

Graphene-based energy storage materials for supercapacitor application



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Award of Degree

DOCTOR OF PHILOSOPHY

By

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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 parents, my sister and teachers for their encouragement and support.

DECLARATION BY THE CANDIDATE

I, **Sanjeev Verma**, certify that the work embodied in this Ph.D. thesis is my bonafide work and carried out by me under the supervision of **Dr. Bhawna Verma** for a period from **July 2018 to December 2022** 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.


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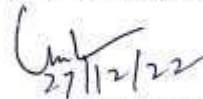
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List of Abbreviations and Symbols

Abbreviation	Nomenclature
EDLC	Electrical double layer capacitance
PANI	Polyaniline
COP	Chemical oxidative polymerization
PPy	Polypyrrole
PEDOT	Poly 3,4-ethylenedioxythiophene
PMeT	Poly(3-methyl thiophene)
PFPT	Poly(3-(4-fluorophenyl)thiophene)
PTh	Polythiophene
PTSA	Para toluene sulfonic acid
APS	Ammonium persulfate
GO	Graphene oxide
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
FESEM	Field emission scanning electron microscopy
EDS	Energy dispersive X-ray spectroscopy
CV	Cyclic voltammetry
CD	Charge-discharge
EIS	Electrochemical impedance spectroscopy
TRGO	Thermally reduced graphene oxide
ACC	Activated carbon cloth
N/P-TRGO	Nitrogen/phosphorous codoped thermally reduced graphene oxide
SWCNT	Single wall carbon nanotube
CNF	Carbon nanofiber
CX	Carbon xerogel
EP	Electrochemical polymerization
IP	Interfacial polymerization
NMP	N-Methyl-2-pyrrolidone

DMSO	Dimethyl sulfoxide
SSA	Specific surface area
CE	Coulombic efficiency
EEC	Equivalent electrical circuit
CPE	Constant phase element

Symbol	Nomenclature
C	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)
FWHM	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)
η	Coulombic efficiency
E _{sp}	Specific energy (Wh/kg)

P_{sp}	Specific power (W/kg)
R_{ct}	Charge transfer resistance (Ω)
Q	Constant phase element
f_k	Knee frequency (Hz)
t_r	Response time (s)

PREFACE

The primary objective of the thesis is to develop graphene oxide-polyaniline-bimetallic oxide based supercapacitor electrodes for energy storage applications.

Energy is becoming more and more in demand, as well as being consumed. From our homes to our workplaces, electrical energy has become a necessary component of daily life. The overuse of non-renewable resources for energy production, such as coal, petroleum, natural gas, etc., is causing their depletion and contributing to global warming. As a result, the focus has turned to environmentally benign renewable energy sources including solar energy, wind energy, tidal energy, hydropower, biomass energy, etc. The production is hampered by the seasonality and irregularity of some renewable resources. In order to store all the energy produced by renewable sources, there is now a greater need for energy storage technology. Currently available energy storage devices include conventional capacitors, batteries, and supercapacitors. Conventional capacitors have a very poor energy density. Batteries are devices with a high energy density and a low power density. They also have a very short cycle life. Supercapacitors have more power density, cycle life, and energy density than capacitors. They fill the gap between batteries and conventional capacitors.

To make supercapacitor electrodes, several carbon-based, conducting polymers, and metal oxide materials are employed. Redox transitions are the basis for the charge storage mechanism in metal oxides and conducting polymers. They have a higher energy density than carbon-based materials because of redox processes, but their cycle life is poor because of the sudden volumetric shift that occurs when charging and discharging. Electrostatic adsorption allows carbon-based materials to hold a charge; as a result, they have a better

power density and cycle life than conducting polymers and metal oxides. So, a ternary hybrid system of carbon based-conducting polymer-metal oxide material was prepared to get the benefits of the individual systems. Graphene oxide was taken as the source of carbon-based material. Polyaniline was taken as the source of conducting polymer as it provides excellent electrochemical activity due to π -conjugation. Bimetallic oxides (CuCo_2O_4 , CuFe_2O_4 , CoFe_2O_4) were synthesized, which provided multiple oxidation states due to the presence of two metals. Very limited work has been done on bimetallic oxides, graphene oxide, and ternary composites. The main objective of the current work is to synthesize graphene oxide-based hybrid ternary composites and use them as supercapacitor electrodes. The primary objective is to increase the specific energy and cycle life of energy storage devices. Various electrochemical characterizations were done to observe the electrochemical activities of the systems.

The current study has been divided into **6 chapters**. **Chapter 1** contains an introduction about supercapacitors and their classifications along with the materials used in synthesizing supercapacitor type systems. **Chapter 2** consists of a literature review on various configurations and materials used in supercapacitors, the research gap, and the objective of the research work. **Chapter 3** deals with the materials, methods, and various characterization techniques used during the research. **Chapter 4** compares between electrochemical properties of graphene oxide-based single, binary, and ternary systems have been done. The ternary composite (graphene oxide-polyaniline-copper cobaltite) based supercapacitor electrodes show outstanding electrochemical performances. It exhibited the highest specific energy of 62.54 Wh/kg. **Chapter 5** compare all the ternary system's structural and electrochemical properties of graphene oxide-polyaniline-copper cobaltite

(GO/PANI/CuCo₂O₄), graphene oxide-polyaniline-copper ferrite (GO/PANI/CuFe₂O₄), and graphene oxide-polyaniline-cobalt ferrite (GO/PANI/CoFe₂O₄) for supercapacitor electrodes. The summary and scope of the future work have been described in **chapter 6**.