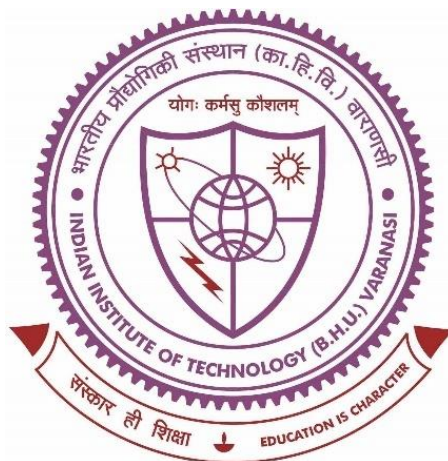


**Electrochemical behaviours of low-cost
sustainable composite materials: Synthesis,
application and optimization studies**



Thesis submitted in partial fulfilment for the

Award of Degree

DOCTOR OF PHILOSOPHY

By

Vikas Kumar Pandey

**DEPARTMENT OF CHEMICAL ENGINEERING &
TECHNOLOGY**

**INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)**

VARANASI-221005

Roll No.: 17041505

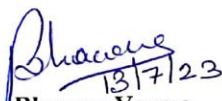
2023

Dedication

I dedicated this Ph.D. thesis to all the people who have directly or indirectly inspired me in my life. I am indebted to my family, teachers, and colleagues for their continuous encouragement and support.

CERTIFICATE

It is certified that the work contained in the thesis titled “**Electrochemical behaviours of low-cost sustainable composite materials: Synthesis, application and optimization studies**” by **Vikas Kumar Pandey** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree. It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy, and SOTA for the award of Ph.D. Degree.


13/7/23
Dr. Bhawna Verma
(Supervisor)

Department of Chemical Engineering & Technology,
Indian Institute of Technology
(Banaras Hindu University),
Varanasi-221005, India

सह प्राध्याप
Associate Professor
रासायनिक अभियंताईयकी एवं प्रौद्योगिकी विभाग
Deptt. of Chemical Engg. & Tech
भारतीय प्रौद्योगिकी संस्थान
Indian Institute of Technology
कशी हिन्दू विश्वविद्यालय
Banaras Hindu University
वाराणसी/Varanasi-22100

DECLARATION BY THE CANDIDATE

I, **Vikas Kumar Pandey**, certify that the work embodied in this Ph.D thesis is my own bonafide work and carried out by me under the supervision of **Dr. Bhawna Verma** for a period from **December 2017 to June 2023** at the Department of Chemical Engineering & Technology, Indian Institute of Technology (Banaras Hindu university), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged, given credit to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any other's work, paragraph, text, data, results, etc. reported in the journals, books, magazines, reports, dissertations, thesis, etc., or available at websites and have not included in this thesis and have not cited as my own work.

Date: 13/07/2023

Place: IIT (BHU), Varanasi

Vikas K. Pandey
Vikas Kumar Pandey

CERTIFICATE FROM THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

Bhawna
13/7/23
Dr. Bhawna Verma
(Supervisor)

Department of Chemical Engineering
& Technology,
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005, India

सह प्राध्यापक
Associate Professor
रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग
Dept. of Chemical Engg. & Tech
भारतीय प्रौद्योगिकी संस्थान
Indian Institute of Technolo
काशी हिन्दू विश्वविद्यालय
Banaras Hindu University
वाराणसी/Varanasi-221005

M.K. Mondal
13/07/23
Prof. M.K Mondal
(Head of the Department)

Department of Chemical Engineering
& Technology,
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005, India

विभागाध्यक्ष/Head
रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग
Dept. of Chemical Engg. & Tech.
भारतीय प्रौद्योगिकी संस्थान/Indian Institute of Technology
काशी हिन्दू विश्वविद्यालय/Banaras Hindu University
वाराणसी/Varanasi-221005

COPYRIGHT TRANSFER CERTIFICATE

Title of Thesis: “**Electrochemical behaviours of low-cost sustainable composite materials: Synthesis, application and optimization studies**”

Candidate’s Name: **Vikas Kumar Pandey**

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the Doctor of Philosophy degree.

Date: 13/07/2023

Place: IIT (BHU), Varanasi

Vikas Kr Pandey
(Vikas Kumar Pandey)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated.

ACKNOWLEDGEMENT

This is a great opportunity to owe immense gratitude to my esteemed supervisor **Dr. Bhawna Verma**, Department of Chemical Engineering & Technology, Indian Institute of Technology (BHU), Varanasi, India for her consistent encouragement, cooperation, and suggestions to improve my research, academic writing, and presentation skills throughout my Ph.D. Her nature and proper direction have provided me an excellent research environment to complete this work.

I owe my personal thanks to **Prof. M.K. Mondal** (Head), Department of Chemical Engineering & Technology, IIT (BHU) for encouraging and providing me all the facilities to carry out my research work.

I would like to express my sincere gratitude to my **RPEC** members **Prof. S. K. Sharma**, Department of Mining Engineering, Indian Institute of Technology (BHU), Varanasi, India, and **Dr. Ravi P. Jaiswal**, Department of Chemical Engineering & Technology, Indian Institute of Technology (BHU), Varanasi, India for all their guidance, encouragement, and support.

I would like to express my sincere thanks to **Prof. V.L.Yadav**, **Prof. H.L.Pramanik**, DPGC convener **Dr. J.P.Chakraborty**, and all the **DPGC** members for their direct or indirect motivation and assistance from different corners during my research work at the institute. Also, I express my sincere thanks to all **faculty members** and **nonteaching staff** of the Department of Chemical Engineering and Technology, Indian Institute of Technology (BHU) for their continued help and co-operation for the completion of this dissertation work.

I also want to acknowledge the In-charge and members of central instrumentation facility (CIF) and office staff of the Chemical Department for their help and support.

I am thankful to all my colleagues, **Dr. Tapas Das**, **Dr. Ahmad Nawaz**, **Mr. Sanjeev Verma**, **Mr. Saurabh Pandey**, **Mr. Ravi Saini**, and **Mr. Gaurav Jaiswal** for their valuable help.

I express my sincere thanks to **Mr. O. P. Patel** for the assistance provided by him during my research work.

I acknowledge the **Ministry of Human Resource Development (MHRD), New Delhi, India** for all the financial support. I am also thankful to the **Indian Institute of Technology (IIT) Varanasi, India**, for providing the laboratory facilities.

Last but not least, I am highly thankful to my Parents; **Mr. Shesh Narain Pandey** and **Mrs. Nirmala Pandey** as well as my wife; **Mrs. Dipali Pandey** and my daughter **Manya** for their continuous support and inspiration throughout the journey.

Date: 13/07/2023

Place: IIT (IIT), Varanasi

Vikas Kr. Pandey
(**Vikas Kumar Pandey**)

Table of Contents

CHAPTER 1: Introduction	1-29
1.1. Introduction.....	2
1.2. Importance of energy storage devices.....	3
1.3. Various electrochemical energy storage and conversion devices.....	4
1.3.1. Conventional electric capacitor	6
1.3.2. Fuel cells.....	8
1.3.3. Batteries.....	10
1.3.4. Supercapacitor.....	11
1.3.5. Other energy storage systems.....	12
1.4. Mechanism of operation of supercapacitors.....	13
1.5. Types of supercapacitors	15
1.5.1. Electric double layer capacitors (EDLC).....	16
1.5.2. Pseudocapacitors	18
1.5.2.1 Underpotential deposition.....	18
1.5.2.2 Redox transitions.....	19
1.5.2.3 Intercalation.....	19
1.5.3. Hybrid supercapacitors.....	20
1.6. Components of a supercapacitor.....	21
1.6.1. Electrode	21
1.6.1.1. Based on conducting polymers.....	21
1.6.1.2. Based on carbon.....	22
1.6.1.3. Based on transition metal oxides.	23
1.6.1.4. Based on perovskite materials.....	23

1.6.2. Electrolyte	23
1.6.3. Separator	25
1.6.4. Current collector	26
1.6.5. Sealants	26
1.7. Advantages of supercapacitors.....	26
1.8. Challenges for supercapacitors.....	28
1.9. Various applications of supercapacitors applications.....	29
1.10. Motivation and scope of work.....	30
CHAPTER 2: Literature review	32-66
2.1. Conducting polymers.....	33
2.2. Polyaniline (PANI).....	35
2.3. Carbon based materials.....	43
2.4. Metal oxides.....	50
2.5. Composite materials.....	53
2.6. Advantages of ternary composite materials.....	60
2.7. Research Gap	61
2.8. Objectives.....	62
CHAPTER 3: Materials, methods, characterization techniques	67-97
3.1. Materials required.....	66
3.2. Synthesis of polyaniline.....	67
3.3. Synthesis of binary metal oxides.....	70
3.4. Synthesis of activated carbon.....	73
3.5. Synthesis of binary composite materials.....	75
3.6. Synthesis of ternary composite materials.....	77

3.7. Fabrication of supercapacitor electrodes.....	79
3.8. Material characterizations.....	81
3.9. Electrochemical characterizations and performance evaluation.....	83
3.10. Experimental design for optimization of ternary composite materials using RSM...96	

CHAPTER 4: Synthesis, application and optimization studies of polyaniline/activated carbon/copper cobaltite based composite material **98-138**

4.1. Introduction	99
4.2. Results and discussions	99
4.2.1. X-ray diffraction.....	99
4.2.2. FTIR.....	101
4.2.3. Morphological analysis.....	103
4.2.4. EDX and elemental mapping.....	104
4.2.5. X-ray photoelectron spectroscopy.....	106
4.2.6. Transmission electron microscopy.....	108
4.3. Electrochemical characterizations.....	109
4.4. Conclusion.....	119
4.5. Central composite design.....	120
4.6. Result and discussion.....	121
4.6.1. Optimization of ternary composite material based on RSM.....	121
4.6.2. X-ray diffraction	127
4.6.3. FTIR.....	128
4.6.4. Morphological analysis.....	129
4.6.5. EDX and elemental mapping.....	130
4.6.6. Electrochemical characterizations.....	132
4.7. Conclusion.....	137

CHAPTER 5: Synthesis, application and optimization studies of polyaniline/activated carbon/cobalt ferrite based composite material **139-177**

5.1. Introduction	141
5.2. Results and discussions	141
5.2.1. X-ray diffraction.....	141
5.2.2. FTIR.....	143
5.2.3. Morphological analysis.....	143
5.2.4. EDX and elemental mapping.....	144
5.2.5. X-ray photoelectron spectroscopy.....	146
5.2.6. Transmission electron microscopy.....	148
5.3. Electrochemical characterizations.....	149
5.4. Conclusion.....	159
5.5. Central composite design.....	159
5.6. Result and discussion.....	160
5.6.1. Optimization of ternary composite material based on RSM.....	160
5.6.2. X-ray diffraction	165
5.6.3. FTIR.....	166
5.6.4. Morphological analysis.....	168
5.6.5. EDX and elemental mapping.....	168
5.6.6. Electrochemical characterizations.....	170
5.7. Conclusion.....	176

CHAPTER 6: Synthesis, application and optimization studies of polyaniline/activated carbon/copper ferrite based composite material **178-216**

6.1. Introduction	179
6.2. Results and discussions	179
6.2.1. X-ray diffraction.....	179
6.2.2. FTIR.....	181
6.2.3. Morphological analysis.....	182
6.2.4. EDX and elemental mapping.....	183

6.2.5. X-ray photoelectron spectroscopy.....	185
6.3. Electrochemical characterizations.....	187
6.4. Conclusion.....	196
6.5. Central composite design.....	197
6.6. Result and discussion.....	198
6.6.1. Optimization of ternary composite material based on RSM.....	198
6.6.2. X-ray diffraction	203
6.6.3. FTIR.....	204
6.6.4. Morphological analysis.....	206
6.6.5. EDX and elemental mapping.....	206
6.6.6. Electrochemical characterizations.....	209
6.7. Comparison of electrochemical properties optimized ternary composite materials.	214
6.8. Conclusion.....	216
CHAPTER 7: Conclusion	217-230
7.1. Conclusion.....	218
7.2. Future studies.....	221
7.3. Commercial and techno-economic aspects.....	224
7.4. Cost comparison of supercapacitor materials.....	227
References	231-251
Appendix	252-255
Publications	256

List of figures

Fig 1.1: Ragone plots for various energy storage devices.....	4
Fig 1.2: Charge storage mechanism in conventional capacitors.....	7
Fig 1.3: Proton exchange membrane fuel cell	9
Fig 1.4: Illustration of the working mechanism of a battery.....	10
Fig 1.5: Double layer models proposed by Helmholtz, Gouy-Chapman, and Stern.....	14
Fig 1.6: Illustration of an electrical double-layer capacitance.....	17
Fig 1.7: Different types of redox mechanisms for pseudocapacitance.....	19
Fig 1.8: Classification of electrolytes for supercapacitors.....	24
Fig 2.1: Different conducting polymers used for supercapacitor applications.....	33
Fig 2.2: Different redox states of polyaniline.....	34
Fig 3.1: (a) Schematic diagram and (b) Experimental set-up for the synthesis of..... polyaniline.....	62-63
Fig 3.2: Flow diagram for synthesis of polyaniline.....	63
Fig 3.3: (a) Schematic diagram, (b) laboratory set-up, and (c) flow-diagram for the synthesis of binary metal oxides.....	65-66
Fig 3.4: (a) Flow diagram and (b) laboratory reactor set-up for synthesis of AC.....	67
Fig 3.5: Flow-diagram for the synthesis of binary composite materials.....	69
Fig 3.6: Flow-diagram for the synthesis of ternary composite materials.....	71
Fig 3.7: (a) a single electrode and (b) a symmetric supercapacitor device.....	73
Fig 3.8: (a) Three electrode and (b) two electrode cell configurations	77
Fig 3.9: (a) Schematic diagram of experimental set-up, (b) experimental set-up used in the laboratory for electrochemical characterization.....	78
Fig 4.1: XRD patterns of pristine PANI, binary PANI/AC, binary PANI/CuCo, and ternary PANI/AC/CuCo.....	99

Fig 4.2: FTIR patterns of pristine PANI, binary PANI/AC, binary PANI/CuCo, and ternary PANI/AC/CuCo.....	100
Fig 4.3: FESEM micrographs of (A) PANI, (B) PANI/AC, (C) PANI/CuCo, and (D) PANI/AC/CuCo.....	102
Fig 4.4: EDX analysis of (A) PANI, (B) PANI/AC, (C) PANI/CuCo, and (D) PANI/AC/CuCo.....	103
Fig 4.5: Elemental mapping of ternary composite material PANI/AC/CuCo.....	104
Fig 4.6: (A) XPS survey scan of PANI, PANI/AC, PANI/CoF, PANI/AC/CoF, (B) to (F) high-resolution spectra for C1s, N1s, O1s, Cu2p and Cu2p,	106
Fig. 4.7: (A) to (D) TEM micrographs of ternary composite material PANI/AC/CuCo at different resolutions.....	107
Fig. 4.8: (A) 3E CV of prepared materials, (B) 3E CV of ternary PANI/AC/CuCo at varying scan rates, (C) 2E CV of prepared materials, (D) 2E CV of ternary PANI/AC/CuCo at varying scan rates from 1-20 mVs ⁻¹	108
Fig. 4.9: GCD characteristics of (A) PANI, PANI/AC, PANI/CuCo, and PANI/AC/CuCo at 1 A/g, (B) ternary PANI/AC/CuCo at varying current density from	112
Fig. 4.10: (A) Ragone plot for the prepared samples, (B) 3E specific capacitance values at different values of voltammetric scan rates, (c) current density vs. coulombic efficiency, (D) Capacitance retention curve.....	113
Fig. 4.11: (A) Electrochemical impedance spectra (EIS) in the complex plane (B) Admittance plots in the complex plane. (C) normalized impedance Z vs. frequency, and (D) normalized admittance vs. frequency.....	116
Fig. 4.12: (A) normalized capacitance C vs. freq, and (B) phase of Z (ϕ) vs. frequenc.	117
Fig. 4.13: (A) Predicted vs. actual response, (B) 3D response surface curve, and (C) contour plot for AC (wt %) vs. CuCo (wt%)	125

Fig. 4.14	XRD patterns for the optimized ternary composite PANI/AC/CuCo.....	125
Fig. 4.15:	FTIR spectra for the optimized ternary composite PANI/AC/CuCo.....	125
Fig. 4.16:	SEM micrographs for the optimized ternary composite PANI/AC/CuCo.....	128
Fig. 4.17:	EDX analysis for the optimized ternary composite PANI/AC/CuCo.....	129
Fig. 4.18:	Elemental mapping for the optimized ternary composite PANI/AC/CuCo.....	130
Fig. 4.19:	(A) 3E CV, (B) 3E CV at varying scan rates, (C) 2E CV, (D) 2E CV of ternary at varying scan rates for the optimized ternary composite PANI/AC/CuCo.....	131
Fig. 4.20:	(A) 2E galvanostatic charge-discharge (B) 2E galvanostatic charge-discharge at varying current density for the optimized ternary composite PANI/AC/CuCo.....	132
Fig. 4.21:	(A) Ragone plot for the prepared samples, (B) 3E specific capacitance values at different values of voltammetric scan rates, (c) current density vs. coulombic efficiency, (D) Capacitance retention curve.....	133
Fig. 4.22:	(A) Electrochemical impedance spectra (EIS) in the complex plane (B) Admittance plots in the complex plane. (C) normalized impedance $ Z $ vs. freq, (D) normalized admittance $ Y $ vs. frequency.....	135
Fig. 4.23:	(A) normalized capacitance $ C $ vs. freq, and (B) phase of $ Z $ (ϕ) vs. frequency..	136
Fig 5.1:	XRD patterns of pristine PANI, binary PANI/AC, binary PANI/CoF, and ternary PANI/AC/CoF.....	140
Fig 5.2:	FTIR spectra of pristine PANI, binary PANI/AC, binary PANI/CoF, and ternary PANI/AC/CoF.....	141
Fig. 5.3:	FESEM micrographs of (A) PANI, (B) PANI/AC, (C) PANI/CoF, and (D) PANI/AC/CoF.....	143

Fig. 5.4: EDX analysis of (A) PANI, (B) PANI/AC, (C) PANI/CoF, and (D) PANI/AC/CoF.....	144
Fig. 5.5: Elemental mapping of ternary composite material PANI/AC/CoF.....	145
Fig 5.6: (A) XPS survey scan of PANI, PANI/AC, PANI/CoF, PANI/AC/CoF, (B) to (F) high-resolution spectra for C1s, N1s, O1s, Co2p and Fe2p,	147
Fig 5.7: (A) to (D) TEM micrographs of ternary composite material PANI/AC/CoF	147
Fig 5.8: (A) 3E CV of prepared materials, (B) 3E CV of ternary PANI/AC/CoF at varying scan rates, (C) 2E CV of prepared materials, (D) 2E CV of ternary PANI/AC/CoF at varying scan rates	149
Fig 5.9: GCD characteristics of (A) PANI, PANI/AC, PANI/CoF, and PANI/AC/CoF at 1 A/g, (B) ternary PANI/AC/CoF at varying current density	151
Fig 5.10. (A) Ragone plot for the prepared samples, (B) Comparison of 2E and 3E specific capacitance values at different values of voltammetric scan rates, (c) current density vs. coulombic efficiency, (D) Capacitance retention curve.....	153
Fig 5.11: (A) Electrochemical impedance spectra (EIS) in the complex plane (B) Admittance plots in the complex plane. (C) normalized impedance $ Z $ vs. frequency, (D) normalized admittance vs. frequency.....	154
Fig. 5.12: (A) normalized capacitance $ C $ vs. freq, and (B) phase of $ Z $ (ϕ) vs. frequency....	156
Fig. 5.13: (A) Predicted vs. actual response, (B) 3D response surface curve, and (C) contour plot for AC (wt %) vs. CoF (wt%) as a function of specific capacitance.....	164
Fig. 5.14: XRD patterns for the optimized ternary composite PANI/AC/CoF.....	165
Fig. 5.15: FTIR spectra for the optimized ternary composite PANI/AC/CoF.....	166
Fig. 5.16: SEM micrographs for the optimized ternary composite PANI/AC/CoF.....	167
Fig. 5.17: EDX spectra of the optimized ternary composite PANI/AC/CoF.....	168
Fig. 5.18: Elemental mapping for the optimized ternary composite PANI/AC/CoF.....	169

Fig 5.19: (A) 3E CV (B) 3E CV at varying scan rates, (C) 2E CV (D) 2E CV of ternary at varying scan rates for the optimized ternary composite PANI/AC/CoF.....170

Fig 5.20: (A) 2E galvanostatic charge-discharge (B) 2E galvanostatic charge-discharge at varying current density for the optimized ternary composite PANI/AC/CoF.....171

Fig 5.21: (A) Ragone plot, (B) 3E specific capacitance values at different values of voltammetric scan rates, (c) current density vs. coulombic efficiency, (D) Capacitance retention curve for the optimized ternary composite PANI/AC/CoF.....172

Fig 5.22: (A) Electrochemical impedance spectra (EIS) in the complex plane (B) Admittance plots in the complex plane. (C) normalized impedance $|Z|$ vs. frequency, (D) normalized admittance $|Y|$ vs. frequency for the optimized ternary composite PANI/AC/CoF.....174

Fig 5.23: (A) normalized capacitance $|C|$ vs. freq, and (B) phase of $|Z|$ (ϕ) vs. freq of the optimized ternary composite PANI/AC/CoF.....175

Fig 6.1: XRD patterns of pristine PANI, binary PANI/AC, binary PANI/CuF, and ternary PANI/AC/CuF.....179

Fig 6.2: FTIR spectra of pristine PANI, binary PANI/AC, binary PANI/CuF, and ternary PANI/AC/CuF.....180

Fig 6.3: FESEM micrographs of (A) PANI, (B) PANI/AC, (C) PANI/CuF, and (D) PANI/AC/CuF.....182

Fig 6.4: EDX analysis of (A) PANI, (B) PANI/AC, (C) PANI/CuF, and (D) PANI/AC/CuF183

Fig 6.5: Elemental mapping of ternary composite material PANI/AC/CuF.....184

Fig 6.6: (A) XPS survey scan of PANI, PANI/AC, PANI/CuF, PANI/AC/CuF, (B) to (F) high-resolution spectra for C1s, N1s, O1s, Cu2p and Fe2p.....185

Fig 6.7: (A) 3E CV of prepared materials, (B) 3E CV of ternary PANI/AC/CuF at varying scan rates, (C) 2E CV of prepared materials, (D) 2E CV of ternary PANI/AC/CuF at varying scan

rates	187
Fig. 6.8: GCD characteristics of (A) PANI, PANI/AC, PANI/CuF and PANI/AC/CuF at 1 A/g, (B) ternary PANI/AC/CuF at varying current density from 1 A/g to 20 A/g.....	189
Fig. 6.9: (A) Ragone plot, (B) specific capacitance values at different values of voltammetric scan rates, (c) current density vs. coulombic efficiency, (D) Capacitance retention curves for the prepared samples.....	190
Fig 6.10: (A) Electrochemical impedance spectra (EIS) in the complex plane (B) Admittance plots in the complex plane. (C) normalized impedance $ Z $ vs. freq, (D) normalized admittance vs. frequency.....	193
Fig. 6.11: (A) normalized capacitance $ C $ vs. freq, and (B) phase of $ Z $ (ϕ) vs. freq for the prepared samples.....	194
Fig. 6.12: (A) Predicted vs. actual response, (B) 3D response surface curve, and (C) contour plot for AC (wt %) vs. CuF (wt%) as a function of specific capacitance	201
Fig. 6.13: XRD patterns of the optimized ternary composite PANI/AC/CuF.....	202
Fig. 6.14: FTIR spectra of the optimized ternary composite PANI/AC/CuF.....	203
Fig. 6.15: SEM micrographs of the optimized ternary composite PANI/AC/CuF.....	204
Fig. 6.16: EDX spectra for the optimized ternary composite PANI/AC/CuF.....	205
Fig. 6.17: Elemental mapping for the optimized ternary composite PANI/AC/CuF.....	206
Fig 6.18: (A) 3E CV, (B) 3E CV at varying scan rates, (C) 2E CV, (D) 2E CV at varying scan rates for the optimized ternary composite PANI/AC/CuF.....	207
Fig 6.19: (A) 2E galvanostatic charge-discharge (B) 2E galvanostatic charge-discharge at varying current density for the optimized ternary composite PANI/AC/CuF.....	208
Fig 6.20. (A) Ragone plot, (B) 3E specific capacitance values at different values of voltammetric scan rates, (c) current density vs. coulombic efficiency, (D) Capacitance retention curve for the optimized ternary composite PANI/AC/CuF.....	209

Fig 6.21: (A) Electrochemical impedance spectra (EIS) in the complex plane (B) Admittance plots in the complex plane. (C) normalized impedance $|Z|$ vs. frequency, (D) normalized admittance $|Y|$ vs. frequency for the optimized ternary composite PANI/AC/CuF.....211

Fig 6.22: (A) normalized capacitance $|C|$ vs. frequency, and (B) phase of $|Z|$ (ϕ) vs. frequency of the optimized ternary composite PANI/AC/CuF.....212

Fig 6.23: Comparison of CV curves for optimized PANI/AC/CuCo, PANI/AC/CoF, and PANI/AC/CuF.....213

Fig. 7.1: Techno-commercial maturity of various energy storage systems (Source: Schlumberger Business Consulting (SBC) Energy Institute).....222

Fig. 7.2: (a) Applications of Supercapacitors (SCs) in India. (b) Optimistic and pessimistic forecast for market penetration of supercapacitors in India.....224

List of Tables

Table 1.1 Important features and limitations of batteries, supercapacitors, and conventional capacitors.....	12
Table 2.1: Electrochemical properties of polyaniline based supercapacitors.....	37
Table 2.2: Electrochemical properties of various carbon based materials.....	44
Table 2.3: Electrochemical properties of metal oxides for supercapacitors.....	48
Table 2.4: Electrochemical properties of various composites for supercapacitors.....	54
Table 2.5: Electrochemical properties of various composite hybrid supercapacitor electrodes and devices.....	53
Table 3.1: Specifications of the chemical compounds.....	60
Table 3.2: Experimental details for the synthesis of binary composites.....	69
Table 3.3: Experimental details of the synthesis of ternary composites.....	71
Table 3.4: Characterization techniques used in the present study.....	73
Table 3.5: Various electronic circuit components and their properties.....	87
Table 3.6: The experimental range and levels of respective independent factors for central composite design.....	88
Table 4.1: The values of specific capacitance (C_{SP}), specific energy-density (E_{SP}), and specific power-density (P_{SP}) for various prepared samples.....	114
Table 4.2: The experimental range and level of respective independent factors for central composite design.....	120
Table 4.3: The experimental data and response values obtained by central composite design.....	121

Table 4.4: ANOVA Response surface quadratic model for specific capacitance.....	122
Table 4.5: The values of specific capacitance (C_{SP}), specific energy-density (E_{SP}), and specific power-density (P_{SP}) for the optimized ternary composite PANI/AC/CuCo.....	134
Table 5.1: The values of specific capacitance (C_{SP}), specific energy (E_{SP}), and specific power density (P_{SP}) for different synthesized materials.....	152
Table 5.2: Level of activated carbon (AC) and cobalt ferrite (CoF) for central composite design.....	159
Table 5.3: The experimental data and response values obtained by central composite design.....	159
Table 5.4: ANOVA Response surface quadratic model for specific capacitance.....	160
Table 5.5: The values of specific capacitance (C_{SP}), specific energy-density (E_{SP}), and specific power-density (P_{SP}) for various prepared samples.....	173
Table 6.1: The values of specific capacitance (C_{SP}), specific energy (E_{SP}), and specific power density (P_{SP}) for different synthesized materials.....	191
Table 6.2: Level of activated carbon (AC) and copper ferrite (CuF) for central composite design.....	196
Table 6.3: The experimental data and response values obtained by central composite design.....	197
Table 6.4: ANOVA Response surface quadratic model for specific capacitance.....	198
Table 6.5: The values of specific capacitance (C_{SP}), specific energy-density (E_{SP}), and specific power-density (P_{SP}) for optimized ternary composite PANI/AC/CuF.....	210
Table. 7.1: Cost comparison for feasibility of synthesized ternary composite materials in this work.....	221

Table. 7.2: Comparison of cost and type of supercapacitor materials based on electrochemical properties.....225

List of Abbreviations and Symbols

Abbreviation	Nomenclature
EDLC	Electrical double layer capacitance
SC	Supercapacitor
TEABF ₄	Tetraethylammonium tetrafluoroborate
CAN	Acetonitrile
EMIM	1-ethyl-3-methylimidazolium
PEO	Polyethylene oxide
PVA	Polyvinyl alcohol
PANI/PA	Polyaniline
PPY	Polypyrrole
PEDOT	Poly 3,4-ethylenedioxythiophene
ST	Synthesis temperature (°C)
DBSA	4-Dodecylbenzenesulfonic acid
CSA	Camphorsulfonic acid
PTSA	Para toluene sulfonic acid
APS	Ammonium persulfate
ED	Energy density
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
FESEM	Field emission scanning electron microscopy
EDX	Energy dispersive X-ray spectroscopy
CV	Cyclic voltammetry
CD	Charge-discharge
EIS	Electrochemical impedance spectroscopy
AN	Aniline
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
SPEEK	Sulfonated polyether ether ketone
NMP	N-Methyl-2-pyrrolidone
DMSO	Dimethyl sulfoxide

PB	Prussian blue
MWCNT	Multi-walled carbon nano tubes
SWCNT	Single-walled carbon nano tubes
BCN	Boron carbonitrides
ACF	activated carbon fibers
CNF	carbon nanofibers
CGNR	Curly graphene nanoribbon
CF	Carbon fiber
NPCNF	Nitrogen, phosphorous codoped carbon nanofiber
g-C ₃ N ₄	Graphitic carbon nitride
EP	Electrochemical polymerization
IP	Interfacial polymerization
EDP	electrodeposition
GD	Galvanostatic deposition
ECD	Electrochemical deposition
COP	Chemical oxidative polymerization

Symbol	Nomenclature
C _{SP}	Specific Capacitance [Farad (F)]
Q	Electric charge (Coulomb)
V	Potential [Volt (V)]
ε _o	Permittivity of free space (8.854×10 ⁻¹² F/m)
A	Area of plate (m ²)
D	Distance between plates (m)
ε	Permittivity of the dielectric material
E	Energy stored [Watt.hour (Wh)]
P _{max}	Maximum power [Watt (W)]
C _{sp}	Specific capacitance (F/g)
D	Average crystallite size (nm)
K	Scherrer's constant
λ	Wavelength of X-ray (Å)
β _L	Full width at half maximum (radians)

Θ	Bragg angle
I	Current (A)
M	Mass (g)
t_c	Charging time (s)
t_d	Discharging time (s)
ΔV	Potential difference (V)
E_{sp}	Specific energy (Wh/kg)
P_{sp}	Specific power (W/kg)
Rct	Charge transfer resistance (Ω)
f_k	Knee frequency (Hz)
τ_r	Relaxation time (s)

List of Abbreviations and Symbols

Abbreviation	Nomenclature
EDLC	Electrical double layer capacitance
SC	Supercapacitor
TEABF ₄	Tetraethylammonium tetrafluoroborate
CAN	Acetonitrile
EMIM	1-ethyl-3-methylimidazolium
PEO	Polyethylene oxide
PVA	Polyvinyl alcohol
PANI/PA	Polyaniline
PPY	Polypyrrole
PEDOT	Poly 3,4-ethylenedioxythiophene
ST	Synthesis temperature ($^{\circ}\text{C}$)
DBSA	4-Dodecylbenzenesulfonic acid
CSA	Camphorsulfonic acid
PTSA	Para toluene sulfonic acid
APS	Ammonium persulfate
ED	Energy density
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy

XPS	X-ray photoelectron spectroscopy
FESEM	Field emission scanning electron microscopy
EDX	Energy dispersive X-ray spectroscopy
CV	Cyclic voltammetry
CD	Charge-discharge
EIS	Electrochemical impedance spectroscopy
AN	Aniline
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
SPEEK	Sulfonated polyether ether ketone
NMP	N-Methyl-2-pyrrolidone
DMSO	Dimethyl sulfoxide
PB	Prussian blue
MWCNT	Multi-walled carbon nano tubes
SWCNT	Single-walled carbon nano tubes
BCN	Boron carbonitrides
ACF	activated carbon fibers
CNF	carbon nanofibers
CGNR	Curly graphene nanoribbon
CF	Carbon fiber
NPCNF	Nitrogen, phosphorous codoped carbon nanofiber
g-C ₃ N ₄	Graphitic carbon nitride
EP	Electrochemical polymerization
IP	Interfacial polymerization
EDP	electrodeposition
GD	Galvanostatic deposition
ECD	Electrochemical deposition
COP	Chemical oxidative polymerization

Symbol	Nomenclature
C _{SP}	Specific Capacitance [Farad (F)]
Q	Electric charge (Coulomb)

V	Potential [Volt (V)]
ϵ_0	Permittivity of free space (8.854×10^{-12} F/m)
A	Area of plate (m^2)
D	Distance between plates (m)
ϵ	Permittivity of the dielectric material
E	Energy stored [Watt.hour (Wh)]
P_{max}	Maximum power [Watt (W)]
C_{sp}	Specific capacitance (F/g)
D	Average crystallite size (nm)
K	Scherrer's constant
λ	Wavelength of X-ray (Å)
β_L	Full width at half maximum (radians)
Θ	Bragg angle
I	Current (A)
M	Mass (g)
t_c	Charging time (s)
t_d	Discharging time (s)
ΔV	Potential difference (V)
E_{sp}	Specific energy (Wh/kg)
P_{sp}	Specific power (W/kg)
Rct	Charge transfer resistance (Ω)
f_k	Knee frequency (Hz)
τ_r	Relaxation time (s)