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

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
Deptt. 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 (BHU) 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 (BHU), Varanasi

Vikas Kr. Pandey

(Vikas Kumar Pandey)

Table of Contents

List of figures

List of Tables

List of Abbreviations and Symbols

Abbreviation	Nomenclature
EDLC	Electrical double layer capacitance
SC	Supercapacitor
TEABF4	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_3N_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	Permitivity of free space (8.854×10^{-12} F/m)
A	Area of plate (m^2)
D	Distance between plates (m)
ε	Permitivity 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
TEABF4	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_3N_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	Permitivity of free space (8.854×10^{-12} F/m)
A	Area of plate (m^2)
D	Distance between plates (m)
ε	Permitivity 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)