

Preface

The development of high-performance efficient energy storage systems devices propelled immense research interest to provide a sustainable energy supply to the world by utilizing the full potential of renewable energy sources. Traditional solutions like lithium-ion batteries suffer from high costs, poor performance at high current rates, and environmental impact restrictions. 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) have garnered significant attention due to their abundance, low cost, efficient energy storage ability, and remarkable electrochemical properties compared to other electrodes.

This thesis entitled “*Synthesis and electrochemical performance of high performing pseudocapacitive sulfide electrodes for the development of supercapacitor/or supercapattery*” explores the potential of TMS as pseudocapacitive materials for efficient energy storage electrodes. The study's primary goals are to understand the fundamental electrochemical processes, elucidate the charge storage mechanisms, and optimize the transition metal sulfide electrode performance. The thesis 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. The following chapters comprise the structure of this current thesis:

The **first chapter** begins with a brief overview of energy sources and explores alternative energy sources of fossil fuels, including renewable and non-renewable. This chapter mainly discusses electrochemical energy storage (EES) systems categorizing

them based on their charge storage mechanism and compiling various phenomena associated with capacitors, batteries and pseudocapacitors. The main section of this chapter concludes by highlighting the significant output of this research, which is the identification of redox-mediated intercalative pseudocapacitive electrodes.

The **second chapter** provides a concise overview of the experimental methodology, encompassing the synthesis techniques for producing materials with controlled morphology and composition and their characterizations along with electrochemical techniques to measure the electrode's performances and to analyze charge storage mechanism.

In the **third chapter**, I discuss in detail about synthesis, characterizations, and electrochemical performances of nanocrystalline β -NiS. The electrode shows the excellent specific capacitance of 1578 F/g at 1 A/g from the galvanostatic discharge profile in 2M KOH aqueous electrolyte due to the reversible transformation of Ni^{2+} to Ni^{3+} through electrosorption (redox) of OH^- ions. Further, the b -value from the power law for charge storage kinetics/mechanisms attributed to semi-infinite diffusion-controlled and surface-control redox (non-diffusion) mediated pseudocapacitance processes responsible for the high specific capacitance of β -NiS nanoparticles.

The **fourth chapter** of the thesis 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 of 761 F/g at 1 A/g current density due to the reversible transformation of $\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+}$ through electrosorption (redox) of OH^- ions coupled with EDLC-type surface contribution of capacitance in 2 M KOH aqueous electrolyte. 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 the **fifth chapter**, nano-chains architectures of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}$ electrode materials consisting of interconnected nano-spheres are rationally designed by tailoring the surface structure to develop high-performance supercapacitive electrodes. Nano-chains of bimetallic sulfide $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}$ 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 $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}/\text{AC}$ two electrode full cell in ASCs mode where AC acted as the negative electrode and the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}$ electrode as the positive electrode in 4 M KOH electrolyte.

In the **sixth chapter**, I present the detailed study of perovskite type $\text{SrFeO}_{3-\delta}$ prepared by flux-method which shows superior pseudo-capacitive charge storage as the negative electrode of a pseudo-capacitor or supercapacitor with superior stability. $\text{SrFeO}_{3-\delta}$ offers high specific capacitances of 743 F/g at a current density of 1 A/g due to the participation of $\text{Fe}^{4+/3+}$ and $\text{Fe}^{3+/2+}$ redox couples. Further $\text{SrFeO}_{3-\delta}$ demonstrates excellent cyclic stability which is attributed to the inherent metallic electrical conductivity of $\text{SrFeO}_{3-\delta}$ and the fortuitous tendency of the robust cation framework structure to accommodate flexible oxygen content.

The concluding **seventh chapter** presents an overview of 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 active participation and the reversible transformation of $\text{M}^{2+/3+}$ redox couple through electrosorption (redox) of OH^- ions coupled with EDLC-type surface

contribution of capacitance. Further metallic SrFeO_{3-δ} 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-δ} electrode.