Chapter 1

Introduction

1.1 Introduction: Importance of energy storage

There is a growing need for energy due to rapid increase in global population and escalating change in climate. It is estimated that the world's energy requirements will become triple of the current values in the year 2030 [1-2]. The fossil fuel reserves are also depleting slowly. Therefore, renewable energy sources are getting priority for delivering clean energy. To reduce dependency on fossil fuels and to facilitate zero carbon emission in the environment, a lot of efforts are being made on the utilization of renewable clean energy sources such as solar energy, wind energy, tidal energy, etc. However, the erratic nature of renewable energy sources and efficient storage of the generated energy from the renewables are two imminent challenges [3-4]. Among various number of existing energy storage technologies, electrochemical energy storage technology such as rechargeable batteries are viewed as one of the promising and efficient technologies because of their high energy and power density, long cycle life, compact size, and ease in assembling [3-5].

Two eminent examples of electrochemical energy storage devices are rechargeable lead-acid and Li-ion batteries (LIBs) [3-7]. Although lead-acid batteries are in the market for over a long period of time, it was the innovation of rechargeable Li-ion battery which radically changed the modern way of living of humanity since its inception in the year 1991. Li-ion batteries power almost all the portable electronic gadgets such as mobile phones and laptops. It is worth to mention here that since the contributions of Li-ion batteries in humankind are magnificent, this invention is recognized with a Nobel Prize in Chemistry in the year 2019. However, in recent times, there are growing concerns over the sustainability of Li-based batteries due to paucity and escalating cost of Li-resources [8-12]. Hence, it is imperative to devise strategies for developing sustainable and affordable electrochemical energy storage technologies based on resources which are largely earth-abundant and, if possible, locally available across diverse geography. Thus, it gives a significant impetus in the research areas of beyond Li-ion batteries such as Na^+, K^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, and Al^{3+} ions [13-48]. Table 1.1 and Figure 1.1 compare the abundance, ionic radius, volumetric/gravimetric capacities of the selective ions [50].

Table 1.1 Comparison of the characteristics of various metal-ions [50].

Category	Atomic mass (g mol^{-1})	Ionic radius (Å)	Volumetric capacity ($mAhcm^{-3}$)	Abundance (Rank)	E Vs SHE
Lithium (Li^+)	6.9	0.76	2042	33	-3.04
Sodium (Na^+)	23	1.02	1050	6	-2.71
Potassium (K^+)	39	1.38	609	7	-2.93
Zinc (Zn^{2+})	65.4	0.74	5857	25	-0.76
Magnesium (Mg^{2+})	24.3	0.72	3868	8	-2.37
Calcium (Ca^{2+})	40	1	2061	5	-2.87
Aluminum (Al^{3+})	27	0.54	8046	3	-1.66

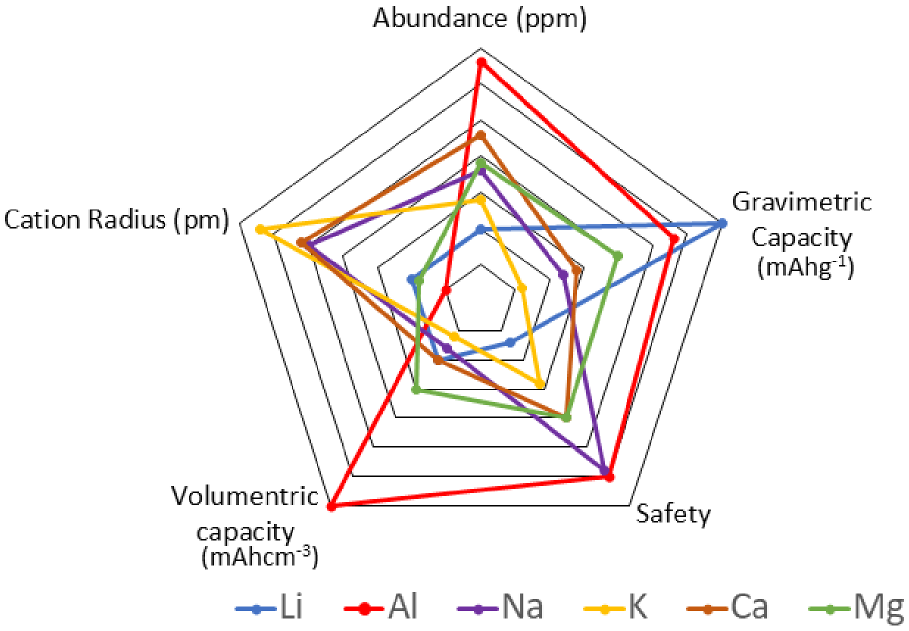

Figure 1.1 Spider chart representation of various ions.

The development of sodium-ion batteries (SIBs) appears to be a viable option for large scale production because of high abundance and low cost of the raw sodium materials [13-17]. It is estimated that the cost of lithium carbonate is 20−30 times higher than that of sodium carbonate [17]. Besides, sodium possesses similar physical and chemical properties to lithium. Research on SIBs started during 1970-1980s. But the immense progress in the research of Li-ion battery overshadows the research activities on SIBs. However, in recent times, intensified endeavors have been made for the development of SIBs [13-24]. In 2000, Dahn and his co-workers showed that hard carbon can act as an anode in SIB that can store Na^+ ion, delivering a reversible capacity of 300 $mAhg^{-1}$ [22]. Similarly, the first cathode properties of α-$NaFeO_2$ for SIBs was reported in the year 2006 by Nishida and his groups [23]. A lot of cathode materials have been explored for SIBs, in particular, layered systems of the P2 and O3 types, organic compounds, etc., [20]. Lithium metal is not suitable for direct use as anode since it is highly reactive [9]. The direct utilization of metallic anodes can further boost the energy densities of such batteries, owing to their high theoretical gravimetric and volumetric capacities as shown in Table 1.1 and Figure 1.1. For example, metallic Zn is regarded as one of the promising anode materials for zinc-ion batteries (ZIBs) due to its low reduction potential (-0.76 V vs. standard hydrogen electrode), high anode capacity of Zn metal (~ 820 $mAhg^{-1}$), environment friendly and cost effective [30-31]. Although ZIBs have attracted a lot of attention over the past few years but the advancements achieved so far are still not satisfactory in comparison to the state-of-the-art LIBs. This is due to the difficulties in finding a suitable cathode material for Zn^{2+} ion insertion, and poor reversibility of Zn metal anode [32]. As an analogue to LIBs, magnesium-ion and calcium-ion batteries are also proposed as alternative options. Magnesium and calcium have the ability to transfer two electrons in contrast to one in case of Li^+ ion [37-47]. Aurbach et al. demonstrated the first rechargeable magnesium battery in 2000 using magnesium as anode and Mo_3S_4 as cathode in magnesium organohaloaluminate salts as electrolyte. Since then, a lot of works have been reported using this type of electrolytes [37]. However, it seems that the progress of magnesium electrochemistry is largely dependent on the composition of the electrolyte. It is worth to mention that reversible magnesium platting/stripping in common electrolyte is one of the detrimental factors for practical magnesium battery application.

Apart from magnesium and calcium batteries, rechargeable battery based on aluminum (Al) could also be a proper fit as a sustainable and affordable system considering Al as the most abundant and low-cost metal. Other two electrochemical traits of Al are also worth mentioning: (i) ability to transfer three electrons per cation and (ii) possession of high volumetric and gravimetric capacities (8046 $mAhcm^{-3}$/2981 $mAhg^{-1}$) [48-50]. This feature makes the energy density of aluminum-ion batteries closer to or higher than Na^+, K^+, Mg^{2+}, Ca^{2+} ions batteries. There are few notable examples of research works in the area of AIBs in the literature that are discussed briefly in the following section.

1.2 A brief history and its current status on cathode material for aluminum batteries

Aluminum metal was first employed in a galvanic cell by M. Hulot in 1855 [51]. There are other systems where aluminum was used. Examples are Al-MnO_2, Al-H_2O_2, Al-Ni, Al-$KMnO_4$ and Al-air batteries [52-61]. These batteries are basically primary batteries. In 2011, Archer and coworkers first investigated the electrochemistry of a non-aqueous aluminum-ion battery using V_2O_5 as cathode and 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl)/$AlCl_3$ as an electrolyte [62]. This work shows the functioning of a rechargeable aluminum-metal battery at room temperature. In 2015, Dai and co-workers demonstrated an ultrafast aluminum-metal battery with 3D graphitic-foam as cathode, which showed a high discharge capacity of 60 $mAhg^{-1}$ over 7500 cycles at a high current rate of 4 Ag^{-1} [63]. Lu et al. reported a free-standing graphene nanoribbon on highly porous 3D graphene foam (GNHPG) as cathode for aluminum-ion battery. This special type of graphene nanoribbons was prepared by chemical vapor deposition (CVD) method and Ar^+-plasma etching technique [64]. The freestanding cathode could deliver a high discharge capacity of 123 $mAhg^{-1}$ with almost no capacity decay over 10000 cycles at a current rate of 5 Ag^{-1}. To further improve the cycling stability and electrochemical performance, Gao and his co-workers reported a novel trihigh tricontinuous graphene film (GF-HC) cathode which showed an ultrahigh discharge capacity of ~ 120 $mAhg^{-1}$ over 250000 cycles at a very high current rate of 400 Ag^{-1} with a Coulombic efficiency of around 91.7% [65]. In addition to carbonaceous material, there are other cathode materials which show promising electrochemical activities in non-aqueous aluminum batteries. These materials are graphite, metal oxides/sulfides, layered double hydroxides

(LDHs), chalcogenide-based materials, MXene, Prussian blue analogous, etc., [50, 62, 66-77].

Here, it is worth to specify two different possible configurations of rechargeable aluminum-batteries: (i) Aluminum-ion battery and (ii) Aluminum-metal battery. The first kind is a "rocking-chair" type electrochemical cell where Al^{3+} ions shuttle in between two Al^{3+} ion storing cathode and anode in an electrolyte (Figure 1.2a) [84-86]. The second configuration directly uses Al metal as anode in conjugation with an Al^{3+} ion storing cathode in an electrolyte (Figure 1.2b) [91-92]. The electrolyte may be aqueous or non-aqueous. Since the present thesis work deals with aqueous electrolyte, the following sections discuss about the aqueous batteries only.

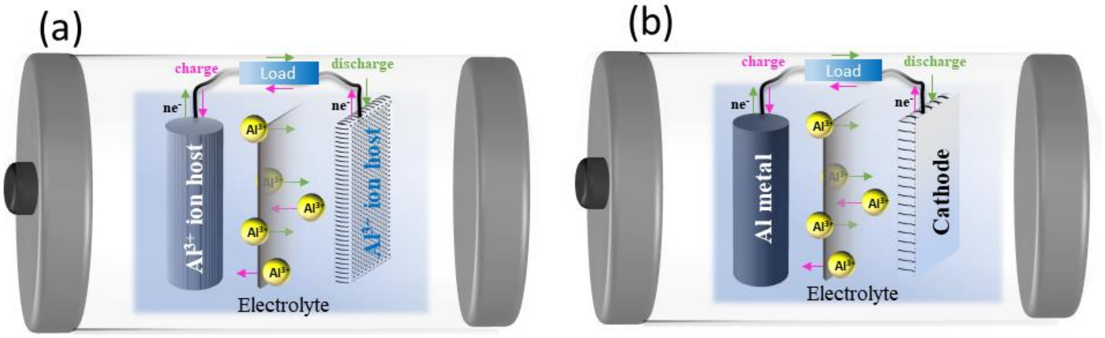

Figure 1.2: Schematic representation of an (a) Aluminum-ion battery, and (b) Aluminum-metal battery respectively.

1.3 The main objectives of the thesis

The primary objectives of the thesis are as follows:

1. Identification and processing of electrode materials for Al^{3+} ion storage in aqueous electrolytes.
2. Structural and electrochemical studies on electrode materials such as graphite, bismuth oxide (Bi_2O_3), bismuth oxychloride (BiOCl), vanadyl ethylene glycolate ($VO(CH_2O)_2$), molybdenum ditelluride ($MoTe_2$), lithium manganese oxide ($LiMn_2O_4$), lithium manganese phosphate ($LiMnPO_4$) for Al^{3+} ion storage.
3. Develop methods for improving the electrochemical performance of the electrode materials.
4. Understanding the electrochemical mechanisms of Al^{3+} ion storage processes.

1.4. A short note on aqueous rechargeable batteries

Research activities on aqueous rechargeable batteries have gained immense importance over the past few years [78]. This is because of the advantages associated with the utilization of aqueous electrolytes. Some of the merits of aqueous electrolytes are as follows: (i) high ionic conductivity, of the order of 2, then other ionic/organic electrolytes, which ensures a good rate capability and high-power density, (ii) low cost due to its abundance, (iii) non-flammability, and (iv) easy to assemble in an open environment. The first prototype of rechargeable aqueous lithium-ion battery was demonstrated by Dahn and coworkers in 1994. The system used $LiMn_2O_4$ as cathode and VO_2 as anode. The electrolyte was 5 M $LiNO_3$/1 mM LiOH aqueous solution. This cell exhibits a discharge voltage of 1.5 V and an energy density of 175 $Whkg^{-1}$ [79]. Thereafter, a variety of cathode materials were investigated for aqueous rechargeable lithium-ion batteries such as $LiFePO_4$, $LiMnPO_4$, $LiNiPO_4$, and other doped polyanionic compounds [80-85]. Generally, the electrochemical stability window of water is very narrow (~ 1.23 V). Very recently, the new concept of "water-in-salt (WiS)" aqueous electrolytes have shown a new path for the next generation aqueous rechargeable batteries [86]. This concept has enabled to achieve a wide operating voltage window of aqueous electrolyte. Su et al. proposed this concept for the first time in aqueous LIB where they demonstrated that a high concentration of lithium bis(tri-fluoromethane sulfonyl)imide (LiTFSI) dissolved in a water solution forms an interphase that protects the electrodes and suppresses the water activity around the electrodes, resulting in the expansion of electrochemical stability window up to 3 V [86]. Although the use of such high super concentrated electrolyte turns attractive, but the cost of lithium-based salts is a limiting factor for large scale production. Aqueous sodium-ion batteries using Na^+ ion as charge carriers is also an attractive option for low-cost energy storage systems [87-90]. A lot of progress has been made in the development of electrode materials for Na^+ ion. Some examples are layered transition metal oxides, polyanionic compounds and Prussian blue analogues etc. [90].

1.5 Rechargeable aqueous aluminum batteries

Chloroaluminate electrolyte-based aluminum-metal or ion batteries have been broadly explored with a plenty of cathode materials with some of them showing stupendous performance [62-77]. Similarly, aluminum-metal/ion batteries based on aqueous electrolyte have also gained a significant research interest in recent times [91-103]. However, one of the significant difficulties in aqueous rechargeable aluminum-batteries is to figure out a steady electrode material within the electrochemical stability window of the electrolyte [50,78]. Despite the difficulties, there are a few significant examples on aqueous aluminum-metal/ion batteries [91-103]. For example, Liu et al. first investigated the electrochemical activity of anatase TiO_2 nanotube in 1 M $AlCl_3$ aqueous electrolyte. It was found that Al^{3+} ion can reversibly intercalate/deintercalation into TiO_2 nanotube in aqueous electrolyte [91]. Later, Holland et al. proposed a functional prototype for rechargeable aqueous AIB using copper hexacyanoferrate cathode, TiO_2 nanotube arrays anode in $Al_2(SO_4)_3$ aqueous electrolyte [92]. This cell delivered a specific capacity of 21 $mAhg^{-1}$ with a discharge potential voltage of 1.6 V [92]. Similarly, He et al. could further improve the storage capacity of Al^{3+} ion in black mesoporous anatase TiO_2 [93]. Besides TiO_2, González et al. demonstrated the possibility of Al^{3+} ion storage in V_2O_5 xerogel in aqueous electrolyte [94]. Recently, Kumar et al. reported the electrochemistry of Al^{3+} ion insertion in $FeVO_4$ [95]. A discharge capacity as high as 350 $mAhg^{-1}$ could be achieved at a current rate of 60 mAg^{-1}. Pang et al. demonstrated the Al^{3+} ion storage behavior in $VOPO_4.2H_2O$ [96]. The Al-metal anode with $VOPO_4.2H_2O$ as cathode exhibits a discharge voltage of ~ 0.9 V with a specific capacity of approximately 125.4 $mAhg^{-1}$ at a current density of 20 mAg^{-1} [96]. In addition, there are only few other cathode materials that has been investigated for aqueous AIBs like MoO_3, $Na_3V_2(PO_4)_3$, Li_3VO_8, MnO_2, Al_xMnO_2, etc. [97-102]. Archer et al. recently proposed a novel way of utilizing Al metal in aqueous AIBs by creating a solid electrolyte interphase on Al metal using chloroaluminate electrolyte and then the treated Al metal was later used in aqueous AIBs. The assembled Al-MnO_2 with treated Al metal shows a discharge voltage of 1.5 V with a stable discharge capacity of 100 $mAhg^{-1}$ at a current rate of 500 mAg^{-1} [100]. Based on these studies, Wu et al. demonstrated a rechargeable aqueous AIB using $Al_xMnO_2{\cdot}nH_2O$ as cathode and Al as anode in 5 M aluminum trifluoromethanesulfonate ($Al(OTF)_3$) [101]. Very recently, the concept of "water-in-salt" aqueous electrolyte is also applied in aqueous AIBs to widen the electrochemical stability window of water [102]. It was found that such high concentration of electrolyte can expand the electrochemical stability window to 4 V

[102]. The research on aqueous AIBs is still at a preliminary stage and, hence, identification of electrolyte and electrode materials are of paramount importance.

Therefore, the present thesis focusses on certain type of electrode materials for Al^{3+} ion storage to be employed for aqueous Al- metal or ion batteries.

1.6 References

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