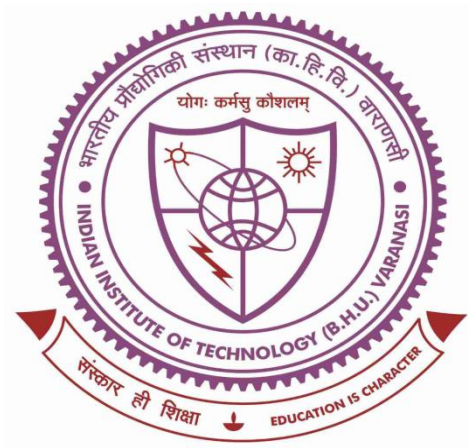


Tuning of Redox energies of transition metal ions in different lattices for grid-scale energy storage applications



**A thesis submitted in partial fulfillment for the
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By**

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Chapter 8

Summary and Future scope

8.1 Summary

To overcome the ever-increasing burden on fossil fuels to fulfil our power demands and to decrease the toxic release and net carbon addition to the environment resulting from global warming due to the burning of fossil fuels, the utilization of the full potential of renewable energy sources such as solar, wind, Tidal, etc. are necessary. Energy storage and conversion devices such as (1) metal-air batteries and (2) hybrid supercapacitor (pseudocapacitive charge storage electrode) are envisaged as bulk grid-scale energy storage and power delivery devices to couple the renewable energy technologies to cater for the energy needs of the society as bulk grid-scale energy storage and power delivery is the biggest challenge the world is facing today in the 21st century. The thesis aimed to develop novel structure-property correlation and tuning of redox energy of active transition metal cation by altering host structure with suitable doping in host lattice to develop superior materials that can be employed as an electrode in both (1) metal-air battery (as OER/ORR electrocatalyst) and (2) hybrid supercapacitor (pseudocapacitive charge storage electrode). Bifunction OER/ORR catalysts and pseudocapacitive electrode materials are important to develop bulk grid-scale energy storage and power-delivering energy storage systems. Materials such as RuO₂, MnO₂, 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 (KCl, Na₂SO₄ media). In this thesis, we 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. In **Chapter 1**, I presented the need for alternative energy solutions especially electrochemical energy storage devices and materials, and the need to develop strategic understanding and guidelines in terms of tuning redox properties with suitable crystal structure or lattice modification with novel doping or substitution

to achieve the targeted electric and electronic properties in the material for the desired application. **Chapter 2** deals with novel preparation methods for material synthesis and presents the know-how and detailed theoretical background of characterization techniques and electrochemical performance measuring techniques utilized in the dissertation

We have shown in **Chapter 3** 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, in **Chapter 4** along with e_g electrons, we 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 $Co(3d)/O(2p)\pi^*$ 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 $Co3d_{z^2}$ and $OH-(2p_z+1s)$ bond.

Similar to multifunction RuO_2 or MnO_2 type materials, we have shown in **Chapter 5** 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 behaviour 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 10 mA/cm^2 current rate in 1 M 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, 282 F/g, 221 F/g, 163 F/g, and 74 F/g was found at a constant current of 1 A/g, 2 A/g, 3 A/g, 5 A/g, and 10 A/g respectively in neutral 0.5 M Na_2SO_4 electrolyte with up to 94% capacitive retention and coulombic efficiency (97%).

In **Chapter 6**, An anion intercalative pseudo-capacitive $\text{La}_{1-x}\text{K}_x\text{FeO}_{3-\delta}$ electrode for supercapacitors application was developed using induced inter-layer potential by altering La^{3+} and K^+ layer in $\text{La}_{1-x}\text{K}_x\text{FeO}_{3-\delta}$, $\text{Fe}^{4+/3+}$, and $\text{Fe}^{3+/2+}$ redox energies can be tuned and made accessible to envisage higher capacity (662 F/g equivalents to $1.32 \text{ e}^-/\text{OH}^-$ diffusion) for $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{2.92}$ 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 $\sim 3594 \text{ W/kg}$ was obtained when specific energy reached $\sim 117 \text{ Wh/kg}$ at 5 A/g of current density for $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{3-\delta}$ electrode in two-electrode $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{3-\delta}$ //AC full cell.

In **Chapter 7**, nanoengineering was employed to develop a superior pseudocapacitive electrode based on $\text{Ni}^{2+/3+}$ 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 293 Wh/kg of maximum specific energy with specific power equivalent to 772 W/kg in the voltage window of 1.6 V in 2 M KOH electrolyte.

8.2 Future Scope

Therefore in this thesis, it was concluded that the role of redox and tuning of redox energy with suitable cation doping in host perovskite lattice can 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. The idea of lowering redox potential using inter-layer potential shown in **chapter 6** can be employed further in accessing the non-accessible redox energies to develop high

voltage electrodes as well as resulting in better electrical conductivities or even in developing superconductors.

The role of doping-induced oxide-ion vacancies can be employed further in developing superior electrocatalysts for other important applications such as hydrogen evolution or oxidation of organic biofuels such as methanol or formic acid to develop Direct methanol fuel cells (DMFC) or direct formic acid fuel cells (DFFC). The developed OER/ORR catalyst can be employed as a cathode in fuel cells. Keeping the electrical and electronic properties intact, Nanoengineering can play a superior role in providing high surface area and catalytic active sites exposed to the reaction can make multifold enhancement of the catalytic properties and electrochemical charge storage properties of the materials.