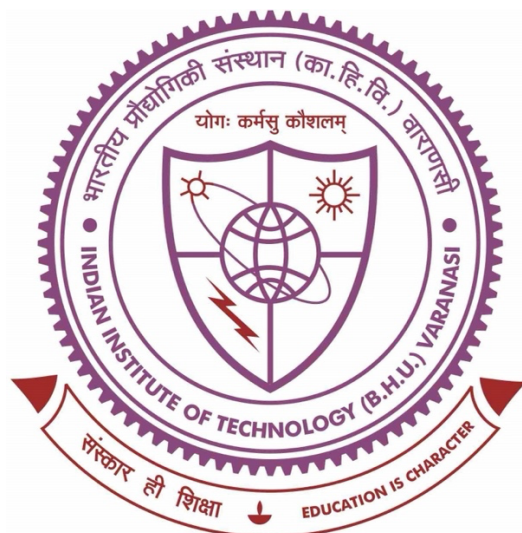


Development of Transition Metal Containing Phosphate Based Pseudocapacitive Electrodes for the Fabrication of High Performing Hybrid Supercapacitors



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By

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Chapter 6

Summary and future scope

6.1 Summary

This thesis aims to synthesize new, structurally competent metal-organic framework materials with a focus to develop intercalating pseudocapacitive electrodes for Hybrid Asymmetric Supercapacitors (HSCs). This research addresses a critical global challenge of harnessing the renewable energy generated from solar, wind, and tidal through electrochemical energy storage systems. Maximizing the energy storage capacity of the electrodes at high rates for bulk grid-scale energy storage and power delivery systems. Materials such as RuO_2 , MnO_2 , and NiOOH are critical because of their Faradic pseudocapacitive behavior in neutral or low-pH aqueous electrolytes, such as KOH , NaOH , KCl , and Na_2SO_4 . In addition, intercalative pseudocapacitance is evident in Nb_2O_5 and V_2O_5 -based materials. The objective of the present study is to design high-capacity pseudocapacitive electrodes with the ability to host guest ions through intercalation and diffusion processes, enabling high charge storage and fast power delivery in grid-scale electrochemical energy storage applications.

Chapter 1, has elaborated on the requirement of new energy storage alternatives and the right materials for grid-scale electrochemical energy storage devices. Again, I have also strongly emphasized the necessity to approach this in a strategic and guideline-based manner in redox property evaluation with an appropriate crystal structure or lattice alteration through innovative doping or substitution to obtain the electrical and electronic characteristics required along with a highly active surface lattice structure for the desired application.

Chapter 2 discuss the sample preparation methods as well as the onboard instruments used in crystal structure analysis, thermal analysis, and microstructure investigation. It also highlighted the principle of each characterization method, as well as discussion of tools for data analysis like X-ray Rietveld refinement and electrochemical impedance spectroscopy, as well as the kinetics of electrochemical reactions through approaches from Trassati and Dunn.

In **Chapter 3** Fluffy, carbonized hexagonal KCoPO_4 powder was prepared by employing maleic acid as a chelating agent via the sol-gel method and high-temperature calcination. This material, evaluated as a positive electrode in aqueous electrolytes, showed outstanding electrochemical performance with a specific capacitance of 725 F/g at 0.5 A/g. Charge storage mechanisms were assigned to both intercalative (37%) and surface capacitive (63%) processes. The electrodes showed excellent durability, with 89% capacity retention after 5000 cycles at 5 A/g with a coulombic efficiency of 96.2 %.

An aqueous Asymmetric Supercapacitor (AASC) device, using KCoPO_4 as the positive electrode and activated carbon (AC) as the negative electrode, showed an energy density of 121.1 Wh/kg and a power density of 6945 W/kg. It retained 86.3% of its capacity after 5000 cycles, with only a 9% loss in coulombic efficiency.

In **Chapter 4** $\text{KCo}_{1-x}\text{Ni}_x\text{PO}_4$ powders (where $x = 0, 0.1, 0.3, \text{ and } 0.5$) were synthesized using a sol-gel auto-combustion method followed by calcination at high temperature (at 600°C). Substitution of Co^{2+} with Ni^{2+} in the phosphate framework improves redox-mediated charge storage, leading to an enhancement of overall capacity. Among all the compositions, the $\text{KCo}_{0.5}\text{Ni}_{0.5}\text{PO}_4$ composition showed the best electrochemical performance, having a specific capacity of 173 mAh/g and capacitance of 1038 F/g. It mainly used the intercalation Pseudocapacitance charge storage mechanism, in which bulk storage was at 58% and surface storage at 42%.

$\text{KCo}_{0.5}\text{Ni}_{0.5}\text{PO}_4$ exhibited excellent cycling stability, wherein 88.93% of the capacity remained after 5000 cycles at a rate of 5 A/g. Energy density value of 183.7 Wh/kg and a power density of 414 W/kg at a rate of 0.5 A/g were noted for a Hybrid Supercapacitor of $\text{KCo}_{0.5}\text{Ni}_{0.5}\text{PO}_4/\text{AC}$. At 10 A/g, the device yielded a power density of 7952 W/kg and an energy density of 36.4 Wh/kg with very minimal degradation after 5000 cycles. The material, owing to its high

specific capacity, cycling stability, and power/energy densities, stands as a promising candidate for large-scale energy storage applications.

In **Chapter 5**, $\text{KCo}_{0.5}\text{Ni}_{0.4}\text{Mn}_{0.1}\text{PO}_4$ was prepared using a sol-gel auto-combustion method followed by calcination at 600°C . The substitution of Co^{2+} by Ni^{2+} and Mn^{2+} would increase redox interactions improving charge storage capacity and offering Hybrid storage behavior. The intercalative pseudocapacitive behavior dominated the $\text{KCo}_{0.5}\text{Ni}_{0.4}\text{Mn}_{0.1}\text{PO}_4$ electrode with a specific capacity of 177 mAh/g and a capacitance of 1062 F/g at 1 A/g.

A Hybrid Supercapacitor (AC// $\text{KCo}_{0.5}\text{Ni}_{0.4}\text{Mn}_{0.1}\text{PO}_4$) showed a specific capacity of 231 mAh/g and capacitance of 521 F/g at 1 A/g and an energy density of 202.7 Wh/kg and power density of 867.2 W/kg at a 2M KOH electrolyte. At 10 A/g, it had a high-power density of 9642 W/kg and good energy storage of 65.7 Wh/kg with excellent cyclic stability.

In summary, $\text{KCo}_{0.5}\text{Ni}_{0.4}\text{Mn}_{0.1}\text{PO}_4$ shows excellent electrochemical performance, which makes it a promising material for high-performance energy storage systems, including grid-scale applications.

Dopants affect the performance of KCoPO_4 -based electrodes due to the interaction of cations d band and results in the accessibility of redox couples to enhance the charge storage capacity of the materials. The synergistic interaction between Ni^{2+} and Co^{2+} ions result in superior energy density or charge storage property of $\text{KCo}_{0.5}\text{Ni}_{0.5}\text{PO}_4$. However similar interaction is not observed in the Co/Mn case as the Mn^{2+} (3d) band is well separated from the Co^{2+} (3d) band resulting in inaccessibility of the $\text{Mn}^{2+/3+}$ redox couple in Mn-doped KCoPO_4 .

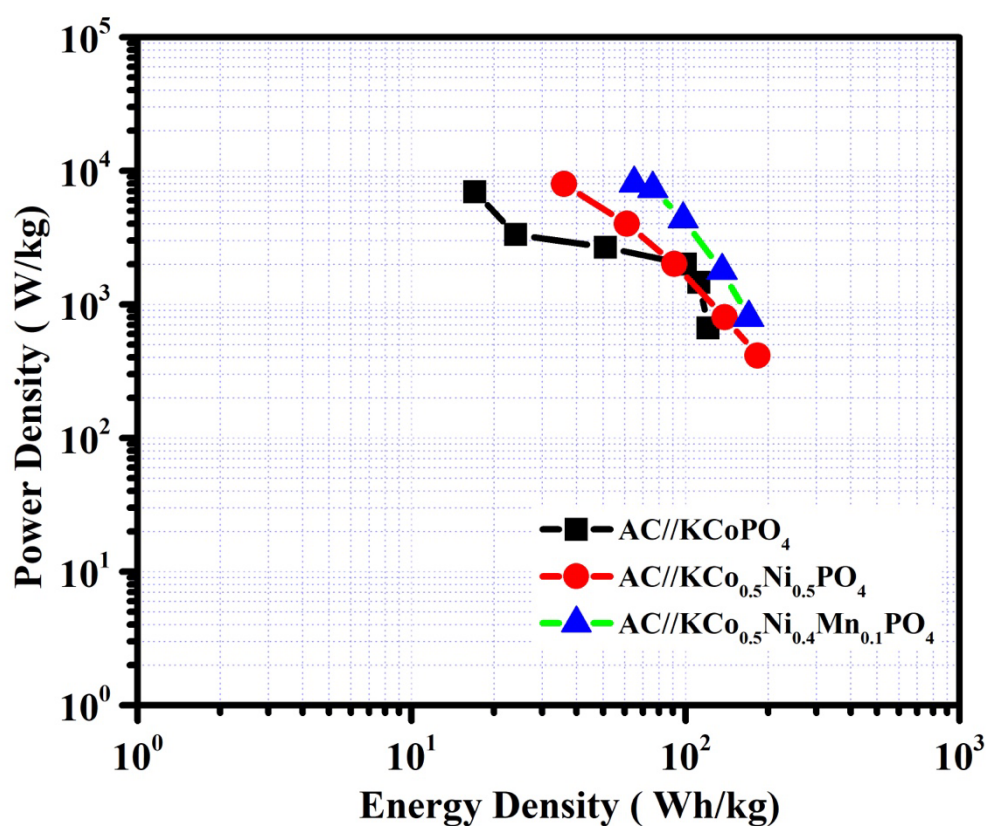


Figure 6.1: Comparison of energy density and power density plot of different Asymmetric Supercapacitor devices developed in this thesis at different current rates

6.2 Conclusion and Future Plans

Transition metal containing Phosphates based electrodes are investigated in this thesis dissertation to develop superior electrodes for intercalating pseudocapacitive charge storage applications. The materials discussed here in the thesis are open-channel frame structure, and they come with multiple applications that seek high-power Faradaic storage such as electrochemical capacitors and high-power battery. Potassium stabilized transition metal phosphates poses high structural stability for reliable, non-degrading and reversible energy storage. Strong bonding between K(4s) and O(2p) of PO₄ tetrahedra stabilized the antibonding O(2p) orbitals too deep to hinder the oxygen evolution in alkaline media to generate non degrading reversible energy storage. The other important aspect offered by this dissertation is complete summarization of the process of design, mechanism of fabrication, and evaluation on

Asymmetric Supercapacitor, "Asymmetric" referring broadly to the various differences in the positive or negative electrodes. I synthesized numerous Potassium stabilized cobalt, nickel and manganese-based Phosphates in various crystal structures to develop superior pseudocapacitive electrodes for an Asymmetric Supercapacitor cell. The following table illustrates the energy storage performance of the developed Asymmetric Supercapacitor devices.

The thesis work represents exploration of phosphate-based framework electrodes for electrochemical energy storage in aqueous electrolytes. The development of new electrode materials for reversible anion intercalation Supercapacitors will help in strengthening the domestic battery industry, supporting the "Make in India" initiative, and contribute to building indigenous energy storage and delivery technologies to meet national energy needs and balance the global imbalance between energy demand and supply.

Table 6.1: Showing energy storage capability of different Asymmetric Supercapacitor devices developed in this thesis at current rate of 1A/g.

Asymmetric device	Electrolyte	Energy density (Wh/kg)	Power density (W/kg)	Ref.
KCoPO ₄ //AC	2 M KOH	121.1	667	Chapter 3
KCo _{0.5} Ni _{0.5} PO ₄ //AC	2 M KOH	139.3	800.6	Chapter 4
KCo _{0.5} Ni _{0.4} Mn _{0.1} PO ₄ //AC	2 M KOH	202.7	867.2	Chapter 5

Despite the many remarkable progresses reported above, much innovation is still needed in Asymmetric Supercapacitors to make them better. The following are some potential future research directions:

1. Further investigation of charge storage mechanisms and understating of the contribution of EDLC and diffusive type charge storage.
2. Optimizing electrolytes is very important for improving the overall performance of Asymmetric Supercapacitor cells.
3. Advanced characterization methods, namely in situ or operando, are essential for probing such complex interfacial EDLC and diffusive charge storage processes.
4. Future designs of the Supercapacitor need to emphasize multi-functional innovation integration. The need is more pressing for highly flexible, wearable energy storage devices that are very easily integrated into fabric to be freed from large and clumsy battery packs.
5. Incorporation of other transition metal ion such as Fe, Ti, Cr and Mn etc. in the phosphate framework and study of electrochemical charge storage properties.
6. Supercapacitors rely much on monitoring the shelf discharge and leakage current in determining the performance in their application in commerce.