RECHARGEABLE LITHIUM ION AND LITHIUM-AIR BATTERY: A BRIEF OVERVIEW

1.1. INTRODUCTION

Energy plays an imperative role in many aspects of human lives. This predicament renders us, in general, to depend on non-renewable fossil fuels such as coal, petroleum, and natural gas. The limitation of the availability and access of natural resources and the climatic consequences arising due to continuous rise in CO₂ levels has made the focus of research be diverted towards renewable energy sources. Notable advancements have been made over the past few decades in renewable energy resources viz., wind, solar, biomass and hydro electricity both in their efficiency and competitiveness. Wind and solar power generation are gaining momentum in their usage around the world, mainly to alleviate some of the negative environmental impacts created by non-renewable sources of energy. However, these renewable sources of electricity pose technical challenges when being integrated on a large scale transmission network. Energy storage is being broadly regarded as one of the probable solutions to deal with this problem. Storing energy may allow us to balance the supply and demand of energy. The added advantage of energy storage devices are their portability.

Despite the fact that there are many modes to store energy, the most convenient method of storing electrical energy is electrochemical storage i.e., in specific “batteries”. Batteries are electrochemical devices, which can convert electrical energy into chemical energy and store the energy. Conversely, it can convert chemical energy into electrical energy through reduction-oxidation (redox) reaction while releasing the energy. There are
three basic components that constitute a battery: an electrolyte (ion conducting medium),
two electrodes i.e., an active negative electrode (anode) and positive electrode (cathode).

Energy density (amount of energy stored per unit mass (Whkg\(^{-1}\)) or volume
(Whl\(^{-1}\)) and power density (the maximum practical sustained power output per unit mass
(Wkg\(^{-1}\)) or volume (Wl\(^{-1}\)) are the two key parameters of batteries. Significant efforts
have been made to improve the energy density of batteries. But it is still decisive for most
of the consumer electronics market and hybrid electric vehicle applications [1].

There are two specific types of batteries: primary battery and secondary battery.

**Primary battery:**

A primary battery is one that is designed to produce electric current through an
electrochemical reaction only once. After single use they are discarded following
discharge. Examples of primary batteries are: Zinc carbon dry cell, alkaline battery,
lithium battery. Though primary batteries are often made from the same base materials as
that of secondary batteries, the design and manufacturing processes are not the same. In
general, primary batteries have high energy density, long storage times and instant
readiness that make them unique over other power sources. Its application includes
pacemakers for heart patients, wristwatches, remote controls, children’s toys etc.

**Secondary battery:**

Secondary battery encompasses the same mechanism as that of primary battery.
The only difference is that the electrochemical actions of secondary batteries are
reversible. As a result the battery may be recharged and reused by passing a current
through the battery in the opposite direction to that of discharge. A secondary battery is usually designed to have a lifetime of between 100 and 1000 recharge cycles. The oldest form of rechargeable battery is the lead-acid battery. Other rechargeable batteries include nickel-cadmium (NiCd), nickel metal hydride (NiMH) and lithium-ion (Li+) battery.

![Figure 1.1. Comparison of specific energy (Wh Kg\(^{-1}\)) of few secondary batteries.](image)

Figure 1.1 shows the comparison of specific energy (Wh Kg\(^{-1}\)) of few secondary batteries. Rechargeable Li\(^+\) batteries are considered widely as efficient energy storage device for portable electronic gadget because they have strong advantages in terms of higher gravimetric energy density of 150 Whkg\(^{-1}\) [2-5] and deliver voltage in the order of 2.5-4.2 V depending on the selection of the electrode materials. In addition to the
high energy density, Li\textsuperscript+ batteries are offering flexible light weight design, low self-discharge and longer cycle life over 500 cycles [6].

1.2. RECHARGEABLE Li\textsuperscript+ BATTERIES

The concept of rechargeable Li\textsuperscript+ batteries was first proposed by J.B. Goodenough in 1979, but was commercialized by Sony at 1991 [7]. Lithium is the lightest metal with high electrochemical potential and thus enables to achieve high energy and power density. Initial attempts with pure lithium as negative electrode in lithium metal batteries failed because of safety problems due to dendrite formation. Later metallic lithium was replaced by lithiated carbon. Since then the development of Li\textsuperscript+ battery technology has been enduring, due to the ever-growing demand in portable electronics, hybrid electric vehicles (HEV) and electric vehicles (EV).

1.2.1. Working principle of Li\textsuperscript+ battery

The main functional components of Li\textsuperscript+ battery include lithium hexafluorophosphate (LiPF\textsubscript{6}) dissolved in organic solvents as the commonly used electrolyte, LiCoO\textsubscript{2} as positive electrode and generally graphitic carbon or any other intercalation compounds as a negative electrode [8].
Figure 1.2. Working principle of rechargeable Li\textsuperscript{+} battery.

The working principle of Li\textsuperscript{+} battery is depicted in Figure 1.2. During charging and discharging, Li\textsuperscript{+} shuttles back and forth between the two electrodes. Hence, Li\textsuperscript{+} battery technology are also known as ‘rocking-chair’ battery technology [9]. Generally, Li\textsuperscript{+} are intercalated (inserted) or de-intercalated (extracted) from the interstitial space in the atomic layers within the electrode components during charge-discharge process. The ideal electrolyte would exhibit high ionic conductivity (> 10\textsuperscript{-2} Scm\textsuperscript{-1} at room temperature) for Li\textsuperscript{+} transport and low electronic conductivity to facilitate the movement of electrons through the circuit.
During the charging process the Li$^+$ leave the LiCoO$_2$ positive electrode (oxidation) and move to the graphite negative electrode to create an intercalated Li$_x$C$_6$ (reduction). Electrons from the positive electrode travel through the external circuit and coalesce with the Li$^+$ at the negative electrode. The reaction involved in the charge process is given below

\[
\text{Positive electrode : } \quad \text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \quad (1.1)
\]

\[
\text{Negative electrode : } \quad x\text{Li}^+ + xe^- + C_6 \rightarrow \text{Li}_x\text{C}_6 \quad (1.2)
\]

\[
\text{Overall (charging) : } \quad \text{LiCoO}_2 + C_6 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6 \quad (1.3)
\]

The discharging process occurs when the battery is in use. In this case, the Li$^+$ move away from the graphite negative electrode (oxidation). Electrons move through the external circuit and coalesce with Li$^+$ at the LiCoO$_2$ positive electrode (reduction). The reaction involved in the discharge process is given below

\[
\text{Negative electrode : } \quad \text{Li}_x\text{C}_6 \rightarrow x\text{Li}^+ + xe^- + C_6 \quad (1.4)
\]

\[
\text{Positive electrode : } \quad \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiCoO}_2 \quad (1.5)
\]

\[
\text{Overall (discharging) : } \quad \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6 \rightarrow \text{LiCoO}_2 + C_6 \quad (1.6)
\]
1.2.2. Advantages of the present Li⁺ battery technology

- High voltage:
  
  Li⁺ batteries exhibit voltages up to 4 V

- High specific energy density and power density:
  
  The energy output is two to four or more times better in lithium battery than that of zinc negative electrode batteries

- Wide operation temperature range:
  
  Most of the lithium batteries will operate over a temperature range from about 70 °C to -40 °C

- High coulombic and energy efficiency

- High rate and rapid charge capability

- Long cycle life and light weight compared to that of other rechargeable battery

- Better shelf life:
  
  Li⁺ batteries can be stored for long periods, even at high temperatures, with no memory effect

1.2.3. Challenges associated with the present Li⁺ battery technology

- The available or working capacity is insufficient/moderate at higher cycling rates.

- The power density is inadequate for the future applications.

- At higher cycling rates, the energy efficiency is too low. This is due to large polarization losses during charge and discharge.

- Due to the capacity loss, the cycling life is limited.
1.3. ELECTROLYTE MATERIALS FOR RECHARGEABLE Li\textsuperscript{+} BATTERY

The electrolyte is a chemical medium that allows the flow of ions between the positive electrode and negative electrode. Li\textsuperscript{+} battery performance depends on the diffusion of Li\textsuperscript{+} within the electrolyte. The types of electrolytes used for Li\textsuperscript{+} battery technology can be broadly classified as,

- Liquid electrolytes
- Polymer electrolytes and
- Solid electrolytes

Conventional Li\textsuperscript{+} batteries use organic liquid electrolyte which is flammable and cause safety issues [10]. The prime advantage of liquid electrolytes is that they exhibit the highest ionic conductivity of $10^{-2}$ Scm\textsuperscript{-1} at ambient conditions. Liquid electrolytes are comprised of lithium salts such as lithium hexafluorophosphate (LiPF\textsubscript{6}), lithium tetrafluoroborate (LiBF\textsubscript{4}), lithium trifluoromethanesulfonate (LiCF\textsubscript{3}SO\textsubscript{3}) and lithium trifluoromethanesulfonimide (LiN(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}) dissolved in organic solvents such as ethylene carbonate (EC) and propylene carbonate (PC). In liquid based Li\textsuperscript{+} batteries, the dendrite formation on the electrode may result due to continuous cycling and cause electrical short circuits, sparks and finally, explosion of the battery. In contrary, solid polymer electrolytes are generally used to avoid the problem of leakage and dendrite formation, although their Li\textsuperscript{+} conductivity is much lower than that of liquid electrolytes.
Drawbacks of liquid and polymer electrolytes

- Major drawback of organic polymer electrolytes is their low ionic conductivity \((10^{-6}\text{ Scm}^{-1})\) at ambient temperatures.
- Poor interfacial stability i.e., formation of solid electrolyte interface (SEI).
- Liquid and polymer electrolytes are not stable with Lithium metal; they cannot be used together with lithium negative electrode.

Switching over to solid electrolyte is the key solution to overcome the drawbacks of liquid and polymer electrolytes. Inorganic solid fast Li\(^+\) based batteries are anticipated to overcome the boundaries over the safety concerns of commercially available organic polymer electrolyte based lithium batteries. Solid electrolyte offer general advantages such as

- Safety
- High energy density
- Less toxic
- Environmental benignity, low cost and easiness of preparation.

The study of all-solid-state lithium batteries started in the middle of the 20\(^{\text{th}}\) century. Solid-state electrolytes are being developed for Li\(^+\) battery, to overcome the problems related to liquid/organic electrolytes. The major advantage of all-solid-state lithium battery technology is that it does not require organic solvents, thus it is quite safer and more tolerable to extreme working conditions, moreover there is no leakage problem, and it has the possibility of easy miniaturization.
The main features required for a successful solid electrolyte for application in Li\(^+\) batteries include [11, 12]:

- High total (bulk + grain-boundary) Li\(^+\) conductivity (~ \(10^{-3}\) Scm\(^{-1}\)) at working temperature.
- Negligible electronic conductivity at high and low lithium activity in negative electrode and positive electrode.
- High chemical stability with lithium electrodes during long-term operation.
- Thermal expansion coefficient must match with lithium electrodes.
- High electrochemical decomposition voltage (up to 5.5V vs. Li).
- Low cost, easy transportation and environmental benignity.

Despite the fact that solid electrolytes proffer many advantages, they display very low ionic conductivities compared to that of liquid electrolytes. Therefore, in the development of all-solid-state lithium rechargeable batteries, it is important to search for solid electrolyte materials with high Li\(^+\) conductivity.

1.4. SOLID FAST Li\(^+\) CONDUCTORS

To simplify the battery design, to improve safety and durability, a solid electrolyte may be utilized instead of the liquid electrolyte. The crystalline solid electrolyte includes perovskite-type lithium lanthanum titanate (Li,La)TiO\(_3\) [13-16], NASICON (Sodium super ion conductor) [17-19], LISICON (Lithium super ionic conductor) [20, 21], thio-LISICON [22] and amorphous lithium phosphorus oxynitride (LIPON) [23] were...
investigated extensively for potential application in all-solid-state lithium batteries. The crystal structures of perovskite, NASICON and LISICON are shown in Figures 1.3(a)-(c), respectively. The room temperature Li$^+$ conductivities of these ceramic electrolytes fall in the range between $10^{-3}$ to $10^{-6}$ Scm$^{-1}$. The most investigated pervoskite-type (Li, La)TiO$_3$ has bulk Li$^+$ conductivity in the order of $10^{-3}$ Scm$^{-1}$ and a total (bulk + grain-boundary) Li$^+$ conductivity of $7 \times 10^{-5}$ Scm$^{-1}$ [24-26]. However, the practical application of (Li, La)TiO$_3$ was restricted as it is not stable in contact with metallic lithium. The reduction of Ti$^{4+}$ to Ti$^{3+}$ during lithium intercalation in (Li, La)TiO$_3$ enhances its electronic conductivity [13, 16]. The crystal structure of (NaM$_2$IV(PO$_4$)$_3$) (M = Ge, Ti, and Zr) NASICON (Na Super Ionic Conductors) was first identified in 1968 [27]. NASICON-related compound Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ (LATP) was reported to have bulk Li$^+$ conductivity of $3 \times 10^{-3}$ Scm$^{-1}$ at 25 °C [28]. However, it was found to be unstable with metallic lithium due to the facile reduction of Ti$^{4+}$ [29]. Structure of LISICON is related to the $\gamma$-Li$_3$PO$_4$ [30-32]. Li$_{3.5}$Zn$_{0.25}$GeO$_4$ and Li$_{2+2x}$Zn$_{1-x}$GeO$_4$ (-0.36 < x < 0.87) are associated with the family of LISICON type lithium conductors. The major concern about LISICON type Li$^+$ conductors are their low Li$^+$ conductivity. LISICON type Li$_{3.5}$Zn$_{0.25}$GeO$_4$ exhibits a room temperature Li$^+$ conductivity of $1 \times 10^{-7}$ Scm$^{-1}$ [33]. Li$_{3.6}$Ge$_{0.8}$V$_{0.4}$O$_4$ exhibits room temperature Li$^+$ conductivity of $4 \times 10^{-5}$ Scm$^{-1}$ [34] Moreover these LISICON type Li$^+$ conductors are highly reactive with lithium metal and atmospheric CO$_2$ [29, 35, 36].
Figure 1.3. Crystal structure of (a) pervoskite-type (Li, La)TiO$_3$ (LLTO) [26], (b) NASICON-type LiA$_2^{IV}$(PO$_4$)$_3$ ($A^{IV} = \text{Ti, Zr, Ge, Hf}$) [37] and (c) LISICON-type Li$_3$Zn$_{0.5}$GeO$_4$ [38] Li$^+$ conductors.
Thio-LISICON also belongs to $\gamma$-Li$_3$PO$_4$ crystal structure [22]. They are generally described by the composition, Li$_x$M$_{1-y}$M$'$$_y$S$_4$ (M = Si, Ge, and M$'$ = P, Al, Zn, Ga, Sb). Among the investigated thio-LISICON Li$^+$ conductors, Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ compound exhibits the highest room temperature Li$^+$ conductivity of 2.17 x $10^{-3}$ S cm$^{-1}$ [39]. Recently, a new composition Li$_{10}$GeP$_2$S$_{12}$ with a one-dimensional conduction pathway has been introduced [40]. It exhibits an extremely high conductivity of 12 mS cm$^{-1}$ at room temperature with the activation energy of 0.1 eV. The negative aspect of this material is the instability of this material with that of ambient air.

Lithium phosphorus oxynitride (LIPON) is an amorphous electrolyte material commonly used for the fabrication of an all-solid-state thin film lithium battery. Generally, LIPON films were fabricated using sputtering method. Lithium orthophosphate (Li$_3$PO$_4$) was used as target material and the thin film fabrication was carried out under a N$_2$ atmosphere [41]. Although the LIPON exhibits poor Li$^+$ conductivity of about 3.3 x $10^{-6}$ S cm$^{-1}$ at 25 °C it exhibits good electrochemical stability with the potential positive and negative electrodes [42].

Among the various Li$^+$ conductors, garnet-like structural compounds reported by Weppner and his co-workers is found to be appropriate for the fabrication of all-solid-state lithium batteries [43-54]. Few lithium garnets were found to be chemically stable against molten lithium, which is the required key property for the development of all-solid-state lithium batteries [46, 47].
1.5. GARNET STRUCTURED LITHIUM RICH SOLID ELECTROLYTES

Garnets are orthosilicates with general formula of $A_3B_2(SiO_4)_3$ ($A^{2+} = Ca, Mg, Fe; B^{3+} = Al, Ti, Cr, Fe$), in which $A$ refer to eight-coordinated cation sites and $B$ refer to six-coordinated cation sites, respectively and it crystallize in the $Ia\bar{3}d$ space group [55]. The crystal structure of $A_3B_2(SiO_4)_3$ ($A^{2+} = Mg, Ca; B^{3+} = Al, Fe, Cr, Ti$) is shown as Figure 1.4.

![Crystal structure of $A_3B_2(SiO_4)_3$.](image)

**Figure 1.4.** Crystal structure of $A_3B_2(SiO_4)_3$ ($A^{2+} = Mg, Ca; B^{3+} = Al, Fe, Cr, Ti$) [55].

Lithium containing garnets $A_3B_2(LiO_4)_3$ are acquired by substituting lithium for silicon in $A_3B_2(SiO_4)_3$. Lithium arrangements in lithium garnets (i.e., $Li_xA_3B_2O_{12}$) were predicted using the neutron diffraction techniques. Neutron diffraction studies on conventional lithium garnets (stoichiometry) $Li_3Ln_3Te_2O_{12}$ ($Ln = Y, Pr, Nd, Sm, Eu, Dy,$
Er and Tm) [56] and Li₃Nd₃W₂O₁₂ [57, 58] shows an unequivocal distributions of Ln³⁺ cations across 8-fold coordination site (A Site) and Te⁶⁺/W⁶⁺ across 6-fold coordinate site (B site) of Li₃A₃B₂O₁₂, respectively. The conventional lithium garnet Li₃Nd₃Te₂O₁₂ exhibits a poor Li⁺ conductivity of around 10⁻⁵ Scm⁻¹ at 600 °C with large activation energy of 1.22 eV [56]. The neutron diffraction analysis also indicated that lithium is solely distributed at the tetrahedrally coordinated position leaving the octahedrally coordinated site unoccupied [56].

Increase in lithium content of Li₃A₃B₂O₁₂ leads to the lithium rich composition Li₅La₃B₂O₁₂ (B = Nb, Ta), which exhibits total (bulk + grain-boundary) Li⁺ conductivity in the order of 10⁻⁶ Scm⁻¹ at 25 °C [43]. Among them tantalum based garnet, Li₅La₃Ta₂O₁₂ has attracted because of its stable nature against lithium metal. Neutron diffraction studies on lithium rich garnet i.e., x > 3 in Li₃A₃B₂O₁₂ indicated that the extra lithium populated in crystallographic octahedral (48 g/96 h) sites that are unfilled for the conventional garnet structure. This is because the tetrahedral (24d) site of conventional garnet structure does not allow more than three lithium per formula unit [44, 46, 47, 59-61]. The foremost difference between the conventional lithium garnets and lithium stuffed garnets is that in conventional lithium garnets, Li⁺ occupies solely tetrahedral coordination sites whereas, for lithium stuffed garnets, Li⁺ occupies both tetrahedral and octahedral coordination sites [62-64].

Following the fast Li⁺ transport properties and the excellent chemical stability of Li₅La₃Ta₂O₁₂ further investigation in conductivity optimization of lithium rich garnets by proper chemical substitutions has been initiated by various research groups. Partial
replacement of divalent ions for trivalent La in $\text{Li}_5\text{La}_3\text{B}_2\text{O}_{12}$ yielded new garnet-like materials with chemical formula $\text{Li}_6\text{ALa}_2\text{B}_2\text{O}_{12}$ ($A = \text{Ca, Sr, Ba, Mg}; B = \text{Nb, Ta}$) [48, 60]. Among them $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ exhibited the maximized total (bulk + grain-boundary) $\text{Li}^+$ conductivity of $4 \times 10^{-5} \text{ S cm}^{-1}$ at $22 \, ^\circ\text{C}$ with an activation energy of 0.40 eV. $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ is found to exhibit low grain-boundary resistance and good electrochemical stability at ambient temperature [60].

1.5.1. High $\text{Li}^+$ conductive cubic phase $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ)

Although $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ offers reasonable $\text{Li}^+$ conductivity and chemical stability against lithium metal the observed total (bulk + grain-boundary) $\text{Li}^+$ conductivity at room temperature was not sufficient for the successful fabrication of all-solid-state lithium secondary battery. Among the reported lithium garnets, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) has been widely investigated owing to its relatively high total (bulk + grain-boundary) $\text{Li}^+$ conductivity of $5.11 \times 10^{-4} \text{ S cm}^{-1}$ at $25 \, ^\circ\text{C}$ [46, 47]. Moreover, it has an excellent stability with lithium metal and possesses large electrochemical voltage window.

LLZ exist in three different crystal phases, viz.; tetragonal phase, high $\text{Li}^+$ conductive cubic phase and low temperature cubic phase. The crystal structure of tetragonal and high $\text{Li}^+$ conductive cubic phase LLZ are shown as Figures 1.5 and 1.6, respectively [46, 47, 65, 66]. Among these three phases, high $\text{Li}^+$ conductive cubic phase is the most desired one due to its high $\text{Li}^+$ conductivity of $10^{-4} \text{ S cm}^{-1}$ [46, 47, 66]. The low temperature cubic phase is related to either CO$_2$ absorption or hydration mechanism [67, 68]. The $\text{Li}^+$ conductivity of the high conductive cubic phase is two orders of
magnitude higher than that of tetragonal and low temperature cubic phases [46, 47, 65, 66-68].

LLZ in tetragonal phase (space group $I4_1/acd$) reported by Awaka et al. is an ordered structure with occupancy of lithium on tetrahedral $8a$ site and octahedral $16f$ and octahedral $32g$ sites [65] as shown in Figure 1.5. LLZ in high Li$^+$ conductive cubic phase (space group $Ia\overline{3}d$) is disordered with lithium on tetrahedral $24d$ and distorted octahedral $96h$ sites [46, 47, 66, 69], which is vacant in conventional garnet structure as shown in Figure 1.6. The high Li$^+$ conductive cubic phase LLZ prepared by sintering around 1230 °C for 36 hours in an alumina crucible exhibits high Li$^+$ conductivity ($10^{-4}$ Scm$^{-1}$). On the other hand, tetragonal phase LLZ prepared with sintering temperature less than 1000 °C exhibits low Li$^+$ conductivity ($10^{-6}$ Scm$^{-1}$) [46, 47, 65]. Hence sintering temperature, duration of sintering and nature of crucible material have major role in determining the phase and Li$^+$ conductivity of the synthesized LLZ.

Following the initial results of high Li$^+$ conduction in the cubic phase LLZ (space group $Ia\overline{3}d$) there has been significant interest in the synthesis, structural analysis, Li$^+$ conductivity and electrochemical stability of lithium rich garnet structured materials. Based on various LLZ studies, it was suggested that the unintentional incorporation of Al$^{3+}$ into LLZ during the high-temperature (1230 °C) solid-state reaction technique using alumina crucibles helps to stabilize the cubic phase against the tetragonal one [70-72]. Geiger et al. reported that Al contamination from the alumina crucible is the key aspect in stabilizing the high conductive cubic phase [72]. Düvel et al. discussed the effects of Al incorporation on both structural and dynamic properties of LLZ [73]. Rangasamy et al.
indicated that the optimized content of Al and Li required for forming high Li$^+$ conductive cubic phase LLZ was 0.24 mole and 6.28 mole, respectively [74]. However, with increasing Al$^{3+}$ content, the La$^{3+}$ and Zr$^{4+}$ in LLZ were progressively replaced by Al$^{3+}$ and greatly affected the corresponding Li$^+$ dynamics [73].

**Figure 1.5(a).** Crystal structure of tetragonal phase Li$_7$La$_3$Zr$_2$O$_{12}$ [65, 66] and (b) the loop structure constructed by lithium atomic arrangements [66].
Figure 1.6(a). Crystal structure of high Li$^+$ conductive cubic phase Li$_7$La$_3$Zr$_2$O$_{12}$ [66] and (b) the loop structure constructed by lithium atomic arrangements [66].

1.5.2. Li$^+$ dynamics in lithium garnets

Crystal structures of garnet-type oxides were studied extensively using both X-ray as well as neutron diffractions. But there exists some dilemma in determining the accurate allocation of lithium between the tetrahedral and octahedral sites of garnet framework. X-ray diffractions have limited application owing to the poor scattering of lithium. In spite of the high sensitivity, neutron diffractions provide only minimal information in terms of atomic displacement parameters. Hence Li$^+$ migration mechanism in garnet framework are still controversial.
Figure 1.7. Occupancy of Li$^+$ with increasing lithium concentration in lithium garnets [69].

Lithium garnet framework are grouped into three models viz., Li$_x$A$_3$B$_2$O$_{12}$ ($x = 3, 5$ and 7). Examination on the neutron diffraction data of aforementioned three models reveal that the first model with chemical composition Li$_3$A$_3$B$_2$O$_{12}$ ($A = Y, Pr, Nd, Sm-Lu; B = Te$) [56] also known as conventional garnet, which has a cubic ordered structure in which the tetrahedral ($24d$) site are completely occupied leaving the octahedral site
(48g) empty. The only plausible path for the Li\textsuperscript{+} migration is to activate it from the occupied tetrahedral site to the neighboring unfilled octahedral site. This is not feasible at the room temperature. Moreover, the energy required for this Li\textsuperscript{+} migration is quite high. The high occupancy of tetrahedral (24d) site and the lack of mobile Li\textsuperscript{+} in octahedral (48g) site are the reason for the low Li\textsuperscript{+} conduction in Li\textsubscript{x}A\textsubscript{3}B\textsubscript{2}O\textsubscript{12} with lithium concentration \(x = 3\).

Schematic representation for the occupancy of Li\textsuperscript{+} with increasing lithium concentration in lithium garnets is shown as Figure 1.7 [69]. Increase in lithium concentration by partial replacement of higher or lower oxidation state of either A or B cations leads to the second model with chemical composition Li\textsubscript{5}A\textsubscript{3}B\textsubscript{2}O\textsubscript{12} (A = La; B = Ta, Nb, Sb and Bi) [51] in which the occupancy of octahedral (48g) takes place along with an increase in the vacancy concentration of the tetrahedral (24d) site. The detailed analysis on neutron diffraction reveals that the Li\textsuperscript{+} occupying octahedral (48g) are displaced to new octahedral position (96h) due to the short Li-Li distance generated through large coulombic repulsion. The co-existence of mobile Li\textsuperscript{+} and vacancies at octahedral (48g) makes the possible lithium migration through the interstice using the neighboring energy barrier route 48g/96h \(\leftrightarrow\) 48g/96h passing through their common tetrahedral (24d) site [69].

The third model with composition Li\textsubscript{7}A\textsubscript{3}B\textsubscript{2}O\textsubscript{12} (A = La; B = Zr) [46, 47] exhibits in two structure viz., high Li\textsuperscript{+} conductive cubic disordered structure with both tetrahedral (24d) and octahedral (48g/96h) sites partially occupied [66]; and a tetragonal ordered structure in which tetrahedral (8a), octahedral (16f), and octahedral (32g) sites are fully
occupied by lithium and tetrahedral (16e) sites are fully empty [65]. The mechanism observed in high Li\(^+\) conductive cubic structure Li\(_7\)La\(_3\)Zr\(_2\)O\(_{12}\) might be originated from the diffusion of mobile Li\(^+\) through the border of 24d-96h and then climbing over other 24d-96h border and finally bypassing the empty octahedral site 48g site [69]. The presence of more mobile Li\(^+\) in octahedral site and simultaneous vacancies in the tetrahedral site help to increase the transportation of Li\(^+\) through the diffusion of Li\(^+\) in the low energy barrier route 24d-96h-24d-96h-48g [69].

The size of the three dimensional A\(_3\)B\(_2\)O\(_{12}\) frame is the prime factor in determining the capability of accommodation and the nature of distribution of lithium atoms among available tetrahedral (24d) and octahedral sites (48g/96h) in the cubic Li\(_x\)A\(_3\)B\(_2\)O\(_{12}\) lithium garnets [75]. The Li\(^+\) conduction in a high Li\(^+\) conductive cubic phase lithium garnet is mainly dependent upon the concentration of lithium and nature of distribution of lithium atoms among tetrahedral and octahedral sites [75].

1.5.3. Fabrication of all-solid-state lithium battery with LLZ solid electrolyte

Fast Li\(^+\) conduction in LLZ and its derivatives instigate various research groups to prepare all-solid-state batteries using garnet metal oxide electrolytes. Battery fabrication with Li\(^+\) conducting LLZ as solid electrolyte and LiCoO\(_2\) as positive electrode revealed the formation of intermediate reaction layer of 50 nm thickness due to the diffusion of Co, La and Zr between the LLZ/LiCoO\(_2\) interfaces as shown in Figures 1.8(a) and (b) which lead poor lithium insertion and extraction between electrode and electrolyte interface [76]. Thus it is important to suppress the formation of intermediate reaction layer at the positive electrode/electrolyte interface.
Figure 1.8(a). Cross-sectional TEM image of an LLZ/LiCoO$_2$ thin film interface and (b) the EDS line profile for elemental analysis obtained from big red arrow in Figure 1.8(a) [76].

1.5.3.1. Interface modification in all-solid-state lithium battery

Interface modification in all-solid-state lithium battery prepared by the deposition of a thin Nb metal layer (~10 nm) onto LLZ solid electrolyte and the thermal heat treatment results the formation of low-resistivity-amorphous layer as shown in Figure 1.9 [77]. The interfacial resistivity between LLZ and LiCoO$_2$ thereby reduce from 2600 $\Omega\text{cm}^2$ to 150 $\Omega\text{cm}^2$. Moreover, the fabricated Li/LLZ/LiCoO$_2$ solid-state battery with interface modifications using Nb metal layer exhibits good cycle stability and rate capability [77].
1.5.3.2. All-solid-state lithium battery prepared by co-sinterable lithium garnet electrolyte with positive electrode.

Fabrication of all-solid-state Li\(^+\) battery with LiCoO\(_2\) as positive electrode, lithium metal as negative electrode and garnet type Li\(_{6.8}(\text{La}_{2.95}\text{Ca}_{0.05})(\text{Zr}_{1.75}\text{Nb}_{0.25})\text{O}_{12}\) (with Li\(^+\) conductivity of 0.36 m Scm\(^{-1}\) at 25°C) as electrolyte prepared by co-sintering the electrolyte and LiCoO\(_2\) (LLZO-AlNb + LCO)/electrolyte (LLZO-AlNb) pellet, followed by coating of lithium metal on the electrolyte displayed charge and discharge capacities.
of 98 mAh g\(^{-1}\) and 78 mAh g\(^{-1}\) corresponding to 72\% and 58\% of the theoretical capacity [78]. Figure 1.10 shows charge-discharge curves of the fabricated battery using lithium metal on the electrolyte side of the co-sintered positive electrode (LLZO-AlNb + LCO)/electrolyte (LLZO-AlNb) pellet [79].

![Charge-discharge curves](image)

**Figure 1.10.** Charge-discharge curves for the model battery fabricated with co-sintered lithium garnet electrolyte with positive electrode [79].

### 1.6. NEXT GENERATION ELECTROCHEMICAL ENERGY STORAGE SYSTEMS

The specific energy density of conventional Li\(^+\) batteries is limited by the amount of active materials stored inside the electrode. To develop the next generation electrochemical energy storage systems, novel type of lithium battery technology are
desirable. So far many efforts have been devoted to realize a high energy density lithium metal based batteries such as Li-air batteries.

Comparison of specific energy densities of various metal-air batteries are shown in Figure 1.11. In this respect, the Li-air battery has attracted attention in recent years due to its high specific energy (13,000 Whkg\(^{-1}\), based on lithium metal alone) [80]. The theoretical specific capacity of Li-air battery is almost 5-10 times higher than that of Li\(^+\) batteries using LiCoO\(_2\) or LiMn\(_2\)O\(_4\) as the positive electrode [81]. However, a practical Li-air expected to provide 2-3 times higher specific capacity compared to that of commercially available Li\(^+\) batteries [80, 82]. Hence the Li-air battery is considered by a number of research groups as the promising technology for the power source of EVs [80, 83].

![Figure 1.11. Specific energy density of various metal-air rechargeable batteries.](image-url)
1.7. Li-AIR BATTERY

Rechargeable Li-air batteries are also called as the lithium-oxygen batteries (Li-O₂). The first Li-air battery was established by Abraham et al., in the year 1996 [84]. The foremost difference between the conventional Li⁺ batteries and Li-air batteries is that the active materials (i.e., oxygen or air) in the positive electrode are not stored in the battery system but is supplied from the environmental atmosphere around the battery to a porous carbon positive electrode [85] as shown in Figure 1.12. The use of ambient air makes Li-air battery safer than commercial Li⁺ batteries.

Figure 1.12. Schematic diagram of a Li-air battery system [86].

1.7.1. Working Principle of Li-air battery

The Li-air battery possesses a very high energy density that instigate from the use of lithium metal as the negative electrode and the consumption of atmospheric oxygen at
the positive electrode with porous carbon and catalyst composites to avoid the contamination from the atmosphere. During the discharge, an oxidation reaction occurs at the negative electrode. The electrons pass through an external circuit and Li\(^+\) transport from the negative electrode to the positive electrode via the electrolyte solution towards the porous carbon positive electrode. The oxygen is filtered from the surrounding air and the Li\(^+\) react with oxygen to form \(\text{Li}_2\text{O}\) or \(\text{Li}_2\text{O}_2\) inside the porous positive electrode. The process is vice versa during charge (i.e., the oxygen is returned to the surrounding air and the Li\(^+\) return to the negative electrode) as shown in Figure 1.13 [87, 88]. In order to avoid the negative effect of humidity and CO\(_2\), most of the fundamental works was carried out in pure oxygen. Owing to the ultrahigh energy density the Li-air battery applications range from portable electronics to electric vehicles.

![Figure 1.13. Working principle of rechargeable Li-air battery [89].](image-url)
1.7.2. Types of Li-air battery

The Li-air batteries were categorized based on the types of electrolyte used with different membranes separator [88, 90-112] such as

- Aprotic (organic) solvents
- Aqueous solvents
- Hybrid (non-aqueous/aqueous) solvents and
- All-solid-state electrolyte

The primary electrochemical reaction mechanisms for charge and discharge depend on the property of an electrolyte used in the Li-air battery. All these four types of Li-air batteries need to overcome the challenges for developing a high efficient electrode that maintains access of oxygen and limit its contaminants (e.g., H₂O, CO₂, N₂) [88].

1.7.2.1. Aprotic (organic) electrolyte based Li-air battery

![Diagram of Aprotic/Nonaqueous electrolyte based Li-air battery](image)

**Figure 1.14(a).** Architecture of Aprotic/Nonaqueous electrolyte based Li-air battery [113].
During the charging process, the \( \text{Li}_2\text{O}_2 \) and \( \text{Li}_2\text{O} \) solids are oxidized to release \( \text{O}_2 \) and \( \text{Li}^+ \) that diffuse to the lithium negative electrode followed by the reduction and deposition of the lithium negative electrode on the surface as shown in Figure 1.14(a).

The fundamental positive electrode discharge reactions are,

\[
\text{O}_2 + 2\text{e}^- + 2\text{Li}^+ \rightarrow \text{Li}_2\text{O}_2 \quad (3.10 \text{ V})
\]

\[
\text{O}_2 + 4\text{e}^- + 4\text{Li}^+ \rightarrow 2\text{Li}_2\text{O} \quad (2.90 \text{ V})
\]

**Advantages of aprotic type electrolyte**

- Exhibits high theoretical energy density
- Better rechargeability (charged for reuse)

**Disadvantages of aprotic type electrolyte**

- Formation of reaction product of lithium peroxide (\( \text{Li}_2\text{O}_2 \)) which is not soluble in the organic electrolytes. Moreover, it blocks the pores on the positive electrode surface and does not allow the oxygen to enter from the atmosphere.
- Decomposition of the electrolyte during the discharge and charge process resulting poor cyclic performance.
- Aprotic Li-air can also cause fire, making it a flammable type of battery.
1.7.2.2. Aqueous electrolyte based Li-air battery

Figure 1.14(b). Architecture of aqueous electrolyte based Li-air battery [113].

The first aqueous type electrolyte in Li-air battery was reported by Galbraith in the year 1976 [114]. An aqueous electrolyte is nothing but a combination of lithium salts dissolved in water. In order to separate the lithium negative electrode with that of aqueous electrolytes, an artificial Li\(^{+}\) conducting membranes is indispensable. This is because the direct contact of H\(_2\)O and lithium can induce severe reactions even for a very short period of time. During discharge process a reaction product layer of water soluble LiOH formed on the positive electrode surface avoids the issues related to positive electrode clogging (Figure 1.14(b)).

The reaction mechanisms for aqueous Li-air battery is,

\[ 4\text{Li} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{LiOH} \text{ (alkaline electrolyte)} \]

\[ 4\text{Li} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Li}^+ + 2\text{H}_2\text{O} \text{ (acid electrolyte)} \]
Advantages of aqueous type electrolyte

- Absence of solid discharge product that causes positive electrode clogging.
- Absence of corrosion of the lithium metal by air moisture.
- Higher practical discharge potential.

Disadvantages of aqueous type electrolyte

- Aqueous type Li-air battery requires a partition (either glass or a lithium-conducting ceramic) to avoid the violent reaction of lithium with the water.

1.7.2.3. Mixed (aprotic-aqueous) electrolytes based Li-air battery

![Diagram of mixed electrolytes based Li-air battery]

**Figure 1.14(c).** Architecture of mixed electrolytes based Li-air battery [113].

This type of battery consists of a non-aqueous electrolyte placed at the negative electrode face and an aqueous electrolyte placed at the positive electrode face. In between the two electrolytes is a Li$^+$ conducting glass ceramic membrane. It works in such a way that the O$_2$ diffuses into the porous carbon positive electrode (where it gets reduced) as
shown in Figure 1.14(c). On the other hand, lithium metal is oxidized to \( \text{Li}^+ \) which diffuses through a non-aqueous solution into an aqueous solution through the membrane.

The reaction mechanisms for mixed electrolytes based Li-air battery is,

\[
4\text{Li} + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{LiOH} \quad \text{(alkaline electrolyte)}
\]

\[
4\text{Li} + \text{O}_2 + 4\text{H}^+ = 4\text{Li}^+ + 2\text{H}_2\text{O} \quad \text{(acid electrolyte)}
\]

**Advantages of mixed type electrolytes**

- The usage of aqueous electrolytes avoids the positive electrode clogging moreover formation of natural SEI on lithium metal negative electrode due to the application of aprotic electrolytes.

**Disadvantages of mixed type electrolytes**

- A lithium metal and water stable artificial SEIs don’t have an effective solid \( \text{Li}^+ \) conductive membrane.
1.7.2.4. Solid electrolyte based Li-air battery

Figure 1.14(d). Architecture of solid electrolyte based Li-air battery [113].

The all-solid-state Li-air battery was first developed by Kumar et al. [110, 111, 115, 116]. Architecture of solid electrolyte based Li-air battery is shown as Figure 1.14(d).

The reaction mechanisms for solid electrolyte based Li-air battery is,

\[ \text{O}_2 + 2e^- + 2\text{Li}^+ \rightarrow \text{Li}_2\text{O}_2 (3.10\text{V}) \]

Advantages of solid type electrolyte

- The all-solid-state Li-air battery eliminates the problems arising due to negative electrode/positive electrode interfaces associated with liquid electrolyte.
- It is quite attractive from a safety point of view.
- Good stability and rechargeability.
- Avoid the formation of lithium dendrite.
Disadvantages of solid type electrolyte

- Solid electrolyte exhibits low Li$^+$ conductivity compared to aqueous/no-aqueous electrolyte

1.7.3. Materials for Li-air battery

1.7.3.1. Negative electrode

Lithium metal is the most promising negative material for high energy density batteries since it has the highest specific capacity (3,860 mAh$^{-1}$) and lowest negative standard reduction potential (-3.04 V vs. standard hydrogen electrode (SHE)) [117]. The major concern using lithium metal negative electrode is the formation of lithium oxidation in the open atmosphere. Hence, a special care in handling of lithium negative electrode in the preparation of the Li-air batteries is necessary.

1.7.3.2. Positive electrode

Porous carbon-based positive electrode needs to be an electrically conductive, high surface area, chemically stable, and porous to allow fast oxygen diffusion to the reaction sites. Different materials, such as porous gold, various morphologies of carbon have been investigated to provide those capabilities [118, 119]. Although porous gold has recently been demonstrated to have better reversibility, carbon-based materials have been applied the most in lithium oxygen batteries because for their light weight, low cost and high surface area. The positive electrode is composed of carbon, a catalyst, and a polymer binder to hold the catalyst on the positive electrode.
1.7.3.3. Catalyst support material

The requirements for catalyst support materials can be summarized as:

- A high specific surface area (which offers high dispersion and high utilization of nano catalysts)
- High conductivity
- High chemical and electrochemical stability under Li-air operating process and low reactivity with electrolytes in Li-air batteries system.

The most attractive material in Li-air system is carbon material owing to its high conductivity, low cost and high surface area. Research activities on other related materials including nitrides, oxides, carbides, etc., in order to brighten the battery performance and life time are in progress.

1.8. SOLID ELECTROLYTES FOR Li-AIR BATTERY APPLICATION

1.8.1. Difference in aqueous and non-aqueous electrolyte based Li-air batteries

Generally, aqueous and non-aqueous electrolyte based Li-air batteries are widely discussed in the literature [120]. The main difference between non-aqueous and aqueous electrolyte based Li-air battery is that the discharge product in the aqueous system is soluble LiOH (in alkaline medium) as shown in Figure 1.15(a), while the non-aqueous system the discharge product is an insoluble insulator Li$_2$O$_2$ precipitate on the positive electrode as shown in Figure 1.15(b). However, Li-air battery with aqueous electrolyte present the best conductivity in respect with the other systems in addition it does not face
the problem of positive electrode blockage because the reaction products of LiOH are soluble in aqueous electrolyte, which continuously maintain the battery performance over time [121] but lithium negative electrode can react with air or in water to produce LiOH and hydrogen gas which lead to a drastic diminution of the performances. Therefore, to avoid this corrosion reaction, Li-air battery with aqueous electrolyte requires a solid electrolyte interface (SEI) to cover the lithium metal (Figure 1.16). Usually, a glass or ceramic, which conducts Li\(^+\), is used as the SEI [121]. Lithium deposition and dissolution occur through the SEI during charge and discharge process is the reaction product of metallic lithium and the electrolyte.

Choosing a suitable electrolyte is crucial for the high performance of Li-air batteries.

Figure 1.15. Difference between reaction product in (a) aqueous and (b) non-aqueous Li-air battery.
Chapter I

38

Figure 1.16. Development of lithium metal and water stable artificial SEIs in aqueous Li-air battery [122, 123].

1.8.2. Solid electrolytes for aqueous electrolyte based Li-air battery

The solid electrolyte is the prime component for aqueous Li-air batteries to avoid the contact between electrode and aqueous electrolyte. The main source of power behind the progress of Li-air battery with aqueous electrolytes is that solid electrolytes that provide a substantial barrier against diffusion of ambient gases and moisture toward the lithium negative electrode. Moreover, battery with solid electrolyte is resistant against aridness. Efforts have been made by various research groups to develop a suitable solid electrolyte to separate the metallic lithium negative electrode from the aqueous
electrolyte. At present, the most prosperous solid electrolyte in Li-air battery is the commercial NASICON-type glass-ceramic \( \text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12} \) (or LTAP, Ohara Inc., Japan). LTAP solid electrolyte has high Li\(^+\) conductivity and better mechanical strength. Moreover it is chemically stable in water, mild acids and bases as shown in Figure 1.17. However the glass-ceramics LTAP is not the decisive solid electrolyte because of the instable nature of LTAP in contact with metallic lithium. Hence there rises the necessity of an inclusion of a buffer layer between the solid electrolyte and that of the lithium metal that compromises the overall energy density. This buffer layer arise many technical problems that influence the performance and stability of Li-air batteries. These drawbacks required a solid electrolyte that is compatible with lithium metal and is stable over a wide pH range.

Hasegawa et al. reported that LLZ cubic garnet structure was stable in saturated LiCl aqueous solution with respect to structure and conductivity [98]. The preliminary results indicated that high Li\(^+\) conductive cubic phase LLZ could be a better solid electrolyte for Li-air batteries.
1.9. SCOPE OF THIS THESIS

The main focus of this thesis is to develop high Li$^+$ conductive cubic phase lithium garnets with dense microstructure for all-solid-state Li$^+$ battery application and lithium garnets stable against aqueous solution for Li-air battery applications. The role of La$_2$Zr$_2$O$_7$ pyrochlore in the formation of LLZ and the effect of lithium concentration in the stabilization of high Li$^+$ conductive cubic phase LLZ through solid-state reaction technique method have been investigated in detail. An attempt has been made to enhance the total (bulk+ grain-boundary) Li$^+$ conductivity of LLZ by partial substitution of hexavalent Te for a tetravalent Zr i.e., with nominal
compositions $\text{Li}_{7-2x}\text{La}_3\text{Zr}_{2-x}\text{Te}_x\text{O}_{12}$ ($x = 0.125$ and 0.25). High $\text{Li}^+$ conductive cubic phase Sn based lithium garnets are successfully prepared by partially substituting Ta for Sn in $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ through solid state reaction technique. The structural stability of tetragonal phase $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ against distilled water, acidic medium (under reflux) and under humid conditions are also investigated. The chemical stability and $\text{Li}^+$ conductivity have been enhanced successfully by partial substitution of $\text{Y}^{3+}$ for $\text{La}^{3+}$ in $\text{Li}_7\text{La}_{3-x}\text{Y}_x\text{Zr}_2\text{O}_{12}$ garnet.
REFERENCES


Chapter I


Chapter I


