Synthesis and Electrochemical Performance of High Performing Pseudocapacitive Sulfide Electrodes for the Development of Supercapacitor/or Supercapattery

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By

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7.1 Summary

We need more efficient methods to store energy as the world dependence on renewable energy sources like wind and solar power increases. We may benefit from energy storage technologies like pseudocapacitors because it provides a dependable and effective method to store and release energy as required. Pseudocapacitive materials, with their high specific capacitance and rapid charge/discharge rates, have emerged as promising candidates for overcoming the limitations of conventional supercapacitors and batteries. Transition metal sulfides (TMS) possess a variety of unique properties that make them highly desirable for use in supercapacitor applications due to their abundance, low cost, efficient energy storage ability, excellent electrochemical stability, high electrical conductivity and remarkable electrochemical properties compared to other electrodes.

This thesis aimed to explore the potential of TMS as pseudocapacitive materials for efficient energy storage electrodes. The thesis explores the fundamental electrochemical processes, elucidate the charge storage mechanisms, and optimize the transition metal sulfide electrode performance. The thesis further explores the kinetics and thermodynamics of the electrochemical charge storage processes occurring at TMS-based electrodes. This involves the study of charge transfer kinetics, surface redox reactions, ion diffusion, and the influence of electrolytes on the overall performance. In this thesis we have developed a concise synthesis scheme for the synthesis of nanocrystalline TMS and study their electrochemical performance for pseudocapacitive energy storage.

Chapter 1, illustrates briefly the general introduction, literature review and scope of this work. This chapter include the need for alternative energy storage solutions from renewable energy systems to portable electronics, and discussed the challenges and limitations that must be overcome in order to fully realize their potential especially electrochemical energy storage devices. There is a detailed explanation of the pseudocapacitive electrode materials and suitability of TMS electrodes for the development of hybrid supercapacitors (HSC) to deliver large scale energy storage system.

Chapter 2, describes a concise overview of the experimental methodology, encompassing the synthesis techniques for producing materials with controlled morphology and composition and their detailed theoretical background of characterizations along with electrochemical techniques to measure the electrode's performances and to analyse their charge storage.

In **Chapter 3**, a systematic study of the nanocrystalline β-NiS towards pseudocapacitive energy storage. The reversible transformation of Ni^{2+} to Ni^{3+} through electrosorption (redox) of OH^- ions coupled with surface-control redox (non-diffusion) mediated pseudocapacitance processes is responsible for the high specific capacitance (1578 F/g at 1 A/g in 2M KOH) of β-NiS nanoparticles. With 90% capacitive retention and 96% coulombic efficiency after continuous 2500 cycles of charge/discharge, the β-NiS electrode//AC (ASC) full cell exhibits excellent long-term cyclic stability. The maximum power density of ~5021 W/kg was obtained when energy density reached ~68 Wh/kg at 10 A/g of current density for nanocrystalline β-NiS electrode in two-electrode β-NiS//AC full cell.

Chapter 4, describes the synthesis and characterization of hexagonal CoS nano-spheres, and put detailed discussion about the structural and electrochemical

properties of layered CoS nano-spheres. The CoS electrode displayed an excellent specific capacitance (761 F/g at 1 A/g in 2 M KOH) due to the reversible transformation of $Co^{2+} \rightleftharpoons Co^{3+}$ through electrosorption (redox) of OH^- ions coupled with EDLC-type surface contribution. An aqueous asymmetric hybrid supercapacitor (HSC) device was fabricated using CoS as the positive electrode and the activated carbon (AC) as the negative electrode. The asymmetric HSC device results in high energy and power densities of ~139.7 Wh/kg and ~7.51 kW/kg, respectively, which shows excellent cyclic stability of up to 87% after 10000 continuous charge-discharge cycles.

In **Chapter 5**, nano-engineering was employed to develop nano-chains architectures of $Ni_{0.5}Co_{0.5}S$ electrode material consisting of interconnected nano-spheres which are rationally designed to develop high-performance supercapacitive electrodes. Nano-chains of bimetallic sulfide $Ni_{0.5}Co_{0.5}S$ electrode exhibited a highly improved electrochemical performance achieving the specific capacity of 2190 F/g at 1 A/g in 4 M KOH aqueous electrolyte. Furthermore, an impressive energy density equivalent to ~257 Wh/kg and power density of ~7.2 kW/kg was achieved by the assembled $Ni_{0.5}Co_{0.5}S$//AC two electrode full cell in ASCs mode where AC acted as the negative electrode and the $Ni_{0.5}Co_{0.5}S$ electrode as the positive electrode in 4 M KOH electrolyte.

Chapter 6, describes the detailed study of perovskite type $SrFeO_{3-\delta}$ prepared by flux-method which shows superior pseudo-capacitive charge storage as the negative electrode of a pseudo-capacitor or supercapacitor with superior stability. $SrFeO_{3-\delta}$ offers high specific capacitances of 743 F/g at a current density of 1 A/g due to the participation of $Fe^{4+/3+}$ and $Fe^{3+/2+}$ redox couples. Further $SrFeO_{3-\delta}$ demonstrates excellent cyclic stability which is attributed to the inherent metallic electrical

conductivity of $SrFeO_{3-\delta}$ and the fortuitous tendency of the robust cation framework structure to accommodate flexible oxygen content. Further the asymmetric ASC device fabricated and results in high energy and power densities of ~191.0 Wh/kg and ~10 kW/kg, respectively, which shows excellent cyclic stability of up to 92.4% after 5000 cycles of GCD experiment.

Chapter 7, describes findings an overview of this thesis for the nano-structured transition metal sulfides (TMS) as a novel pseudocapacitive electrode for adequate electrochemical energy storage. Superior performances of the electrodes were obtained due to clear-cut redox mediated pseudocapacitance i.e. reversible transformation of $M^{2+/3+}$ redox couple through electrosorption (redox) of OH^- ions coupled with EDLC-type surface contribution of capacitance. The diffusion coefficient (D) of OH^- ions based on the Randles-Sevick equation is low for CoS (2.16×10^{-9} cm^2/s) compared to NiS ($3.13\times10^{-7}cm^2/s$), whereas the D value for $Ni_{0.5}Co_{0.5}S$ lies between them (3.14×10^{-8} cm^2/s). In fact, in the solution, D of the species is in the range of tens of micro cm^2/s, indicates rapid transportation of ions. The *b*-value from the power law for NiS, CoS and $Ni_{0.5}Co_{0.5}S$ are 0.58, 0.77 and 0.68, respectively, indicating the dominance of semi-infinite diffusion-controlled intercalative processes in the NiS electrode and in the CoS electrode, it is primarily due to from surface capacitive reactions rather than from diffusion-controlled insertion reactions. In contrast, energy storage for $Ni_{0.5}Co_{0.5}S$ contributes linear combination of diffusion-controlled insertion processes and pseudocapacitive processes (diffusion-controlled redox-mediated intercalative processes). The redox activity for $Ni_{0.5}Co_{0.5}S$ is increased as the substitution of Ni atom to the Co-site. This may be due to increase in redox mediated intercalative charge storage at Ni-site coupled with double layered capacitance. The synergistic interaction between Co and Ni leads to very high charge storage capacity of electrodes. Further metallic

$SrFeO_{3-\delta}$ is presented as a robust negative pseudocapacitive electrode as an alternative to AC. Redox mediated interconversion $O^{2-} + H_2O \rightleftharpoons 2OH^-$ was found as the key component behind superior pseudocapacitive charge storage in the perovskite $SrFeO_{3-\delta}$ electrode. The specific capacitance of electric double-layer capacitors (EDLCs) relies on the charge accumulated on the surface of the electrode, and when the specific surface area increased up to a certain level, the capacitance increased, but over that level, it may decrease because micropores reduce conductivity. As the specific surface area of the electrode materials increases it facilitate the diffusion of electrolyte ions (OH^-) into the electrode surface thus increases the diffusion-controlled intercalation process, which increases the capacitance of the electrode materials.

The BET-specific surface area of the different materials used in this thesis are summarized in Table-7.1, and result shows that effect of high surface area in storing high surface charge is clearly visible. However, we have not found any direct effect of high surface area in resulting superior capacitance.

Table 7.1 Displays the comparative study of BET-specific surface area and capacitance of the different electrode materials used

Electrode Material	**BET-Surface area (m^2/g)**	**Pore diameter (nm)**	**Capacitance at 1mV/s**
β-NiS	64.0	23.0	1611
CoS	13.7	14.5	776
$Ni_{0.5}Co_{0.5}S$	13.5	14.3	2378
$SrFeO_{3-\delta}$	37.0	27.0-54.0	733

Additionally, Table-7.2 compares the electrochemical characteristics of all TMS electrodes (β-NiS, CoS, and $Ni_{0.5}Co_{0.5}S$) with perovskite $SrFeO_{3-\delta}$ electrodes.

Table 7.2 Displays the electrochemical characteristics of the fabricated ASC full cells

Material	Energy density (Wh/kg)	Power density (kW/kg)	Cycling stability (%) after "n" cycles	Capacitance (three-electrode system)
β –NiS//AC	~163.0	~0.51	90.0%, 2500	1578 F/g at 1 A/g
CoS//AC	~139.7	~0.75	87.0%, 10000	761 F/g at 1 A/g
$Ni_{0.5}Co_{0.5}S$//AC	~257.0	~0.73	89.5%, 8000	2190 F/g at 1 A/g
$SrFeO_{3-\delta}$	~191.0	~0.99	92.4%, 5000	743 F/g at 1 A/g

7.2 Future Scope

Supercapacitors (SCs), which are recognised for their high power densities, are replacing rechargeable lithium-ion batteries, which formerly dominated the energy storage industry. The global supercapacitor market growth and history forecast their rapid rise in numerous applications. Hybrid and fuel cell vehicles need such a surge of energy to start than can be supplied by standard batteries. SCs are also necessary for various engineering and electrical applications whenever a large energy burst is needed. Due to the excellent features of SCs, such as longer cycle-life, high power density, and fast and simple charging even at low temperatures, have generated much attention for commercial electronics and are used in various applications. The high performance of β-NiS, CoS & $Ni_{0.5}Co_{0.5}S$ electrodes in aqueous asymmetric capacitors can make the path to develop superior high performance battery. Even the cost of Ni & Co is high and they have a very high applicability in Li-ion batteries but the performance of β-NiS, CoS & $Ni_{0.5}Co_{0.5}S$ electrodes can make aqueous asymmetric supercapacitors as an alternative for conventional non-aqueous Li-ion batteries.

Future scope of present work that could improve the performance are as follows

1. Development of novel electrode materials for reversible anion intercalation type pseudocapacitors which enhance and strengthen the energy storage
2. Nano-engineering in the synthesis of electrode materials to improve its surface and electronic properties
3. Search of framework and hybrid structured materials to enhance the energy density and stability of pseudocapacitive electrodes
4. Optimization of electrolyte concentration and operating voltage window for best activity of the cell and developing new electrolytes that can improve the charge/discharge rates and cycle life of pseudocapacitors
5. Pseudocapacitive electrode-based supercapacitors assembly (HSC/ASC) performances and optimisations at the device level.
6. Try to reach energy density (> 50Wh/Kg) and superior power (>200 W/Kg) for sulfide-based full cell SCs.
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 sulfide-based pseudocapacitive anion intercalative electrodes delivering energy and power capabilities similar to Li-ion batteries.