1.1. INTRODUCTION

Concerns over the diminution of fossil fuels and the greenhouse effect caused by CO₂ emissions have stimulated strong interest in harvesting more clean energy such as wind and solar energies. The major challenge of the efficient use of renewable energy includes the exploration of suitable electrical energy storage devices for both off-grid and on-grid schemes. The global market for electrical energy storage devices is expected to be around 55 billion US dollars in 2019 for applications such as laptops, mobile phones, watches and toys [1].

Electrochemical energy storage systems such as batteries and super capacitors are expedient source of choice to store and deliver energy. Compared to super capacitors, batteries continue to dominate the market of consumer and portable electronic systems. Batteries store electricity by converting the chemical energy contained in its active materials (negative electrode (anode), positive electrode (cathode) and an electrolyte (separator)) by an electrochemical redox (reduction-oxidation) reaction.

1.1.1. Types of batteries

Batteries are classified into two kinds namely, primary battery and secondary battery.
Primary batteries

Primary batteries also known as single-use or “throw-away” batteries are batteries in which the electrochemical reactions are not reversible. During discharging the electrical energy is released until the original compounds are completely exhausted. Thus the cells can be used only once. Primary batteries are more commonly used in portable devices that have low current drain. Primary Batteries include Zinc-carbon, Alkaline, and Lithium batteries.

Secondary batteries

Secondary batteries also known as rechargeable batteries are the batteries in which the electrochemical reactions are reversible and the original chemical compounds can be reconstituted. Secondary batteries can be recharged many times for reuse. Secondary batteries include Lead-acid, Nickel-cadmium, Nickel-metal hydride and Lithium ion (Li\(^+\)).

1.1.2. Basic concepts used to evaluate the electrochemical performance of batteries

Cell potential

It is the potential difference between the positive and negative electrodes.

Ampere-Hour (Ah) capacity

It is defined as the amount of current delivered by a battery for one hour before the battery gets discharged.
Specific energy (SE)

It is defined as the energy per unit mass.

Specific capacity

The amount of electric charge the battery can store per unit mass.

The theoretical specific capacity \( Q_{TSC}, \text{mAh g}^{-1} \) is given by

\[
Q_{TSC} = n \times F/M
\]  
(1.1)

where \( n \) is the number of moles of electrons exchanged, \( F \) is the Faraday constant \((96,485.33 \text{ C mol}^{-1})\) and \( M \) is the molecular weight of the active materials. The specific charge capacity \( Q_c, \text{mAh g}^{-1} \) or specific discharge capacity \( Q_d, \text{mAh g}^{-1} \) can be calculated from the following equation:

\[
Q_c \text{ (or } Q_d) = I \times t/m
\]  
(1.2)

where \( I \) is the charge or discharge current (mA), \( t \) is the charge or discharge time (s), \( m \) is the mass of the active materials (g).

Energy density (ED)

It is defined as the amount of energy stored in a given system.

The specific energy \( SE, \text{Wh kg}^{-1} \) and energy density \( ED, \text{Wh L}^{-1} \) can be calculated from the following equations:

\[
SE = (E \times Q) / 1000
\]  
(1.3)

\[
ED = (E \times Q \times m) / (1000 \times V)
\]  
(1.4)
C-rate

The C rate is a unit which is used to signify a charge or discharge rate. The rate of current that is numerically equal to the Ah rating of the cell.

Irreversible capacity ($Q_I$)

It is used to define the capacity loss after each cycle.

For positive electrode: $Q_I = n^{th} Q_d - n^{th} Q_c$  \hspace{1cm} (1.5)

For negative electrode: $Q_I = n^{th} Q_c - n^{th} Q_d$  \hspace{1cm} (1.6)

Coulombic efficiency: a term to represent the ratio of discharge capacity to the charge capacity.

\[
\mu = \frac{n^{th} Q_d}{n^{th} Q_c} \times 100\%
\]  \hspace{1cm} (1.7)
1.2. RECHARGEABLE Li⁺ BATTERIES

Figure 1.1. Comparison of specific energy (WhKg⁻¹) of few secondary batteries [2, 3].

Figure 1.1 shows the comparison of the specific energy (WhKg⁻¹) of few secondary electrochemical energy storage batteries. Among the various electrochemical energy storage devices, rechargeable lithium ion (Li⁺) batteries are attaining significant attention for various applications ranging from portable electronics to electric vehicle because of its high energy density compared to other battery systems.

Li⁺ batteries are at least 30% lighter in weight than Ni-MH batteries and provide at least 30% more capacity. Experimentation to develop rechargeable lithium battery i.e.,
using lithium metal as negative electrode failed due to the safety issues (dendrite growth) raised due to metallic lithium. Further analysis on rechargeable lithium battery gives rise to a solution using non metallic Li$^+$. This technology is named as Li$^+$ battery technology. Unlike lithium primary batteries the specific energy of Li$^+$ battery technology is quite low but are safer. The concept of rechargeable Li$^+$ batteries was first commercialized by Sony at 1991 [2]. Since then Li$^+$ battery technology has became the most exciting and escalating battery technology. Its application includes popular electronic devices such as mobile phone, laptops, MP3’s and others. Extensive research and development activities in various research laboratories are in progress to develop Li$^+$ battery technology for hybrid electric vehicles (HEV) and electric vehicles (EV).

1.2.1. Working principle of Li$^+$ battery

The commercialized Li$^+$ batteries introduced by Sony in the year 1991 used coke (coal product) as the negative electrode; lithium metal oxide (e.g. LiCoO$_2$/LiMnO$_2$) as positive electrode and a lithium salt such as hexafluorophosphate (LiPF$_6$) dissolved in an organic solvent as liquid electrolyte [3]. Later coal has been replaced by graphite (a form of carbon). This technology is also named as a “rocking-chair” battery as the Li$^+$ “rock” back and forth between the two positive and negative electrodes during battery charging and discharging. The working principle of rechargeable Li$^+$ battery is shown in Figure 1.2.
Figure 1.2. Working principle of rechargeable Li\textsuperscript{+} battery [2, 3].

During charging process, Li\textsuperscript{+} are de-intercalated from the layered LiCoO\textsubscript{2} positive electrode, pass across the electrolyte and then inserted between the graphite layers in the negative electrode. At the same time, electrons flow from the positive electrode to the negative electrode through the external circuit. This process is completely reversed while discharging. The Li\textsuperscript{+} battery operation are based on the reversible shuttling of Li\textsuperscript{+} between the positive and negative electrode materials. As a result, the intrinsic properties of electrode materials will strongly confine the feat of batteries.

The reaction involved during Li\textsuperscript{+} battery charging and discharging process are given below

<table>
<thead>
<tr>
<th>Positive electrode</th>
<th>LiCoO\textsubscript{2}</th>
<th>Charge \rightleftharpoons Discharge</th>
<th>\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative electrode</td>
<td>6C + xLi\textsuperscript{+} + xe\textsuperscript{-}</td>
<td>Charge \rightleftharpoons Discharge</td>
<td>Li_xC_6</td>
</tr>
<tr>
<td>Overall</td>
<td>LiCoO\textsubscript{2} + 6C</td>
<td>Charge \rightleftharpoons Discharge</td>
<td>Li_xC_6 + Li_{1-x}\text{CoO}_2</td>
</tr>
</tbody>
</table>
1.2.2. Advantages of the Li$^+$ rechargeable battery compared to other rechargeable batteries

- Li$^+$ batteries exhibit high voltages up to 4 V
- Have high specific energy and power density than other rechargeable batteries
- Wide operation temperature range
- High Coulombic and energy efficiency
- High rate and rapid charge capability
- Light weight compared to the other rechargeable batteries
- Long cycle life

1.2.3. Disadvantages of the present Li$^+$ battery technology

- The power density is inadequate for the future applications.
- Degrade much faster if they are exposed to heat as compared to the normal temperature exposure because they are extremely sensitive to high temperatures.
- Li$^+$ batteries are ruined if they are completely discharged.
- The cost of Li$^+$ battery is high compared to the other existing rechargeable batteries.
- There are safety concerns because of the usage of high energy materials.
- Problems arise with over charge and discharge.
- Thermal runaway and venting can occur when cells are crushed or punctured. Such conditions can cause fires.
1.3. MATERIALS FOR Li⁺ RECHARGEABLE BATTERIES

1.3.1. Positive electrode materials for rechargeable Li⁺ battery

The positive electrode is one of the main components in the Li⁺ battery pack. It is essential to explore a positive electrode material that exhibits high operating voltages in order to improve the energy density of present rechargeable Li⁺ batteries. Most of the positive electrode materials used in present Li⁺ battery technology are based on lithium transition metal oxides like, lithium cobalt oxide (LiCoO₂), lithium manganese oxide (LiMn₂O₄) and lithium iron phosphate (LiFePO₄).

1.3.1.1. Lithium cobalt oxide (LiCoO₂)

Layered transition metal oxide LiCoO₂ was introduced by John B Goodenough in the year 1980 [4]. The lithium cobalt oxide used as the positive electrode in rechargeable Li⁺ battery was first commercialized by Sony in 1991. Over a decade, LiCoO₂ still remains as a most exploited commercial positive electrode material for Li⁺ battery application due to its high stability during electrochemical cycling, superior capacity and ease of preparation in bulk quantities. LiCoO₂ belongs to α-NaFeO₂ structure. The layered structure of LiCoO₂ shown in Figure 1.3 consists of a close packed network of oxygen ions with Li and Co ions on alternative (111) planes of the cubic rock salt sublattice. The edges of CoO₆ octahedral are shared to form CoO₂ sheets and Li⁺ can move in two-dimensional directions between CoO₂ sheets.
Advantages: LiCoO$_2$ exhibits a high theoretical specific capacity and volumetric capacity of 274 mAh g$^{-1}$ and 1363 mAh cm$^{-3}$, respectively. In addition to these LiCoO$_2$ exhibits a high discharge voltage, good cycling performance and low self-discharge. All these features makes LiCoO$_2$ a very attractive positive electrode material for consumer applications like cell phones, laptops and cameras [6].

Drawbacks:

- high costs (owing to the limited resources of cobalt)
- low discharge current
- increase of the internal resistance with respect to cycling and aging.
• Environmental hazards (owing to high toxicity of cobalt).

1.3.1.2. Lithium iron phosphate (LiFePO$_4$)

Padhi et al. reported on the electrochemical properties of a new class of cathode materials known as the phospho-olivines in the year 1997 [7]. LiFePO$_4$ belongs to the olivine structure-type orthorhombic structure with a space group Pnma as shown in Figure 1.4. Li$^+$ and Fe$^{2+}$ occupy half of the octahedral sites, whereas P is located in 1/8th of the tetrahedral sites of LiFePO$_4$. The FeO$_6$ octahedra share corners and LiO$_6$ octahedra share edges along tunnels down the b-axis, through which the Li$^+$ can diffuse.

![Figure 1.4](image_url)

**Figure 1.4.** The structure of monoclinic Li$_3$Fe$_2$(PO$_4$)$_3$ looking down the unique axis, P is located in the blue tetrahedral and Fe in the green octahedral. Yellow spheres represent the Li$^+$ [7]
Advantages:

The major advantages of LiFePO\(_4\) are that it has a reversible capacity of \(~160\) mAh g\(^{-1}\) and an operating voltage of \(~3.45\) V \(v.s.\) Li\(^+\)/Li. More importantly the raw materials for the preparation of LiFePO\(_4\) are abundant in nature and are of low in cost and environmentally friendly. LiFePO\(_4\) are considered to be safer than the transition metal oxides owing to their high stability. No major capacity fading is observed and it is possible to enhance the electrochemical performances at high temperature (up to 85 °C) over a long cycle life.

Drawbacks:

The major drawback of LiFePO\(_4\) is poor electronic conductivity, which prevents full use of its theoretical capacity.

1.3.1.3. Lithium manganese oxide (LiMn\(_2\)O\(_4\))

LiMn\(_2\)O\(_4\) that forms a spinel structure is a promising cathode material that was proposed by Thackeray et al. in 1983 [8]. In case of LiMn\(_2\)O\(_4\) structure, manganese occupies the octahedral sites whereas lithium occupies the tetrahedral sites [9]. The path for lithiation and delithiation of LiMn\(_2\)O\(_4\) are a 3-dimensional network of channels rather than planes. Compared to LiCoO\(_2\) the LiMn\(_2\)O\(_4\) is low in cost and are safe [10].

Advantages:

Manganese is relatively lesser toxic, cheap, thermally stable and environmentally friendly. LiMn\(_2\)O\(_4\) has a flat operating voltage of 3.95 – 4.1 V with theoretical capacity of 148 mA h g\(^{-1}\).
Drawbacks:

- low capacity.
- Exhibits phase changes during cycling.

1.3.2. Negative electrode materials for rechargeable Li$^+$ battery

1.3.2.1. Lithium metal

Lithium metal is the most favored negative electrode for lithium primary batteries because of its low molecular weight and higher specific capacity. It is possible to achieve a capacity of 3861 mAh.g$^{-1}$ using lithium metal as negative electrode. However use of metallic lithium as negative electrode in rechargeable batteries cause difficulty in terms of safety and reversibility. The morphology of lithium deposited during charging process is different from that of lithium metal. The needle like deposit thus produced is known as dendrite and may become electrically isolated from the lithium metal due to non-uniform dissolution of lithium at different portions during continuous charge-discharge cycles leading to capacity loss. These dendrites may penetrate the separator and can cause internal short circuit. The problem of lithium dendrite formation is overcomed by the use of lithium intercalation compounds.

1.3.2.2. Graphite

The substitution of lithium metal electrodes with insertion materials with relatively high lithium activities initiated the breakthrough in the rechargeable lithium battery technology. Several insertion materials, including transition-metal oxides and chalcogenides, carbons and lithium alloys have been proposed for negative electrodes.
Since its first introduction in the market of Li$^+$ battery, graphite has become most attractive electroactive material for the negative electrode fabrication, due to its unique characteristics in terms of safety, capacity, cyclability and low voltage of the lithium insertion/deinsertion mechanism. The advantage of using carbonaceous materials is that they are cheap and largely abundant. The major improvement of the Li$^+$ battery technology in terms of energy density could be reached by increasing the crystallinity of the carbon negative electrode, i.e. by replacing amorphous carbon by graphite. The crystal structure of lithiated graphite is shown as Figure 1.5 [11]. Out of the maximum theoretical capacity of 372 mA h g$^{-1}$, practical values of about 350 mA h g$^{-1}$ is generally attained with graphite. However, many problems of the current configuration are related to the use of graphite-based negative electrode, that present poor performances under some particular operating conditions, i.e. low temperatures and high charge/discharge rates and high irreversible capacity in the first cycle due to the solid electrolyte interface (SEI) formation.
Hence, there is considerable interest in finding alternative negative electrode materials with both larger capacities and slightly more positive intercalation voltages vs. Li⁺/Li in order to minimize any risks of high-surface-area lithium plating at the end of fast recharge.

1.3.2.3. Spinel Li₄Ti₅O₁₂

Spinel Li₄Ti₅O₁₂ has been considered as one the most hopeful negative electrode candidates in Li⁺ batteries for HEVs or EVs because this “zero-strain material” Li₄Ti₅O₁₂ has high voltage platform, no volume change and perfect cycling performance.
Li$_4$Ti$_5$O$_{12}$, has a spinel structure with a cubic space group $Fd\bar{3}m$, as illustrated in Figure 1.6, where the octahedral $16d$ sites are shared by lithium and titanium with an atomic ratio of 1 : 5 and all the tetrahedral $8a$ sites are occupied by lithium [13]. It is astonishing that the occupation of intercalated three Li$^+$ in $16c$ sites during the intercalation process does not change the structure of Li$_4$Ti$_5$O$_{12}$. The shortcomings like low electronic conductivity and poor rate performance must be solved before Li$_4$Ti$_5$O$_{12}$ can realize practical application in the area of high energy density applications.

1.3.3. Electrolyte materials for rechargeable Li$^+$ battery

The development of high energy density Li$^+$ battery technology truly depends on the development of robust electrolyte which can sustain with high performance electrodes. On that account the choice of electrolyte depends on the chemistry of electrodes. The electrolyte materials for rechargeable Li$^+$ battery are broadly classified as
• Liquid electrolytes
• Ionic liquids
• Polymer electrolytes
• Solid electrolytes

1.3.3.1. Liquid electrolytes

Owing to their high ionic conductivity of ~$10^{-2}$ Scm$^{-1}$ the liquid electrolyte retains their importance in rechargeable Li$^+$ battery technology. In general liquid electrolytes are composed of lithium salts such as LiClO$_4$, LiAsF$_6$, LiPF$_6$, LiSO$_3$CF$_3$, LiN (SO$_2$CF$_3$)$_2$ etc. dissolved in solvents. Based on the solvent used they are classified into aqueous (water), mixed aqueous (water mixed along with co-solvent) and non-aqueous (organic or inorganic solvent) electrolyte solutions, respectively. The non-aqueous aprotic organic solvent comprise either one or mixture of the following: propylene carbonate (PC), diethyl carbonate (DEC), ethylene carbonate (EC), dimethyl carbonate (DMC), or ethyl methyl carbonate (EMC). These solvents have good conductivity and electrochemical stability towards the highly oxidizing positive electrode. The initial Li$^+$ battery design was made using LiClO$_4$ as electrolyte. Later it was found that LiClO$_4$ lithium salt undergoes violent decomposition, resulting safety issues [14] Hence LiClO$_4$ was replaced by LiPF$_6$. The major concern of using liquid electrolytes is that they are thermodynamically unstable in combination with negative electrode. Moreover the formation of intermediate layers of reaction products (SEI) between the electrode and
electrolyte reduce the kinetics of charge and discharge process and therefore results in capacity fading.

1.3.3.2. Ionic liquids

Ionic liquids are organic salts composed of ionic species that are liquid at (or close to) room temperature. Most ionic liquids are liquids at room temperature and exhibits melting temperatures as low as -96 °C [15]. Ionic liquids offer great advantages that include low volatility, high thermal stability, good electrochemical stability, recyclability and non flammability. These remarkable properties makes ionic liquids as green solvents for Li⁺ battery applications [16]. Based on the cation segment the ionic liquids are generally classified into alkylammonium, dialkylimidazolium, phosphonium and N-alkylpyridinium. Ammonium-based ethanolammonium nitrate (EOAN), was the first synthesized ionic liquid in 1888 by Gabriel [17]. Comparison of few room temperature ionic liquid containing quaternary ammonium cation and imide anion by Sakaeb et al. revealed that quaternary ammonium cations, including EMI (1-ethyl-3-methylimidazolium) cation, TMPA (trimethylpropylammonium) cation, P13 (N-methyl-N-propylpyridinium) cation, PP13 (N-methyl-N-propylpiperidinium) cation and TFSI (bis(trifluoromethanesulfonyl)imide) cation, could stabilize the reduction on the lithium metal [18]. The ionic conductivities of ionic liquids are three to four orders of magnitude lower, than those of liquid electrolytes [19,20].
1.3.3.3. **Polymer electrolytes**

The usages of liquid electrolyte in rechargeable Li$^+$ batteries were replaced by the introduction of polymer electrolytes in the year 1999 [21]. Polymer electrolytes are obtained by dissolving the solvent free polymer membrane such as poly ethylene oxide (PEO) and lithium salts (LiPF$_6$ or LiCF$_3$SO$_3$). The most common type of polymer electrolyte studied is PEO$_6$:LiMF$_6$ (where M = P, Sb, As). However, PEO-based electrolytes exhibits a low ionic conductivity of $10^{-8}$ Scm$^{-1}$ to $10^{-4}$ Scm$^{-1}$ at temperature between 40°C and 100°C owing to their high degree of crystallinity [22]. Later PEO was replaced by polyacrylonitrile (PAN). Nevertheless the usage of PAN results in an increase in internal resistance of the Li$^+$ polymer battery. Polyvinylidene fluoride (PVDF) is the most common polymer used at present in Li$^+$ polymer battery technology due to its strong electron withdrawing functional group (-C-F) and high dielectric constant. But PVDF exhibits low ionic conductivity compared to liquid electrolyte system. Introduction of composite filler such as SiO$_2$, ZrO$_2$, TiO$_2$, Al$_2$O$_3$, in PVdF improves the ionic conductivity of polymer electrolytes [23-25].

Among the investigated fillers SiO$_2$ ceramic oxide filler in PVDF matrix exhibits a maximized ionic conductivity of $3.5 \times 10^{-2}$ Scm$^{-1}$ [26-29].

**Major advantages of polymer electrolytes based batteries**

Although conductivity of the order of $10^{-4}$Scm$^{-1}$ obtained for a many polymer electrolytes at elevated temperatures, this is not as high as required. By configuring the electrolytes as very thin layer and large-area elements the internal resistance of the fabricated cell may be reduced into an acceptable range. Also, the cells can be operated at
relatively low values of current density, while still permitting the battery at practical rates. It is the combination of a unique battery cell structure with the properties of these polymer electrolytes that can, in principle, permit high values of specific energy and power to be achieved [30].

The polymer electrolyte plays three important roles in the polymer electrolyte (PE) battery.

- It is a Li\(^+\) carrier and can be formed into thin films to improve the energy density.
- It acts as an electrode spacer hence eliminates the need to incorporate an inert porous separator.
- It is a binder, which ensures good electrical contact with the electrodes.

The flexibility and mechanical resilience are the major advantages.

**Disadvantages of Polymer electrolytes**

However, there exists a phase separation between the polymer matrix and the absorbed electrolyte solution resulting in leakage of electrolyte solution and failure of the electrode/electrolyte contact thereby reducing the ionic conductivity [31]. Polymer electrolytes are not stable with lithium metal; they cannot be used together with lithium negative electrode.

**1.3.3.4. Solid fast Li\(^+\) conductors**

Solid-state Li\(^+\) batteries are considered to be the potential contender for the safety issues raised by the conventional organic liquid/polymer electrolyte based Li\(^+\) batteries.
The foremost futures of solid Li\(^+\) conducting electrolytes include large electrochemical stability windows, good thermal stability, pollution free, absence of leakage, less internal short circuit, resistance to shocks and vibrations and simplicity of manufacture. Hence recent researches have been devoted to realize a solid electrolyte with high Li\(^+\) conductivity and excellent chemical stability against lithium metal electrode.

Although the advantages of non-flammable solid electrolytes are widely accepted, their low ionic conductivities and low chemical and electrochemical stabilities prevent them being used in practical applications. Therefore, the search for solid electrolyte materials with high Li\(^+\) conductivity (> 10\(^{-4}\) Scm\(^{-1}\)) became a prime factor in the advancement of all-solid-state lithium rechargeable batteries.

1.4. INORGANIC SOLID ELECTROLYTES

So far, a wide range of layered two-dimensional (2D) and three-dimensional (3D) inorganic solid Li\(^+\) conducting electrolytes (SLICEs) such as Li\(_3\)N [32]; Li-\(\beta\)-alumina [33, 34]; amorphous lithium phosphorus oxynitride (LIPON) [35], Li\(_4\)SiO\(_4\) [36]; Li\(_{14}\)ZnGe\(_4\)O\(_{16}\) (lithium superionic conductors, LISICON) [37, 38]; Li\(_{1.3}\)Al\(_{0.3}\)Ti\(_{1.7}\)(PO\(_4\))\(_3\) (sodium superionic conductors, NASICON) [39, 40]; Li\(_3\)PO\(_4\) and perovskite (Li,Ln)TiO\(_3\) (Ln = rare earths) [41-43] had been investigated for possible application in rechargeable batteries. A comparison of the Arrhenius plot of ionic conductivity of few well known crystalline and amorphous inorganic solid Li\(^+\) conductors is shown as Figure 1.7 [44].
Figure 1.7. Arrhenius plots of ionic conductivity of important crystalline and amorphous inorganic solid Li$^+$ conductors [44].

1.4.1. Perovskite type lithium lanthanum titanate (LLTO)

Among the investigated crystalline inorganic solid Li$^+$ conductors, the perovskite (ABO$_3$)-type lithium lanthanum titanate Li$_{3}$La$_{(2/3)-x}$La$_{(1/3)-2x}$TiO$_3$ (0.04 < x < 0.16) (LLT) exhibits a maximized room temperature bulk Li$^+$ conductivity of about 1 x 10$^{-3}$ Scm$^{-1}$ with an activation energy of 0.4 eV for x corresponds to 0.11 [42] which is comparable to that of existing polymer/liquid based electrolytes in the Li$^+$ battery technology. The crystal structure of LLT is given as Figure 1.8. However LLT undergoes fast lithium insertion with the consequent reduction of Ti$^{4+}$ to Ti$^{3+}$, while in direct contact with elemental lithium and thereby resulting high electronic conductivity [45]. Therefore the
application of LLT is not favorable to employ as an electrolyte in the high-energy density all-solid-state batteries using lithium metal negative electrode.

Figure 1.8. The crystal structure of the perovskite (Li,La)TiO$_3$ [46].

1.4.2. NASICON type lithium aluminum titanium phosphate (LATP)

The family of sodium superionic conductors, (NASICON) with nominal compositions LiM$_2$(PO$_4$)$_3$ (M = Ti, Zr, Ge, Hf) exhibits a highest Li$^+$ conductivity of $3 \times 10^{-3}$ Scm$^{-1}$ at 25 °C for Al doped Ti based compound Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ (LATP) [47-49]. The crystal structure of LiM$_2$(PO$_4$)$_3$ (M = Ti, Zr, Ge, Hf) is given as Figure 1.9. The substitution of smaller Al$^{3+}$ (0.53 Å) for larger Ti$^{4+}$ (0.60 Å) cations reduces the unit cell dimension of the NASICON framework and enhance the ionic conductivity. However the application of NASICON-type materials for all-solid-state lithium batteries failed due to facile reduction of Ti$^{4+}$. 
1.4.3. Lithium phosphorus oxynitride (LIPON)

Lithium phosphorus oxynitride (LIPON) has Li$^+$ conductivity of about $3.3 \times 10^{-6}$ Scm$^{-1}$ at 25 °C and are widely used for the fabrication of an all-solid-state thin film type lithium battery. LIPON films have good electrochemical stability with both lithium metal negative electrode and transition metal positive electrodes with a cell potential of 5.5 V versus Li. The major drawback of LIPON system is that the films can be fabricated only by means of sputtering method. Moreover the LIPON exhibits a poor ionic conductivity [35].

So far, all the discovered inorganic compounds had either high ionic conductivity or high electrochemical stability, but not the both. In order to develop high-energy density all-solid-state lithium batteries the electrolyte must possess both high Li$^+$ conductivity as well as high electrochemical stability.
Among the investigated fast Li\textsuperscript{+} conductors, garnet-like structural compounds reported by Weppner and his group received considerable attention for potential application as electrolytes in all-solid-state lithium batteries owing to their high ionic conductivity [50-58].

1.5. GARNET STRUCTURED SOLID FAST Li\textsuperscript{+} CONDUCTORS

Garnets are orthosilicates with general formula of A\textsubscript{3}B\textsubscript{2}(SiO\textsubscript{4})\textsubscript{3} (A\textsuperscript{2+} = Ca, Mg, Fe; B\textsuperscript{3+} = Al, Ti, Cr, Fe), in which A and B refer to eight- and six-coordinated cation sites, respectively and it crystallize in the I\textit{a}3\textit{d} space group [59]. The crystal structure of ideal garnet A\textsubscript{3}B\textsubscript{2}C\textsubscript{3}O\textsubscript{12} where A (Ca, Mg, Y), B (Ga, Mn, Ni, Fe, Al, Cr), and C (Al, Si, Ge, V) are eight-, six- and four-oxygen-coordinated cation sites, respectively, is shown as Figure 1.10.

Lithium containing garnets are obtained by replacing silicon with lithium to provide the general composition A\textsubscript{3}B\textsubscript{2}(LiO\textsubscript{4})\textsubscript{3}. So far, a number of diffraction studies have been employed using both X-rays and neutrons to determine the crystal structure of lithium garnets. Among them neutron diffraction measurements are found to be more sensitive in detecting the distribution of lithium cations across the possible sites (tetrahedral or octahedral) of lithium containing garnets [61-66]. The initial neutron diffraction studies on lithium containing garnets confirmed the presence of a cubic unit cell with a space group I\textit{a}3\textit{d}.
Figure 1.10. The crystal structure of an ideal garnet of general formula $A_3B_2C_3O_{12}$, where the orange spheres represent B cations and blue and green polyhedrons represent A and C cations, respectively [60].

Neutron diffraction studies on conventional garnet stoichiometry $Li_3Ln_3Te_2O_{12}$ ($Ln = Y, Pr, Nd, Sm - Lu$) by O’Callaghan et. al. indicated that lithium precisely occupy tetrahedrally coordinated site (24$d$) leaving the octahedrally coordinated site empty as shown in Figure 1.11 [67]. Moreover, the conventional garnet stoichiometry $Li_3A_3B_2O_{12}$ does not allow the occupancy of more than three lithium cation per formula unit in the tetrahedral (24$d$) site. Examination on the transport properties of $Li_3Nd_3Te_2O_{12}$ revealed a very poor $Li^+$ conductivity of around $10^{-5}$ Scm$^{-1}$ at 600 °C with high activation energy of 1.22 eV [67]. Investigations on Li-excess $Li_{3+x}Nd_3Te_{2-x}Sb_xO_{12}$ ($x = 0.05–1.5$) by
O’Callaghan et al. indicated that the Li$^+$ conductivity increase with increasing Li content and reach a maximized value of $1 \times 10^{-2} \text{Scm}^{-1}$ at 400 °C for the composition Li$_{3.5}$Nd$_3$Te$_{1.5}$Sb$_{0.50}$O$_{12}$ [68].

![Figure 1.11. The lithium cations in Li$_3$Nd$_3$W$_2$O$_{12}$ are in LiO$_4$ tetrahedron (grey) linked with tungsten (blue) which is octahedrally coordinated by oxide anions (red) [69].](image)

**Figure 1.11.** The lithium cations in Li$_3$Nd$_3$W$_2$O$_{12}$ are in LiO$_4$ tetrahedron (grey) linked with tungsten (blue) which is octahedrally coordinated by oxide anions (red) [69].

### 1.5.1. Lithium stuffed garnets

Li$_x$A$_3$B$_2$O$_{12}$ with lithium concentration $x > 3$ is identified as lithium stuffed garnets. It is possible to increase the lithium content in Li$_x$A$_3$B$_2$O$_{12}$ by partial replacement of either A or B cations with higher or lower oxidation state. Figure 1.12 shows the evolution of family of garnet structured solid Li$^+$ conductors.
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Figure 1.12. Evolution of new family of garnet structured solid Li$^+$ conductors.

Increase in the lithium content of Li$_i$A$_3$B$_2$O$_{12}$ leads to the lithium rich composition Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta). Thangadurai et al. was the first to report the Li$^+$ transport properties of Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta) in 2003 [50]. The total (bulk + grain-boundary) Li$^+$ conductivity was found to be in the order of $10^{-6}$ S cm$^{-1}$ at 25 ºC. More importantly, tantalum based Li$_5$La$_3$Ta$_2$O$_{12}$ was found to be stable against reaction with molten lithium, which is the key property to develop all-solid-lithium battery. Initial bond valence analysis on Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta) to find the possible pathways for Li$^+$ migration predicted that the Li$^+$ move in a three-dimensional network of energetically equivalent partially occupied (tetrahedral and octahedral) sites [70]. Neutron diffraction refinements by Cussen et al. on Li$_5$La$_3$M$_2$O$_{12}$ (M = Ta, Nb) revealed that the Li$^+$ occupies both
tetrahedral and octahedral and suggests that the octahedral sites are responsible for the observed Li$^+$ mobility via a clustering mechanism [61]. The occupancy of Li$^+$ in Li$_5$La$_3$Ta$_2$O$_{12}$ predicted by Cussen et al. is shown as Figure 1.13 [61]. The structure of Sb containing system Li$_5$Ln$_3$Sb$_2$O$_{12}$ (Ln = La, Pr, Nd, Sm) has been reported by Percival et al. [71]. Li$_5$La$_3$Sb$_2$O$_{12}$ showed the partial occupancy of lithium across two crystallographic sites with 79% Li$^+$ over tetrahedral site and 44% Li$^+$ over distorted octahedral site and is isostructural with that of Li$_5$La$_3$Nb$_2$O$_{12}$ and Li$_5$La$_3$Ta$_2$O$_{12}$ [69, 71].

![Figure 1.13](image-url)

**Figure.** 1.13. (a) The La$_3$M$_2$O$_{12}$ garnet framework showing MO$_6$ octahedral units and Ln$^{3+}$ cations. The occupancy of lithium in (b) trigonal prismatic, (c) octahedral coordination and (d) tetrahedral coordination [61].

Systematic investigation on Li$_5$La$_3$M$_2$O$_{12}$ (M = Ta, Nb, Sb and Bi) by Murugan et al. [53, 55] revealed that bismuth containing lithium garnet exhibits a maximized cubic lattice constant and enhanced Li$^+$ conductivity with low activation energy. Moreover,
there exist a correlation between the lattice parameter and Li$^+$ conductivity. It was found that the Li$^+$ conductivity increases with increase in the lattice parameter in the order Ta < Nb < Sb < Bi containing aluminium garnet [55]. The correlation between the Li$^+$ conductivity and activation energy versus lattice parameter of the Li$_5$La$_3$M$_2$O$_{12}$ (M = Ta, Nb, Sb and Bi) series are shown as Figure 1.14 [55].

![Figure 1.14. Correlation between total (bulk + grain-boundary) Li$^+$ conductivity and activation energy vs lattice parameter of the Li$_5$La$_3$M$_2$O$_{12}$ (M = Ta, Nb, Sb and Bi) series [55].](image)

Following the discovery of garnet structured Li$_5$La$_3$M$_2$O$_{12}$ (M = Ta, Nb), many research work has been attempted to improve Li$^+$ conductivity by various chemical substitution and structural modifications. Substitution of alkaline earth elements for La in
Li$_5$La$_3$M$_2$O$_{12}$ ($M = \text{Nb, Ta}$) and adding excess lithium results in new members of the class of materials with the chemical composition ($A=\text{Ca, Sr, Ba, Mg; } M= \text{Nb, Ta}$) [51, 52, 72]. Among the investigated materials, in this series Li$_6$BaLa$_2$Ta$_2$O$_{12}$ exhibited the maximized total (bulk + grain-boundary) Li$^+$ conductivity of $4 \times 10^{-5}$ S cm$^{-1}$ at 22 °C with activation energy of 0.40 eV [51]. The variation of Li$^+$ conductivity and activation energy against ionic radii of the divalent Mg, Ca, Sr, Sr$_{0.5}$Ba$_{0.5}$ and Ba ions substituting a trivalent La in Li$_5$La$_3$Ta$_2$O$_{12}$ is shown as Figure 1.15.

**Figure 1.15.** Plot of total (bulk + grain-boundary) (Open square) and bulk ionic conductivity (Open circle) observed at 50 °C and activation energy (Open triangle) vs the eight-coordinated ionic radii of the divalent Mg, Ca, Sr, Sr$_{0.5}$Ba$_{0.5}$ and Ba ions substituting a trivalent La in Li$_5$La$_3$Ta$_2$O$_{12}$ [72].
Structural refinement on $\text{Li}_6\text{CaLa}_2\text{Ta}_2\text{O}_{12}$ reported by Awaka et al. revealed that $\text{Li}^+$ occupy partially at the tetrahedral $24d$ site Li(1) and distorted octahedral $96h$ site Li(2), as shown in Figure 1.16.[73]

![Crystal structure of Li$_6$CaLa$_2$Ta$_2$O$_{12}$](image)

**Figure 1.16.** The crystal structure of Li$_6$CaLa$_2$Ta$_2$O$_{12}$ [73].

Substitution of tetravalent Zr for M in Li$_5$La$_3$M$_2$O$_{12}$ leads to the discovery of Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) lithium garnet by Murugan et al. in 2007 [74, 75]. Among the reported lithium garnets Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) exhibits high $\text{Li}^+$ conductivity of $5.11 \times 10^{-4}$ Scm$^{-1}$ at 25 °C and chemical stability with lithium metal [74, 75]. Comparison of $\text{Li}^+$ conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$ with other well known fast $\text{Li}^+$ conductors is shown in Figure 1.17. [74, 75].
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Figure 1.17. The comparison of Li$^+$ conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$ with other reported Li$^+$ conductors [74,75].

The experimental and theoretical studies on lithium stuffed garnets suggested that the Li$^+$ conductivity as well as the possible pathways for Li$^+$ migration mainly depend on the lithium content in the garnet-type materials and the distribution of lithium cations across various crystallographic sites.

1.5.1.1. Crystal structure of tetragonal and high Li$^+$ conductive cubic phase 

Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ)

LLZ exist in three different crystal phases, viz.; tetragonal phase (I4$_1$/acd), high Li$^+$ conductive cubic phase (Ia$\bar{3}$d) and low temperature cubic phase. The crystal
structure of tetragonal and high Li\textsuperscript{+} conductive cubic phase are shown as Figures 1.18 and 1.19, respectively [76, 77].

Tetragonal phase LLZ with a space group $I4_1/acd$ is an ordered structure where the Li atom occupy three different sites i.e., Li(1) atoms occupy tetrahedral 8$a$ sites, Li(2) and Li(3) atoms occupy octahedral 16$f$ and 32$g$ sites, respectively [76] as shown in Figure 1.18. The high Li\textsuperscript{+} conductive cubic phase LLZ with a space group $Ia\bar{3}d$ is a disordered structure where the lithium atoms occupy two sites i.e., Li(1) atom occupied tetrahedral 24$d$ site and Li(2) atom occupied distorted octahedral 48$g$/96$h$ site which is vacant in ideal garnet structure, respectively [77] as shown in Figure 1.19.

The low temperature cubic phase is related to either CO\textsubscript{2} absorption or hydration mechanism [78, 79]. Among these three phases, high Li\textsuperscript{+} conductive cubic phase is the most desired one due to its high Li\textsuperscript{+} conductivity of $10^{-4}$ Scm\textsuperscript{-1} [74, 75]. The high Li\textsuperscript{+} conductive cubic phase LLZ prepared by sintering at 1230 °C for 36 hours in an alumina crucible exhibits high Li\textsuperscript{+} conductivity in the order of $10^{-4}$ Scm\textsuperscript{-1}. On the other hand, tetragonal phase LLZ sintered at 980 °C for 5 hours exhibits low Li\textsuperscript{+} conductivity in the order of $10^{-6}$ Scm\textsuperscript{-1} [76]. The Li\textsuperscript{+} conductivity of the high conductive cubic phase $Ia\bar{3}d$ is two orders of magnitude higher than that of tetragonal and low temperature cubic phases [74-76, 78]. The phase and Li\textsuperscript{+} conductivity of LLZ depend upon the sintering temperature, duration of sintering and nature of crucible material used for sintering.
Figure 1.18. The crystal structure of tetragonal phase Li$_7$La$_3$Zr$_2$O$_{12}$ [76].

Figure 1.19. The crystal structure of high Li$^+$ conductive cubic phase Li$_7$La$_3$Zr$_2$O$_{12}$ [77].
1.5.2. Synthesis techniques for the preparation of lithium garnets

Lithium garnets can be obtained by different synthesis methods, such as solid-state reactions from mixtures of oxide, carbonate and hydroxide [74-76], sol–gel method based on hydrolysis and condensation of alkoxide and nitrates [80-82], Pechini [83], spray pyrolysis [84] and organic chemical vapour deposition techniques [85].

1.5.2.1. Solid-state reaction method

Solid-state synthesis is the most widely used method for the preparation of battery materials. The method involves intimate grinding of solid precursors and then annealed/sintered at various temperature and duration.

Grinding by hand in an agate mortar remains a useful method in modern synthesis. Ball mills, also known as centrifugal or planetary mills, are devices used to rapidly grind materials to colloidal fineness by developing high grinding energy via centrifugal and/or planetary action. The samples are placed in one of the bowls and several balls are added. Samples can be run wet or dry. In planetary action, centrifugal forces alternately add and subtract. The grinding balls roll halfway around the bowls and then are thrown across the bowls, impacting on the opposite walls at high speed. Grinding is further intensified by interaction of the balls and sample. Once the homogenous precursor powder was obtained, it was placed into a furnace and heated to a suitable temperature. Gases were generated and released followed by chemical interaction to form final product(s). Generally, this product may be ground finely again and then put into a furnace a second time (for a “2nd sinter”, or to allow crystals to form and grow in size). Finally powder materials are hydraulically pressed into a pellet shape to increase the
interactivity between the powder grains and form a higher quality and/or higher density final product. Therefore solid-state synthesis normally requires intermittent grinding, high temperature and long duration of heating for the formation of final product. Hence, formation of product depends on thermodynamic and kinetic (rate of reaction) factors.

The better ionic conductivity (~$10^{-6}$ Scm$^{-1}$) along with good chemical stability of Li$_5$La$_3$Ta$_2$O$_{12}$ acquainted the attraction of researchers towards lithium garnets. However a breakthrough in the field of lithium garnets electrolytes came after the successful introduction of cubic phase Li$_7$La$_3$Zr$_2$O$_{12}$ with high Li$^+$ conductivity of $10^{-4}$ Scm$^{-1}$ by Murugan et al. [74, 75] Li$_7$La$_3$Zr$_2$O$_{12}$ was synthesized using solid-state reaction technique followed by a high sintering temperature of 1230 °C for 36 hours [74, 75].

Following the initial results of Li$_7$La$_3$Zr$_2$O$_{12}$ there have been a significant interest in the synthesis, structure and electrical properties of Li$_7$La$_3$Zr$_2$O$_{12}$ using various dopants through solid state reaction method. Among them Ta, Nb, Al, Ga, Ge, Si, Y, In, Sb, Te substituted LLZ [86-96] and related system Li$_7$La$_3$M$_2$O$_{12}$ (M = Sn, Hf) [97, 98] prepared via solid-state reaction method has received a notable attention.

Though solid-state reaction method is a simple synthesis technique it has a lot disadvantages. The high sintering temperature and long exposure of heating results a possible evaporation of lithium from the product structure. Moreover it is also difficult to control the chemical stoichiometry of the lithium garnets through solid-state synthesis due to volatile nature of lithium at high temperature sintering. Another major issue of solid-state reaction method is inhomogeneity in the end product and formation of impure phases.
1.5.2.2. Sol gel method

The wet chemical (sol gel) process begins with liquid precursors, so provides molecular level mixing of the components [80, 81]. The result is that the precursors can react relatively at lower temperatures and in shorter times, without the need for intermittent grinding, and this synthesis route typically yields finer powders with a more uniform size distribution [99]. The powder obtained from the sol gel method generally expected to show better performance due to their higher homogeneity in composition, finer crystal size, higher purity and surface area.

Wide ranges of battery materials have been successfully prepared in recent times using sol-gel technique. Sol-gel technique follows the route line of hydrolysis and polymerization to form amorphous or crystalline material at low temperature processing in solution state.

The sol-gel process takes up two different routes for the preparation of various types of materials; (a) colloidal process and (b) alkoxide routes. Colloidal process involves the dispersion of particle of colloidal size in aqueous solvent medium to form a sol and then the sol is destabilized in a controlled manner, by allowing the particles to approach each other to overcome the stabilising barrier. This could be achieved by heating, freezing, adjusting the pH of the sol to obtain a gel. The solvent from the gel can be removed by maintaining it at a particular temperature and then sintered to give a crystalline/dense amorphous solid material.

Sol-gel process through alkoxide route involves the following steps; mixing, casting, gelation, aging drying, chemical stabilization and densification. Metal alkoxide is
the main precursor chemical, which requires the use of an organic solvent, normally an alcohol, in order to act as mutual solvent for the alkoxide and water for hydrolysis. The citrate gel process is a modified sol-gel technique in which the precursor ingredients include metal nitrates dissolved in citric acid and water.

Various garnet structured electrolyte materials have been reported using sol gel synthesis technique. Janani et al. reported the preparation of LLZ and high Li\(^{+}\) conductive 0.9wt.% of Al doped LLZ i.e., Li\(_{6.16}\)Al\(_{0.28}\)La\(_{3}\)Zr\(_{2}\)O\(_{12}\) (Al-LLZ) in cubic phase by modified sol-gel technique [99]. The flow chart used for the preparation of LLZ and high Li\(^{+}\) conductive 0.9 wt.% of Al doped LLZ i.e., Li\(_{6.16}\)Al\(_{0.28}\)La\(_{3}\)Zr\(_{2}\)O\(_{12}\) (Al-LLZ) in cubic phase using modified sol-gel technique by Janani et al. [99] is shown as Figure 1.20.
**Figure 1.20.** Flow chart for the preparation of LLZ and Al-LLZ by modified sol-gel technique.
1.5.2.3. Pechini method

The polymerized complex method (also referred to as the Pechini process) begins with liquid precursors. In this an alpha hydroxyl carboxylic acid is used as chelating agent that binds with the metal precursors to form a sol. In a typical pechini method, aqueous solutions of metal nitrate are mixed with chelating agent like citric acid. This chelate with the metal ions presents to form a sol. A polyhydroxy alcohol (ethylene glycol) is then added and the solution is heated to 100-150 °C. The sol polymerizes to form a gel like cross linked polymer. This polymer on decomposition yields the oxide product. The product formed is highly homogeneous with reduced particle size. Jin et al. reported the stabilization of cubic phase LLZ by the incorporation of Al through a polymerized complex method [83].

1.5.2.4. Thin film processing techniques

Pulsed laser deposition (PLD)

LLZ in bulk forms have been synthesized by solid-state reaction and sol–gel method [74-76, 80-82]. However, there are only few reports regarding the fabrication of LLZ thin films [100, 101]. Tan et al. fabricated LLZ thin film on SrTiO₃ (100) and sapphire (0001) substrates by pulsed laser deposition (PLD) with subsequent post-annealing [100]. Pulsed laser annealed LLZ films were found to have a Li⁺ conductivity of $7.36 \times 10^{-7}$ Scm⁻¹. Moreover, it was found to be electrochemically stable against lithium metal. Kim et al. reported the epitaxial growth of LLZ films on garnet Gd₃Gd₅O₁₂
substrate prepared by PLD exhibits the ionic conductivities of $2.5 \times 10^{-6}$ Scm$^{-1}$ and $1.0 \times 10^{-5}$ Scm$^{-1}$ at 298 K in the grains of the (001) and (111) films, respectively [101].

**Metal-organic chemical vapor deposition (MOCVD)**

Metal-organic chemical vapor deposition (MOCVD) is a versatile technique for fabricating of thin films at high deposition rates and moderate vacuum conditions. Moreover, the morphology and phase formation of the thin films can be controlled by this technique to design all-solid-state thin-film batteries.

Katsui et al. prepared cubic and tetragonal LLZ films on polycrystalline Al$_2$O$_3$ by metal organic chemical vapor deposition and investigated the effect of deposition temperature on the formation of phase, morphology and deposition rates [85]. The morphology of tetragonal and cubic LLZ film prepared by MOCVD varies depending upon the deposition temperature. [85]

**1.5.2.5. Nebulized spray pyrolysis (NSP) technique**

Organic components used as a complexing agent in the solution-based techniques leaves a large quantity of organic residue after synthesis. As a result post-annealing and grinding are necessary in case of solution-based techniques [80]. Nebulized spray pyrolysis (NSP) is a solution-based aerosol technique in which the use of organic solvents can be excluded due to the readily available nitrate based precursors. It is possible to synthesise nanocrystalline powders using NSP owing to the simultaneous thermolysis of precursors and annealing treatment. Moreover NSP offers less synthesis
time compared to other techniques. The dense films with controlled thickness can be deposited on appropriate substrate using this NSP technique.

Al-doped Li$_{7-3x}$La$_3$Zr$_2$Al$_x$O$_{12}$ ($x = 0–0.25$) (LLZ) with ultra-fine grained ceramics prepared using NSP exhibits a room temperature ionic conductivity of $1.2 \times 10^{-6}$ Scm$^{-1}$ and $4.4 \times 10^{-6}$ Scm$^{-1}$ for tetragonal ($x=0$) and cubic ($x=0.15$) LLZ, respectively, with a relative density of 47–56% [84]. Further increase in Al-content, leads to the formation of secondary phase.[84].

Other processing methods like hot press technique [86], spark plasma sintering [102], etc have also been reported in literature to enhance the density. Each method has its own advantages and disadvantages. However, the best synthesis method is expected to meet the following criteria,

- The synthetic method has to be of low cost
- Product formed should be phase pure and homogeneous.
- Materials with proper physical and chemical characteristics suitable for battery application

Thus exploration of novel synthetic method and processing technology plays a vital role for the development of high performance lithium batteries.

1.5.3. Li$^+$ dynamics in lithium garnets

The occupancy of lithium in lithium stuffed garnets prolongs to be controversial. The garnet framework is made of cubic structure consisting tetrahedral sites bridged by means of a single octahedron. The arrangement is made in such a way that each
tetrahedron faces (24d) share to four octahedral (48g/96h) and each octahedron face share to two tetrahedra that are facing opposite [61]. Cussen et al. predicted that the additional lithium in lithium stuffed garnets (i.e., $x > 3$ in $\text{Li}_x\text{A}_3\text{B}_2\text{O}_{12}$) occupy the octahedral site (48g/96h) that are empty in case of conventional garnets [61]. The octahedral site (48g/96h) can accommodate a total of six lithium cations per formula unit. Later, Callaghan et al. with neutron diffraction studies on $\text{Li}_{5+x}\text{Ba}_x\text{La}_{3-x}\text{Ta}_2\text{O}_{12}$ ($x = 0–1.6$) reported that the displacement in lithium stuffed garnets are due to static disorder and there must exist a short Li...Li distance of 2.44 Å between the majority occupied sites that promoting a high Li$^+$ mobility [65]. Moreover, a displacement of Li$^+$ at any of these site (octahedral (48g/96h) /tetrahedral (24d)) would reflect a shift towards different neighboring Li site, provided the neighboring Li site must be empty i.e., it is not possible for a Li$^+$ to occupy an octahedral site (48g/96h) that has a Li$^+$ on both face-sharing tetrahedral sites (24d) [65]. Among the investigated compounds it was found that the octahedral sites reach a maximum of 57%, with a tetrahedral vacancy of 14% for the composition $\text{Li}_{6.6}\text{Ba}_{1.6}\text{La}_{1.4}\text{Ta}_2\text{O}_{12}$ [65]. Reverse Monte Carlo (RMC) modeling and classical molecular dynamics studies on the local lithium structure and dynamics of garnet type $\text{Li}_3\text{La}_3\text{Ta}_2\text{O}_{12}$ predict that Li$^+$ hopping is not through the direct octahedral to octahedral movement but through a triangular bottle neck via 3D continuous network of tetrahedral (24d)/ octahedral (48g/96h) sites and thereby leads to fast ionic conduction [103].

Compositions with 7 Li$^+$ per formula unit (i.e., $\text{Li}_7\text{A}_3\text{B}_2\text{O}_{12}$, A=La, B=Zr) exhibits in two crystallographic phase viz., high Li$^+$ conductive cubic and tetragonal phase.
However the tetragonal phases are considered to be thermo-dynamically stable and exhibit an ordered structure of the lithium cations across tetrahedral (8a), octahedral (16f) and (32g) and a tetrahedral (16e) sites that are fully empty [76]. On the other hand Li$_7$La$_3$Zr$_2$O$_{12}$ with high Li$^+$ conductive cubic phase is a disordered structure with lithium cations on both tetrahedral (24d) and octahedral (48g/96h) sites that partially occupied [77]. Density-functional theory (DFT) studies on Li$_7$La$_3$Zr$_2$O$_{12}$ shows that the stability of tetragonal phase depends on two parameters (i) simultaneous ordering of the Li$^+$ on the Li sublattice and (ii) a volume-preserving tetragonal distortion that alleviate internal structural strain. Hence, doping supervalent cations leads to lithium vacancies thereby enables the possibility of stabilizing the cubic phase. Ab initio studies based on molecular dynamics within the cubic Li$_7$La$_3$Zr$_2$O$_{12}$ framework by Randy Jalem et al. predicts that the distribution of Li$^+$ is high at octahedral site and the transportation of Li$^+$ takes place through a three dimensional distorted octahedral-tetrahedral-distorted octahedral (48g/96h-24d-48g/96h) diffusion path [104]. The conduction pathway forecasted by M. Xu et al. based on DFT suggest that the occupancy of Li$^+$ in tetrahedral coordinated sites is reduced to ~50% with a simultaneous increase in the occupancy of octahedral sites to ~90% . The Li$^+$ migrate from one octahedral site (48g/96h) to the adjacent vacant octahedral site (48g/96h) through the common tetrahedral site (24d) [105]. Investigation on crystal structure of Li$_7$La$_3$Zr$_2$O$_{12}$ using internal friction (Figure 1.21) by X.P.Wang et al. revealed a prominent peak at 7 °C, comprised of two sub-peaks P1 and P2, suggesting a possible 3D diffusion pathway of Li$^+$ consisting of Li(24d)–Li(96h)–Li(48g)–Li(96h)–Li(24d) chain segments [106].
Figure 1.21. (a) The Crystal structure model of cubic Li$_7$La$_3$Zr$_2$O$_{12}$ projected in the (001) direction (space group $Ia\overline{3}d$). (b) Possible migration routes for Li$^+$ via 96$h$ $\leftrightarrow$ 48$g$; (c) possible migration routes of lithium ions via 24$d$ $\leftrightarrow$ 96$h$. The yellow balls are occupied lithium ions, and the open circles and squares are proposed lithium vacancies [106].
Neutron diffraction studies by Xie et al. suggest that $x = 7.5$ in $\text{Li}_x\text{A}_3\text{B}_2\text{O}_{12}$ is the theoretical upper limit that a garnet framework can tolerate. However, this upper limit requires half occupancy of the tetrahedral ($24d$) sites with a complete occupancy of the octahedral sites ($48g/96h$) [107]. But the occupancy of octahedral sites ($48g/96h$) reaches a maximum (~90%) for the composition $x=7$, i.e., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. Hence, further increase in the lithium concentration of garnet frame $\text{Li}_x\text{A}_3\text{B}_2\text{O}_{12}$ (i.e., for $x>7$) leads to an insufficient vacancies for the Li$^+$ migration [105]. Systematic investigation on the structure and Li$^+$ transport properties of garnet structure $\text{Li}_x\text{A}_3\text{B}_2\text{O}_{12}$ ($\text{A} = \text{Y}^{3+}, \text{La}^{3+}, \text{Sr}^{2+}, \text{Ba}^{2+}; \text{B} = \text{Te}^{6+}, \text{Ta}^{5+}, \text{Zr}^{4+}$ and $3 \leq x \leq 7.5$) revealed an increase in the hopping of Li$^+$ with the increase in Li$^+$ concentration and the Li$^+$ conductivity reaches a maximized value ($\sigma_{\text{total}} = 5.10 \times 10^{-4} \text{Scm}^{-1}$) for the nominal composition $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ then decreases with further increase of lithium concentration [108] as shown in Figure. 1.22 [106]. Hence an optimized lithium vacancy is required to achieve high Li$^+$ conduction in case of lithium stuffed garnets.
Figure 1.22. Change in the bulk (solid triangle) and total (solid square) Li\(^+\) conductivity measured at 33 °C and activation energy (solid circle) for the composition Li\(_{x}\)A\(_3\)B\(_2\)O\(_{12}\) (5 ≤ x ≤ 7.5) [108].

The Li\(^+\) conduction in garnet framework depends on the size of the three dimensional A\(_3\)B\(_2\)O\(_{12}\) frame, concentration of lithium and nature of distribution of lithium atoms among tetrahedral and octahedral sites.

1.6. SCOPE OF THIS THESIS

A solid electrolyte with high Li\(^+\) conductivity, low electronic conductivity, fast charge transfer at the electrode and electrolyte interface and wide electrochemical window is strongly required for the safe, high power and high capacity all-solid-state lithium secondary battery. Hence, significant research effort is directed towards
developing novel fast Li\textsuperscript{+} conductors for potential application as electrolytes in all-solid-state Li\textsuperscript{+} batteries. Recently, garnet-type metal oxides received considerable attention for potential application as electrolytes in all-solid-state lithium secondary batteries.

In addition to the high Li\textsuperscript{+} conductivity, dense microstructure related to grains and grain-boundaries is also a critical issue for the successful application of LLZ as solid electrolyte membrane in all-solid-state lithium and Li-air battery applications. The dense microstructure is expected to enhance the total (bulk + grain-boundary) Li\textsuperscript{+} conductivity by reducing the grain-boundary resistance and also expected to cordon the dendritic growth during lithium deposition.

The major focus of this thesis is to develop high Li\textsuperscript{+} conductive cubic phase lithium garnets with dense microstructure for all-solid-state Li\textsuperscript{+} battery application. Simple combustion synthesis technique was employed for the rapid synthesis of nanosized high Li\textsuperscript{+} conductive cubic phase Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZ) and Li\textsubscript{6.28}Al\textsubscript{0.24}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (Al-LLZ) relatively at lower sintering temperature. The phase stability of the tetragonal and high Li\textsuperscript{+} conductive cubic phase LLZ against distilled water, acidic medium and under humid atmosphere was probed. The effect of partial substitution of hexavalent W for a tetravalent Zr in LLZ on the structure and Li\textsuperscript{+} dynamics was also investigated.
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