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## Abstract

With the ever-growing increase in population, it is estimated that nearly 1 billion households worldwide are yet to attain the benefits of electrification. While hundred percent rural or urban electrification is a primary target of majority of the developing countries, it also must be cautiously tackled to substantially mitigate the global CO<sub>2</sub> emission. This has led to the foundation for the very need of clean and affordable energy. Hence, there is an upsurge in the utilization of various small/large-scale renewable energy sources. Consequently, this unequivocally demands for appropriate technologies to store electricity and call it forth when required. In this regard, the contributions of rechargeable batteries are commendable. The interventions of these batteries in the society at various capacities have brought a paradigm shift in the modern way of living. At this juncture, it would be apt to acknowledge two merely ubiquitous rechargeable battery systems in modern society. These are lead-acid and lithium-ion batteries. While the functioning of these state-of-the-art batteries is prolific, there are growing global concerns over the chronic pollution attributed by the residues of certain components of spent batteries such as lead and cobalt if discarded in the environment without regulation. Another issue is the gradual depletion of certain important natural resources necessary for manufacturing these batteries, which results in price escalation. Therefore, the need for rechargeable batteries based on earth abundant but non-toxic materials is becoming critical than ever before.

The charm of aluminum (Al) has not gone unnoticed in the domain of rechargeable batteries in recent times. Al being the third most abundant element in Earth's crust, it has lot more to offer in the overall performance of Al-metal or Al-ion batteries. Two important electrochemical properties are worth mentioning. First, Al has the ability to exchange three electrons per cation. Second, Al possesses the highest storage capacity per volume basis compared to some of its counterparts like Li, Na, K, Mg, Ca and Zn. Additionally, Al resources are economical and handling them under an ambient atmosphere is relatively easy. Therefore, the electrochemical coupling of Al as an anode with a high-voltage cathode such as graphene or graphite could be considered as a remarkable battery system. The research works on Al-metal batteries with various types of graphene cathodes are a testimony of it. On the other hand, aqueous electrolytes are in general inflammable, affordable, highly ionic conducting and environment friendly. These beneficial properties make aqueous electrolyte an attractive option for aqueous

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rechargeable aluminum batteries. Therefore, the present thesis focusses on the investigations on electrode materials for  $\text{Al}^{3+}$  ion storage in aqueous electrolytes.

**Chapter 1** gives the brief introduction of various energy storage devices, the overall background of the research work and literature review.

**Chapter 2 (Part I)** discusses a simple and facile concept of a rechargeable aqueous Al-metal battery with electrochemically pretreated Al and exfoliated graphite foam as electrodes. The long-term stability of the aqueous Al-graphite cell is found to be limited by the dissolution of Al anode, but we show greater sustainability of the system by mechanical rejuvenation of the Al electrode in the cell. The specific capacities are relatively low ( $\sim 88 \text{ mAhg}^{-1}$  at  $0.5 \text{ A g}^{-1}$ / $25 \text{ mAhg}^{-1}$  at  $1 \text{ Ag}^{-1}$ ) compared to state-of-art Li-ion battery electrodes, but such an investigation as discussed herein provides an important basis for future studies in aqueous Al-ion or Al-metal battery. The discussed aqueous Al-metal battery takes the advantage of raw materials that are locally available in high abundance, low priced, and ecofriendly. Besides, the ease in handling the materials and assembling the battery system at ambient atmosphere open exciting opportunities for safe, sustainable, and affordable energy storage devices. Utilizing ex-situ XRD, XPS and electron microscopy techniques, the  $\text{Al}^{3+}$  ion storage mechanism is also highlighted.

**Chapter 2 (Part II)** discusses a novel strategy to significantly improve the electrochemical performance of a rechargeable Al-graphite battery in aqueous electrolyte. It is done by thermal treatment of the electrochemically exfoliated graphite electrode. It results in enhancement in the storage capacity of  $\text{Al}^{3+}$  ion. The influence of ‘water-in-salt’ electrolyte in the electrochemical performance was also investigated.

**Chapter 3 (Part I)** illustrates the  $\text{Al}^{3+}$  ion storage behavior in bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) in aqueous electrolyte. There are no detailed studies on  $\text{Al}^{3+}$  ion insertion/extraction in  $\text{Bi}_2\text{O}_3$  in aqueous electrolytes so far. The advantage of exfoliated graphite as current collector is also shown in this chapter. It was noticed that distinct electrochemical redox activities and long-term cycling stability of  $\text{Bi}_2\text{O}_3$  in  $\text{Al}^{3+}$  ion conducting aqueous electrolyte could be observed in the in-situ derived electrodes. When assembled with an Al anode,  $\text{Bi}_2\text{O}_3$  delivers a stable specific capacity of  $103 \text{ mAhg}^{-1}$  at a current rate of  $1.5 \text{ Ag}^{-1}$  over 70 cycles. It is also demonstrated that an integrated approach of tethering  $\text{Bi}_2\text{O}_3$  particles to an exfoliated graphite current collector is required for mitigating the sharp decline in the storage capacity of  $\text{Bi}_2\text{O}_3$  in aqueous electrolyte. Taking a lead from the previous work, the thesis also focused in

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understanding the  $\text{Al}^{3+}$  ion storage capability in bismuth oxychloride ( $\text{BiOCl}$ ) in aqueous electrolyte.

**In Chapter 3 (Part II)**, it is demonstrated that  $\text{Al}^{3+}$  ion could be stored in bismuth oxychloride ( $\text{BiOCl}$ ). It delivers a stable specific capacity of  $145 \text{ mAhg}^{-1}$  over 200 cycles. It was found that capacity decline is a major concern. However, a simple and innovative strategy was adopted to dramatically improve the electrochemical stability by synthesizing a binder-free  $\text{BiOCl}$  electrode on a thermally exfoliated graphite current collector. Utilizing ex-situ XRD, XPS and electron microscopy techniques, the  $\text{Al}^{3+}$  ion storage mechanism is also highlighted.

**In Chapter 4**, the  $\text{Al}^{3+}$  ion electrochemistry of vanadyl ethylene glycolate ( $\text{VO}(\text{CH}_2\text{O})_2$ ) is discussed. Vanadyl ethylene glycolate is an organic-inorganic hybrid material. A binder free vanadyl ethylene glycolate electrode was synthesized on carbon cloth substrate using solvothermal method. Vanadyl ethylene glycolate nanorods were found to be tethered on the carbon cloth due to in-situ deposition. It is highlighted that binder free vanadyl ethylene glycolate shows significant improvement in the electrochemical stability in comparison to pristine vanadyl ethylene glycolate with binder. The binder free electrode shows specific capacity values of approximately  $77 \text{ mAhg}^{-1}$  over 600 cycles. Contrarily, pristine vanadyl ethylene glycolate shows negligible capacity. Utilizing ex-situ XRD, XPS, Raman spectroscopy and electron microscopy techniques, the  $\text{Al}^{3+}$  ion storage mechanism is also highlighted.

**In Chapter 5**, the electrochemical activities of molybdenum ditelluride ( $\text{MoTe}_2$ ) for various metal ions such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  ion in aqueous electrolytes is illustrated. It is found that  $\text{MoTe}_2$  exhibits superior  $\text{Al}^{3+}$  ion storage in comparison to  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ions. A stable discharge capacity of  $100 \text{ mAhg}^{-1}$  over 250 cycles at a current density of  $1 \text{ Ag}^{-1}$  could be obtained with an excellent long term cycling performance ( $50 \text{ mAhg}^{-1}$  over 2000 cycles at a current density of  $5 \text{ Ag}^{-1}$ ) in case of  $\text{Al}^{3+}$  ion, while  $\text{Li}^+$  and  $\text{Na}^+$  could deliver a discharge capacity of  $10 \text{ mAhg}^{-1}$  over 250 cycles. However, in case of  $\text{Mg}^{2+}$  ion, a discharge capacity of  $50 \text{ mAhg}^{-1}$  could be achieved. In addition, the polarization is estimated to be lowest for  $\text{Al}^{3+}$  ion. Utilizing ex-situ XRD, XPS and electron microscopy techniques, the  $\text{Al}^{3+}$  ion storage mechanism is also highlighted.

**Chapter 6 (Part I)** discusses the possibility of  $\text{Al}^{3+}$  ion storage in lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) in aqueous electrolyte. It is found that  $\text{LiMn}_2\text{O}_4$  exhibits specific capacity of  $20 \text{ mAhg}^{-1}$  over 120 cycles. It was also found that the initial cycle

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in case of  $\text{LiMn}_2\text{O}_4$  is completely different from the rest of the cycles. It is noted that dissolution of Mn species is an issue and, hence, the cycling stability could be significantly enhanced by pre-addition of a low-valence Mn salt in the electrolyte. A stable discharge capacity of  $65 \text{ mAhg}^{-1}$  at a current rate of  $800 \text{ mA g}^{-1}$  at the 75<sup>th</sup> cycle could be achieved with a discharge potential plateau of 1.5 V. The post mortem analysis of the electrodes shows formation of amorphous  $\text{MnO}_2$  after discharge. Utilizing ex-situ XRD, XPS and electron microscopy techniques, the  $\text{Al}^{3+}$  ion storage mechanism is also highlighted.

**Chapter 6 (Part II)** discusses another possibility of  $\text{Al}^{3+}$  ion storage in lithium manganese phosphate ( $\text{LiMnPO}_4$ ) in aqueous electrolyte. It is found that  $\text{LiMnPO}_4$  can store  $\text{Al}^{3+}$  ion and it possesses two discharge plateaus at 1.09 V and 0.86 V (vs  $\text{Ag/AgCl}$ ). The initial discharge capacity obtained is as high as  $146 \text{ mAhg}^{-1}$  at a current rate of  $1 \text{ Ag}^{-1}$  with capacity retention of  $50 \text{ mAhg}^{-1}$  over 450 cycles at current rate of  $2.5 \text{ Ag}^{-1}$ . Based on this, a rechargeable aqueous Al-ion cell is also assembled with  $\text{LiMnPO}_4$  as cathode and tungsten oxide ( $\text{WO}_3$ ) as anode. This Al-ion cell shows discharge plateau in the potential range of 1-1.4 V with specific capacity of  $32 \text{ mAhg}^{-1}$  over 200 cycles.

**Chapter 7** summarizes the main outcomes of the thesis work and outlines the future prospects.

**KEYWORDS**

Energy storage; aqueous electrolytes; electroactive materials; aluminum-metal/ion battery.

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