Dedicated to my Beloved Parents and Family

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It is certified that the work contained in the thesis titled ***Tuning of Redox energies of transition metal ions in different lattices for grid-scale energy storage applications"*** by ***"RAKESH MONDAL*** 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 there quirements of the comprehensive examination, candidacy, and SOTA for the award of Ph.D. Degree.

Dr. Preetam Singh
Supervisor
Assistant Professor,
Department of Ceramic Engineering,
Indian Institute of Technology (BHU),
Varanasi - 221005, (U.P.),

Dr. Anil Kumar
Co-Supervisor
Associate Professor
Department of Ceramic Engineering,
Indian Institute of Technology (BHU),
Varanasi - 221005, (U.P.), India

Associate Professor
Department of Ceramic Engineering
भारतीय प्रौद्योगिकी संस्थान (का०हि०वि०वि०)
Varanasi-221005/वाराणसी-221005

Prof. Vinay Kumar Singh
Head of Department
Department of Ceramic Engineering,
Indian Institute of Technology (BHU)
Varanasi - 221005, (U.P.), India

HEAD/विभागाध्यक्ष
Department of Ceramic Engineering
सिरामिक अभियान्त्रिकी विभाग
Indian Institute of Technology (B.H.U.)
भारतीय प्रौद्योगिकी संस्थान (का०हि०वि०वि०)
Varanasi-221005/ वाराणसी-221005

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

DECLARATIONBYTHECANDIDATE

I, ***RakeshMondal***, certify that the work embodied in this thesis is my own bonafide work carried out by me under the supervision of ***Dr. Preetam Singh*** from ***July 2016***to ***July 2022***, at the ***Department of Ceramic Engineering***, Indian Institute of Technology (BHU), 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 and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not will fully copied any other's work, paragraphs, text, data, results, *etc*., reported in journals, books, magazines, reports dissertations, thesis, *etc*., or available on websites and have not included them in this thesis and have not cited as my own work.

Rakesh Mondal
Signature of the student

Date:

Place: IIT (BHU), Varanasi

(*Rakesh Mondal*)

CERTIFICATEBYTHESUPERVISOR

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

Dr. Preetam Singh
Supervisor
Assistant Professor,
Department of Ceramic Engineering,
Indian Institute of Technology (BHU),
Varanasi - 221005, (U.P.), India

Dr. Anil Kumar
Co-Supervisor
Associate Professor
Department of Ceramic Engineering,
Indian Institute of Technology (BHU),
Varanasi - 221005, (U.P.), India

Associate Professor
Department of Ceramic Engineering
सहायक आचार्य, सिरेमिक अभियांत्रिकी विभाग
Indian Institute of Technology (B.H.U.)
भारतीय प्रौद्योगिकी संस्थान (का०हि०वि०वि०)
Varanasi-221005/ वाराणसी-221005

Prof. Vinay Kumar Singh
Head of Department
Department of Ceramic Engineering,
Indian Institute of Technology (BHU)
Varanasi - 221005, (U.P.), India

HEAD/Ceramic Engineering
Department of Ceramic Engineering
विभागाध्यक्ष, सिरेमिक अभियांत्रिकी विभाग
Indian Institute of Technology (B.H.U.)
भारतीय प्रौद्योगिकी संस्थान (का०हि०वि०वि०)
Varanasi-221005/ वाराणसी-221005

भारतीय
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Rakesh Mondal
Signature of the Student
(*Rakesh Mondal*)

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LIST OF ABBREVIATIONS

XRD-X-ray Diffraction

HR-SEM-High Resolution Scanning Electron Microscopy

HR-TEM-High Resolution Transmission Electron Microscopy

TGA- Thermogravimetric analysis

FTIR-Fourier Transforms Infrared Spectroscopy

XPS-X-ray Photoelectron Spectroscopy

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

LSV- Linear Sweep Voltammetry

CV- Cyclic Voltammetry

EIS- Electrochemical Impedance Spectroscopy

EDLC- Electric double layer capacitor

ASCs – Asymmetric Supercapacitors

AC-activated carbon

Csp - specific capacitance

E_{RHE} – Potential respect to the Reversible Hydrogen Electrode

E_{fb} - Flat Band Potential

OER -Oxygen Evolution Reaction

ORR -Oxygen Reduction Reaction

η = overpotential

A = Tafel slope

j = current density, mA/cm^2

j_0 =Exchange current density", mA/cm^2.

QDs- Quantum Dots

g-gram

A,mA- Ampere, milli-Ampere

PREFACE

Energy storage is the biggest challenge the world is facing today in the 21st century to utilize the full potential of renewable energy sources such as solar, wind, Tidal, etc. to overcome the ever-increasing burden on fossil fuels to fulfill our power demands and to decrease the toxic release and net carbon addition edition to the environment resulting global warming due to burning of fossil fuels. Electrochemical Energy storage devices are also important to overcome power and current fluctuations associated with renewable energy sources to be utilized as power supply units in electric grids. Thus major attention in the energy storage device section is to develop a gird scale bulk energy storage and delivery system with superior energy storage and power delivering capabilities. Therefore redox flow batteries, Metal-air batteries, and hybrid supercapacitors are technologically important and materials development to enhance their capabilities is the major area of focus in the energy materials section.

- Bifunctional OER/ORR catalyst and pseudocapacitive electrode materials are important to developbulk grid-scale energy storage and power delivering energy storage systems.
- Materials such as RuO_2, MnO_2, and NiOOH become very important because they show superior electrocatalytic OER/ORR properties in basic media (KOH electrolyte) and Faradic pseudocapacitive storage in neutral or low pH aqueous electrolyte (KOH, KCl, and Na_2SO_4 media).
- Perovskite such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF), and $LaNiO_{3\pm\delta}$ are also known to have superior and stable electrocatalytic OER/ORR activity in aqueous high pH KOH electrolyte and recently pseudocapacitiveanion charge-storage through oxygen intercalation was discovered in $LaMnO_3$ perovskite electrodes.
- Thus there is a need to develop strategic understanding and guidelines to develop superior materials that can be employed as an electrode in both (1) metal-air batteries (as OER/ORR electrocatalyst) and (2) hybrid supercapacitors (pseudocapacitive charge storage electrode).
- Tuning redox properties with suitable crystal structure or lattice modification with novel doping or substitution strategies is important to achieve the

- Targeted electric and electronic properties in the material for the desired application. In this thesis, I attempted to map the electronic structure of the material with suitable doping of guest cations in the host lattice and draw a structure-property correlation in the materials to be applied for electrochemical energy storage application.

I have shown that the rock-salt structure can act as a model host structure similar to perovskite where e_g electrons can be varied to obtain superior electro-catalytic activity. Incorporation of Nickel into CoO lattices helps to stabilize the rock salt structure and tune the e_g electrons to develop superior OER and ORR electrocatalysts. $Ni_{0.3}Co_{0.7}O$ with 1.3 e_g electrons showed superior electrocatalytic activity for oxygen evolution reaction. Further, along with e_g electrons, I explored the role of Sr in $Ba_{1-x}Sr_xCoO_{3-\delta}$perovskite toward higher electrocatalytic OER/ORR activities and showed that the incorporation of Sr ion in $Ba_{1-x}Sr_xCoO_{3-\delta}$ ($0\leq x\leq 0.5$) perovskite lattice, facilitates the formation of ligand hole by decreasing the Fermi level position into the Co(3d)/O(2p)π* band. The decrease in the bandgap of the materials and superior electrical conductivity (p-type conduction) suggest a large number of oxygen vacancies or oxygen vacant BO_5 octahedra formation that yields more active sites as this type of oxygen vacancy in perovskite lattice get more reaction surface or active sites because (011) plane contains transition metal (Co) in $Ba_{1-x}Sr_xCoO_{3-\delta}$ perovskite that forms $Co3d_{z2}$ and $OH^-(2p_z+1s)$ bond.

Similar to multifunction RuO_2 or MnO_2type materials, I have shown that $La_{1-x}K_xCoO_{3-\delta}$ ($0 \leq x \leq 0.5$) shows a pH-dependent bifunctional electrocatalyst (OER/ORR) and electrochemical charge storage behavior in different electrolytes.30 % K doped p-type $La_{0.7}K_{0.3}CoO_{3-\delta}$ show superior OER activity with an overpotential of 335 at $10mA/cm^2$ current rate in 1M KOH electrolyte. Further, the double exchange mechanism enhances OER catalytic properties and additionally, improves charge storage kinetics and activities as electrode material $La_{1-x}K_xCoO_{3-\delta}$ **(**$0 \leq x \leq 0.5$**)** for supercapacitors application. High Gravimetric capacitance of $La_{0.5}K_{0.5}CoO_{3-\delta}$ electrode equivalent to 378 F/g, 282F/g, 221F/g, 163F/g, 74F/g was found at a constant current of 1A/g, 2A/g, 3A/g, 5A/g, and 10A/g respectively in neutral 0.5M Na_2SO_4 electrolyte with up to 94% capacitive retention and coulombic efficiency (97%).

An anion intercalative pseudo-capacitive $La1\text{-}xK_xFeO_{3-\delta}$ electrode for supercapacitors

application was developed using induced inter-layer potential by altering La^{3+} and K^{+} layer in $La_{1-x}K_xFeO_{3-\delta}$, $Fe^{4+/3+,}$ and $Fe^{3+/2+}$ redox energies can be tuned and made accessible to envisage higher capacity (662 F/g equivalents to 1.32 e^-/OH^- diffusion) for $La_{0.5}K_{0.5}FeO_{2.92}$ electrode. Higher b values (>0.8) obtained for diffusion-controlled reaction suggest a high faradaic pseudocapacitive contribution to the electrode. Up to 88.6% capacitive retention and coulombic efficiency (95%) were obtained after continuous 5000 cycles of charge/discharge and Maximum specific power of ~3594 W/kg was obtained when specific energy reached ~117 Wh/kg at 5A/g of current density for $La_{0.5}K_{0.5}FeO_{3-\delta}$ electrode in two-electrode $La_{0.5}K_{0.5}FeO_{3-\delta}$//AC full cell.

Further Nano-engineering was employed to develop a superior pseudocapacitive electrode based on $Ni^{2+/3+}$ redox couple in framework structure as Anhydrous NiC_2O_4 Quantum dots that showed large-scale pseudocapacitive energy storage in aqueous KOH and neutral Na_2SO_4 electrolyte. Predominant diffusion control over surface control mechanism seems to operate behind high charge storage as intercalative (Inner) and surface (outer) charges stored by porous anhydrous NiC_2O_4 QDs were close to high at 38% and 62% respectively. Anhydrous NiC_2O_4 QDs //AC full cell resulted in 293Wh/kg of maximum specific energy with specific power equivalent to 772W/kg in the voltage window of 1.6V in 2M KOH electrolyte.

Therefore in this thesis, I conclude the role of redox and tuning of redox energy with suitable cation doping in host perovskite lattice be employed as an efficient tool to alter its electrical and electronic properties so that the materials can show pH-dependent electrocatalytic (OER/ORR) properties and pseudocapacitive energy storage capabilities. The correlation of lattice structure and electronic state of active transition metal cation in the host lattice is established to develop novel OER/ORR catalyst and pseudocapacitive energy storage materials. This tuning of redox energies coupled with structure alteration can open the gate to explore novel new alternative materials for desired electrochemical energy storage applications