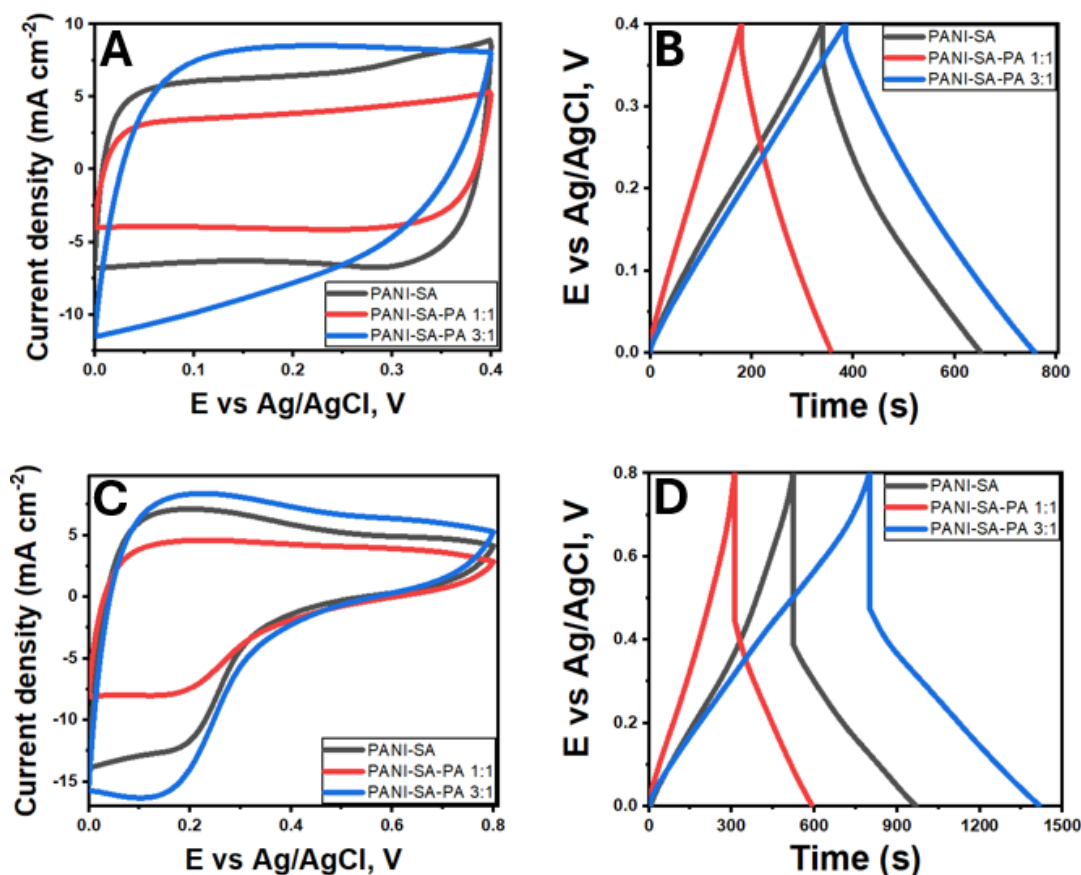


Figure 5.5 (a) CV curves of the three supercapacitors measured at a scan rate of 50 mV/s over voltage range of 0 to 0.4 V. (b) GCD profiles of the same supercapacitors, measured at a current density of 1 mA/cm² over a voltage range of 0 to 0.4 V. (c) CV curves of the three supercapacitors measured at a scan rate of 50 mV/s over a voltage range of 0 to 0.8 V. (d) GCD profiles of the same supercapacitors, measured at a current density of 1 mA/cm² over a voltage range of 0 to 0.8 V.

Further electrochemical analysis was carried out on **PANI-SA-PA 3:1** to confirm the results obtained above and to accentuate further its actual optimum performance. Figure 6a displays CV curves recorded at different scan rates of 10, 50 and 100 mV/s. According to these curves, the integral area increases with increase in the scan rate and the supercapacitor displays more of EDLC behavior than the pseudocapacitive behavior. Capacitance calculated from this data using Equation 2 reveals that the capacitance of this supercapacitor decreases with increasing the scan rate as shown in Figure 6b. The most probable reason for this effect could be due to lower penetration of electrolytic ions at faster voltage scan while at lower voltage scan, the electrolytic ions have sufficient time to diffuse into the system [6], [146]. Over the same voltage range of 0 V to 0.4V, GCD technique was employed to the performance of this supercapacitor at three different current densities of 1, 3 and 5 mA/cm². Figure 6c displays the result of this measurement where discharge time of this device decreases with increasing the current density. Capacitance calculated at the three different current densities reveals that at higher current densities, capacitance decreases. The calculated values of capacitance of this supercapacitor are 933.8 mF/cm², 837.3 mF/cm² and 745.3 mF/cm² at current densities of 1, 3 and 5 mA/cm² respectively. The nearly equilateral triangle of the GCD curves indicates a dominance of EDLC nature with little pseudocapacitive nature. It can be said that at lower current density, electrolytic ions have sufficient time penetrating the electrode material, making it deliver more capacitance [2].

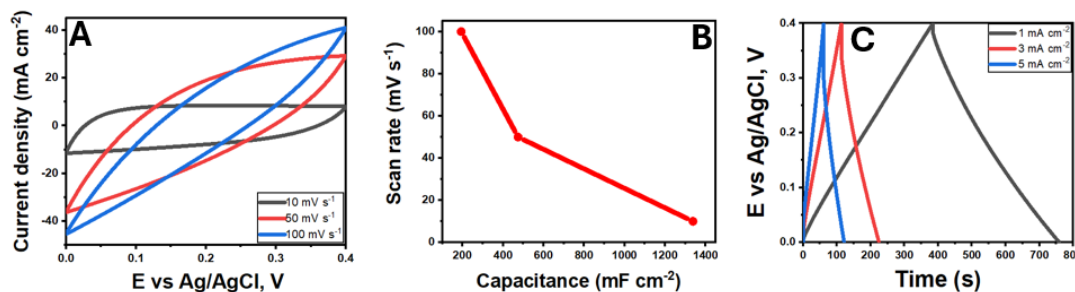


Figure 5.6 (a) CV curves of PANI-SA-PA 3:1 supercapacitor at different scan rates over a voltage range of 0 to 0.4 V. (b) Capacitance vs. scan rate relationship plot derived from CV data over a voltage range of 0 to 0.4 V (c) GCD profiles of the PANI-SA-PA 3:1 supercapacitor at varying current densities over a voltage range of 0 to 0.4 V.

Electrochemical analysis on **PANI-SA-PA 3:1** supercapacitor was also carried out at voltage range of 0 – 0.8V. Figure 7a shows the result of CV measurements taken at scan rates of 10, 50 and 100 mV/s where area under the curve and the current read by this supercapacitor increase with increasing the scan rate. The CV curves in this case display a dominant pseudocapacitive behavior due to redox reaction of PANI, where oxidation peak for oxidation of leucoemeraldine to emeraldine and reduction peak for the reverse process are clearly seen. Figure 7b shows that capacitance of this device decreases with an increase in the applied scan rate. GCD analysis was also carried out at current densities of 1, 3 and 5 mA/cm² as shown in Figure 7c. The values of capacitance calculated were 766.5 mF/cm², 707.9 mF/cm² and 626.3 mF/cm² respectively at 1 mA/cm², 3 mA/cm² and 5 mA/cm². Energy density and power density were both calculated from this GCD data at the three current densities of 1, 3 and 5 mA/cm² using equations 3 and 4 respectively, the result of which was presented in a Ragone plot shown in Figure 8a. According to the Ragone plot, as energy density increases, power density decreases concurring with typical behavior of

supercapacitor [147]. It is noticeable that at voltage range of 0 V to 0.4V this optimum supercapacitor records the highest value of capacitance while at voltage range of 0 V to 0.8V, it records highest values of energy density and power density. Apparently speaking, the practical choice of using this supercapacitor for energy storage application will depend on the purpose it is intended for. This data is presented in Table 5.1.

Table 5.1 Comparing the performance of *PANI-SA-PA 3:1* based on voltage ranges of 0 to 0.4V and 0 to 0.8V

Voltage Range	Current density mA/cm ²	Capacitance mF/cm ²	Energy density μ Wh/cm ²	Power density μ W/cm ²
0 to 0.4V	1	933.8	20.8	
0 to 0.8V	1	766.5	69.0	405.2

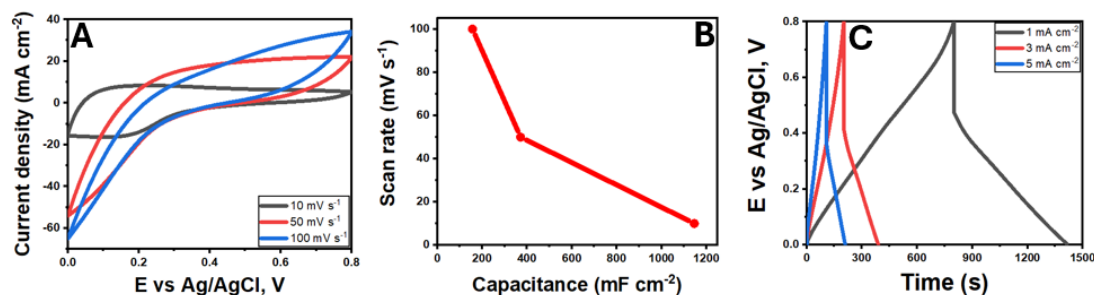


Figure 5.7 (a) CV curves of PANI-SA-PA 3:1 supercapacitor at different scan rates over a voltage range of 0 to 0.8 V. (b) Capacitance vs. scan rate relationship plot derived from CV data over a voltage range of 0 to 0.8 V (c) GCD profiles of the PANI-SA-PA 3:1 supercapacitor at varying current densities over a voltage range of 0 to 0.8 V.

Stability test of the optimum supercapacitor *PANI-SA-PA 3:1* over multiple charge and discharge cycles was carried out. During this analysis, the device was subjected to **1000**

GCD cycles at current density of 10 Ma/cm² operating at voltage range of 0 V – 0.4V. It is revealed according to Figure 8b that there is no significant decrease in the capacitance of this device before and after the stability test which maintains a capacitance retention of 91%. Figure 8c shows Nyquist plots obtained from EIS measurements of the three fabricated supercapacitors while Figure 8d shows Nyquist plots of EIS measurements on the optimum supercapacitor before and after stability test. The essence of this measurement is to bring out the information regarding the mobility of electrolytic ions within the electrochemical system. This ionic mobility takes place at the electrode electrolyte interfaces which is best encoded using equivalent circuit inset on the Nyquist plots. On the Equivalent circuit diagram, R_s is known as solution resistance which entails ionic mobility between the two electrodes within the system, R_{CT} denotes charge transfer resistance which tells about the resistance encountered by the ions while travelling to the electrode surface from the electrolyte and W is the Warburg resistance, which is an indicator of diffusion of the electrolytic ions within the system. C_{dl} is known as double layer capacitance which is the sign to show that the result of the capacitance measurement being carried out on the supercapacitor comes from layers of ions at the electrode electrolyte interface. R_s is determined from the first intersection of the curve with the X-axis of the Nyquist plot while R_{CT} is determined from the diameter of semicircle on the X-axis at high frequency region of the plot. W is determined from the slope of the straight line on the low frequency region of the plot [146]. Comparing the three supercapacitors according to Figure 8c, **PANI-SA-PA 3:1** displays moderate diffusion of ions even though it shows the best supercapacitive performance. Considering its performance according to Fig 8d, the values of R_s , R_{CT} and

W before the stability test are 1.6 Ω , 0.2 Ω and 2.9 Ω respectively while after the test they are 1.3 Ω , 0.2 Ω and 3.0 Ω respectively.

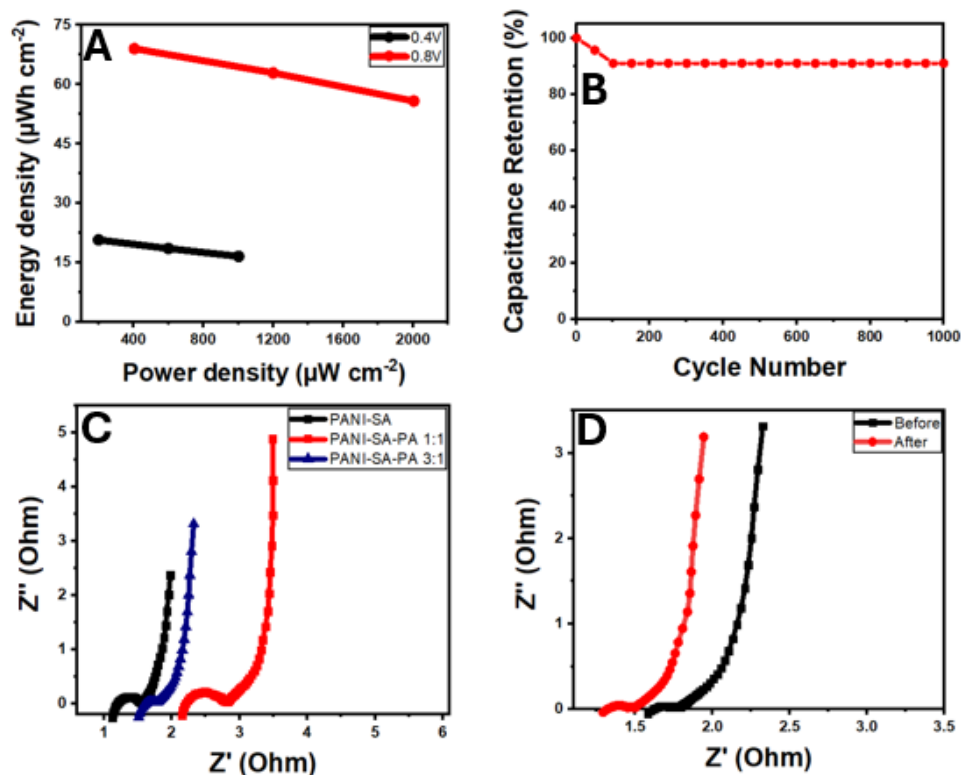


Figure 5.8 (a) Ragone plot illustrating the relationship between energy density and power for PANI-SA-PA 3:1 supercapacitor, using GCD data over voltage ranges of 0 to 0.4 V and 0 to 0.8 V. (b) Plot displaying cyclic stability and capacitance retention by **PANI-SA-PA 3:1** over 1000 cycles. (c) Nyquist plot comparing the ionic mobility within the electrochemical systems of the three supercapacitors (d) Nyquist plots illustrating impedance for **PANI-SA-PA 3:1** supercapacitor showing impedance characteristics before and after the stability test.

This work is compared with other works from literature where the performance of the supercapacitor designed herein in terms of capacitance, energy density, power density is compared in Table 5.2.

Table 5.2 Comparing the performance of PANI-based supercapacitor developed in this work based on dual doping with other supercapacitors previously reported from literature.

Electrode Composition	Electrolyte	Current density (mA/cm ²)	Areal capacitance (mF/cm ²)	Energy density (μWh/cm ²)	Power density (μW/cm ²)	Cyclic stability (No. of cycles, %)	Ref.
PANI-HCl-H ₃ PO ₄	PVA/H ₂ SO ₄	0.5	177.6	-	-	5000, 91.2	[148]
PANI-H ₂ SO ₄ -HClO ₄	PVA/H ₂ SO ₄	0.5	149.3	13.0	400	5000, 93.3	[6]
PANI/Phytic acid	PVA/H ₂ SO ₄	0.5	135.9	49.9	400	10000, 76	[149]
rGO-PANI-CH ₄	PVA/H ₂ SO ₄	0.2	45	-	-	1000, 100	[150]
PANI-GO-H ₂ SO ₄ -DBSA	PVA/H ₂ SO ₄	5	97.38	-	-	93.33	[151]
PANI-H ₂ SO ₄	0.1 M H ₂ SO ₄	1	353	26.4	199	-	[14]
PNA/G	H ₃ PO ₄ /PVA	0.1	230	37.2	...	8000, 86.9	[90]
PANI/Graphene nanosheets	H ₂ SO ₄ /PVA	0.5	355.6	320	54	...	[96]
CNF/CNT, CNT/PANI	H ₃ PO ₄ /PVA	0.5	67.31	...	...	5000, 90	[95]
PANI-H ₂ SO ₄ -H ₃ PO ₄	1M H ₃ PO ₄	1	933.8	69.0	405.2	1000, 91	This work

CHAPTER 6

CONCLUSION AND RECOMMENDATION

The first study presents a comprehensive examination of the impact of porosity of woven steel mesh as a current collector on the performance of supercapacitors, culminating in significant findings. The electropolymerization of PANI on woven steel meshes of four different sizes (20, 50, 100, and 200 mesh) was successfully achieved, with subsequent structural and morphological characterizations via FESEM/EDX, TEM, XRD, and FTIR confirming the uniform deposition of PANI on each mesh. Electrochemical characterization of the prepared electrodes and the assembled supercapacitors was meticulously conducted using CV, GCD, and EIS. Among various electrodeposition cycles tested (5, 15, 25, 35), the 35-cycle deposition emerged as optimal, exhibiting the highest capacitance, energy density, and power density. Analysis of GCD data at a current density of 1 mA/cm^2 across different OPWS (0 to 0.4 V, 0 to 0.6 V, 0 to 0.8 V) allowed for the calculation of key performance metrics. The 20 mesh supercapacitors demonstrated superior performance, with a peak capacitance of 4730 mF/cm^2 at 0 to 0.4 V. The highest energy density and power density for this mesh size were $317.8 \text{ }\mu\text{Wh/cm}^2$ and $400 \text{ }\mu\text{W/cm}^2$, respectively, measured at 0 to 0.8V. Cyclic stability tests on the optimally assembled supercapacitor (20 mesh) revealed remarkable durability, with 100% capacitance retention after 1000 GCD cycles, underscoring the stability and suitability of electropolymerized PANI as a cost-effective and environmentally friendly electrode material for supercapacitor fabrication.

The second study scrutinizes the effect of mixed-dopant PANI towards enhancing the supercapacitor's performance. According to the electrochemical assessment of this study, introducing phosphoric acid into sulfuric acid-based electrodeposition solution of polyaniline can improve the supercapacitive performance of PANI. mixed-dopant PANI demonstrates a desirable nanorod-shaped morphology with a noticeable dense structure which explains better performance. This morphology facilitates shorter ionic diffusion path along with high electrode-electrolyte contact area which enhances easy accessibility of ions. Among the three supercapacitors studied in this work, **PANI-SA-PA 3:1** shows the highest performance, exhibiting areal capacitance of 933.8 mF/cm^2 as compared to that of sulfuric acid doped PANI **PANI-SA** having areal capacitance of 775.5 mF/cm^2 at current density of 1 mA/cm^2 . This best performing supercapacitor can dissipate a high energy density of $69.0 \text{ }\mu\text{Wh/cm}^2$ at a power density of $405.2 \text{ }\mu\text{W/cm}^2$ while retaining 91% of its initial capacitance after 1000 GCD cycles. It is also revealed that volume of phosphoric acid in the electrodeposition solution plays role in the supercapacitive performance of these PANI based supercapacitors. This is highlighted based on the areal capacitance of 351.8 mF/cm^2 read by **PANI-SA-PA 1:1** supercapacitor in which the volume of phosphoric acid in its electrodeposition solution is two times the volume in the electrodeposition solution of **PANI-SA-PA 3:1**.

In conclusion, this investigation not only underscores the critical role of steel mesh porosity and mix-doping of PANI in determining supercapacitor performance but also highlights the promising potential of PANI as a high-performance electrode material. The findings from these studies open avenues for the development of more efficient, durable, and eco-friendly supercapacitors for energy storage applications.

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VITAE

Name | Ahmad Abbas Dalhatu |

Nationality | Nigeria |

Date of Birth | 9/24/1990 |

Email | abbati0857@gmail.com |

Address | No. 10 Kabiru Gote Street by KEDCO Office Rijiyar Zaki
Kano State Nigeria |

Academic Background | Received BSc. Chemistry 2015, from Bayero University
Kano, Kano State Nigeria. P.O. Box 3011 |

| Received MSc. Degree in Chemistry from King Fahd University of Petroleum and
Minerals Dhahran Kingdom of | Saudi Arabia |

Research Interest

Energy Storage

Publications

- Enhancing the performance of supercapacitors through optimized electrodeposition of polyaniline on various woven steel mesh substrates (submitted under review)
- Enhance performance symmetric supercapacitor by electrochemical co-doping of polyaniline with phosphoric acid in sulphuric acid medium (under review)