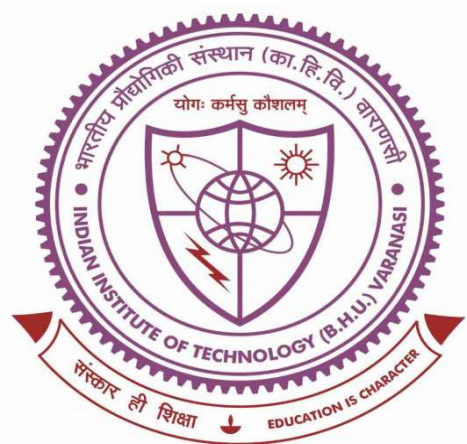


Development of novel metal-oxalate electrodes for intercalative battery type hybrid capacitor



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

Neeraj Kumar Mishra

**DEPARTMENT OF CERAMIC ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI – 221005
INDIA**

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Chapter-6

SUMMARY AND FUTURE SCOPE

6.1 Summary

The thesis aimed to develop novel structured metal-organic framework materials, especially the simple ones such as metal oxalates to develop as pseudocapacitive electrodes to be applied as hybrid Asymmetric supercapacitor mode where activated carbon can work as a negative electrode as bulk grid-scale energy storage and power delivery is the biggest challenge the world is facing today is to utilize the full potential of renewable energy sources such as solar, wind, Tidal, etc. to decrease the ever-increasing burden on fossil fuels and also to decrease the toxic exhaust and net carbon addition edition to the environment resulting global warming due to burning of fossil fuels. Materials such as RuO_2 , MnO_2 , and NiOOH become very important because they show Faradic pseudocapacitive storage in neutral or low pH aqueous electrolytes (KOH , KCl , and Na_2SO_4 media). Further intercalative pseudocapacitance is also evident in Nb_2O_5 and V_2O_5 -based materials. In this thesis, we attempted to develop the high capacity pseudocapacitive electrode materials that can host guest ions through interactive diffusion inside the electrode material that enables high charge storage and fast power delivery to be applied for grid-scale electrochemical energy storage application.

In Chapter 1, I presented the need for alternative energy solutions and materials developed especially for grid-scale electrochemical energy storage devices and the need to develop strategic understanding and guidelines in terms of accessing redox properties with suitable crystal structure or lattice modification with novel doping or substitution to achieve the targeted electric and electronic properties and high surface active host lattice structure in the material for the desired application.

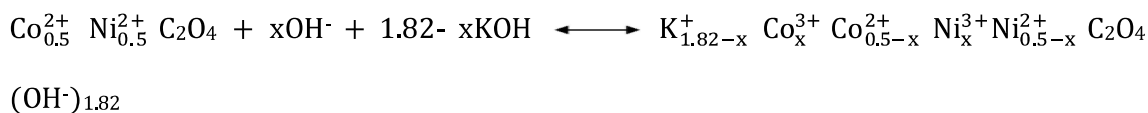
Chapter 2 deals with novel preparation methods for material synthesis and presents the know-how and detailed theoretical background of characterization techniques and electrochemical performance measuring techniques utilized in the dissertation.

We have shown in **Chapter 3** that the 3-d open pore structured $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ flakes due to the formation of hydrogen bonding through hydrated water were synthesized using a single-step co-precipitation method in an aqueous medium. $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ -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 due to the available site in the open pore framework structure of the host lattice. $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ 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. Predominant intercalative mechanism seems to be operative behind high charge storage as intercalative (Inner) and surface (outer) charges stored on $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ electrodes were found to be 84% and 16% respectively. In 2M KOH electrolyte, $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} // \text{AC}$ full cell resulted in 141.5 Wh/kg of maximum specific energy with specific power equivalent to 559 W/kg in the voltage window of 1.4 V in 2M KOH electrolyte at 0.2 A/g current density.

Further, in **Chapter 4**, I present the synthesis of porous anhydrous CoC_2O_4 nanorods using a two-step process, first $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was synthesized by co-precipitation method in an aqueous medium followed by heating the precipitate at 210 °C to produce porous CoC_2O_4 nanorods. TGA/DTA study was coupled in synthesis scheme to develop control dehydration step in the synthesis process that resulted in nanorod morphology for CoC_2O_4 that can enable fast diffusion of guest ions to have capacity pseudocapacitance in the material. 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 high 75% and 25% respectively. Porous anhydrous

CoC2O4// 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.

Chapter 5 presents the study on Ni-doped Co-oxalates. Porous anhydrous Co_{0.5}Ni_{0.5}C₂O₄ was successfully synthesized using a two-step process; first, Co_{0.5}Ni_{0.5}C₂O₄·2H₂O was synthesized by co-precipitation method in an aqueous medium, and then Co_{0.5}Ni_{0.5}C₂O₄·2H₂O was heated at 230 °C for 5 h, which resulted in porous anhydrous Co_{0.5}Ni_{0.5}C₂O₄. The anhydrous Co_{0.5}Ni_{0.5}C₂O₄ 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. Predominant intercalative mechanism coupled with strong surface absorption seems to operate behind high charge storage capacity of the materials as intercalative (inner) and surface (outer) charges stored by porous anhydrous Co_{0.5}Ni_{0.5}C₂O₄ were close to high 38% and 62%, respectively. The ultra-high capacitance of the Co_{0.5}Ni_{0.5}C₂O₄ electrode can be represented as a combination of redox reaction as well as double layer formation because the electron transfer is more than 1 per molecule of Co_{0.5}²⁺ Ni_{0.5}²⁺ C₂O₄·2H₂O. The redox reaction for the high capacitance of the electrode is given below and the value of x varies with the scan rate.



The porous anhydrous Co_{0.5}Ni_{0.5}C₂O₄//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.

These studies confirm that metal framework materials can be employed successfully to develop intercalative pseudocapacitive electrodes. Thermochemical characterization techniques such as TGA/DTA or DSC can be employed successfully to develop synthesis for

control precipitation or synthesis of high surface area porous nanostructures that can enable fast mobilization of ions inside the host structure that can result in very high pseudocapacitance in the materials. High electrochemical charge storage performance coupled with long-term stability studies make the porous transition-metal oxalate electrodes suitable for large-scale energy storage application in ASC mode.

6.2 Future Scope

As can be seen from the study on Ni and CO based oxalate materials, a systematic increase in charge storage capacity of electrodes were achieved. A table is presented below showing comparative charge storage performances of developed electrodes in this thesis.

Electrode Material	Specific Surface area	Capacitance at 1A/g
NiC ₂ O ₄ ·2H ₂ O	22.9 m ² /g	1150 F/g
CoC ₂ O ₄	60.9 m ² /g	2116 F/g
Co _{0.5} Ni _{0.5} C ₂ O ₄	129.82 m ² /g	2396 F/g

Table 6.1: Showing charge storage capacity of different electrodes developed in this thesis.

As can be seen that surface area of the materials is increase with anhydrated Co-Ni oxalate solid solutions and along with redox mediated intercalation, high surface become a once of the key factor to increase the energy capacity of the electrode. Thus Nano-engineering of developed materials can result superior performances of the developed electrodes in the Thesis. Further, it is know that several safety concerns are associated with negative electrode stability in Li-ion batteries during cation intercalation and reversible de-intercalation as SEI and dendrite formation is a key issue that is responsible for battery bursting and stability. However, anion intercalations don't have any such issue. Anion intercalation involves OH⁻, Cl⁻ or SO₄²⁻ as transport ion that is very stable, much cheaper, and much more widely available that can make a much cheaper energy storage alternative to the current generation of reversible Li-ion batteries and Lead-acid batteries provided suitable materials can be

developed as a host structure which can have superior performance as an electrode of anion intercalative battery type supercapacitors. In this project, the focus will be on the exploration of oxalates-based framework electrodes that can have superior performances in non-aqueous electrolytes. Development of novel electrode materials for reversible anion intercalation battery type supercapacitors will enhance and strengthen the domestic battery industry and will certainly contribute to the “make in India drive” and will help to build indigenous (swadeshi) energy storage and delivery technology to fulfill our domestic energy needs and overcome the global imbalance in Energy demand vs. supply.

Further studies can be carried out are

1. Performance study and operating voltage window optimization of the electrode in a different type of electrolytes.
2. Optimizing of high voltages Ni-Mn-Co based metal framework electrodes and Fe based low voltage electrodes.
3. Fabrication of full architecture of framework electrode-based supercapacitors.
4. Performance analysis in full cell mode
5. Performances and optimizations of pseudocapacitive electrode-based supercapacitors assembly at the device level.
6. Achieving energy density ($> 50\text{Wh/Kg}$) and superior power $> (200\text{ W/Kg})$ for oxalate-based full cell battery type capacitor.
7. And the ultimate goal can be to develop coin cell as well as pouch cell type full cell fabrication asymmetric supercapacitor (ASC) mode using oxalate-based pseudocapacitive anion intercalative electrodes delivering energy and power capabilities similar to Li-ion batteries.