Development of novel metal-oxalate electrodes for intercalative battery type hybrid capacitor

A thesis submitted in partial fulfillment for the
Award of Degree
Doctor of Philosophy
By

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YEAR: 2022

Dedicated to my Beloved Parents and Family

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Acknowledgments

The journey towards Ph.D. has been a turning point in my life, and it would not be possible without the constant support, assistance, and guidance that I have received from countless people. I would like to take this opportunity to acknowledge and appreciate those people who have given their valuable time during my Ph.D.

I am indebted to my thesis supervisor Dr. Preetam Singh for his constant monitoring, enthusiastic encouragement, continued guidance, and unconditional support throughout my Ph.D. journey. I always admire his knowledge of the subject, his unconventional thinking, and his enthusiastic nature for research. His ingenious approach to research is a source of inspiration, and this approach is reflected in his simple but clear writing style, which I want to carry forward in my career. I have been fortunate enough to be part of his group. His suggestions and advice will always be beneficial in life, whether it is academic or non-academic. I am very thankful to you sir for being a mentor academically as well as philosophically and wish to continue to seek this mentorship in future life too.

I am thankful to my RPEC members, Prof. Rajiv Prakash (SMST, IIT-BHU), Dr. Anil Kumar, and Dr. M.R. Majhi, for their knowledgeable, motivational, and umpteen suggestions throughout this research work.

I want to express my gratitude to the Ex-Head of Department, Prof. D.Kumar, and Head of Department Prof. Vinay Kumar Singh for providing me required facilities of the department. I also wish to thank all the faculty members of the Department of Ceramic Engineering, Prof . D. Kumar, Prof. Om Prakash, Prof. S.P. Singh, Prof. Ram Pyare, Prof. Vinay Kumar Singh, Dr. Anil Kumar, Dr. M. R.

Majhi, Dr. P. K. Roy, Dr. AshutoshDubey, Dr. Preetam Singh, Dr. Santanu Das, Dr. Imteyaz Ahmed, Dr. Subrta Panda, Dr. Kundan Kumar Dr. Sudama Singh, Dr. R.K. Chaturwedi, Dr.Akanksha Dwivedi, Dr. Kalyani Mohanta, for their motivation, selfless support, and suggestions during course work as well as my whole Ph.D. time.

I would also like to thank Prof. Rajiv Prakash for providing experimental facilities during the entire course of research work at CIFC, IIT (BHU). Along with that, I am also thankful to all the staff at CIFC, IIT(BHU).and Prof. Rajiv Prakash (SMST, IIT-BHU), Dr. T. Maiyalagan Department of Chemistry, SRM University Chennai, for their valuable discussions over the scientific work.

I would like to extend thanks to Dr. Asha Gupta, Department of Chemistry IIT(BHU) for providing a lab facility during the time of crisis. I also gratefully acknowledge the financial support of the Ministry of Education, India (formally known as the Ministry of Human Resource and Development; MHRD, India).

I am also thankful to all non-teaching staff, Mr. Shailendra, Mr. Pawan, Mr. Prasant, Mr. K. K. Maurya, (office staff)Mr. Ashish Tripathi, Mr. BhagmalJi, and Mr. Mansa Ram(all Technical and workshop staff) of the Department of Ceramic Engineering for their kind cooperation. I am very thankful to the labmates Akanksha, Rakesh, Krishna, Neeraj, Himanshu, Saurabh,and Abhay for cooperating and maintaining the lab culture. I also want to thank Dr. Asha mam research group, Vishal, Vaishali and Shraddha for their help and cooperation. I wish to express my sincere gratitude to all those who have extended their helping hands in various ways during my tenure at the Indian Institute of Technology (Banaras Hindu University),

Varanasi, India. I am also thankful for the negative energies which teach me life lessons and help me to grow.

I am highly obliged to my parent, my family, and my wife Dr. Varsha Tripathi for their continuing support, love, laughter, and motivation to keep me coherent and to make this project possible especially during many rough patches of time. I would also include my In-laws in the list for being understanding and supportive. I would like to mention my friend Mahatim, Vikas, Neeraj, Sanjo, Ashutosh, Rishi, Vipin, Sharad, Sudhanshu, Ratnesh, etc for having that emotional and motivational support during the tenure.Lastly, I want to thank almighty God for all positive opportunities and negative situations which prepare me to handle situations in the future life.

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LIST OF ABBREVIATIONS

XRD-X-ray Diffraction

HR-SEM-High-Resolution Scanning Electron Microscope

HR-TEM-High-Resolution Transmission Electron Microscope

TGA- Thermogravimetric analysis

FTIR-Fourier transform Infrared Spectroscopy

XPS-X-ray Photoelectron Spectroscopy

BET - (Brunauer, Emmett, and Teller) specific surface

CV- Cyclic Voltammetry

ASCs – Asymmetric Supercapacitors

Csp - specific capacitance

A, mA (unit) - Ampere, milliamp

AC - Activated Carbon

AM - Active mass

C, μC (unit) - Coulomb, microcoulomb

C - Capacitance

C^+/R^+ - Cationic species in electrolyte

C^* - Complex differential capacitance

C^{+ve} - Capacitance of positive electrode

C^{-ve} - Capacitance of negative electrode

C_{Cell} - Overall cell capacitance

C_{Diff} - Capacitance from diffuse layer

C_{dl} - Capacitance from double layer

Cg - Gravimetric capacitance

C_H - Capacitance from Helmholtz plane

CIH - Capacitance from inner Helmholtz plane

COH - Capacitance from outer Helmholtz plane

e^- - Electron

ε - Permittivity of vacuum

E - Electrode potential

E° - Standard electrode potential

E_{Total} - Total energy stored in capacitor

EDLC - Electrochemical double layer capacitor

EIS - Electrochemical impedance spectroscopy

ES - Electrochemical supercapacitor

f - Frequency

F - Faraday constant

F, mF, μF (unit) - Farad, millifarad, microfarad

g, mg, μg (unit) - Gram, milligram, microgram

h (unit) – Hour

Hz, mHz, kHz (unit) - Hertz, millihertz, kilohertz

I - Current

K (unit) - Temperature in Kelvin

K – Boltzmann's constant

M - Mass of active materials

m, cm, μm, nm (unit) - Meter, centimeter, micrometer, nanometer

M - Molar concentration

Q - Charge stored

V - Voltage

V_{Max} - Maximum voltage

V_{Min} - Minimum voltage

W (unit) - Watt

Wh (unit) - Watt hour

wt% - Weight percentage

ω - Angular frequency

X - Fraction of ion occupancy in lattices

z - Number of electrons transferred in redox reactions

Z^* - Total impedance

Z' - Real component of impedance

Z'' - Imaginary component of impedance

ΔV - Voltage window

°C (unit) - Temperature in Celsius

θ_H - Surface coverage of H^+ in underpotential deposition

[Ox] - Concentration of oxidized species

[Red] - Concentration of reduced species

PREFACE

The energy supply based on fossil fuels To fulfill the ever-increasing energy demands to sustain the continuous growth and development of society has increased the inaccessible burden on fossil fuel resources and is decisively adding to climate change concerns and global warming. Renewable energy generation (including solar energy, wind energy, geothermal energy, etc.) has drawn significant attention as an alternative to fossil fuels and a remedy of concern related to pollution, global warming, and climate change due to net carbon addition to the earth environment. However, the power supply through renewable sources is irregular or fluctuating due to the time and weather-dependent nature of renewable sources and can not be used directly in electrical and electronic appliances. Though costly, yet most efficient, Electrochemical energy storage is key to harnessing the full potential of renewable energy sources, and thus gid-scale energy storage solutions are required to reduce the burden of fossil fuel-based energy solutions and instead use renewable power sources.

In this thesis, we focus on development of high energy-high power delivering redox-mediated intercalative supercapacitor to establish grid-scale energy storage solutions. In pseudocapacitors, energy is stored by fast and reversible redox reactions at the surface of active materials. Compared to EDLCs, pseudocapacitors offer 10 to 100 times higher capacitance because charge storage is not limited to the surface only, but also to the near-surface region where ions can diffuse. Pseudocapacitance arises when electrode potential is dependent logarithmically on the extent of reactions and involves charge transfer across the double layer. The intercalative pseudocapacitance is also based on redox reactions, which arise when ions intercalate into tunnels or layers of active materials accompanied by faradic charge transfer without crystallographic phase change but involve redox reactions in a 3-

dimensional structure rather than a 2-dimensional surface in redox pseudocapacitance. Metal oxalate framework structures are employed here to develop superior electrodes for hybrid intercalative battery-type supercapacitors. Thermochemical properties especially coupling of TGA/DTA techniques with strategic precipitation schemes to develop novel highly porous nanostructures that can enable fast transport or diffusion of ions in the host structure to have large-scale charge storage capabilities are employed here to develop effective electrodes for intercalative battery type supercapacitors.

$NiC_2O_4.2H_2O$ flakes were synthesized using a single-step co-precipitation method in an aqueous medium. $NiC_2O_4.2H_2O$ -based electrode showed intercalative charge storage behavior exhibiting specific capacitance of 990 F/g at a current density of 1 A/g with excellent cyclic stability. $NiC_2O_4.2H_2O$ electrode showed superior specific capacitance equivalent to 990 F/g in the potential window of 0.45 V was observed in an aqueous KOH electrolyte and 440 F/g in 1M neutral Na_2SO_4 electrolyte in the potential window of 0.85 V.

Highly porous, anhydrous CoC_2O_4 nanorods were successfully synthesized using a two-step process, first $CoC_2O_4.2H_2O$ was synthesized by co-precipitation method in an aqueous medium followed by heating the precipitate at 210 ºC to produce porous CoC_2O_4 nanorods. Porous CoC_2O_4 nanorods showed pseudocapacitive energy/charge storage behavior with a specific capacitance of the materials reaching as high as 2116 F g^{-1} at a current density of 1Ag^{-1} with excellent cyclic stability. The predominant intercalative mechanism seems to operate behind high charge storage as intercalative (inner) and surface (outer) charges stored by porous anhydrous CoC_2O_4 were close to 75% and 25% respectively. Porous anhydrous CoC_2O_4// AC full cell resulted in maximum specific energy of 129 W h kg^{-1} and specific power of ~647 Wkg^{-1} at 0.5 A g^{-1} current density in the voltage window of 1.3 V in 2 M

KOH electrolyte.

Anhydrous $Co_{0.5}Ni_{0.5}C_2O_4$ was successfully synthesized using a two-step process; first, $Co_{0.5}Ni_{0.5}C_2O_4 \cdot 2H_2O$ was synthesized by the co-precipitation method in an aqueous medium, and then $Co_{0.5}Ni_{0.5}C_2O_4 \cdot 2H_2O$ was heated at 230 °C for 5 h, which resulted in porous anhydrous $Co_{0.5}Ni_{0.5}C_2O_4$. The anhydrous $Co_{0.5}Ni_{0.5}C_2O_4$ electrode showed a highly pseudocapacitive performance with a specific capacitance of 2396 F/g at a current density of 1 A/g and excellent cyclic stability. The porous anhydrous $Co_{0.5}Ni_{0.5}C_2O_4$ //AC full cell resulted in 283 W h/kg of maximum specific energy with a specific power equivalent to 817 W/kg in the voltage window of 1.6 V in the 2 M KOH electrolyte at a 1 A/g current rate.

In this thesis, I conclude that framework structure material containing transition metal ions can be an excellent host to develop novel electrodes that can enable fast charge-discharge to develop high energy high power delivering battery type capacitors. The use of TGA/TDA techniques can be an important tool to modify the synthesis schemes to develop highly porous nanostructured materials to employ as an electrode in batteries and capacitors. Ni/Co oxalate framework was shown to have redox-mediated charge storage capability that can dissipate power or current at fast rates to power electronic and electrical appliances and to be applied as grid-scale energy storage solutions. I found that the transition metal oxalate electrodes in full cell asymmetric supercapacitor (ASC) mode where activated carbon is utilized as a negative electrode can deliver power performance and rate capabilities comparable to lead acid batteries and further studies can bring superior aqueous redox-mediated battery type capacitor that can be employed for grid-scale energy storage solution and can also be utilized as an alternate to lead acid batteries to power inverters.