Chapter 6

Conclusions

“A good storage battery is the most perfect thing in the world for holding electricity until you are ready to use it.”

-Thomas A. Edison

6. Conclusions

In conclusion, this thesis offers a thorough analysis of different aqueous monovalent and multivalent energy storage systems (primarily K^+ and Al^{3+}), examining their behaviour and performance across a diverse array of electrode materials. These systems, which are of growing interest due to their potential for sustainable and cost-effective energy storage, were studied using a combination of electrochemical and morphological analyses to better understand their underlying mechanisms and performance. Through detailed experimentation, a number of critical parameters were identified that significantly influence the efficiency and durability of these systems, which includes the chemical composition and structural properties of the electrode materials, the nature of the electrode–electrolyte interface, the concentration and type of the electrolyte, as well as modifications made to the surfaces of the current collectors etc. Strategies, such as doping, substrate modification were adopted to enhance the specific capacities and overall rate performance of the electrode materials. The results consistently demonstrate that these intrinsic and extrinsic factors collectively play a pivotal role in determining the electrochemical stability, reversibility, and long-term cycling performance of the energy storage devices. This work contributes valuable insights that may guide future research and development in the design of high-performance, environmental friendly aqueous energy storage systems.

Chapter 1: Introduction

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: Aqueous electrolyte mediated reversible K^+ ion insertion in graphite.

Chapter 2 describes aqueous electrolyte mediated reversible potassium ion insertion in graphite for the first time. Two types of graphite such as natural and pyrolytic were utilized in order to investigate the K^+ ion electrochemistry in various concentrations of KOH electrolyte. 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 insertion. Another set of experiments were carried out using the exfoliated graphite electrodes which showed reduced overpotential and better electrochemical performance than the natural graphite. The EIS measurements show that the charge transfer resistance for the natural graphite electrode is much lower in comparison to the pyrolytic graphite electrode. It is also revealed that the K^+ ion insertion significantly enhanced the wettability of the graphite electrode which promotes ion insertion kinetics. The contact angle measurement values of the discharged state electrode show reduction in comparison to natural graphite electrodes. It is obtained that K^+ ion insertion leads to a 55 % rise in disorder in the graphite electrode. The XPS analysis confirms the presence of K^+ ion species in the discharged state electrode depicting insertion of K^+ ion during cycling. The AFM and FESEM images obtained after cycling support these findings.

Chapter 3: The Active-Inactive Interface for K^+ Ion Storage- A Case Study with $Bi_5Nb_3O_{15}$

Chapter 3 highlights the significance of the current collector when evaluating electrode materials for aqueous potassium-ion batteries. In order to investigate these, four types of current collector/ substrate such as titanium, stainless steel, nickel and graphite are utilized in different potassium ion conducting electrolytes. Bismuth niobate ($Bi_5Nb_3O_{15}$) is used as a model electrode material for the investigation. While evaluating the electrochemical performance of $Bi_5Nb_3O_{15}$ in titanium, prominent electrochemical activity can be witnessed. The initial discharge and charge capacities are 146 $mAhg^{-1}$ and 90 $mAhg^{-1}$ respectively, although $Bi_5Nb_3O_{15}$ suffers severe capacity fading. As an alternate substate, stainless steel has been procured and $Bi_5Nb_3O_{15}$ shows distinct electrochemical activity here too. But continuing the similar trend, the capacity fading phenomena is far more severe in this case. Subsequent experimentation with nickel as substrate even shows worst electrochemical behavior of $Bi_5Nb_3O_{15}$. Although some electrochemical activity could be observed around -0.7 V to -0.2 V, there is rapid fall of current response in the negative potential range. The charge/discharge profile also could not be completed for the initial cycle. But quite surprisingly, graphite as current collector significantly impedes the capacity fading phenomena of $Bi_5Nb_3O_{15}$. A stable discharge capacity of around 110 $mAhg^{-1}$ was achieved after 50th discharge cycle which clearly outperforms the previous discussed results in terms of stability. Also, the rate capability of graphite is also quite impressive in case of graphite substrates. For example, it can sustain a stable storage capacity over 60 $mAhg^{-1}$ at current rate of 2 Ag^{-1} over 400 cycles. To figure out these contrasting behaviors, EIS measurements were carried which shows lower electrochemical charge transfer resistance of $Bi_5Nb_3O_{15}$ in graphite substrate in comparison to the others in the discharged state electrode. A time dependent study of the bare substrates was also carried out to investigate these contrasting behaviors. It was obtained that there is significant rise of interface resistance values with time for stainless steel, nickel and titanium substrates whereas it is quite smaller in case of graphite. The contact angle measurements of the $Bi_5Nb_3O_{15}$ on graphite substrate decreases significantly after discharge cycle, whereas no such changes were noticeable for other substrates. The decreased contact angle value may also indicate a reduction in the overpotential to drive K^+ ion insertion in the electrode material. Additionally, it is also found that there is a reduction (approximately by 15%) of the contact angle of the bare graphite substrate after soaking it in the electrolyte for. This is not the case for the other three bare substrates. FESEM images of the pristine graphite and graphite dipped in the electrolyte for 48 h indicates a change of the overall roughness. The corrosion study illustrates that the corrosion rate is highest in case of nickel current collector whereas graphite shows the lowest corrosion rate. Supporting it, the polarization resistance value is much higher in case of the graphite in comparison to the others. The ex-situ measurements confirm the insertion of K^+ ion in the $Bi_5Nb_3O_{15}$ which results in the change in XRD, FTIR, and XPS spectra. In a nutshell, 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. Considering $Bi_5Nb_3O_{15}$ as a model system, we show the importance of the interface of the electrode and the current collector in achieving better cycling stability.

Chapter 4: Investigation on Al^{3+} ion storage in Bi_2MoO_6 and Bi_2WO_6 for rechargeable aqueous aluminum-ion battery

Chapter 4 explores the of reversible Al^{3+} ion intercalation in aurivillous phase bismuth molybdate (Bi_2MoO_6) and bismuth tungstate (Bi_2WO_6) in aqueous electrolyte. Firstly, the electrochemical activities of Bi_2MoO_6 were investigated in different Al^{3+} ion conducting electrolytes. Prominent electrochemical activities could be witnessed although it suffers drastic capacity fading. On the other hand, Bi_2WO_6 also shows prominent electrochemical activity towards Al^{3+} ion insertion although it suffers capacity retention issues. But by reducing the concentration the severe capacity fading problem can be impeded. In short, it is found that the electrochemical activities are different for different aqueous electrolytes for both the materials. Although capacity fading is a severe problem for both the materials in 1 M $AlCl_3$ aqueous electrolyte, the electrochemical stability could be seen for 0.5 M $AlCl_3$ aqueous electrolyte only for Bi_2WO_6. While the charge-discharge profiles are almost identical for both Bi_2MoO_6 and Bi_2WO_6, it is to be noted that Bi_2WO_6 exhibits better electrochemical long-term stability and severe capacity decline is noticeable for Bi_2MoO_6. The specific discharge capacity is 94 $mAhg^{-1}$ at a current density of 1 Ag^{-1} over 50 cycles for Bi_2WO_6 in an optimized $AlCl_3$ aqueous electrolyte. By adopting an optimized current collector, the specific capacity could be significantly enhanced to above 200 $mAhg^{-1}$ at a current density of 1 Ag^{-1}. The electrochemical impedance spectra (EIS) of natural and exfoliated graphite show less charge transfer resistance in case of exfoliated graphite substrates which results in the improved electrochemical storage behavior of Bi_2WO_6. A mechanistic study using various ex-situ techniques like XRD, Raman, FTIR, XPS, FESEM and contact angle measurement reveals probable transformation of Bi_2WO_6 to BiOCl during the electrochemical process.

Chapter 5: High-rate performance of H_xMoO_3 for aqueous aluminium-ion battery

Chapter 5 discusses the impact of hydrogen doping on enhancing the Al^{3+} ion storage capacity of MoO_3 in aqueous electrolytes. To verify the presence of hydrogen doping in MoO_3 methods of different classes like XRD, Raman, FESEM, HRTEM, FTIR, XPS and PL spectra experiments were pursued and results obtained gives us a clear indication regrading successful H-doping. Proceeding further electrochemical measurements were carried out for MoO_3 and hydrogen doped MoO_3 (H_xMoO_3) in Al^{3+} ion conducting electrolytes. Cyclic voltammetry analysis predicts reduced polarization in case of H_xMoO_3. MoO_3 shows a stable discharge capacity of around 100 mAg^{-1} although there is capacity decline at higher current rates. However, a significant improvement in capacity could be noticed in H_xMoO_3 in comparison to pristine MoO_3. The 1st discharge capacity is now 417 $mAhg^{-1}$, whereas it was 274 mAg^{-1} for MoO_3. This enhancement in capacity continues over repeated cycling and around 37 % of increase could be noticed over 130 cycles. Even higher current rates H_xMoO_3 shows much better specific capacities as a stable discharge capacity of 54 mAh g^{-1} at a high current rate of 20 Ag^{-1} could be achieved over 1200 cycles. The EIS and bode analysis predict better charge transfer phenomena in case of H_xMoO_3. An enhanced diffusion rate could also be predicted for H_xMoO_3 from the calculation of diffusion coefficient using GITT and EIS techniques. Ex-situ XRD and HRTEM analysis predicts possible contraction and expansion of crystal planes of H_xMoO_3 after Al^{3+} ion insertion. Briefly, it can be commented 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. Additionally, the high-rate performance of MoO_3, mediated by hydrogen doping is demonstrated.