Preface

The world can be viewed from inside to outside, only through an energy prism. Therefore, energy can be considered as the currency of the universe. Energy exists in many forms such as electromagnetic radiation, electric, magnetic, nuclear, chemical, thermal, and mechanical processes. These different forms of energy can be converted from one to another, but the total amount of energy in a closed system remains constant. This idea leads to the foundation of basic laws of physics, known as the conservation of energy. Standards of living and energy use have been growing exponentially and in the upcoming future two things are certain: (1) the world population will increase exponentially and (2) economic reserves of fossil fuels, particularly oil, coal, and natural gas, will decrease substantially. New technology and better living habits must be developed to fulfill the ever-increasing energy demand, and the environment's quality needs to be preserved for a promising future. Renewable energy sources are plentiful in nature and can be naturally replenished and also safe for the environment, these include Solar energy, geothermal energy, wind energy, biomass, and hydro energy. However, most of the renewable energy coming to the Earth's surface is time, location, and weather-dependent and cannot be used directly in electrical and electronic appliances. So, energy storage and conversion become a key challenge to harnessing the full potential of renewable energy sources, and thus grid-scale energy storage solutions are needed to reduce the reliance on fossil fuels.

Of the many ways to store energy, electrochemical energy storage (EES) such as batteries and supercapacitors have garnered tremendous attention due to their high theoretical efficiency in converting chemical to electrical energy. There are several processes by which EES occurs at solid-state electrodes via; (i) the formation of an electrical double-layer (EDL), (ii) surface redox reactions, (iii) intercalation/de-intercalation of ions, and (iv) alloying, decomposition, or conversion reactions. The latter three processes are Faradaic in origin; that is, they obey Faraday's law and involve charge transfer reactions at the electrode-electrolyte interface. Among these, surface redox and ion insertion reactions have been considered pseudocapacitive because their thermodynamic and kinetic behavior can be described with the same mathematical models as those for surface adsorption/desorption. The concept of pseudocapacitance emerged in the early 1960s to describe surface Faradaic processes such as under-potential deposition and hydrogen adsorption. Further, it was extended to energy storage in the early 1970s with the observation that thin films of hydrous RuO_2 cycled in an acidic electrolyte exhibited cyclic voltammograms that resembled those of capacitors, while single-crystal RuO_2 did not. The exact atomistic mechanism is often unknown but is typically ascribed to reversible charge transfer reactions that are not limited by solid-state diffusion. The technological motivation for the search for pseudocapacitive electrode materials is to overcome the kinetic limitations of Li-ion batteries while achieving higher energy densities compare to the electrical double-layer capacitors (EDLCs).

This thesis aims to provide a comprehensive understanding of pseudocapacitors, that leads to the identification of a novel category of electrode materials. It emphasizes the importance of the electrochemical reaction pathway underlying pseudocapacitors and elucidates the structural requirements that enable materials to exhibit pseudocapacitance. This thesis further underscores the requirement of in situ or operando methods to investigate electrochemical behavior and outlines recent efforts in developing fundamental theories of pseudocapacitors. Moreover, it acknowledges the current progress in material designing for the emergence of diverse energy storage devices, more particularly asymmetric supercapacitor devices. The present thesis is organized in the form of the following chapters:

In the **first chapter**, we provide a brief overview of energy and explore different types of energy sources, including renewable and non-renewable. Our focus is on the future outlook of global energy and finding the most suitable alternatives to fossil fuels, taking into concerns such as global warming and climate change. Additionally, we provide a concise overview of electrochemical energy storage (EES) systems, categorizing them based on their charge storage principles. The final section of this chapter concludes by highlighting the significant output of this research, which is the identification of redox-mediated intercalative pseudocapacitive electrodes.

In **chapter second**, we provide a concise overview of the methodologies employed for sample preparation, along with the onboard instrumentations used for crystal structure, thermal, and microstructural analyses. We also discuss data calibration tools such as X-ray Rietveld refinement, electrochemical study, and impedance spectroscopy. In the end, we describe the kinetics of electrochemical reactions with the help of Trassati and Dunn's methods.

The third chapter of the thesis describes the synthesis and characterization of Layered delafossite $AgFeO_2$, and a put detailed discussion about the structural and electrochemical properties of Layered $AgFeO_2$, having a mixed phase of 2H and 3R-phase. The 2H phase was aimed to synthesize as a majority phase because it has larger interlayer spacing than the 3R phase, and is responsible for superior performance of 2H-$AgFeO_2$.

In the fourth chapter, we have successfully grown the crystallites of $K_{0.4}MnO_2. xH_2O$, having a birnessite-type layered structure. An asymmetric cell was fabricated using birnessite- $K_{0.4}MnO_2. xH_2O$ as a positive electrode (cathode), and the thin carbon layer coated $AgFeO_2$ as a negative electrode (anode) in aqueous 1M Na_2SO_4 electrolyte that exhibited high energy density and high power density with excellent stability up to cell voltages close to 1.8 V. The newly developed high-voltage aqueous asymmetric battery-type supercapacitors device has a low-cost and enviro-friendly, that can replace market-available hazardous lead-acid batteries.

In the fifth chapter, we have investigated Sr-doped $YMnO_3$ i.e. $Y_{1-x}Sr_xMnO_{3-\delta}$ perovskite, as electrode material for pseudocapacitance. The formation of the mostly cubic phase, with 50% Sr-doping $YMnO_3$ (YSMO-50) provides an equivalent three-dimensional network and superior conductivity due to Mn^{3+}–O^{2-}–Mn^{4+} hopping conduction, resulting in superior performance has been observed. Redox-mediated interconversion of oxide to hydroxide ($M^{2+}O^{2-} + H_2O + e^- \leftrightarrow M^+OH^- + OH^-$) in aqueous media is shown to be the reason behind the high capacitance of YSMO-50. Our study reveals that the doping of low valence Sr^{2+} at the A-site in perovskite manganite ($YMnO_3$) may be an effective tool to enhance the pseudocapacitive performance of perovskite-based electrodes.

In the **sixth chapter**, we have synthesized $LiMnO_2$-Li_2MnO_3 nanocomposite via a two-step hydrothermal method. The nanocomposite exhibited excellent bi-functional OER/ORR activity in an alkaline medium. The stabilization of metastable $LiMnO_2$ ($Mn^{3+)}$ in Li-rich-Li_2MnO_3, in the form of a composite $LiMnO_2$-Li_2MnO_3 (0.56-0.44), produces a large number of oxygen vacancies and stacking faults into the structure. These defects can act as an oxygen-evaluating center in the catalyst. Additionally, the formation of the Mn^{3+}-di-μ-oxo-Mn^{4+} compound in strongly alkaline conditions contributes to the superior catalytic activity of the composite material. Therefore, the mixed $Mn^{3+/4+}$ valence state in the form of a layered structure exhibits superior catalytic activity compared to γ-MnOOH and spinel $LiMn_2O_4$.

The seventh chapter provides the scientific output of the present thesis and summarizes all the results, which offer valuable insights for the advancement of new energy storage and conversion devices. These devices have the potential to surpass the currently existing energy storage technology and can minimize the use of fossil fuel-based energy solutions.

A list of journals and books used to bind up the thesis has been given at the end as references.