Ac Conductivity Studies Of Polyethylene-Oxide-Garnet Type Li7La3Zr2O12 Hybrid Composite Solid Polymer Electrolyte For Li-Ion Battery

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AC CONDUCTIVITY STUDIES of POLYETHYLENE-OXIDE-GARNET TYPE Li$_7$La$_3$Zr$_2$O$_{12}$ HYBRID COMPOSITE SOLID POLYMER ELECTROLYTE for Li-ION BATTERY

by

PARISA BASHIRI

DISSERTATION

Submitted to the Graduate School

of Wayne State University,

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MAJOR: PHYSICS

Approved by

______________________________
Advisor                        Date
DEDICATION

“To my parents and sister”
ACKNOWLEDGMENTS

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CHAPTER 1
INTRODUCTION AND BACKGROUND: COMPOSITE SOLID POLYMER ELECTROLYTE FILMS FOR Li-ION BATTERY

1.1 Batteries as Energy Storage Systems

The accelerating demand on high energy density, high power density and high voltage per battery cell for portable electronics, hybrid/full electric vehicle (EV) and energy storage devices have brought up the concern to develop new types of energy storage devices such as batteries. Batteries are electrochemical energy storage devices which convert chemical energy to electrical energy and release it on demand. A battery has three main parts: cathode, anode and electrolyte. When a charged battery is connected to a load, the oxidation reaction starts at anode and the released electron in the process reaches the cathode through external circuit.

Batteries can be divided into two main categories:

- Primary Batteries, which are non-rechargeable, and the chemical reaction is irreversible such as: Zinc-Carbon batteries, alkaline-manganese batteries, Lithium metal batteries, etc.

- Secondary Batteries are rechargeable, and the battery can be regenerated by applying the current in the opposite direction. Some examples of secondary batteries are Lead-Acid batteries, Ni-Cd alkaline batteries, Ni-metal-hydride batteries, Lithium ion batteries, etc.

1.2 Li-ion Battery (LIB): Structure and Functional Mechanism

LIBs are the most popular rechargeable batteries because of their high energy and power density. The development of advanced materials for LIBs is the focus of research in material
science, chemistry, physics and chemical engineering. LIBs are now the major power sources for portable electronic devices and are expected to be utilized in EVs.

The fundamental mechanism of LIBs is based on series of reversible chemical reactions known as “redox” (reduction and oxidation) reactions which take place at the surface of the electrodes. The anode electrode is where the oxidation reaction occurs, while reduction happens at the surface of the cathode. Figure 1.1 is a schematic energy level diagram of electrons in electrodes and electrolyte. In a thermodynamically stable battery, the chemical potential energy of anode $\mu_A$ should fall below the lowest unoccupied molecular orbital (LUMO) of electrolyte and the chemical potential of cathode $\mu_C$ should be higher than highest occupied molecular orbital (HOMO) of electrolyte. This will prevent oxidation of electrolyte at anode side and reduction of electrolyte at the cathode side. The energy difference between LUMO and HOMO ($E_g$) is the electrolyte voltage stability window and the energy difference between electrodes chemical potential is cell’s open circuit voltage $V_{oc}$.

$$\mu_A - \mu_C = eV_{oc}$$

Figure 1.1 Schematic energy diagram of thermodynamically stable Li ion battery [2]
The reversible chemical reaction in Li-ion battery consists of two half reactions which happens at the electrodes. Figure 1.2 below represents the structure of a lithium ion battery with LiCoO₂ as cathode and graphite as anode.

Charging

(Cathode half reaction): \( \text{LiCoO}_2 \rightarrow \text{Li}^+ + e^- + \text{CoO}_2 \) \((0.6 \text{ V})\)

(Anode half reaction): \( \text{Li}^+ + e^- + 6\text{C} \rightarrow \text{LiC}_6 \) \((-3.0 \text{ V})\)

Full reaction: \( \text{LiCoO}_2 + 6\text{C} \rightarrow \text{CoO}_2 + \text{LiC}_6 \) \((V_{oc} = 3.6 \text{ V})\)

1.3 Components of a Li-ion Battery

1.3.1 Cathode

Electrode materials are compounds that can accommodate Li-ions and release them when needed in an irreversible process. Electrode materials can store Li-ions in their empty (1D, 2D or 3D) channels, vacant sites or even react with Li-ions in different ways such as conversion [2] or alloying [3]. The cathode materials are mainly in the form of layered structure such as lithium transition metal oxides LiMO₂ where \( M = \text{V}, \text{Cr}, \text{Mn}, \text{Ni}, \text{Co}, \ldots \). For example LiCoO₂
LCO was first introduced by Goodenough in 1980 [4] and, commercialized by SONY [4] in 1991. LCO is a great cathode material because of its high theoretical specific capacity (280 mAh/g), low self-discharge, high cycle life and high discharge voltage (3.6 V) [5]. However, charging to higher voltages may cause safety concerns due to oxygen evolution. Other forms of layered materials are Spinels (LiMn$_2$O$_4$), Olivines (LiFePO$_4$) and other transition metal oxides such as MnO$_2$, V$_2$O$_5$, etc. [6].

1.3.2 Anode

The anode electrode is where Li ions are stored in the fully charged battery. One of the widely used materials as anode in Li-ion battery is graphite which provides high gravimetric capacity as high as 1200 mAh/g in first cycle and 850 mAh/g in 40th cycle [7]. Another type of anode material which has high capacity are alloyed anode materials: xLi$^+$ + xe$^-$ + M $\rightarrow$ Li$_x$M where examples of M are Si, Ge, Sn, P and etc. In general, the alloyed materials show higher capacity compared to graphite [8]. The main challenge with alloyed materials is drastic change in volume due to lithiation/de-lithiation (3 times in Si) which can cause fracture in structure and capacity fading. Despite various available anode materials, Li metal is still the ideal anode for Li-ion batteries due to its high specific capacity 3860 mAh/g [9]. However, repeated Li metal deposition and stripping during the charge/discharge process on the anode surface lead to the formation of Li-dendrites, internal short circuiting and battery failure [10]. Different studies have been done in order to understand dendrite formation mechanism and ways to suppress it [11–13].

1.3.3 Electrolyte
The performance of a battery strongly depends on the properties of its electrolyte. The electrolyte in battery provides pathway for Li-ions to travel between anode and cathode. Because of the crucial role of electrolyte in a battery, its primary requirements need to be satisfied. First and the most important, the electrolyte material needs to be an ion-conductor. In other words, Li-ions can freely pass through electrolyte without any other unwanted side reactions. It is believed that the potential electrolyte should have minimum bulk conductivity of $10^{-3}$ S cm$^{-1}$ at room temperature. The electrolyte is directly in contact with electrodes, which are the centers of chemical reactions (redox), hence it is necessary for the electrolyte to be chemically stable against cathode and anode to prevent side reactions and decomposition of electrolyte which leads to capacity fade, heat generation, and gas production. Finally, the electrolyte materials need to be resistant to thermal, electrical and mechanical shocks.

The efforts in finding the perfect formulation to match the requirements ended up in LiPF$_6$ dissolved in ethylene carbonate (EC)/ dimethyl carbonate (DMC). However, LiPF$_6$ reacts with both anode and cathode materials which leads to the formation of the solid electrolyte interface (SEI) on the surface of the electrodes. The SEI layer inhibits further reactions, decomposition of electrolyte and capacity fade. The breakdown of the passivation layer specially at voltages above 4.3 V results in power and capacity loss [14]. Liquid electrolyte is not electrochemically and physically stable to be used against high voltage cathodes or Li metal anode. In order to safely expand the voltage window of battery cell, thermally and electrochemically stable electrolytes against redox reactions, Li dendrite growth, mechanical and electrical shocks are needed. Other than liquid electrolytes, polymer electrolytes, gel electrolytes, solid electrolytes, and composite solid polymer electrolytes have been studied. However, challenges still remain regarding ionic
conductivity, mechanical integrity, and thermal stability. Moving from low density liquid electrolytes \((\rho \sim 0.8 \sim 0.9 \text{ g/cm}^3)\) to high theoretical density solid electrolytes \((\rho \sim 2.5 \sim 6 \text{ g/cm}^3)\) results in losing gravimetric energy density \([15]\). Thus, thin film solid electrolytes are needed. However, thin film processes such as physical vapor deposition including pulsed laser deposition or magnetron sputtering are not suitable for large scale manufacturing \([16–19]\).

1.3.3.1 Polymer Electrolytes

In 1973, Fenton and co-workers showed that polymer-Li salt complexation shows ionic conductivity properties \([20]\). This study and many others have become the initial realization to use polymer salt complex as solid electrolytes. There are several advantages of using polymer electrolytes over liquid electrolytes and inorganic solid electrolytes such as: excellent flexibility and resistance against electrodes volume changes during charge/discharge, ease of processing, improved safety, etc. \([21]\). Yet there are some key requirements for polymer-Li salt complex to be used as electrolyte in Li ion batteries, which are listed as below:

- High ionic conductivity
- High \(\text{Li}^+\) transference number
- Mechanical integrity
- Wide electrochemical stability window
- Improved chemical and thermal stability

The ability of the polymers to dissolve alkali metal salts is the crucial factor to choose the right category of polymers for this specific application. Polymers with polar groups, such as \(--\text{O}--, --\text{S}--, --\text{N}--, --\text{P}--, =\text{O}, \text{C} = \text{O}, \text{C} = \text{N}, \) are able to dissolve salts \([22]\). Dissociation of inorganic salts in polymer matrix is easier in polymers with high dielectric constant and when
salts have low lattice energy such as LiClO$_4$, LiPF$_6$, LiBF$_6$, LiCF$_3$SO$_3$, etc. [23,24]. However, the ionic conductivity of polymer-salt complex is highly controlled by the crystalline structure of polymer. Figure 1.3 (a) shows the schematic of semi-crystalline structure in polymers. In solid polymer electrolytes, the Li ions are located at coordination sites near polar group of the polymer chains (e.g. — O — in polyethylene oxide, PEO). When the polymer chain undergoes segmental motions (T>T$_g$), free volume will be created. Li ions then migrate from one site to another site along the polymer chain (intra-chain) or hop between chains through free volume (inter-chain) Fig. 1.3 (b). Thus, the amorphous regions of the polymer which contains less

Figure 1.3 a) schematic of crystalline and amorphous regions in polymer b) Li ion conduction mechanism in polymer-salt matrix [20]

ordered structure and more flexible to move are responsible for ion conduction [20]. PEO is the most propitious solid solvent for Li salts due to its strong ether group which makes PEO a special solvate for Li metal salts. However, The ionic conductivity of PEO – based membranes vary from $10^{-8}$ to $10^{-6}$ S cm$^{-1}$ at room temperature; below its melting point (~ 60°C) due to the coexistence of crystalline and amorphous regions which prevent the use of PEO as practical polymer electrolyte [26,27].
Several approaches have been attempted in order to improve the ionic conductivity of polymer complex, for example; adding lower molecular weight polymers (plasticizers) such as dimethyl carbonate (DMC), ethylene carbonate (EC), poly-ethylene glycol (PEG) which improve the mobility of polymer chains and provide free volume for ion transfer inside the polymeric structure which results in enhanced ionic conductivity [28,29]. Another method which has been used, is the inclusion of small amount of oxide nanoparticles as fillers such as SiO$_2$, Al$_2$O$_3$, SnO$_2$, ZnO etc. [30–33]. Al$_2$O$_3$ nanoparticles as fillers have also been shown to suppress dendrite growth in composite polymer electrolyte films [34]. Although the addition of plasticizers and nanoparticles can improve ionic conductivity by enhancing the amorphous regions of polymer, the main drawback of these electrolytes is their low mechanical and thermal integrity. This has led to the development of a new category of inorganic solid electrolytes containing Li-ions.

1.3.3.2 Inorganic Solid Electrolytes

Inorganic solid electrolytes have the advantages of simple design, wide potential stability window and resistance to vibrations shocks, temperature and pressure variations. Different groups of inorganic solid electrolytes have been studied in detail such as LISICON (lithium super ionic conductor), perovskite, LIPON (lithium phosphorous oxynitride), garnet type, and many more. A brief review on some of these inorganic compounds is presented below.

Perovskite

The first perovskite structure solid electrolyte was introduced by Inaguma as Li$_{3x}$La$_{2/3}$-xTiO$_3$ (LLTO) with bulk ionic conductivity as high as 1x10$^{-3}$ S cm$^{-1}$ [35]. The main problem with LLTO is instability against potentials bellow 1.8 V vs. Li/Li$^+$ due to Ti$^{4+}$ reduction at low voltages [36]. This
issue has been resolved in different studies such as partial substitution of Ti$^{4+}$ by Zr$^{4+}$, Sn$^{4+}$, Zn$^{4+}$ [37–39]. However, the doped perovskites show lower ionic conductivity, e.g. in Li Sr$_{1.65}$Zr$_{1.3}$Ta$_{1.7}$O$_9$ (LSZT) the ionic conductivity is $1.3 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C [40].

**LISICON**

LISICON is an acronym for lithium super ionic conductor. Li$_{1.6}$Zn (GeO$_4$)$_4$ as the first LISICON structure solid electrolyte with high ionic conductivity of $1.25 \times 10^{-1} \text{ S cm}^{-1}$ at 300 °C [41]. More studies have reported conductivity of $2 \times 10^{-6} \text{ S cm}^{-1}$ at 50 °C and $1.3 \times 10^{-6} \text{ S cm}^{-1}$ at 33 °C [42,43]. Other examples of LISICON – type solid electrolytes such as Li$_{3.5}$Ge$_{0.5}$VO$_4$ and Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$ have been prepared and showed ionic conductivity of $4 \times 10^{-5} \text{ S cm}^{-1}$ and $\sim 10^{-5} \text{ S cm}^{-1}$ at 18 °C [44]. The ionic conductivity of LISICON-type solid electrolytes is very low to be practically used in solid state lithium ion batteries.

**LIPON**

LIPON type electrolytes are lithium phosphorous oxynitride compounds. The first LIPON was synthesized by radio frequency magneto sputtering using Li$_3$PO$_4$ as target in N$_2$ atmosphere which showed ionic conductivity of $2 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C [45,46]. LIPONs’ low ionic conductivity hinders practical use in bulk all solid – state batteries.

**Garnet**

Different classes of solid-state compounds and their examples have been briefly introduced above. However, they are far from being applicable in lithium ion batteries due to their low ionic conductivity at room temperature which is affected by high grain boundary resistance. Garnet structure compounds exhibit general formula of A$_3$B$_2$C$_3$O$_{12}$ where (A = Ca, Mg, Y, La or rare earth elements; B = Al, Fe, Ge, Ga, Mn, Ni and C = Si, Ge, Al) and are arranged in
faced centered cubic [47]. The first garnet like structure Li ion conductor was investigated in 2003 by Weppner et al. as Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta) and its bulk ionic conductivity was reported as ~ $10^{-6}$ S cm$^{-1}$ at 25 °C [48]. Among all the garnet like materials which are Li – rich and potential as solid electrolytes, Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) has exhibited the highest total ionic conductivity at room temperature ($2.2 \times 10^{-4}$ S cm$^{-1}$ at 25°C) [49].

**Li-rich garnet like structure: Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO)**

Weppner et al. synthesized Li-rich compound garnet structure LLZO in cubic structure using solid state reaction for the first time in 2007 [50]. LLZO has been characterized in two different structures as tetragonal (a = 13.077 Å and c = 12.715 Å) and cubic (a = 13.002 Å) with $I4_1/acd$ and $Ia3$D space group respectively [42–44]. In LLZO, isotropic edge sharing ZrO$_6$ octahedra and LaO$_8$ dodecahedra create framework in which the tetrahedral ($24d$) and distorted octahedral sites ($48g$ or $96h$) of Li ions and Li ion vacancies percolate as shown in Fig. 1.4 [54,55].

![Figure 1.4 Crystal structure of cubic LLZO](image-url)
Several parameters can have crucial effects on structure of LLZO such as sintering temperature and time, Li content, and contaminants. The LLZO in cubic structure usually forms at high temperatures and it seems that it is stabilized by small amount of Al due to using alumina crucible at temperatures > 1200 °C [56,57]. According to Sakamoto et al., the optimized amount of Al and excess Li in order to stabilize cubic phase is 0.24 mol and 6.24 mol respectively which are hot pressed under Ar flow at 1000 °C for 1 hour [51]. It has been reported that tetragonal structure exhibits lower ionic conductivity compared to cubic structure mainly due to different crystal structure, Li content, atomic displacement and Li diffusion pathway [53]. As the total ionic conductivity is the contribution of both bulk and grain boundary hence the density of the LLZO pellets plays a crucial role as tetragonal LLZO with 60% relative density (with respect to theoretical density) exhibits $\sigma_b = 1.63 \times 10^{-6} \text{ S cm}^{-1}$ and $\sigma_{gb} = 5.59 \times 10^{-7} \text{ S cm}^{-1}$ at 300 K, while $\sigma_{tot} = 2.23 \times 10^{-5} \text{ S cm}^{-1}$ and $3-4 \times 10^{-5} \text{ S cm}^{-1}$ for 98% and 100% relative density respectively which indicates that the total ionic conductivity in tetragonal structure is hindered by grain boundary resistance [52,58]. However, the total ionic conductivity of cubic structure stabilized by Al or Ta is reported to be $1 \times 10^{-4} \text{ S cm}^{-1}$ and $1 \times 10^{-3} \text{ S cm}^{-1}$ when the relative density is 93% and 98% respectively [59 – 67]. It is also reported that, the activation energy in tetragonal LLZO is 0.4 eV while it is 0.26 – 0.35 eV in cubic structure [52]. Although the shear modulus of LLZO is about 12 times higher than Li metal (~60 GPa), dark features due to formation of Li filament have been observed in LLZO pellet for high current density (0.1 mA cm$^{-2}$ at room temperature). It has been shown that the propagation of Li dendrite through LLZO pellet is through grain boundary (intergranular) rather than grains [68].
1.3.3.3 Composite Solid Polymer Electrolytes

Hybrid composite solid polymer electrolytes (CSPEs), which combine the merits of two or more types of solid electrolytes, have been proposed to create better electrolytes with both high ionic conductivity and good mechanical properties [69]. Recently, LLZO has been used as one of the fillers that can be used to enhance the Li⁺ ion conductivity, as the channel structure in LLZO contributes to enhancement of Li⁺ conduction, and the addition of LLZO particles to PEO provides mechanically and thermally stable framework. Further, the bonding of the PEO polymer matrix to the Li metal anode permits electrolyte and electrodes to create a large contact area, benefiting the solid/solid interfacial compatibility, and the stable chemical and electrochemical performance of LLZO with Li metal allows the electrolyte/Li interface to achieve a stable state [15].

Recently, Zheng et.al have studied various Li local structural environments within PEO-LiClO₄-cubic LLZO composite polymer electrolyte using high resolution ⁶Li NMR [70]. Fig 1.5 (a) shows a schematic of the possible Li local environments and Fig. 1.5 (b) shows high resolution ⁶Li NMR spectra of LiClO₄-cubic LLZO composite along with pure LLZO and LiClO₄ in PEO as references. Clearly the NMR spectrum of composite shows three distinct components corresponding to LLZO, LLZO/PEO interface and PEO matrix regions. Further, they were able to track Li ion pathways within the composite electrolyte by monitoring the replacement of ⁷Li by ⁶Li ions in LLZO fillers in PEO-LiClO₄ electrolyte, when used in a symmetric ⁶Li electrode/composite electrolyte/⁶Li electrode battery before and after battery cycling. Fig. 1.5 (c) and (d) clearly demonstrate that Li ions favor the pathway through the LLZO particles instead of the PEO-LLZO interface or PEO matrix. [70]. A previous study has shown that composite PEO-
LiClO₄ (molar ratio 15:1) films impregnated with tetragonal-LLZO particles (42.5 to 82.5 wt%) exhibited much enhanced conductivity compared to PEO films (~5×10⁻⁸ S cm⁻¹ at 35 °C) without LLZO [71]. This study also showed that the conductivity was maximum when PEO was loaded with ~52.5 wt% LLZO. However, another study showed that the conductivity of composite PEO-LiClO₄ (molar ratio 20:1) films prepared using cubic-LLZO particles (30 to 50 vol %) was lower than that of pure PEO-LiClO₄ films (~5×10⁻⁷ S cm⁻¹ at 20 °C) [15].

Figure 1.5 (a) Schematic of local Li environments in PEO-LiClO₄-cubic LLZO composite, (b) High resolution ^6 Li NMR spectra of LiClO₄-cubic LLZO composite, pure LLZO, and PEO-LiClO₄, (c) Comparison of ^6 Li NMR spectra of PEO-LiClO₄-cubic LLZO composite before and after battery cycling, (d) Quantitative analysis of the amount of ^6 Li in LLZO, interface, and the PEO matrix.[70]

1.4 Motivation and scope of the thesis

The aim of this thesis is to investigate CSPE films with high conductivity around room temperature while having robust mechanical properties. In the present thesis, we have studied free standing ~100-130 μm thick CSPEs films of comprised of sub-micron sized aluminum substituted cubic LLZO particles (purchased from MSE Supplies) dispersed in PEO (Mw=10⁶)-LiClO₄ matrix.
Chapter 2 describes synthesis (solution casting), characterization (x-ray diffraction, scanning electron microscopy, electrical impedance spectroscopy and linear sweep voltammetry) and analysis methods for investigating PEO-LiClO$_4$-LLZO films. The AC dielectric permittivity and ionic conductivity of the films without and with LLZO have been analyzed using an expression that generalizes the power-law dependence of complex dielectric permittivity and conductivity including electrode polarization [72]. The temperature dependence of ionic conductivity has been investigated, and the data were analyzed using Vogel- Tammann-Fulcher- (VTF) empirical equation to estimate the change in the activation energy PEO-LiClO$_4$ upon the addition of LLZO particles. In Chapter 3, the effect of LiClO$_4$ content on PEO crystallinity, ionic conductivity, segmental motion of PEO polymer chains are investigated. Chapter 4 compares the results of AC conductivity and dielectric permittivity studies of tetragonal versus cubic LLZO particles in PEO-LiClO$_4$ (EO/Li = 15:1)-LLZO (50 wt %)- composite films. Thermal stability and electrochemical stability measurements are also performed on CSPE films with and without LLZO. In Chapter 5, the results of our investigation on different amounts (30-75 wt %) of cubic LLZO particles in PEO-LiClO$_4$ (EO/Li = 15:1)-LLZO films are presented. Chapter 6 presents the results of our investigation on composite solid polymer electrolyte PEO-50 wt% cubic LLZO-LiClO$_4$ with varying [EO]:[Li] concentrations of 15:1, 12:1, and 10:1. In Chapter 7 we have briefly studied the effect of aging on ionic conductivity of PEO-50 wt% LLZO-LiClO$_4$ (15:1) CSPE. We have also shown the effect of heating on ionic conductivity of an aged CSPE. Chapter 8 provides a summary of the work performed and future directions.
CHAPTER 2
SYNTHESIS, CHARACTERIZATION, AND ANALYSIS METHODS

This chapter presents synthesis, characterization, and analysis methods for investigating composite solid polymer electrolyte (CSPE) films of PEO-LiClO₄-LLZO. We have used solution casting method to prepare free-standing CSPE films. The structural and morphological characterizations were done using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The thermal stability of the films was tested for by placing them in an oven held at 120 °C for 1 hour and subsequently cooled to room temperature. The mechanical integrity of the films was examined by inspection. We have used electrochemical impedance spectroscopy (EIS) measurements to evaluate AC conductivity and dielectric permittivity as a function of frequency. The data have been analyzed using an expression that generalizes the power-law dependence of complex dielectric permittivity and conductivity including electrode polarization. Temperature dependent DC ionic conductivity have been fitted using Vogel-Tammann-Fulcher (VTF) empirical equation to determine the activation energy. In addition, the principle of linear sweep voltammetry (LSV) is also described which was used to measure the voltage stability window of the composite polymer electrolytes against Li/Li⁺ electrode.

2.1 Solution Casting Method

CSPE films were prepared by solution casting method using polyethylene oxide (PEO) with $M_W = 10^6$ as the polymer, obtained from Alfa Aesar, complexed with LiClO₄ (99.99%, Sigma Aldrich) as a Li – salt at different concentrations. Cubic-LLZO stabilized with Al was purchased from MSE Supplies (Tucson, AZ) which consists of submicron-sized (0.4 - 0.6 µm) particles. For
PEO films without the inclusion of Li$_2$La$_3$Zr$_2$O$_{12}$ (LLZO) particles, proper molar ratio of PEO and LiClO$_4$ with [EO]:[Li] = 15:1, 12:1, 10:1 were dissolved in acetonitrile (ACN, 99.8% Sigma Aldrich) and stirred with a magnet for 24 hours at room temperature. The homogenous solution was then cast on a glass plate and let dry at ambient temperature for another 24 hours as shown in Fig. 2.1 (a). The dried film was then peeled off and placed in desiccator in order to remove all residual ACN and moisture. The membrane was punched into circular pieces with a diameter of ~2 cm for various measurements. To prepare the films with LLZO (30 - 75 wt%), appropriate amount of LLZO particles dispersed in acetonitrile was added to the PEO-LiClO$_4$ solution and then magnetically stirred and the films were cast as described above. The average thickness for membranes were ~100 - 130 µm depending on the concentration of Li-salt and LLZO content. Figure 2.1 shows the solution casting method on glass substrate (a), a circular cut sample of dried electrolyte film (b), and the images of PEO films with and without LLZO (c) and (d).
2.2 Structural and Morphological Characterization Methods

2.2.1 X-ray Diffraction (XRD)

When the X-rays are incident on the sample, diffraction peaks are detected when the scattered x-rays from the lattice planes satisfy Bragg’s law \(2d \sin \theta = n \lambda\) as shown in Fig. 2.2 (a), where, \(d\) is the spacing between two consecutive planes in the crystal, \(\theta\) is the diffraction angle, \(\lambda\) is X-ray wavelength and \(n\) is the order of diffraction. X-ray diffraction is a powerful tool to determine the crystal structure. XRD was used in this research in order to monitor the evolution of crystalline phase of PEO as Li-salt or LLZO content changed. XRD patterns were collected using a Rigaku MiniFlex Diffractometer (Fig 2.2 (b)). The instrument operates in \(\theta-2\theta\) scanning mode (Fig. 2.2 (c)), and the Cu-K\(\alpha\) x-rays (\(\lambda = 1.54 \text{ Å}\)) are produced with a source operating with 40 kV and 14 mA. The XRD patterns were recorded in the range of \(2\theta = 10^\circ\text{-}80^\circ\), with a \(2\theta\) step size \(0.01^\circ\), and a scan rate of \(0.25^\circ/\text{min}\).

![Figure 2.2](image.png)

Figure 2.2 a) Bragg's law b) bench top Rigaku 600 c) inside the X-ray instrument

2.2.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is one of the versatile techniques for studying surface morphology, analysis of chemical composition and size distribution of ultrafine particles. A
A schematic of the operation principle of an SEM is shown in Fig. 2.3. Basic elements of an SEM include an electron gun, accelerating potential of 1 to 30 kV, electron focusing magnetic lenses, an electron detector for collecting electrons, scanning coils, and an image display unit.

![Schematic of an SEM](image)

**Figure 2.3 schematic diagram of an SEM [73]**

When the electrons strike the specimen the incident electrons interact with the specimen producing elastically scattered electrons (backscattered electrons), inelastically scattered electrons leading to emission of secondary electrons, characteristic X-rays, Auger electrons. Figure 2.4 shows a schematic of the interaction of the incident electron beam with the sample and the interaction volume.

The secondary electrons are the electrons that are emitted from the outer atomic shells arising from the interaction of incident electrons with atoms of the specimen. These electrons have low energy (3-5 eV) and come from within a few nanometers of the sample the surface. The
secondary electrons generated deep inside the specimen are quickly reabsorbed by the specimen. The secondary electrons are sensitive to the surface morphology and hence are used in studying the sample morphology. The backscattered electrons have higher energy than the secondary electrons and are sensitive to the chemical composition, and their analysis can provide chemical composition and information about the deeper regions of the sample. In this work, we have taken images using SEM model JSM-6510-LV-LGS with electron beam energy 2 keV for low (<1000x) magnification and 5 keV for higher magnification (>10,000x). The samples were slightly coated with Au in order to prevent charge accumulation in insulating polymeric sample. Figure 2.5 shows the photograph of the SEM instrument used in this work.
2.3 Electrochemical Characterization

2.3.1 Electrochemical Impedance Spectroscopy (EIS)

The ionic conduction mechanism of solid polymer electrolytes is not well understood because of complex contribution of polymer chains dipole-dipole interaction and polymer segments and salt molecules interaction in overall conductance [74]. Electrochemical impedance spectroscopy is a well-suited method to elucidate the mechanism of ionic conductivity in complex systems such as polymer electrolytes from the point of view of polarization, alignment and relaxation of dipoles. In impedance spectroscopy, an alternating electric signal is applied to the cell and the response of the system is measured in a wide range of frequencies. In this research, the frequency dependent electrical impedance (EI) of the films was measured using a Gamry electrochemical impedance analyzer in the frequency range of 1 Hz - 300 kHz. The samples were sandwiched between two stainless steel blocking electrodes, and the sandwich structure was placed on a compact ceramic heater for temperature dependent EI measurements. The impedance spectrum can be presented as Bode plot (magnitude and phase of complex
impedance $Z^*$ versus frequency ($f$). Figure 2.6 shows an example for one of our polymer electrolyte film.

![Figure 2.6 Bode plot](image)

An alternate and a common way of presenting the same data is to plot $-Z''$ (Im $Z^*$) vs. $Z'$ (Re $Z^*$), called Nyquist plot (see Fig. 2.7). Generally, the Nyquist plot shows a depressed semicircle at high frequency region which arises from a non-ideal capacitive behavior with a low frequency tilted spike represents the electrical double layer due to the charge accumulation at the interface of electrode/electrolyte. One can assign an equivalent circuit (see Fig. 2.7) to simulate the experimental Nyquist plot. The impedance of resistors ($R$), capacitors ($\frac{1}{j\omega C}$) and constant phase element (CPE) ($\frac{1}{Q_0(I\omega)^n}$) where $Q_0 = 1/|Z|$ at $\omega = 1$ rad/s and $0<n<1$ to describe imperfect capacitor, are adjusted to generate the Nyquist curve corresponding to the measured one [75].
2.3.2 AC Conductivity and Dielectric Permittivity

The polymer electrolyte which is sandwiched between two blocking electrodes (stainless steel) can be characterized as a capacitor filled with a polymer dielectric where the conductance of Li-ions is strongly affected by both ionic and segmental dipolar relaxation times. The principle of ionic conduction in polymer electrolyte is complex and not yet fully understood [76]. However, conductivity and dielectric permittivity dispersion relation can reveal information about polymer segmental motion and ionic conduction mechanisms.

The measured complex impedance is related to complex permittivity by:

$$Z^* = \frac{t}{i\omega \varepsilon_o A \varepsilon'}$$

(2.1)

where, $A$ is the area of the blocking electrode, $t$ is the thickness of the film, $\omega$ is the angular frequency of the applied AC field, and $\varepsilon_o$ is the vacuum permittivity. The measured complex impedance $Z^* = Z' + iZ''$ was used to calculate the complex permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, using,
\[ \varepsilon' = \frac{t}{\omega \varepsilon_0} \frac{Z''}{Z'^2 + Z''^2} \]  
(2.2)

\[ \varepsilon'' = \frac{t}{\omega \varepsilon_0} \frac{Z'}{Z'^2 + Z''^2} \]  
(2.3)

The complex conductivity \( \sigma^* = \sigma' + i\sigma'' \) was calculated from the relation:

\[ \sigma^* = i\varepsilon_0 \omega \varepsilon^* = i\varepsilon_0 \omega (\varepsilon' - i\varepsilon'') \]  
(2.4)

Figures 2.8 and 2.9 show AC dielectric permittivity and conductivity dispersion curves calculated using the example complex impedance data shown in Figs. 2.6 and 2.7. Both the curves show a strong dependence on the frequency of the applied electric field. At low frequencies, the magnitude of \( \varepsilon' \) and \( \varepsilon'' \) are 4 to 6 orders of magnitude higher than the corresponding high frequency limits, because the ions are able to follow the alternating electric field at low frequency.

Figure 2.8 Real and imaginary part of AC dielectric permittivity dispersion
Figure 2.9 Real and imaginary components of AC conductivity

< $f_{on}$ (see Figs 2.9 and 2.10), where long-distance motion of ions becomes possible and as a result the charges accumulate at opposite electrode. This process leads to huge increase in dielectric permittivity and decrease in electric field inside the polymer which results in conductivity drop. The full development of electrode polarization takes place at $(f_j)$, from which the ionic relaxation time can be calculated.

The ratio of mobile to the stored can be described by $\tan \delta = \frac{\varepsilon''}{\varepsilon'}$, loss tangent, appears with a maximum peak at $f_\rho = f_{on}$, as shown in Fig. 2.11. This peak corresponds to the characteristic coupled ion-polymer segmental chain dipolar relaxation frequency.
2.3.3 Analysis of AC Conductivity and Dielectric Permittivity

The real and imaginary part of AC conductivity data, extracted from impedance measurement, have been shown to follow a power law dependence. However, the power law equation does not describe the electrode polarization region (low frequency). We have analyzed the complex AC conductivity and dielectric permittivity data using a generalized expression for AC conductivity in ion-conducting materials that takes into account the electrode polarization.

The modified conductivity is given by [77],

\[ \sigma^*(f) = \sigma_{dc} - \frac{\sigma_{dc} - \sigma_o}{1 + (if/f_j)^\alpha} + i\omega\varepsilon_o \frac{\Delta \varepsilon}{(1 + (if/f_R)^\beta)^\gamma} \]  \hspace{1cm} (2.5)

where, \( \sigma_{dc} \) is the frequency independent DC conductivity, \( \sigma_o \) is pre-factor used in describing the AC conductivity in the region not affected by electrode polarization, \( f_j \) is the frequency corresponding to the full development of electrode polarization (see Figs. 2.6 and 2.7), \( f_R \) is the characteristic frequency of the dipole relaxation, \( \varepsilon_o \) is the permittivity of free space, \( \Delta \varepsilon = \varepsilon_o - \varepsilon_\infty \)
(static and high frequency limit of dielectric constant), and \( f \) is the frequency of the applied AC electric field. \( \alpha, \beta \) and \( \gamma \) are <1. The complex dielectric permittivity is calculated using,

\[
\varepsilon^*(\omega) = \frac{\sigma^*(\omega)}{i\omega \varepsilon_0}
\]

(2.6)

2.4 Temperature Dependent Conductivity Measurements

The conductivity of films has been measured over a temperature range from room temperature to 60 °C in order to calculate the average activation energy of ions. The ionic conductivity mechanism in polymer electrolytes are quite complex and in general can be described in terms of Arrhenius behavior or VTF model. Arrhenius model describes the ion hopping when it is decoupled from segmental motion e.g. polymer electrolytes below their glass transition temperature (\( T_g \));

\[
\sigma = \sigma_0 e^{-\frac{E_a}{k_B T}}
\]

(2.7)

where \( \sigma_0 \) is pre-exponential factor which is related to the number of charge carriers and \( E_a \) is activation energy and \( k_B \) is Boltzmann constant. Above the glass transition temperature, the plots logarithmic conductivity versus reciprocal temperature do not show strictly linear relationship indicating a non-Arrhenius temperature dependence of conductivity. Many electrolytes exhibit such temperature dependence and its origin is attributed to the coupling of ionic motion and polymer segmental dynamics. The non-Arrhenius temperature dependence of conductivity in many polymer electrolytes is quantitatively described by VTF empirical equation. We have used the following form of the VTF equation for analyzing temperature dependence of conductivity [74],
\[ \sigma = \sigma_0 e^{-\frac{E_a}{k_B(T-T_o)}} \]  
(2.8)

where \( T_o \) is usually called equilibrium glass transition temperature. Above the glass transition temperature (\( T_g \)), polymeric materials become macroscopically rubbery rather than glassy and it is only the thermal energy in excess of \( T_g \) (i.e. \( k_B (T - T_g) \)) that provides actual mobility of the polymer chain segments [74].

2.5 Linear Sweep Voltammetry

Linear sweep voltammetry (LSV) is a simple method to determine the electrochemical potential stability window of the electrolyte vs. Li/Li\(^+\). In this method the electrolyte is sandwiched between Li metal as reference electrode and stainless-steel disk as working electrode. The voltage is then applied across the sandwich structure and increased linearly at a scan rate of 10 mV/s from -1 V to +8 V. Within negative working electrode voltage range the Li ions from Li metal electrode migrate and get deposited on to stainless-steel (cathodic current). This process will continue up to (ideally) 0 V. In positive potential sweep, however, the deposited Li ions will be stripped from working electrode and deposited on Li metal electrode until all the deposited Li ions are stripped and the current will remain zero. As the voltage further increases, the electrolyte will reach the breakdown voltage which means polymer electrolyte will no longer act as an electronic insulator. The voltage at which the current starts to increase steeply determines the electrochemical voltage stability window. A typical LSV curve is shown in Fig. 2.11.
In the following chapters, the results of XRD, SEM and AC conductivity and dielectric permittivity studies of various PEO-LiClO$_4$-LLZO composite films (without and with LLZO particles) will be presented.
CHAPTER 3
AC CONDUCTIVITY STUDIES OF POLYETHYLENEOXIDE (PEO)-LiClO4 FILMS WITH DIFFERENT [EO]:[Li] CONCENTRATION

This chapter presents the results of our study on the effect of Li concentration on ionic conductivity of PEO complexed with LiClO4 as polymer electrolyte. A comparative study of structural (XRD), morphological (SEM), and electrochemical (EIS) characterizations has been done on PEO-LiClO4 films with different [EO]:[Li] ratio of 15:1, 12:1 and 10:1.

3.1 Introduction

Polymer electrolytes as a sub-category of solid electrolytes for LIBs are introduced in order to address the safety issues caused by traditional organic liquid electrolytes, which are flammable and reactive. High molecular weight polymers with large number of monomers are capable to dissolving Li salts leading to increase in ionic conductivity. However, crystalline regions in polymer matrix slow down the polymer segmental motion and hinder the ionic conductivity. Thus, reducing the crystalline phase in a polymer matrix is key to enhancing the ionic conductivity. Desirable properties of solid electrolytes are high ionic conductivity at room temperature (> $10^{-4}$ S cm$^{-1}$), high mechanical strength and thermal stability (> 60 °C), wide electrochemical potential window (> 5 V), and electrochemical stability against Li metal [78]. Here, we have used PEO ($M_w$ 10$^6$ daltons) as a polymer matrix complexed with LiClO4 as Li salt with three different [EO]:[Li] ratio of 15:1, 12:1 and 10:1. We have used XRD and SEM to study the crystalline structure and surface morphology of PEO-LiClO4 films as a function of Li-
concentration. AC conductivity and dielectric permittivity data have also been analyzed to obtain corresponding polymer segmental motion and ionic relaxation times. The temperature dependence of electrical conductivity data is analyzed using Vogel-Tammann-Fulcher (VTF) model, and activation energy associated with ionic conductivity has been determined.

3.2 Materials and Methods

The calculated amounts of polyethylene oxide (M_w 10^6 daltons, Alfa Aesar) and LiClO_4 (99.99%, Sigma Aldrich) ([EO]:[Li] = 15:1, 12:1 and 10:1) were added to acetonitrile (ACN) and stirred for 24 hours at ambient temperature (22 °C). The homogenous viscous solution is then cast on glass substrate using tape casting method and allowing ACN to evaporate at ambient temperature for another 24 hours. The film was then peeled off from the substrate and placed in a desiccator for another 24 hours to remove any extra CAN, and moisture. The mechanical integrity of films is affected by the amount of Li concentration in the films. In what follows, we have labeled these films as PEO-LiClO_4 (15:1), PEO-LiClO_4 (12:1), and PEO-LiClO_4 (10:1). We find PEO-LiClO_4 (15:1), PEO-LiClO_4 (12:1) films to be mechanically more robust compared to PEO-LiClO_4 (10:1). The latter film was hard to handle and sticky in nature. In order to have a free standing PEO-LiClO_4 (10:1) film, a thicker film had to be cast. The thickness of films is listed in Table 1.

3.3 Structural Analysis: XRD

Figure 3.1 (a) shows the XRD patterns of PEO-LiClO_4 (15:1), PEO-LiClO_4 (12:1), and PEO-LiClO_4 (10:1) in the range of 2θ = 10° to 80°. Two strong characteristic crystalline peaks, (100) and (010) of PEO are observed at 2θ = 19° and 23.5°, riding on a broad XRD background indicating
a semi-crystalline structure of polymer complex. The enlarged region of $2\theta = 18^\circ$ to $25^\circ$ in Fig. 3.1 (b) provides further useful information about its structural evolution when the Li content is increased. The increased peak width as well as the broad XRD background demonstrate an enhanced amorphous phase of PEO.

![XRD patterns of PEO-LiClO$_4$ with different Li concentrations](image)

Figure 3.1 a) XRD pattern of PEO (1M) with different Li concentrations. b) Expanded region of XRD pattern from $2\theta = 18^\circ$ to $25^\circ$.

3.4 Surface Morphology: SEM

The SEM images of PEO films with different Li concentrations are shown in Fig. 3.2 under two different magnifications: 100x (Fig. 3.2 a, b, c), and 1000x (Fig. 3.2 d, e, f). The rough surface features observed in Fig.3.1 (a and d) corresponding to PEO-LiClO$_4$(15:1) are due to the crystalline domains of PEO, while these domains are reduced in size in images (Fig.3.1 (b-f)) corresponding to PEO-LiClO$_4$(12:1) and PEO-LiClO$_4$(10:1). We also observe several hundred microns long
features (Fig. 3.2 c) on the surface of PEO-LiClO$_4$(10:1) film, which may be responsible for its poor mechanical stability.

Figure 3.2 SEM images of PEO-LiClO$_4$ [EO]:[Li] with 15:1 (a, d), 12:1 (b,e), 10:1 (c, f) at two different magnifications (100x and 1000x). The scale bars are 100 µm in a, b, c and 10 µm in d,e,f.
3.5 Electrochemical Characterization (EIS)

The fully dried samples were cut into circular pieces (diameter ~ 2 cm) and the thickness was carefully measured (values are listed in Table 1). The film was placed between two stainless steel discs as blocking electrodes to carry out EIS measurements using 10 mV AC signal in the frequency range of 1 Hz to 300 kHz. The Nyquist plots obtained at 30 °C are shown in Fig. 3.3 for PEO-LiClO$_4$ (15:1), PEO-LiClO$_4$ (12:1), and PEO-LiClO$_4$ (10:1) films. The depressed semicircle in the high frequency region is the result of non-ideal capacitive behavior of the polymer film and the spiked tail is the result of electrode polarization in the low frequency region.

![Figure 3.3 Nyquist plot of PEO–LiClO$_4$ [EO]:[Li] = 15:1, 12:1 and 10:1 at 30°C. The inset represents the enlarged area of low resistance PEO–LiClO$_4$ [EO]:[Li] = 12:1 and 10:1.](image)

The low frequency intercept on x-axis corresponds to bulk resistance which can be used to calculate total bulk ionic conductivity (S cm$^{-1}$) using equation $\sigma = \frac{t}{AR}$, where, t is thickness in cm, A is the area of the sample (cm$^2$) and R is the bulk resistance (Ω) of the film.
3.6 AC Conductivity and Dielectric Permittivity

The complex AC dielectric permittivity ($\varepsilon'$, $\varepsilon''$) and conductivity ($\sigma'$, $\sigma''$) were calculated from the measured values of $Z'$ and $Z''$ versus frequency data using Eqs. 2.1-2.4 (see Ch. 2), and are plotted in Fig 3.4 (a) and (b) (symbols) for PEO-LiClO$_4$ (15:1), PEO-LiClO$_4$ (12:1), and PEO-LiClO$_4$ (10:1) films at 30 °C. Both conductivity and dielectric permittivity are strongly dependent on frequency. At low frequency where the ions are able to follow the alternating electric field, both $\varepsilon'$ and $\varepsilon''$ are 4 to 6 orders of magnitude greater than the corresponding high frequency limit. This is because of accumulation of opposite charges at the interface of blocking electrode (stainless steel). In the low frequency region, where the full development of electrode polarization occurs, the electric field in the sample decreases, hence $\sigma'$, and $\sigma''$ steeply decrease. The frequency ($f_j$) corresponding to the full development of electrode polarization which also appears as maximum in $\sigma''$ can be used to calculate ionic relaxation time ($\tau_j = 1/2\pi f_j$) (see Table 3.1) [77,79]. Figure 3.4 (c) shows the frequency dependent loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) with a peak at $f_p$ corresponding to polymer chain segmental relaxation time, $\tau_s = 1/2\pi f_p$. The presence of single peak in loss tan vs. frequency indicates that the ions are closely coupled with polymer chain which means the ionic motion is facilitated by segmental motion of polymer.

The experimental data of $\varepsilon'$, $\varepsilon''$ and $\sigma'$, $\sigma''$ versus frequency ($f$), were fitted using generalized Eqns. 2.5 and 2.6 (see Ch. 2), and the corresponding best fit parameters ($\sigma_{dc}$, $\tau_j$, $\tau_R$, $\alpha$, $\beta$, $\Delta\varepsilon$) are listed in Table 3.1. The fitted data are shown by solid lines in Figs. 3.4 (a, b, c). As the [EO]:[Li] ratio increases from 15:1 to 12:1, the ionic conductivity ($\sigma_{dc}$) enhances by two orders of magnitude. This is consistent with the observation of an order of magnitude decrease in the ionic ($\tau_j$) and segmental ($\tau_s$) relaxation times (see Table 3.1)
Figure 3.4 a) Complex dielectric permittivity, (b) Complex AC conductivity and c) Loss tangent of PEO-LiClO$_4$ [EO]:[Li] (15:1, 12:1, 10:1) films at 30 °C. The symbols represent the experimental data and the solid lines represent the fitted data.
Table 3.1: The ionic relaxation time $\tau_j$, polymer chain segmental relaxation time $\tau_s$, decoupling ratio $R_{ji}$, and other best fit parameters obtained by fitting the complex conductivity and dielectric permittivity at 30 °C Activation energy, $E_a$, and equilibrium glass transition temperature, $T_0$, are obtained by fitting temperature dependent conductivity, $\sigma_{dc}$ to VTF model (see section 3.5.2).

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>$\sigma_{dc}$ (S/cm)</th>
<th>$\tau_j$ (µs)</th>
<th>$\tau_s$ (µs)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\Delta\varepsilon$</th>
<th>$R_{ji}$</th>
<th>$E_a$ (eV)</th>
<th>$T_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-LiClO$_4$ (15:1)</td>
<td>102</td>
<td>$5.80 \times 10^{-7}$</td>
<td>1.22</td>
<td>38.8</td>
<td>0.35</td>
<td>0.68</td>
<td>0.65</td>
<td>15</td>
<td>0.032</td>
</tr>
<tr>
<td>PEO-LiClO$_4$ (12:1)</td>
<td>92</td>
<td>$6.00 \times 10^{-6}$</td>
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<td>1.38</td>
<td>0.32</td>
<td>0.82</td>
<td>0.6</td>
<td>18</td>
<td>0.009</td>
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<tr>
<td>PEO-LiClO$_4$ (10:1)</td>
<td>196</td>
<td>$9.50 \times 10^{-5}$</td>
<td>0.11</td>
<td>1.33</td>
<td>0.29</td>
<td>0.84</td>
<td>0.53</td>
<td>20</td>
<td>0.012</td>
</tr>
</tbody>
</table>

3.7 Temperature Dependent Dielectric Permittivity and AC Conductivity

In order to study the temperature dependence of ionic conductivity ($\sigma_{dc}$) of PEO-LiClO$_4$ (15:1, 12:1 and 10:1) films, we have measured frequency dependent $\varepsilon'$, $\varepsilon''$ and $\sigma'$, $\sigma''$ in the temperature range of 30 - 60 °C (at every 3 °C step allowing the sample to equilibrate for 10 minutes). Figure 3.5 (a, b) shows the plots for PEO-LiClO$_4$ (15:1) film, as an example. The inset in Fig. 3.5 (a) shows the temperature dependent loss tangent versus frequency curves. As temperature increases, clearly the peak in loss tangent shifts to higher frequency indicating a thermally activated conduction process. Correspondingly, the peak in $\sigma''$ spectra also shifts to higher frequency indicating a coupled ion-polymer segmental motion.
3.8 Activation Energy: Non-Arrhenius Behavior

We have analyzed the temperature dependence of conductivity to determine the activation energy. Figure 3.6 shows the plots of logarithmic conductivity ($\sigma_{dc}$) versus reciprocal temperature (i.e. $1000/T$) for PEO-LiClO$_4$ (15:1), PEO-LiClO$_4$ (12:1) and PEO-LiClO$_4$ (10:1) films. Symbols show the experimental data and the solid lines represent the fitted data using Eqn. 2.8. The plots do not show strictly linear relationship indicating a non-Arrhenius temperature dependence of conductivity. As described in Chapter 2, this behavior is better described by VTF model using Eqn. 2.8. The same logarithmic conductivity data plotted (graphs not shown) versus reduced temperature (i.e. $1000/(T-T_o)$) fall on a straight line and the linear fits are excellent with goodness of fit indicator $R^2 > 0.99$, where $T_o$ is the equilibrium glass transition temperature.
The fact that the temperature dependence of electrical conductivity is described by VTF equation implies a coupled motion of Li-ions with the polymer segmental motion is consistent with the decoupling ratio (see Table 3.1) found using ionic and polymer segmental relaxation times as discussed earlier (see Chapter 2). The values of activation energy ($E_a$) and the equilibrium glass transition temperature ($T_o$) change from 0.32 eV and 175 K for PEO-LiClO$_4$ (15:1) to 0.09 eV and 189 K for PEO-LiClO$_4$ (12:1), and 0.08 eV and 197 K for PEO-LiClO$_4$ (10:1). The values of $T_o$ are 70 K - 80 K below the glass transition temperature ($T_g \approx 245$ K) and are in agreement with the values observed for other PEO based electrolytes [80–83]. Nearly a factor of four reduction in the activation energy in PEO-LiClO$_4$ (12:1) and PEO-LiClO$_4$ (10:1), compared to PEO-LiClO$_4$ (15:1), enhances the hopping transport of ions through the films thus explaining the observed increase in conductivity.
3.9 Conclusions

Three polymer-salt complex systems of PEO-LiClO$_4$ with [EO]:[Li] ratios of 15:1, 12:1, and 10:1 have been studied with the aim of understanding the effect of Li salt concentration on ionic conductivity of the polymer electrolyte. The complex AC conductivity and dielectric permittivity were determined using the measured electrical impedance spectra. The experimental data were fitted using a generalized form of power law to determine ionic conductivity ($\sigma_{dc}$), ionic, and polymer segmental relaxation times. The fitted parameters show a close coupling between ionic and polymer segmental motions. Furthermore, the temperature dependent ionic conductivity data have been fitted to a VTF model to calculate the activation energy of Li ion motion in the polymer matrix. A two order of magnitude increase in the conductivity and a factor of four decrease in the activation energy was observed when the Li ion concentration was increased from [EO]:[Li] = 15:1 to 12:1. However, no significant change in conductivity was observed when the Li content was increased from [EO]:[Li] = 12:1 to 10:1.
CHAPTER 4

HYBRID COMPOSITE SOLID POLYMER ELECTROLYTE FILMS OF
PEO-Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO)-LiClO$_4$

In the previous chapter the results of our study on the effect of Li concentration on ionic conductivity of PEO-LiClO$_4$ complex were presented. Among three concentrations investigated, \([\text{EO}]:[\text{Li}] = 15:1, 12:1 \text{ and } 10:1\), PEO-LiClO$_4$ films with latter two concentrations showed two orders of magnitude higher conductivity compared to PEO-LiClO$_4$ (15:1) film. In this chapter, we have investigated the effect of the addition of micron-sized particles of Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO), a garnet-type solid electrolyte, on the ionic conductivity of PEO-LiClO$_4$ (15:1) complex. We have used both cubic and tetragonal phases of LLZO in investigating their effects on the ionic conductivity of PEO-LiClO$_4$-LLZO composite films. The structural, morphological, and electrochemical characterization of these hybrid composite polymer solid electrolyte (CPSE) films of PEO- tetragonal LLZO-LiClO$_4$ and PEO- cubic LLZO-LiClO$_4$ have been carried out using XRD, SEM and EIS measurements and analysis. The films have been tested for their thermal stability and hence indirectly their mechanical integrity by visual inspection. The voltage stability window has also been measured against Li/Li$^+$. 

4.1 Introduction

Among polymer based solid electrolytes (SEs), PEO is the widely studied semi-crystalline polymer electrolyte host matrix due to its ability to solvate a wide variety of salts through interaction of its ether oxygen with cations [84–87]. Despite PEO’s light weight and good viscoelastic properties, its low room-temperature ionic conductivity and poor mechanical
stability at higher temperatures limit its applications in commercial batteries [1]. Thus, hybrid CSPEs, which combine the merits of two or more types of SEs, are proposed to create better electrolytes with both high ionic conductivity and good mechanical properties. LLZO ceramic is one of the fillers used to enhance the Li⁺ ion conductivity as the channel structure in LLZO contributes to enhancement of Li⁺ conduction, and the addition of LLZO particles to PEO provides mechanically stable framework against the growth of dendrites [88]. Al₂O₃ nanoparticles as functional fillers have also been shown to suppress dendrite growth in composite polymer electrolyte films [7]. Further, the bonding of the PEO polymer matrix to the Li metal anode permits electrolyte and electrodes to create a large contact area, benefitting the solid/solid interfacial compatibility, and the stable chemical and electrochemical performance of LLZO with Li metal allows the electrolyte/Li interface to achieve a stable state [90–92]. The Li⁺ ion transport in CSPEs occurs by intra-chain and inter-chain hopping via interaction between Li⁺ ions and the functional groups of the polymer host [93,94]. It has been shown that the inclusion of LLZO in PEO increases the amorphous phase of PEO, thus leading to increased flexibility of polymer chains and increased segmental motion of host polymer [93]. LLZO crystallizes in both cubic and tetragonal crystal structures. Tetragonal LLZO has been shown to have a low lithium ion conductivity of ~10⁻⁶ S/cm [13], whereas the cubic polymorph has a desirable high conductivity of ~10⁻⁴ S/cm [96]. However, the cubic structure is unstable under ambient conditions and it is often stabilized by adding small amount of multivalent elements such as Al, Ta and Ga [95,97–99].

A previous study has shown that composite PEO-LiClO₄ ([EO]:[Li] = 15:1) films impregnated with tetragonal-LLZO particles (42.5 to 82.5 wt%) exhibited much enhanced
conductivity compared to PEO films (~ $5 \times 10^{-8}$ S cm$^{-1}$ at 35 °C) without LLZO [100]. This study also showed that the conductivity was maximum when PEO was loaded with ~ 52.5 wt% LLZO. However, another study showed that the conductivity of composite PEO-LiClO$_4$ (molar ratio 20:1) films prepared using cubic-LLZO particles (30 to 50 vol %) was lower than that of pure PEO-LiClO$_4$ films (~$5 \times 10^{-7}$ S cm$^{-1}$ at 20 °C) [101]. In this research, we have studied free standing CSPE films of PEO-LiClO$_4$ ([EO]:[Li] = 15:1) with 50 wt% micron-sized tetragonal LLZO particles as well as PEO-LiClO$_4$ [EO]:[Li] = 15:1 with 50 wt% Al-substituted sub-micron size cubic LLZO particles to compare with PEO-LiClO$_4$ [EO]:[Li] = 15:1 film without LLZO.

4.2 Materials and Methods

The calculated molar ratio of PEO ($M_w 10^6$, Alfa Aesar) and LiClO$_4$ (99.99%, Sigma Aldrich) ([EO]:[Li] = 15:1) were dissolved in 15 mL of acetonitrile (CAN) and stirred using magnetic stirring for 24 hours. The Al stabilized cubic LLZO with submicron particle size (0.1 – 0.5 µm) and tetragonal LLZO particles with an average size of 2-5 µm were purchased from MSE Supplies (Tucson, AZ). The calculated amount of 50 wt% with respect to total mass of PEO, LiClO$_4$ and LLZO were dissolved separately in 5 mL ACN for 24 hours. The polymer solution and the dispersed LLZO solution were then mixed together and let to mix thoroughly for 24 hours at room temperature in order to achieve a homogenous and uniform viscous solution. The uniform solution was then cast on glass substrate and let to let ACN evaporate at room temperature. The fully dried free-standing films are peeled off and placed in a desiccator to remove the remaining moisture. The completely dried films were punched into circular shapes of diameter of ~2 cm. The average film thickness was ~ 100 µm. In the following sections, the films are labelled as: PEO-Tetragonal LLZO-LiClO$_4$ (15:1), PEO-Cubic LLZO-LiClO$_4$ (15:1), and PEO-LiClO$_4$ (15:1).
4.3 Structural Analysis: XRD

The XRD patterns of tetragonal and cubic LLZO powders are shown in Fig 4.1. The diffraction peaks are labeled by their corresponding hkl Miller indices, characteristic of garnet type crystal structure [102]. The XRD peaks of LLZO particles are consistent with their cubic and tetragonal crystal structure. Several differences between the two XRD patterns are the peak splitting observed in tetragonal LLZO at $2\theta = 16.8, 19.5, 25.6,$ and $30.5$ degrees corresponding to (211), (220), (321), (420) diffraction peaks as well as the presence of additional peaks such as (411), (431), (440), etc. which are signatures of tetragonal LLZO structure.

Figure 4.2 (a) shows the XRD pattern of PEO-LiClO$_4$ (15:1), PEO-tetragonal LLZO-LiClO$_4$, and PEO-Cubic LLZO-LiClO$_4$ CSPE films in the range of $2\theta = 10^\circ - 80^\circ$. Clearly, the XRD patterns of CSPE films are dominated by LLZO (either tetragonal or cubic) diffraction peaks and with much reduced intensity of PEO peaks (marked with *). Figure 4.2 (b) shows an enlarged region of Fig 4.2 (a) to highlight the differences. The peak observed at $19.5^\circ$ in PEO-tetragonal LLZO- LiClO$_4$ film is due to (220) peak of tetragonal LLZO. We notice that cubic LLZO has several of its characteristic peaks (although very weak) overlapping with the diffraction peaks of PEO thus broadening the diffraction peaks in PEO-cubic LLZO-LiClO$_4$ film. A weak peak around
Figure 4.1 The X-ray diffraction pattern of cubic and tetragonal LLZO

Figure 4.2 a) The XRD diffraction pattern pure PEO-LiClO$_4$ and CSPE films comprised of 50 wt % tetragonal and cubic LLZO, b) Expanded region of corresponding XRD patterns from $2\theta = 18^\circ$ to $25^\circ$. The asterisks correspond to PEO peaks.
2θ = 21.5° due to cubic LLZO is somewhat enhanced in intensity in PEO-LLZO-LiClO₄ indicating some orientational interaction between the LLZO crystallites and the PEO matrix. Similar effect has been observed by adding oxide nanoparticles (ZnO, Al₂O₃ and SnO₂ and SiO₂) into polymer electrolytes [79].

4.4 Surface Morphology: SEM

Figures 4.3 (a) and (b) show the SEM image of tetragonal and cubic LLZO powders. The former consists of aggregates of micron sized (~ 3-6 µm) particles, whereas the latter consists of much smaller sub-micron sized (0.1-0.5 µm) particles coalesced to form much porous grains.

![SEM images of tetragonal LLZO powder](image1)
![SEM images of cubic LLZO powder](image2)

Figure 4.3 SEM images of a) Tetragonal LLZO powder (scale bar 10 µm) b) Cubic LLZO powder (scale bar 1 µm)

Figures. 4.4 (a) and (b) show the surface morphology of PEO-tetragonal LLZO-LiClO₄ (15:1) and PEO-cubic LLZO-LiClO₄ (15:1) films at low (200 x) magnification while Figs 4.4 (c) and (d) show the same at 20000 x. The latter images show uniform distribution of LLZO particles in CSPE films with pore free surface structure (obtained using sub-micron size particles of cubic LLZO), compared to PEO-tetragonal LLZO-LiClO₄ film (micron sized particles).
Figure 4.4 Low magnification (200 x) SEM images of: a) PEO-tetragonal LLZO-LiClO4 (15:1) and b) PEO-cubic LLZO-LiClO4 (15:1) films (scale bar 100 µm); Corresponding higher magnification (20,000 x) images are shown in c) and d) (scale bar 1 µm).

4.5 Electrochemical Characterization: EIS

The ionic conductivity of the films was measured by conducting EIS measurement by placing the films between two stainless steel disks as blocking electrodes and the frequency dependent impedance were measured. The Nyquist plots for PEO-LiClO4, PEO-cubic LLZO-LiClO4, and PEO-tetragonal LLZO-LiClO4 at 30 °C are plotted in Fig. 4.5. The addition of 50 wt% LLZO particles (tetragonal or cubic) to PEO-LiClO4 (15:1) has significantly reduced the bulk resistance of the CSPE films. The results of detailed analysis of frequency dependent complex AC conductivity and dielectric permittivity data of these films are presented in Section 4.5.1.
Figure 4.5 The Nyquist plots for pure PEO-LiClO$_4$, PEO-cubic LLZO-LiClO$_4$ and PEO-tetragonal LLZO-LiClO$_4$ at 30 °C

4.5.1 AC Conductivity and Dielectric Permittivity

The complex dielectric permittivity ($\varepsilon'$, $\varepsilon''$) and conductivity ($\sigma'$, $\sigma''$) of PEO-LiClO$_4$, PEO-cubic LLZO-LiClO$_4$ and PEO-tetragonal LLZO-LiClO$_4$ are calculated using Eqs. 2.1-2.4 (see Ch 2) from the measured complex impedance at 30 °C. The experimental data (symbols) are fitted (solid line) using Eqns. 2.5 and 2.6 (see Ch 2) and are shown in Fig 4.6 (a,b). The dielectric loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) (symbols) and the fitted curves are also shown in Fig 4.6 (c). At low frequencies, the ions are able to follow the alternating electric field and can transverse long distance. The mobile ions accumulate at the electrode-electrolyte interface (electrode polarization) which results in large magnitude of dielectric permittivity and decrease in conductivity. As the frequency increases, the ionic conductivity increases and shows the ionic relaxation peak in $\sigma''$ ($\tau_i = 1/2\pi f_i$) which is attributed to ion mobility.
Figure 4.6 a) Complex dielectric permittivity, (b) Complex AC conductivity of pure PEO-LiClO4, PEO-cubic LLZO-LiClO4 and PEO-tetragonal LLZO-LiClO4 at 30 °C. The symbols represent the experimental data and the solid lines are the fit. c) Loss tangent pure PEO-LiClO4, PEO-cubic LLZO-LiClO4 and PEO-tetragonal LLZO-LiClO4 at 30 °C.

At low frequency region where the electrode polarization is developed, tanδ is less than unity while increasing non-linearly with frequency and exhibits dielectric relaxation peak at high
frequency \( \tau_s = \frac{1}{2\pi f_p} \) which explains the polymer chain dynamic. The corresponding relaxation times and other parameters are summarized in Table 4.1. The data shows that the addition of LLZO particles to pure PEO-LiClO\(_4\) reduces \( \tau_j \) and \( \tau_s \). This reduction is more dominant in PEO-cubic LLZO-LiClO\(_4\) compared to PEO-tetragonal LLZO-LiClO\(_4\) which can be seen in shifting of the peak positions of tan\( \delta \) and \( \sigma'' \) peaks toward higher frequencies (Fig. 4.6). This is because the smaller particle size cubic LLZO introduces more amorphous phase into polymer matrix which facilitates the ion mobility and polymer chain motion. The decoupling ratio \( (R_{sj} = \tau_s/\tau_j) \) is the ratio of polymer segmental relaxation time to the ionic relaxation time. The decoupling ratio \( (R_{sj}<1) \) describes that the ions motion is facilitated by polymer chain motion and the ionic conductivity is assisted by segmental motion [103]. The \( R_{sj} \) is calculated for each case and summarized in Table 4.1.

Table 4.1 The ionic relaxation time \( \tau_j \), polymer chain segmental relaxation time \( \tau_s \), decoupling ratio \( R_{sj} \), and other best fit parameters obtained by fitting the complex conductivity and dielectric permittivity at 30 °C Activation energy, \( E_a \) and equilibrium glass transition temperature, \( T_0 \), are obtained by fitting temperature dependent conductivity, \( \sigma_{dc} \), to VTF model.

<table>
<thead>
<tr>
<th>Thickness ((\mu m))</th>
<th>( \sigma_{dc} (S cm^{-1}) )</th>
<th>( \tau_j (ms) )</th>
<th>( \tau_s (ms) )</th>
<th>( \gamma )</th>
<th>( \Delta \varepsilon )</th>
<th>( T_0 (K) )</th>
<th>( E_a (eV) )</th>
<th>( R_{sj} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-LiClO(_4) (15:1)</td>
<td>102</td>
<td>5.8 x 10(^{-7})</td>
<td>1.10</td>
<td>38.8</td>
<td>0.35</td>
<td>0.68</td>
<td>0.65</td>
<td>1.00</td>
</tr>
<tr>
<td>PEO-LLZO-LiClO(_4) (15:1) (Tetragonal)</td>
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<td>4.3 x 10(^{-6})</td>
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<td>11.0</td>
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<td>0.74</td>
<td>0.68</td>
<td>0.57</td>
</tr>
<tr>
<td>PEO-LLZO-LiClO(_4) (15:1) (Cubic)</td>
<td>113</td>
<td>1.4 x 10(^{-4})</td>
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<td>0.28</td>
<td>0.24</td>
<td>0.80</td>
<td>0.70</td>
<td>1.00</td>
</tr>
</tbody>
</table>

4.5.2 Activation Energy: Non-Arrhenius Behavior

We have analyzed the temperature dependence of conductivity in order to determine the activation energy. In Fig 4.7 the logarithmic conductivity \( (\sigma_{dc}) \) vs reciprocal temperature (i.e. 1000/T) are shown (symbols). The plots are not linear indicating a non-Arrhenius behavior.
The non-Arrhenius temperature dependent conductivity is fitted (solid line) using Vogel-Tammann-Fulcher (VTF) model using Eq. 2.8 and the activation energy ($E_a$) and the equilibrium glass transition temperature ($T_0$) are determined as fitting parameters.

The ionic conductivity data is described by the VTF model which shows that the ion motion is coupled with polymer motion which is also consistent with decoupling ratio ($R_{sj}$). The Li ion activation energy and equilibrium glass transition temperature in pure PEO-LiClO$_4$ has changed from 0.32 eV and 175 K to 0.16 and 179 K in PEO-tetragonal LLZO-LiClO$_4$ and to 0.07 eV and 185 K in PEO-cubic LLZO-LiClO$_4$ due to the amorphous phase in CSPE, which is consistent with the fact that the ionic conductivity depends on activation energy.
4.6 Thermal Stability Measurements

We have indirectly tested the mechanical integrity of CSPE films by observing their thermal stability after subjecting them to 120 °C for 1 hour in an oven, and then allowed to cool to room temperature after removal from the oven. The images taken before and after heating are shown in Fig. 4.8. We observe that PEO-LiClO₄ (15:1) film has shrunk at the edges and also stuck to the glass substrate making it difficult to peel. On the other hand, CSPE films with LLZO particles remain mechanically robust after the heat treatment.

![Figure 4.8 The images of a) PEO-LiClO₄ (15:1), b) PEO-tetragonal LLZO-LiClO₄ (15:1), and c) PEO-cubic LLZO-LiClO₄ (15:1) films before and after heating at 120 °C for 1 hour.](image)

4.7 Electrochemical Stability - Linear Sweep Voltammetry

Electrochemical stability window is one of the key parameters of solid polymer electrolytes, and a good electrolyte must have a stability window of over 4.5 V (vs. Li metal). Linear Sweep Voltammetry (LSV) measurements were performed to determine the electrochemical stability window of PEO-LiClO₄ (15:1) and PEO-cubic LLZO-LiClO₄. The films were placed between Li metal as reference electrode, and a stainless-steel plate (SS) as working electrode.
The DC voltage is applied to the working electrode from -1 V to +8 V with scan rate of 10 mV/sec and the current is measured (see Fig. 4.10). From -1 V to 0 V, Li\(^+\) ions leave the Li metal and get deposited on SS electrode. As the voltage increases toward positive voltage, the deposition process slows down and stops (zero current) and the Li ions are stripped off of the SS and deposited back on the Li metal. The electrolyte film in this system acts as dielectric and, increasing the voltage further results in dielectric break down and the current starts to increase steeply. We have measured the breakdown voltage for these films as shown in Fig. 4.10. PEO- Cubic LLZO-LiClO\(_4\) is stable up to ~ 5.2 V against Li metal. In addition, composite electrolyte exhibits lower oxidation current compared to PEO-LiClO\(_4\). This means that adding LLZO to PEO-LiClO\(_4\) polymer electrolyte results in a better interfacial stability.

Figure 4.9 The linear sweep voltammetry curve and breakdown voltage of PEO-LiClO\(_4\) (15:1) and PEO-cubic LLZO-LiClO\(_4\) (15:1) films
4.8 Conclusions

We have investigated and compared the effect of addition of 50 wt% tetragonal LLZO and cubic LLZO into PEO-LiClO₄ (15:1). The addition of 50 wt% LLZO particles as fillers in PEO-LiClO₄ film affects the complex polymer structure, surface morphology, ionic conductivity and other properties. Addition of sub-micron sized cubic LLZO particles improves the ionic conductivity by two orders of magnitude from $5.8 \times 10^{-7}$ S cm$^{-1}$ to $1.4 \times 10^{-4}$ S cm$^{-1}$ at 30 °C, whereas the ionic conductivity has been improved by an order of magnitude by adding tetragonal LLZO. The SEM images show smoother surface in CSPE films compared to polymer complex. The addition of LLZO fillers into polymer electrolytes make the films mechanically strong with ability to withstand heating up to 120 °C. Complex dielectric permittivity and AC conductivity studies confirm that the ionic conductivity is facilitated by polymer segmental motion. The Li ion activation energy decreases from 0.32 eV in PEO-LiClO₄ to 0.16 eV in PEO-tetragonal LLZO-LiClO₄, and to 0.07 eV in PEO-cubic LLZO-LiClO₄ which improves the ion motion and results in higher ionic conductivity in PEO-cubic-LLZO-LiClO₄. Composite solid polymer electrolytes composed of 50 wt% Al-LLZO is stable against Li/Li$^+$ up to 5 V.
CHAPTER 5

EFFECT OF LLZO CONCENTRATION ON THE IONIC CONDUCTIVITY OF PEO-CUBIC LLZO-LiClO$_4$ COMPOSITE SOLID POLYMER ELECTROLYTES

In the previous chapter, we compared the effect on ion conductivity of adding 50 wt% micron sized tetragonal LLZO particles (3-6 µm) with sub-micron sized cubic LLZO particles (0.1 – 0.5 µm) as fillers in PEO-LiClO$_4$ (15:1) polymer matrix. In this chapter, we have studied the effect of concentration of cubic LLZO particles on the ionic conductivity of PEO-Cubic LLZO-LiClO$_4$ [EO]:[Li] = 15:1 by including 30 and 75 wt% of cubic LLZO particles. The structural, morphological and electrochemical characterization of these hybrid composite solid polymer electrolyte (CSPE) films have been done using XRD, SEM and EIS measurements.

5.1 Introduction

The ionic conductivity of CSPE films is complex as it is highly affected by the ratio of ceramic fillers to polymer [104–106]. It was shown that 52.5 wt% tetragonal LLZO is the optimum LLZO content to enhance the ionic conductivity of PEO-LiClO$_4$ [EO]:[Li] = 15:1 [4]. It is well known that the amorphous phase in polymer matrix is responsible for ionic conduction, but based on some finite element simulations it has been shown that the ionic conduction happens at ceramic-polymer interface [34,108,109]. The NMR study of Li-ion pathway in PEO-LLZO-LiClO$_4$ composite polymer has revealed that the Li ions favor the pathway through LLZO particles instead of PEO or PEO-LLZO interface [8]. The addition of fast ion conductor garnet type LLZO as filler in PEO-LiClO$_4$ polymer complex provides channel structure pathway for Li ions that enhances the conductivity at room temperature and improves the mechanical integrity of polymer matrix against Li dendrite
growth [88]. In chapter 4, we have shown that hybrid CSPE films consisting of 50 wt% cubic LLZO micron-sized particles in PEO-LiClO$_4$ matrix exhibit both enhanced ionic conductivity ($1.4 \times 10^{-4}$ S cm$^{-1}$) and mechanical integrity compared to that of PEO-LiClO$_4$ ($5.8 \times 10^{-4}$ S cm$^{-1}$). In this chapter, we have varied the concentration of cubic LLZO particles in PEO-LiClO$_4$ matrix to include 30 wt% and 75 wt% and studied the structural, morphological and electrochemical characteristics.

5.2 Materials and Methods

The calculated molar ratio of PEO ($M_w \ 10^6$ g/mol, Alfa Aesar) and LiClO$_4$ (99.99%, Sigma Aldrich) ([EO]:[Li] = 15:1) were dissolved in 15 mL acetonitrile (CAN) and stirred using magnetic stirring for 24 hours. The Al stabilized cubic LLZO with submicron size particles (0.1 – 0.5 µm) was purchased from MSE Supplies (Tucson, AZ). The calculated amounts of 30, 50 and 75 wt% of LLZO with respect to total mass of PEO, LiClO$_4$ and LLZO were dissolved separately in 5 mL ACN for 24 hours. The polymer solution and the dispersed LLZO solutions were then mixed together and let to mix thoroughly for 24 hours at room temperature in order to achieve a homogenous and uniform viscous solution. The uniform solution is cast on glass substrate and let to dry at room temperature to remove ACN. The fully dried free-standing film were peeled off and placed in a desiccator to remove remaining moisture and ACN. The completely dried films were punched into circular pieces of diameter of ~2 cm. The thicknesses of the films are listed in Table 5.1. In the following, the films are labeled as: PEO-30 wt% LLZO-LiClO$_4$, PEO-50 wt% LLZO-LiClO$_4$ and PEO-75 wt% LLZO-LiClO$_4$.

5.3 Structural Analysis: XRD

Figure 5.1 (a) shows the X-ray diffraction patterns of PEO-30 wt% LLZO-LiClO$_4$, PEO-50 wt% LLZO-LiClO$_4$ and PEO-75 wt% LLZO-LiClO$_4$ films in the range of $2\theta = 10^\circ$ to $80^\circ$. The diffraction
peaks of crystalline cubic LLZO are dominant in all composite patterns. The two characteristic crystalline peaks of PEO are observed at $2\theta = 19.2^\circ$ and $23.4^\circ$ (indicated by asterisks), riding on a broad XRD background indicating a semi-crystalline structure of polymer complex. Figure 5.1 (b), shows the enlarged region of $2\theta = 18^\circ$ to $25^\circ$.

![XRD patterns](image)

Figure 5.1 a) XRD pattern of PEO-30 wt% LLZO-LiClO$_4$, PEO-50 wt% LLZO-LiClO$_4$ and PEO-75 wt% LLZO-LiClO$_4$ b) the expanded region of XRD pattern from $2\theta = 18^\circ$ to $25^\circ$. The asterisks correspond to PEO peaks.

It is interesting to note that the PEO diffraction peaks are broader in PEO-50 wt% LLZO-LiClO$_4$ compared to PEO-30 wt% LLZO-LiClO$_4$ and PEO-75 wt% LLZO-LiClO$_4$ samples, indicating higher fraction of amorphous PEO.
5.4 Surface Morphology: SEM

The low magnification (200x) SEM images of PEO-30 wt% LLZO-LiClO₄, PEO-50 wt% LLZO-LiClO₄ and PEO-75 wt% LLZO-LiClO₄ surface are shown in Fig 5.2 (a, b and c) and the high magnification (20,000 x) images of corresponding films are shown in Fig 5.2 (d, e and f).

Figure 5.2 The SEM images of PEO-30 wt% LLZO-LiClO₄ (a,d), PEO-50 wt% LLZO-LiClO₄ (b,e) and PEO-75 wt% LLZO-LiClO₄ (c,f). The scale bars are 100 mm in a, b, c, and 10 mm in d,e,f.
It can be clearly seen that the film surface gets rougher as the concentration of LLZO is increased from 30 wt% to 75 wt% perhaps due to large agglomeration of particles. The high magnification SEM images confirms a uniform distribution of LLZO particles/agglomeration in CSPE films.

5.5 Electrochemical Characterization (EIS)

Figure 5.3 shows the Nyquist plots of PEO-30 wt% LLZO-LiClO$_4$, PEO-50 wt% LLZO-LiClO$_4$ and PEO-75 wt% LLZO-LiClO$_4$ films at 30 °C. The composite polymer films with 30 wt% and 50 wt% cubic LLZO particles show lower and almost similar values of $R_{\text{bulk comp}}$ compared to 75 wt% sample. Reduced amount of PEO-LiClO$_4$ in the latter sample may have led to reduced connectivity between the LLZO particles for Li-ion conduction causing higher bulk resistance.

![Nyquist plots](image)

**Figure 5.3** The Nyquist plots of PEO-30 wt% LLZO-LiClO$_4$, PEO-50 wt% LLZO-LiClO$_4$ and PEO-75 wt% LLZO-LiClO$_4$ at 30 °C
5.5.1 AC Conductivity and Dielectric Permittivity

The complex dielectric permittivity ($\varepsilon'$, $\varepsilon''$) and conductivity ($\sigma'$, $\sigma''$) of PEO-30 wt% LLZO-LiClO$_4$, PEO-50 wt% LLZO-LiClO$_4$ and PEO-75 wt% LLZO-LiClO$_4$ are calculated using Eqs. 2.1-2.4 (see Ch 2) from the measured complex impedance at 30 °C (Fig. 5.3). The experimental data (symbols) are fitted (solid line) using Eqns. 2.5 and 2.6 (see Ch 2) and are shown in Fig 5.4 (a,b). The dielectric loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) (symbols) and the fitted curve are also shown in Fig 5.4 (c). As explained in previous two chapters, the experimental data of $\varepsilon'$, $\varepsilon''$ and $\sigma'$, $\sigma''$ versus frequency ($f$), were fitted using generalized Eqns. 2.5 and 2.6 (see Ch. 2), and the corresponding best fit parameters ($\sigma_{dc}$, $\tau_j$, $\tau_R$, $\alpha$, $\beta$, $\Delta\varepsilon$) obtained are listed in Table 5.1. The fitted data are shown by solid lines in Figs. 5.4 (a, b, c). PEO-75 wt% LLZO-LiClO$_4$ film shows the lowest ionic conductivity at 30 °C among the three concentrations investigated. This is further demonstrated by the observation of slower polymer segmental and ionic relaxation times. Perhaps large agglomeration of particles at this high concentration, as observed in SEM images, may not be well connected by the polymer chains to facilitate Li ion motion. Although PEO-30 wt% LLZO-LiClO$_4$ sample shows slightly lower conductivity compared to that of PEO-50 wt% LLZO-LiClO$_4$ film, we need to further optimize the concentration of LLZO between 30 to 60 wt% to obtain the highest conductivity.
Figure 5.4 a) Complex dielectric permittivity, (b) Complex AC conductivity and c) loss tan PEO-30 wt% LLZO-LiClO₄ and PEO-50 wt% LLZO-LiClO₄ films at 30°C. The symbols represent the experimental data and the solid lines represent the fitted data.
5.5.2 Activation Energy: Non-Arrhenius Behavior

The temperature dependent conductivity of PEO-30 wt% LLZO-LiClO₄, PEO-50 wt% LLZO-LiClO₄ and PEO-75 wt% LLZO-LiClO₄ films are measured from 30 °C to 60 °C. The ionic conductivity of PEO-75 wt% LLZO-LiClO₄ was not much affected by the temperature variation, exhibiting average conductivity of (5.8 ± 0.8)×10⁻⁶ S cm⁻¹. For PEO-30 wt% LLZO-LiClO₄ and PEO-50 wt% LLZO-LiClO₄ films, the logarithmic conductivity (σₐc) versus reciprocal temperature (i.e. 1000/T) are plotted in Fig. 5.5, where the symbols show the experimental data. The plots do not show strictly linear relationship indicating a non-Arrhenius temperature dependence of conductivity. As described in Chapter 2, this behavior is better described by VTF model using Eqn. 2.8. Both the activation energy (Eₐ) and equilibrium glass temperature (T₀) are determined from the VTF fitting and are summarized in Table 5.1. The activation energy in PEO-50 wt% LLZO-LiClO₄ is lower by factor of two compared PEO-30 wt% LLZO-LiClO₄. As explained in previous sections, this is due to higher amorphous fraction of PEO in the former providing more free volume for polymer chains for faster polymer segmental motion, and hence efficient ion motion through the CSPE film.

Table 5.1 The ionic relaxation time τᵢ, polymer chain segmental relaxation time τₛ, decoupling ratio Rₛ, and other best fit parameters obtained by fitting the complex conductivity and dielectric permittivity at 30 °C Activation energy, Eₐ, and equilibrium glass transition temperature, T₀, are obtained by fitting temperature dependent conductivity, σₐc, to VTF model.

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Thickness (µm)</th>
<th>σₐc (S cm⁻¹)</th>
<th>τᵢ (µs)</th>
<th>τₛ (µs)</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>Δε</th>
<th>Eₐ (eV)</th>
<th>T₀ (K)</th>
<th>Rₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-30 wt% LLZO-LiClO₄</td>
<td>122</td>
<td>5.3×10⁻⁵</td>
<td>0.30</td>
<td>2.00</td>
<td>0.82</td>
<td>0.50</td>
<td>0.85</td>
<td>22</td>
<td>0.12</td>
<td>188</td>
<td>0.007</td>
</tr>
<tr>
<td>PEO-50 wt% LLZO-LiClO₄</td>
<td>113</td>
<td>1.4×10⁻⁴</td>
<td>0.06</td>
<td>0.28</td>
<td>0.80</td>
<td>0.70</td>
<td>1.00</td>
<td>15</td>
<td>0.07</td>
<td>185</td>
<td>0.004</td>
</tr>
<tr>
<td>PEO-75 wt% LLZO-LiClO₄</td>
<td>145</td>
<td>5.8×10⁻⁶</td>
<td>0.20</td>
<td>9.00</td>
<td>0.65</td>
<td>0.65</td>
<td>1.00</td>
<td>50</td>
<td></td>
<td></td>
<td>0.045</td>
</tr>
</tbody>
</table>
5.6 Conclusions

The total ionic conductivity in composite solid polymer electrolytes is the combination of Li ion motion through ceramic, polymer matrix, and ceramic-polymer interface, where the ceramic channels are more favorable pathways. The hybrid composite solid polymer electrolyte comprised of PEO- cubic LLZO-LiClO$_4$ with different LLZO content (30, 50 and 75 wt%) has been studied. It is shown that the ionic conductivity of CSPE has been increased by increasing the LLZO content from 30 wt% ($5.3 \times 10^{-5}$ S cm$^{-1}$) to 50 wt% ($1.4 \times 10^{-4}$ S cm$^{-1}$). Further increasing LLZO results in a lower ionic conductivity ($5.8 \times 10^{-6}$ S cm$^{-1}$) due to slower segmental motion of polymer chains and hence slower ion-motion.
CHAPTER 6

EFFECT OF [EO]:[Li] CONCENTRATION ON THE IONIC CONDUCTIVITY OF PEO-CUBIC LLZO-LiClO₄ COMPOSITE SOLID POLYMER ELECTROLYTES

In Chapter 5, the CSPE films of PEO-Cubic LLZO-LiClO₄ with 50 wt % LLZO particles as fillers in PEO-LiClO₄ matrix with [EO]:[Li] = 15:1 showed the highest ionic conductivity at 30 °C among three concentrations of LLZO studied (30, 50 and 75 wt%). In this Chapter, we have studied the effect of changing the Li ion concentration on the characteristic properties of PEO-50 wt% Cubic LLZO-LiClO₄ by changing the ratio of [EO]:[Li] to 12:1 and 10:1.

6.1 Introduction

The Li ionic conductivity in PEO-LiClO₄ films has been clearly shown to be affected by [EO]:[Li] concentration (see Chapter 3). Two orders of magnitude increase in the conductivity and a factor of four decrease in the activation energy was observed when the Li ion concentration was increased from [EO]:[Li] = 15:1 to 12:1. However, no significant change was observed when the Li content was increased from [EO]:[Li] = 12:1 to 10:1. XRD patterns demonstrated an enhanced amorphous phase of PEO in PEO-LiClO₄ (12:1) and PEO-LiClO₄ (10:1) films, compared to PEO-LiClO₄ (15:1) films. It has been shown that amorphous regions provide higher free volume for polymer chains to move and thus aiding coupled Li ion and polymer segmental motion [111,112]. In the following sections, we have compared the role of cubic LLZO particles (50 wt%) on the electrical conductivity and mechanical integrity of PEO-Cubic LLZO-LiClO₄ films with [EO]:[Li] = 15:1, 12:1 and 10:1.
6.2 Materials and Methods

Free-standing CSPE films of PEO-50 wt% cubic LLZO-LiClO$_4$ [EO]:[Li] = 15:1, 12:1 and 10:1 were prepared with a similar procedure described in Chapter 5 (see section 5.2). The structural, morphological, and electrochemical characterizations were done using XRD, SEM, and EIS measurements. In the following, the films are labeled as: PEO-LLZO-LiClO$_4$ (15:1), PEO-LLZO-LiClO$_4$ (12:1) and PEO-LLZO-LiClO$_4$ (10:1). The film thickness is listed in Table 6.1.

6.3 Structural Analysis: XRD

Figure 6.1 (a) shows the XRD patterns of PEO-LLZO-LiClO$_4$ (15:1), PEO-LLZO-LiClO$_4$ (12:1) and PEO-LLZO-LiClO$_4$ (10:1) in the range of 2\(\theta\) = 10° - 80°. The patterns are dominated by cubic LLZO diffraction peaks, but we can also observe weaker PEO peaks (marked with *) around 2\(\theta\) = 19.3° and 23.5°. Figure 6.1 (b) shows the expanded pattern in the range of 2\(\theta\) = 18° - 25°. The peak observed at 19.5°, with very similar intensity, is assigned to (220) peak of cubic LLZO overlapping with that of PEO (100) peak at 19.3°. However, we do observe significant reduction in intensity of PEO (110) peak ~ 23.5°, especially in PEO-LLZO-LiClO$_4$ (12:1), indicating reduced crystallinity of PEO matrix. In addition, the development of new features, especially in PEO-LLZO-LiClO$_4$ (10:1) film around 2\(\theta\) ~ 22° indicate some orientational interaction between the LLZO crystallites and the PEO matrix. It is interesting to note that such features are absent in PEO-LLZO-LiClO$_4$ (12:1) film.
Figure 6.1 a) The XRD diffraction pattern pure PEO-50 wt% LLZO-LiClO$_4$ with [EO]:[Li] = (15:1), (12:1) and (10:1), b) Expanded region of corresponding XRD patterns from $2\theta = 18^\circ$ to $25^\circ$. The asterisks correspond to PEO peaks.

6.4 Surface Morphology: SEM

The surface morphology of PEO-LLZO-LiClO$_4$ (15:1), PEO-LLZO-LiClO$_4$ (12:1) and PEO-LLZO-LiClO$_4$ (10:1) films at low magnification (200x) are shown in Fig. 6.2 (a-c), respectively. At this magnification, the film surface become smoother with increasing Li concentration. Corresponding SEM images at higher magnification (20000x, Fig. 6.2 (d-f)) show uniform distribution of sub-micron LLZO particles in polymer matrix. It is not clear whether the surface asperities observed in PEO-LLZO-LiClO$_4$ (12:1) film are LLZO agglomerates or a rearrangement of PEO matrix. Although the PEO-LLZO-LiClO$_4$ (10:1) films look the smoothest, we also observe
several pores (~ 10 µm) uniformly distributed throughout the surface. These features may affect the electrical conductivity behavior.

Figure 6.2 The SEM images of PEO-50 wt% LLZO-LiClO₄ (15:1) (a,d), PEO-50 wt% LLZO-LiClO₄ (12:1) (b,e) and PEO-50 wt% LLZO-LiClO₄ (10:1) (c,f). The scale bars are 100 µm in a, b, c, and 10 µm in d,e,f.
6.5 Thermal Stability Measurements

We have indirectly tested the mechanical integrity of PEO-LLZO-LiClO$_4$ (15:1), PEO-LLZO-LiClO$_4$ (12:1) and PEO-LLZO-LiClO$_4$ (10:1) films by observing their thermal stability after subjecting them to 120 °C for 1 hour in an oven, and then allowed to cool to room temperature after removal from the oven. The images taken before and after heating are shown in Fig. 6.3. We observe that the films with LLZO particles remain mechanically robust after the heat treatment.

![Image of films before and after heating](image)

Figure 6.3 The images of a) PEO-cubic LLZO-LiClO$_4$ (10:1), b) PEO-cubic LLZO-LiClO$_4$ (12:1) and c) PEO-cubic LLZO-LiClO$_4$ (15:1) films before and after heating at 120 °C for 1 hour.

6.6 Electrochemical Characterization: EIS

The ionic conductivity of films was determined by conducting frequency dependent EIS measurements, as described in previous chapters. The Nyquist plots for PEO-LLZO-LiClO$_4$ (15:1), PEO-LLZO-LiClO$_4$ (12:1) and PEO-LLZO-LiClO$_4$ (10:1) films at 30 °C are presented in Fig. 6.4. It can be seen that PEO-LLZO-LiClO$_4$ (10:1) film shows a slightly higher value of $R_{\text{bulk}}$ compared to other two films indicating a reduction in conductivity although this film has a higher Li concentration. This could be due to ion-pairing effects [113].
Figure 6.4 The Nyquist plots for PEO-50 wt% LLZO-LiClO$_4$ [EO]:[Li] = 15:1, 12:1 and 10:1 at 30 °C.

6.7 AC Conductivity and Dielectric Permittivity

The complex dielectric permittivity ($\varepsilon'\varepsilon''$) and conductivity ($\sigma'\sigma''$) of PEO-50 wt% LLZO-LiClO$_4$ (15:1), (12:1) and (10:1), calculated using calculated using Eqs. 2.1-2.4 (see Ch 2) from the measured complex impedance at 30 °C are shown in Fig. 5.3. The experimental data (symbols) are fitted (solid line) using Eqns. 2.5 and 2.6 (see Ch 2) and are shown in Fig 6.5 (a,b). The dielectric loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) (symbols) and the fitted curve are also shown in Fig 6.5 (c). As explained in previous three chapters, the experimental data of $\varepsilon'$, $\varepsilon''$ and $\sigma'$, $\sigma''$ versus frequency ($f$), were fitted using generalized Eqns. 2.5 and 2.6 (see Ch. 2), and the corresponding best fit parameters ($\sigma_{dc}$, $\tau_j$, $\tau_R$, $\alpha$, $\beta$, $\Delta\varepsilon$) are listed in Table 6.1. The fitted data are shown by solid lines.
in Figs. 6.5 (a, b, c). PEO-50 wt% LLZO-LiClO$_4$ (10:1) film shows the lowest ionic conductivity at 30 °C among the three Li concentrations investigated. This is further demonstrated by the observation of slower polymer segmental and ionic relaxation times. Perhaps ion-pairing effects at this high Li ion concentration, may the cause of this reduction [114] due to fewer Li-ions participating in the ion transport. The decoupling ratio $R_{sj}$ which is the ratio of polymer segmental relaxation time to the ionic relaxation time is << 1 in all three films, indicating that the ions motion is facilitated by polymer chain motion. The corresponding relaxation times and other parameters are summarized in Table 6.1.

Table 6.1 The ionic relaxation time $\tau_j$, polymer chain segmental relaxation time $\tau_s$, decoupling ratio $R_{sj}$, and other best fit parameters obtained by fitting the complex conductivity and dielectric permittivity at 30 °C. Activation energy, $E_a$ and equilibrium glass transition temperature, $T_0$, are obtained by fitting temperature dependent conductivity, $\sigma_{dc}$, to VTF model.

<table>
<thead>
<tr>
<th></th>
<th>Thickness (µm)</th>
<th>$\sigma_{dc}$ (S cm$^{-1}$)</th>
<th>$\tau_j$ (ms)</th>
<th>$\tau_s$ (µs)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\Delta \varepsilon$</th>
<th>$E_a$ (eV)</th>
<th>$T_0$ (K)</th>
<th>$R_{sj}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-50 wt% LLZO-LiClO$_4$ (15:1)</td>
<td>113</td>
<td>$1.40 \times 10^4$</td>
<td>0.06</td>
<td>0.28</td>
<td>0.24</td>
<td>0.80</td>
<td>0.7</td>
<td>1.00</td>
<td>15</td>
<td>0.07</td>
<td>185</td>
</tr>
<tr>
<td>PEO-50 wt% LLZO-LiClO$_4$ (12:1)</td>
<td>111</td>
<td>$2.20 \times 10^4$</td>
<td>0.05</td>
<td>0.12</td>
<td>0.04</td>
<td>0.88</td>
<td>0.7</td>
<td>0.65</td>
<td>20</td>
<td>0.05</td>
<td>198</td>
</tr>
<tr>
<td>PEO-50 wt% LLZO-LiClO$_4$ (10:1)</td>
<td>114</td>
<td>$3.00 \times 10^4$</td>
<td>0.45</td>
<td>3.30</td>
<td>0.40</td>
<td>0.85</td>
<td>0.6</td>
<td>0.65</td>
<td>24</td>
<td>0.09</td>
<td>185</td>
</tr>
</tbody>
</table>
Figure 6.5 a) Complex dielectric permittivity, (b) Complex AC conductivity and c) Loss tangent of PEO-50 wt% LLZO-LiClO4 [EO]:[Li] = 15:1, 12:1 and 10:1 at 30 °C. The symbols represent the experimental data and the solid lines are the fit.
6.8 Activation Energy: Non-Arrhenius Behavior

The temperature dependent conductivity has been measured in order to determine Li ion activation energy. In Fig 6.5 the logarithmic conductivity ($\sigma_{dc}$) vs reciprocal temperature (1000/T) are shown (symbols) for PEO-50 wt% LLZO-LiClO$_4$ (15:1), (12:1) and (10:1) films. The plots are not exactly linear as expected in an Arrhenius behavior. The non-Arrhenius temperature dependent conductivity is fitted (solid line) using VTF model (Eq. 2.8), and the activation energy ($E_a$) and the equilibrium glass transition temperature ($T_0$) are determined as fitting parameters (see Table 6.1). The lower activation energy and hence higher ionic conductivity in PEO-50 wt% LLZO-LiClO$_4$ (15:1) and PEO-50 wt% LLZO-LiClO$_4$ (12:1) compared to PEO-50 wt% LLZO-LiClO$_4$ (10:1) shows better coupled motion between Li ions and polymer segments.

Figure 6.6 The non-Arrhenius behavior of ionic conductivity vs. 1000/T and the fitting VTF model.
6.9 Conclusions

We have investigated the effect of Li content on structural and characteristics of PEO-50 wt% LLZO-LiClO$_4$ CSPE by varying the ratio of [EO]:[Li] = 15:1, 12:1 and 10:1. We have shown that the ionic conductivity of CSPE has enhanced when [EO]:[Li] changes from 15:1 to 12:1, but further increase in Li concentration lowers the ionic conductivity, perhaps due to ion-pairing effects.
CHAPTER 7

EFFECT OF AGING ON IONIC CONDUCTIVITY OF SOLID COMPOSITE POLYMER ELECTROLYTES

In this chapter we discuss the effect of aging on structure and ionic conductivity of PEO-50 wt% LLZO-LiClO$_4$ (15:1). We have studied the effect of aging on structure of PEO-50 wt% LLZO-LiClO$_4$ (15:1) by comparing the XRD pattern of a fresh sample and after four months. We have also measured and compared the ionic conductivity at room temperature. We have also presented our observations on the effect of heat on structure and ionic conductivity of an aged PEO-50 wt% LLZO-LiClO$_4$ (15:1).

7.1 Introduction

Aging is an inevitable process in polymers which affect the physical and chemical properties of polymers. Due to the wide application of polymers and polymer-based materials, aging can drastically influence their performance [115]. The aging effect can originate from the surrounding environment such as heat, moisture, UV light and so on, and affect their volume, density, mechanical strength or change their chemical reactivity [116]. It has been shown that the ionic conductivity of polymers degrade over time [117]. Polymer materials specially nanocomposite polymers are nonequilibrium and it is known that re-crystallization occurs during aging [118].
7.2 Materials and Methods

The composite solid polymer electrolyte comprised of PEO-LiClO$_4$ (15:1) and 50 wt% LLZO has been prepared as discussed in Chapter 5 (see section 5.2). The sample was kept in desiccator over 4 months and the ionic conductivity was measured after 6 days, 50 days and 4 months at room temperature ($23 \, ^\circ \text{C}$).

7.3 Aging Effects

Ionic Conductivity

In Fig. 7.1 (a) the Nyquist plot of PEO-50 wt% LLZO-LiClO$_4$ (15:1) is shown when the film was fresh, after 6 days, and after 50 days. The effect of aging in total resistance can be clearly observed as the intercept on x-axis moves toward higher resistance. In Fig. 7.1 (b) the Nyquist plot of the similar sample is shown after 4 months and the drastic decrease in ionic conductivity can be clearly observed.

![Nyquist plots](image)

Figure 7.1 a) Nyquist plots of PEO-50 wt% LLZO-LiClO$_4$ (15:1) fresh (black), after 6 days (red) and after 50 days (blue) b) after 4 months.
X-ray Diffraction

Figure 7.2 shows the XRD pattern of PEO-50 wt% LLZO-LiClO₄ (15:1) when the film was fresh and after 4 months. The PEO peaks at 2θ = 19.2° and 23.5° are labeled with asterisks. By comparing the XRD pattern of both fresh film and aged one with LLZO powder, we have noticed changes on the intensity and presence of shoulders on two peaks corresponding to LLZO (shown by arrow) which can be caused by some side reactions.

Figure 7.2 The XRD patterns of PEO-50 wt% LLZO-LiClO₄ (15:1) when it was fresh and after 4 months of aging.
Heat Treatment

We have investigated the effect of heat treatment on the structure and ionic conductivity of a 4 months aged PEO-50 wt% LLZO-LiClO$_4$ (15:1) film. The films were placed in an oven at 120 °C for one hour and then placed the film in desiccator for 24 hours to cool down to room temperature and lose any moisture and measured the ionic conductivity afterward Fig. 7.3 (a). In Fig. 7.3 (b) we have shown the XRD pattern of the film both before and after heating. As it can be seen the two LLZO peaks (shown by asterisks) have changed to the shape as it can be seen in fresh film pattern (7.2 middle panel). We have shown that the ionic conductivity of the aged film can be improved by heating.

Figure 7.3 a) The Nyquist plots of PEO-50 wt% LLZO-LiCl$_4$ (15:1) after 4 months before and after heating at room temperature. b) The XRD pattern of same film before and after heating.
7.4 Conclusions

Based on our observation, the structural and ionic conductivity of CSPE are affected over time. The ionic conductivity of PEO-50 wt% LLZO-LiClO₄ (15:1) film has decreased drastically after 4 months and the XRD patterns have shown major differences corresponding to LLZO peaks. We have also observed an improvement in ionic conductivity after heating the sample up to 120 °C for one hour.
CHAPTER 8

SUMMARY AND FUTURE DIRECTIONS

Solid electrolytes seem to be the ultimate substitute for resolving the safety concerns of lithium ion batteries which currently use flammable and reactive organic liquid electrolytes. Polyethylene oxide (PEO) is a well-studied polymer which is considered as a suitable candidate for polymer electrolytes due to its flexibility and ability for dissolving Li-salts through its ether group interaction with Li⁺. However, the coexistence of crystalline and amorphous phases in PEO hinders the ionic conductivity at room temperature ($10^{-8} - 10^{-6}$ S cm⁻¹). Garnet type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is a fast ion conductor and is often studied solid ion conductor as pure on its own or as polymer composite with PEO. LLZO crystallizes in cubic and tetragonal structures and can have room temperature of conductivity of up to $10^{-4}$ S cm⁻¹ depending on compaction density. The cubic structure LLZO exhibits a higher ionic conductivity at room temperature compared to the tetragonal phase due to its channel structure which is favorable ion conduction. The combination of PEO and LLZO as a filler is expected to exhibit favorable ionic conductivity, mechanical integrity and high potential stability window against Li. In this thesis we have studied the PEO-LLZO-$\text{LiClO}_4$ as hybrid composite solid polymer electrolyte (CSPE) for all solid-state lithium ion batteries.

As our first project in (Chapter 3), we have investigated the effect of Li concentration on structural, morphological and electrochemical properties of PEO-$\text{LiClO}_4$ by varying the ratio of ethylene oxide monomers per Li-ion ([EO]:[Li]). We have investigated the films with [EO]:[Li] ratios of 15:1, 12:1 and 10:1. Both X-ray diffraction studies and scanning electron microscope images have shown that increasing the Li content results in more amorphous structure and films
with smoother surface. We have shown that the Li-ion motion is coupled with polymer segmental motion and is assisted by the motion of polymer chains in the amorphous phase. The highest ionic conductivity has been observed for PEO-LiClO$_4$ (10:1).

In our second project in (Chapter 4), we have studied PEO-50 wt% LLZO-LiClO$_4$ (15:1) using sub-micron size Al substituted cubic LLZO particles and compared with PEO-50 wt% LLZO-LiClO$_4$ (15:1) comprised of micron size tetragonal LLZO inspired by previous studies. According to previous studies, the channel structure pathway in LLZO is more favorable for Li-ions to traverse in PEO-LLZO-LiClO$_4$ composite polymers compared to PEO-LLZO interface or PEO matrix. We have shown that the ionic conductivity improves by two orders of magnitude using cubic LLZO compared to tetragonal LLZO. This is explained as due to increase in PEO amorphous phase in the composite films upon addition of sub-micron sized cubic-LLZO particles which facilitate enhanced ionic motion leading to a higher total conductivity in composite films. The dispersed LLZO particles in the polymer matrix also increase the physical strength of the composite polymer films which show stability at elevated temperatures up to 120 °C.

In Chapter 5, we presented the results of the investigation on the effect of the amount of cubic-LLZO content on the ionic conductivity of CSPE films. The amount of LLZO was varied from 30 wt% to 75 wt% in PEO-LiClO$_4$ (15:1) films. We observed that increasing the LLZO content from 30 wt% to 50 wt% increased the ionic conductivity. However, a further increase in LLZO to 75 wt% resulted in a decreased ionic conductivity, which we attribute to the formation of increased crystalline phase of PEO as well as agglomeration of LLZO particle leading to discontinuities in the contacts among LLZO particles.
The effect of Li concentration on ionic conductivity of PEO-50 wt% cubic-LLZO-LiClO$_4$ was investigated and the results are presented in Chapter 6. The [EO]:[Li] ratio was varied from 15:1, 12:1 and 10:1. The increase in Li content from [EO]:[Li] = 15:1 to 12:1 showed an expected increase in ionic conductivity. However, opposite result was observed by further addition of LiClO$_4$ ([EO]:[Li] = 10:1). The decrease in the films with higher Li content may be due to ion-pairing and agglomeration of LLZO particles. We have also observed that heat treatment may possibly recover the ionic conductivity of an aged CSPE by rearranging polymer chains.

In summary, in order to increase the ionic conductivity in polymer electrolytes and understand their ionic transport behavior, we have studied polyethylene oxide complexed with lithium salt and the addition of LLZO ceramic particles, which are known to be Li ion conductors. In order to optimize the conductivity and mechanical strength of the polymer-salt-ceramic composite films, we have varied the lithium concentration ([EO]/Li ratio), concentration of LLZO in the films, and different crystalline phases of LLZO. Our studies show that is an optimal concentration for Li, and LLZO where the conductivity is highest. Further, composite films with cubic form LLZO compared to its tetragonal phase. We have analyzed the ionic relaxation process in complex permittivity and conductivity formalism. The analyses of the data shows that the conduction occurs primarily through amorphous regions of the films with key contributions from the segmental motion of polymer backbone and ionic association effects. In these composite polymer electrolytes with ceramic fillers conduction relaxation time is coupled to the segmental relaxation time of polymer matrix.

Although, we have investigated the effects of Li-ion concentration, LLZO concentration and the two crystallographic polymorphs of LLZO on the ionic conductivity of polymer-Li-LLZO
complexes at selected concentrations, several additional studies could be undertaken to understand the mechanism of ionic transport behavior in these composite polymer films.

We have used a PEO of molecular weight $10^6 \text{ g/mol}$ and it would be interesting to study the effect of molecular weight on the ionic conductivity using the optimized concentrations in the current study. The effect of crystallite size of the ceramic fillers. In our study the cubic-LLZO particles were of sub-micron size whereas tetragonal-LLZO particles had larger size (~ $\mu \text{m}$). In order to compare the two results, it is desirable to use the particle of similar size. It is also desirable to investigate the effect of particle size. However, preparing or obtaining the LLZO with different particle size could be a challenge in itself. It has been suggested that LLZO may not be thermodynamically stable forming Li$_2$O$_3$ which is an insulator. Addition of high concentration of LLZO in PEO matrix may reduce the ionic conductivity due to a layer of Li$_2$O$_3$ covering the LLZO particle in the polymer matrix which renders LLZO a poor Li-ion conductor. The presence of thin layer of Li$_2$O$_3$ could to be investigated using high resolution transmission electron microscopy and X-ray dispersive spectroscopy. It is known that ion conductivity of PEO films decreases with aging, perhaps due to recrystallization of PEO. A systematic study could be undertaken to assess the effect of aging in the PEO-Li-LLZO composite films, including heat treatment to remove aging effects.
REFERENCES


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ABSTRACT

AC CONDUCTIVITY STUDIES of POLYETHYLENE-OXIDE-GARNET TYPE Li$_7$La$_3$Zr$_2$O$_{12}$ HYBRID COMPOSITE SOLID POLYMER ELECTROLYTE for Li-ION BATTERY

by

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Solid electrolytes including ceramics and polymers are considered to be the ultimate substitute for organic liquid electrolytes, which are currently being used in commercialized lithium ion batteries, to address the safety concerns due to Li dendrite growth and internal short circuiting. However, low ionic conductivity in ceramics due to high grain boundary resistance and semi-crystalline nature of polymers has held back the solid electrolytes from being used in Li-ion batteries. Polyethylene oxide (PEO) complexed with a Li-salt is a well-studied polymer electrolyte because of its ionic conductivity properties at room temperature and its ability to form flexible membranes. However, the coexistence of amorphous and crystalline regions at room temperature has limited its ionic conductivity to $\sim 10^{-8} - 10^{-6}$ S cm$^{-1}$. On the other hand, Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) is a fast Li-ion conductor in its cubic crystalline form showing high ionic conductivity up to $10^{-4}$ S cm$^{-1}$ at room temperature but challenging to form flexible membranes.
In the present thesis, we have investigated hybrid composite solid polymer electrolyte films of PEO-LLZO-LiClO₄ with different [EO]:[Li] ratio and LLZO concentrations to optimize their near room temperature conductivity while maintaining the robust mechanical properties. We have synthesized free-standing flexible films of PEO-LLZO-LiClO₄ with a thickness of ~100-130 µm, comprised of sub-micron sized aluminum substituted cubic LLZO particles dispersed in PEO (Mw=10⁶)-LiClO₄ matrix using a solution cast method. The structural, morphological and electrochemical properties were studied using X-ray diffraction, scanning electron microscopy, electrical impedance spectroscopy (EIS) and linear sweep voltammetry. The AC dielectric permittivity and ionic conductivity of the films, determined using EIS measurements, were analyzed using an expression that generalizes the power-law dependence of complex dielectric permittivity and conductivity including electrode polarization. The temperature dependence of ionic conductivity were investigated, and the data were analyzed using Vogel-Tammann-Fulcher (VTF) empirical equation to estimate the changes in the activation energy of PEO-LiClO₄ upon the addition of LLZO particles. The PEO-50 wt% LLZO-LiClO₄ films with [EO]:[Li] = 15:1 and 12:1 show a high ionic conductivity of ~ 10⁻⁴ S cm⁻¹ at room temperature. The films are mechanically robust and stable against Li metal up to 5 V, and thermally stable up to 120 °C.
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2. MRS spring meeting, Phoenix, AZ, March 2019 (Poster Presentation)

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