# Abstract

It is well-known that rechargeable energy storage technologies are of paramount importance for a modern society. Over the decades, it has been witnessed that there are profound advancements in building better and safer energy storage devices based on sustainable resources. While there are several such platforms for integration with energy generation systems, the electrochemical energy storage devices, particularly the rechargeable batteries, are quite attractive due to the merits of easy handling, minimal space requirements, relatively long-life time and low maintenance. Rechargeable batteries primarily the lithium-ion batteries (LIBs) are now deeply enrooted into the lives of common people as this technology has certainly fulfilled some of our greatest energy aspirations over the decades. However, in spite of the tremendous success of LIBs, there is unrelenting focus for the development of state-of-the-art rechargeable batteries which are economically affordable and safer in repeated operation. The use of organic electrolytes is prevalent in current high energy dense batteries. However, a possible replacement of these electrolytes by appropriate aqueous electrolytes holds immense promise in mitigating the safety issue. In addition, the convenience of handling and processing of an aqueous electrolyte under ambient conditions presents a unique opportunity for large scale manufacturing of aqueous batteries even in geographically remote locations. Aqueous electrolytes are also fundamentally important due to its higher ionic conductivity in comparison to organic counterpart which is an essential criterion for driving a high-power device. The growing demand for sustainable and safe energy storage solutions, particularly for grid-scale applications, continues to drive innovation and exploration in the field of aqueous battery technologies.

The present thesis aims to study monovalent and multivalent (primarily $K^+$ and $Al^{3+}$ ion) ion-based energy storage devices. It explores the electrochemical behavior, advantages, and challenges associated with each ion type, with a particular focus on developing and optimizing electrode materials and electrolyte suitable for stable operation. Additionally, the complex electrochemical mechanisms associated with these systems which governs the ion transport and ion storage are also investigated.

**Chapter 1** briefly discusses the crucial role of energy storage in advancing the global transition toward a green and sustainable future. It highlights the significance of aqueous monovalent and multivalent ion storage devices in addressing current global energy demands. The chapter also explores the importance of developing a comprehensive library of electrode materials to support the expansion of these aqueous-based energy storage technologies.

**Chapter 2** describes aqueous electrolyte mediated reversible potassium ion insertion in graphite. It is observed that the type of graphite as well as the concentration of electrolytes plays a pivotal role in the potassium ion electrochemistry. It was investigated that pyrolytic graphite fails to host $K^+$ ion whereas natural graphite shows good cycling stability towards potassium ion intercalation. It is also revealed that the $K^+$ ion insertion significantly enhanced the wettability of the graphite electrode which promotes ion insertion kinetics. The EIS measurements show that the charge transfer resistance for the natural graphite electrode is much lower in comparison to the pyrolytic graphite electrode.

**Chapter 3** highlights the significance of the current collector when evaluating electrode materials for aqueous potassium-ion batteries. It is observed that the choice of current collector plays a crucial role in mitigating unwanted side reactions by forming an active interface. The current collector is shown to significantly influence the electrochemical performance of $Bi_5Nb_3O_{15}$. Graphite, in particular, is identified as the optimal current collector due to its ability to form a favorable electrode-electrolyte interface. Under these conditions, the $Bi_5Nb_3O_{15}$ particles can maintain a stable $K^+$ ion storage capacity of 100 mAh $g^{-1}$ at a current rate of 2 A $g^{-1}$. While titanium and stainless-steel current collectors exhibit some degree of electrochemical activity, nickel current collectors show the poorest performance.

**Chapter 4** explores the of reversible $Al^{3+}$ ion intercalation in Bismuth molybdate ($Bi_2MoO_6$) and Bismuth tungstate ($Bi_2WO_6$) in aqueous electrolyte. It is shown that $Al^{3+}$ ion storage capacity is strongly dependent on the concentration of the electrolytes. While facile $Al^{3+}$ ion electroreactivity is possible in both the materials, $Bi_2WO_6$ depicts the best cycling performance in aqueous $AlCl_3$ electrolyte. It is obtained that capacity fading is a severe problem for both the materials in 1 M $AlCl_3$ aqueous electrolyte while electrochemical stability could be seen for 0.5 M $AlCl_3$ aqueous electrolyte only for $Bi_2WO_6$. The specific capacity has been enhanced using exfoliated graphite current collectors (above 200 mAhg$^{-1}$). The mechanistic study after the charge/discharge process suggests a possible phase transformation of $Bi_2WO_6$ which was identified to be BiOCl phase.

**Chapter 5** discusses the impact of hydrogen doping on enhancing the $Al^{3+}$ ion storage capacity of $MoO_3$ in aqueous electrolytes. It is shown that hydrogen doping significantly improves the storage behaviour of $Al^{3+}$ ions in $MoO_3$. This doping notably reduces the charge transfer resistance and enhances the diffusion rate of the $Al^{3+}$ ions, with the hydrogen-doped $MoO_3$ showing an increase in diffusion rate by almost a factor of 8. Additionally, the high-rate performance of $MoO_3$, mediated by hydrogen doping, is demonstrated. A discharge capacity exceeding 100 mAh g$^{-1}$ is achieved at an extremely high current rate of 20 Ag$^{-1}$.

**Chapter 6** summarizes the entire thesis work highlighting the important and major findings.

# KEYWORDS

Energy storage; aqueous electrolytes; electroactive materials; potassium ion batteries, aluminum ion battery, doping, graphite.