TUNING OF REDOX ENERGIES BY SYNERGISTIC INTERACTION OF DIFFERENT TRANSITION METAL IONS FOR THE DEVELOPMENT OF HIGH-PERFORMANCE HYBRID SUPERCAPACITORS

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By

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Chapter 7

Conclusions and Future Plan

In this chapter, we briefly describe the scientific output of the present thesis and summarize all our results, which offer valuable insights for the advancement of new energy storage and conversion devices. We also outline the future prospects of these scientific works.

7.1 Summary

One of the biggest scientific and societal challenges is to develop safe and sustainable clean energy for the future. Cost-effective, bulk grid-scale energy storage systems are highly desirable for different applications such as consumer electronics, power tools, and transportation. Supercapacitors (SCs) are a promising solution for storing electrical charges, offering advantages such as higher power densities, quicker charging times, and longer lifespan compared to lithium-ion batteries. This thesis aims to establish a connection between the crystal structure and the electronic properties of materials in order to develop highly efficient electrodes for pseudocapacitors. The focus is on developing layered transition metal oxides with open channel structures, which can facilitate rapid ion diffusion within their framework. These characteristics enable the electrodes to exhibit high energy density with exceptional power-delivering capabilities. Additionally, this thesis provides an understanding of the electrochemical reaction mechanism underlying pseudocapacitors and identifies the structural requirement for the materials to display pseudocapacitive behavior. The redox energy of the materials depends on their local electronic structure, via the formation of metal-ligand bonds. Hence, tailoring the crystal structure through suitable dopant concentration can significantly shift these energy bands and provide an opportunity to enlarge the operating potential window is the main finding of this thesis. Another achievement of this thesis is an aqueous-based asymmetric supercapacitor devices (ASCs) that comprise an optimized matching of electrode materials in combination with appropriate electrolytes and the current collector. Therefore, an ASC device having a wider operating potential window can be considered as an alternative to batteries for grid-scale energy storage solutions. Furthermore, the altering of structure with suitable dopant concentration could shift the redox energies of transition metal ions, providing valuable insights for the development of bi-functional OER/ORR catalysts, which can be utilized as a cathode material in the form of metal-air batteries for large-scale energy storage applications.

In the first chapter, we provided a concise overview of energy and discuss various sources of energy, encompassing both renewable and non-renewable. Our main focus was on the future prospects of global energy and identifying the most suitable alternatives to fossil fuels, considering global warming and climate change, which result in the net carbon addition in the Earth's atmosphere. Furthermore, we gave a brief description of electrochemical energy storage (EES) systems, classifying them based on their charge storage principles, and compiling various phenomena associated with them. The chapter concluded by identifying different types of electrode materials, specifically redox-mediated intercalative pseudocapacitor electrodes, as potential solutions for future grid-level energy storage technology.

The second chapter dealt with sample preparation methods, and onboard instruments used for crystal structure analysis, thermal analysis, and microstructural studies. We have also discussed the working principle of each characterization technique and covered data analysis tools like X-ray Rietveld refinement, and electrochemical impedance spectroscopy. Finally, Trassati and Dunn's methods was employed to explain the kinetics of the electrochemical reactions.

In chapter third, layered delafossite $AgFeO_2$ with an open channel structure was envisaged as a pseudocapacitor electrode using Fe^{2+}/Fe^{3+} redox couple. A co-precipitation method was employed to form the delafossite $AgFeO_2$ phase, resulting in a combination of 2H and 3R phases. The synthesis aimed to produce predominantly 2H phase, due to its larger inter-layer spacing compared to the 3R phase. The flower-like microarchitectures of $AgFeO_2$ exhibited superior electrochemical performance, with a high specific capacitance of 110.4 F

g^{-1} at a current density of 1 A g^{-1} in a 1 M Na_2SO_4 electrolyte. In an asymmetric device configuration, the AFO-400//AC full cell demonstrated excellent electrochemical performance, delivering high energy density (33.5 Wh kg^{-1}) and high-power density (454.3 W kg^{-1}), while maintaining excellent cycling stability (86% retention) up to the 2000th cycles.

Chapter four described the successful growth of $K_{0.4}MnO_2.\ xH_2O$ crystallites using a simple chemical flux method. These crystallites exhibited a birnessite-type layered structure with a lateral dimension ranging from 2 to 5 μm. In an asymmetric cell (ASC) configuration ($AgFeO_2$@C//$K_{0.4}MnO_2.\ xH_2O$), in which birnessite- $K_{0.4}MnO_2.\ xH_2O$ served as the positive electrode (cathode), and a thin carbon layer coated $AgFeO_2$ as the negative electrode (anode) demonstrated high energy density and power density, along with excellent cycle life in 1M Na_2SO_4 electrolyte, achieving cell voltages of up to 1.8 V. The presented asymmetric cell (battery-type supercapacitor) showed a maximum energy density of 61.51 Wh kg^{-1} and a power density of 450 W kg^{-1} at a current density of 0.5 A g^{-1}. These values surpassed previously reported aqueous electrolyte-based asymmetric supercapacitors and position this technology as a potential replacement for hazardous lead-acid batteries in fast energy storage applications.

In the fifth chapter, Sr-doped $YMnO_3$ perovskite was prepared and studied for pseudocapacitance in a 2M KOH aqueous electrolyte. YSMO-50 with 50% strontium doping provided an equivalent three-dimensional network and superior conductivity due to Mn^{3+}–O^{2-}–Mn^{4+} hopping conduction. The key finding of this chapter was the water-mediated interconversion of oxide-ion to hydroxide ion ($M^{2+}O^{2-} + H_2O + e^- \leftrightarrow M^+OH^- + OH^-$), incorporating Mn^{2+}/Mn^{3+} and Mn^{3+}/Mn^{4+} redox couples which generated a large amount of charge over the perovskite electrode. An energy density equivalent to 65.13 Wh kg^{-1} was achieved using YSMO-50 as a negative electrode and activated carbon as a positive electrode in the PVA-KOH gel electrolyte. Our study revealed that the doping of low valence atom (Sr) at the A-site in perovskite manganite ($YMnO_3$) might be an effective tool to enhance the pseudocapacitive performance of perovskite-based electrodes.

In chapter six, a hydrothermal method was used to synthesize various Mn-based layered compounds (γ-MnOOH, $LiMnO_2$-Li_2MnO_3, and spinel $LiMn_2O_4$) and investigated as bi-functional OER/ORR catalysts in a 1M KOH aqueous electrolyte. Among the synthesized materials, a composite consisting of 56% $LiMnO_2$ and 44% Li_2MnO_3 showed the highest catalytic activity, attributed to the stabilization of metastable $LiMnO_2$ (Mn^{3+}) within Li-rich Li_2MnO_3. The structural analysis, including XRD, Rietveld refinement, SAED pattern, and HR-TEM image, clearly indicated the presence of structure defects, such as ordered oxygen vacancies that resulted in stacking faults in the composite. These ordered oxygen-vacant sites in the form of stacking faults were likely responsible for the formation of terminal hydroxyl and Mn^{3+}-di-μ-oxo-Mn^{4+} complexes, which further enhanced the catalytic activity of the composite. Overall, this study demonstrated the potential of stabilizing Mn^{3+} in a layered composite with ordered oxygen vacancies as a promising approach for developing efficient water oxidation electrocatalysts.

7.2 Conclusion and Future Plans

The materials discussed in this thesis have an open channel framework structure and could be used in a number of applications that require high-power Faradaic storage, from electrochemical capacitors to high-power batteries. Additionally, this dissertation summarized the insight into the design, mechanism, fabrication, and evaluation of asymmetric supercapacitors, where the term “asymmetric” was broadly referred to the difference between positive and negative electrodes. We have introduced various iron and manganese-based compounds into the different crystal structures in order to make an asymmetric supercapacitor cell. The table presented below shows the comparative energy storage performances of developed asymmetric supercapacitor devices:

The present thesis utilized two different types of aqueous asymmetric supercapacitor devices, pseudocapacitive materials//carbon electrodes-based ASCs ($AgFeO_2$//AC & YSMO-50//AC) and all pseudocapacitive material-based aqueous ASCs ($K_{0.4}MnO_2.x H_2O$//$AgFeO_2$@C). From the Table 7.1, it can be seen that all pseudocapacitive material-based ASCs (Chapter 4) exhibited higher energy density than pseudocapacitive materials//carbon electrodes-based ASCs (Chapters 3 & 5). Thus, building an ASC with two different types of pseudocapacitor electrodes put forward an effective tool to enhance the energy density of SCs.

Table 7.1: Showing energy storage capability of different asymmetric supercapacitor devices developed in this thesis.

Asymmetric device	Electrolyte	Current density (A g^{-1})	Potential window (V)	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Ref
$AgFeO_2$//AC	1 M Na_2SO_4	0.4	1.8	33.8	454	Chapter 3
$K_{0.4}MnO_2.$ $x$$H_2O$// $AgFeO_2$@C	1 M Na_2SO_4	0.5	1.8	61.51	450	Chapter 4
YSMO-50//AC	2 M KOH	0.5	1.8	65.13	450	Chapter 5

Therefore, the future perspective will be to design the ASCs which have a wider operating voltage window, hence achieving high energy performance in aqueous electrolytes. Additionally, the development of novel electrode materials (both positive and negative), which show superior performance in a separate potential window, strengthen the domestic battery industry and will help to build indigenous (swadeshi) energy storage and delivery technology, which can overcome the global imbalance in Energy demand vs. supply. Despite the aforementioned impressive progress, innovative approaches are still needed to enhance the performance of asymmetric supercapacitors. Here, we suggest some prospective and future research to be carried out:

(1) The charge storage mechanisms need further understanding including both EDLC and pseudocapacitance.

(2) Electrolyte optimization is also essential to increase the overall performance of the asymmetric supercapacitor cells.

(3) Advanced characterization techniques including in situ or operando methods are essential to study the complex interfacial process of EDLC and pseudocapacitance.

(4) Future supercapacitor design utilizes the incorporation of device innovation with multi-functionality. There is a growing demand for the development of highly flexible and

wearable energy storage devices that can be seamlessly integrated into fabrics, thereby eliminating the need for conventional bulky battery packs.

(5) The shelf discharge and leakage current of supercapacitors should be monitored as it has a significant impact on how supercapacitors are used in commercial devices.