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NEXT-GENERATION SOLID-STATE LITHIUM BATTERIES ENABLED BY ULTRA-FAST ION TRANSPORT IN HYBRID CERAMIC–POLYMER ELECTROLYTES

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Abstract

The design of the next generation solid-state lithium batteries is highly reliant on the electrolytes that integrate high ionic conductivity, mechanical stability, and electrochemical safety. Polymer electrolytes (PEO): These are highly flexible polymer electrolytes with outstanding flexibility and interfaces between electrodes but have low ionic conductivity at room temperature because of their semi-crystalline structure. To bypass this shortcoming, this paper examines a hybrid electrolyte that is ceramic-polymer which is a mix of PEO matrix and garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) ceramic fillers. Generally, the system of the incorporation of LLZO notably modifies the crystallinity of the PEO and forms continuous lithium-ion-conducting routes, improving the lithium-ion transport. Structural, thermal, and electrochemical studies ensure effective polymer-ceramic interactions, lowered crystallinity, increased thermal stability, and expanded electrochemical stability. The hybrid electrolyte has a much higher ionic conductivity and less activation energy than pure PEO, and its behavior is that of a thermally activated ultra-fast ion transport. These findings provide the opportunity to discuss the synergistic nature of LLZO fillers to overcome the inherent drawbacks of polymer electrolytes and emphasize the opportunities of PEO-LLZO hybrid systems as *promising solid electrolytes to high-performance and safe solid-state lithium batteries.*

INTRODUCTION

The increased demand of lithium-based batteries with higher energy density, enhanced safety and increased operational life time has been cropped up by the rapid growth of electric vehicles, portable electronics, and large-scale energy storage systems[1]. The traditional lithium-ion batteries that use flammable liquid electrolytes have issues related to inherent risks of safety such as leakage of electrolytes, thermal runaway, and development of lithium dendrites[2]. Such restrictions have also prompted serious research efforts to solid-state lithium batteries (SSLBs), that substitute liquid electrolytes with solid electrolytes and have higher safety, broader electrochemical stability ranges, and better thermal stability[3]. Polymer systems have received a lot of attention as solid electrolytes owing to their flexibility, lightweight, simple processing and good interfacial contact with electrodes[4]. Poly (ethylene oxide) (PEO) is a polymer matrix of solid polymer electrolytes that has been studied most widely due to its great coordination capacity with lithium salts and good electrochemical stability[5]. PEO-based electrolytes however possess low ionic conductivity at room temperature mostly because they are semi-crystalline in nature, which limits the movement of polymer chains and the transport of lithium-ions[6]. This inherent weakness is an important issue that still needs to be overcome in order to practically apply PEO-based solid-state batteries[7]. On the other hand, inorganic ceramic electrolytes like garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) have high lithium-ion conductivity, and are highly electrochemically stable with lithium metal and strong mechanical strength. The following characteristics of LLZO suggest that it is an excellent candidate in inhibiting the growth of lithium dendrites and facilitating long-time cycling. Although these have these benefits, ceramic electrolytes are fragile and usually have poor interfaces with electrodes, which results in high interfaces resistance and processing challenges[8]. This has restricted the practical use of stand-alone ceramic electrolyte in a battery. In an attempt to counter the shortcoming of both polymer and ceramic electrolytes, hybrid ceramic-polymer electrolytes have been considered as an effective solution that incorporates the mechanical flexibility of polymers with high ionic conductivity and stability of ceramic fillers[9]. In these hybrid systems, the dispersal of ceramic particles in the polymer mass may break the crystallinity of the polymer, increase the dissociation of lithium salt, and develop other transport routes fast ion in the polymer-ceramic faces. Such synergistic effects are capable of enhancing ionic conductivity to a large extent without compromising mechanical integrity and processability[10]. As recent studies have shown, the addition of LLZO to PEO-based electrolytes can be used to increase ionic conductivity and electrochemical stability. Nevertheless, the reported systems continue to be reported as having suboptimal ion transport performance at ambient temperature, commonly because of poor filler dispersibility, interfacial incompatibility or inadequate knowledge of ion transport mechanisms in the hybrid matrix[11].

In addition, polymer-ceramic interfaces in facilitating the lithium-ion flow in ultra-fast velocity is a poorly studied area, especially with regard to filler loading commerce and interfaces. Although the PEO-based hybrid electrolytes have been studied extensively, the systematic knowledge of the effect of the optimized incorporation of LLZO on the polymer crystallinity, interfacial structure, and lithium-ion transport behavior has not been properly understood in combination. Specifically, the challenge of attaining the ultra-fast ion mobility and maintaining mechanical vulnerability and electrochemical stability remains a significant challenge facing the next-generation solid-state lithium batteries. The aim of the current work is to design and research a hybrid PEO-LLZO ceramic-polymer electrolyte with higher ionic conductivity and solid-state battery. This paper critically reviews the influence of incorporation of LLZO on the structure, thermal, mechanical and electrochemical properties of the hybrid electrolyte. Particular attention is put on the study of the ion transportation processes and interfaces interactions that cause ultra-fast lithium-ion conduction. The long-term aim is to show that PEO-LLZO hybrid electrolytes can be regarded as good alternatives in the upcoming solid-state lithium batteries.

2 Literature review

Polymer-ceramic hybrid electrolytes have also been developed as an attractive category of solid electrolytes to be used in all-solid-state lithium batteries through the synergistic mixture of the desirable characteristics of both polymer matrices and ceramic fillers. Conventional solid polymer based on PEO complexed with lithium salts have good processability and interfacial contact with the electrodes but have low ionic conductivity at room temperature because they are semi-crystalline which inhibits the movement of the polymer segments and the lithium-ion. PEO-LiTFSI pure systems can typically exhibit conductivities of the order of 10^{-6}-10^{-5} S cm^{-1} at room temperature, which is significantly lower than the conductivities of ceramic conductors, including LLZO with conductivities at 3×10^{-5} -3×10^{-4} S cm^{-1}[12]. Addition of ceramics fillers to polymer matrices has been greatly identified as an efficient approach in overcoming these constraints. Some ceramic materials like $Li_7La_3Zr_2O_{12}$ (LLZO) do not only offer high intrinsic lithium-ion conductivity, but also can break crystallinity of polymers and form continuous channels of ion movement. The literature reviews indicate that the ion conduction is highly dependent on the surface chemistry, size, and distribution of ceramic fillers. As an example, inorganic fillers have the ability to prevent the ion clusters formation in the polymer, cause the lithium salts dissociation, and the fraction of free Li^+ carriers, leading to an increase in ionic conductivity[13]. Also, filler particles with the high surface area and smaller sizes are more active in interaction with the polymer matrix, resulting in enhanced changes in conductivity. PEO-LLZO hybrid electrolytes have been studied specifically by experimental studies and have provided varied outcomes with regard to composition and processing. Chen et al. have reported that PEO_8-LiTFSI composite electrolytes with about 10 wt% LLZTO (Ta-doped garnet) made good ionic conductivities (exceeding 10^{-4} S cm^{-1}) at 30°C, but additions of additional ceramic led to numerous ionic conductivity reductions owing to the loss of polymer continuity[14]. Other studies have shown that further increases in conductivity and electrochemical stability can be achieved by incorporating other polymer materials into the LLZO such as PVDF or PVDF-HFP; a PEO/PVDF-HFP/LLZTO composite had conductivities of approximately 2.65×10^{-4} S cm^{-1} and electrochemical stability up to 5.55 V.

Moreover, composite membranes using LLZO particles as part of mixed polymer assemblies have demonstrated the capability to increase rate and cycling stability in $LiFePO_4$ full cells and have indicated that hybrid architectures may be more able to support viable battery behavior. With these developments, it is still difficult to maximize the performance of hybrids in terms of understanding them fully[15]. A number of studies point out that the conduction mechanism in these composites remains a point of contention with some studies indicating that ion transport may occur preferentially via the ceramic phase as opposed to via the polymer phase or just via the polymer-ceramic interface. As an example, isotope-labeled NMR experiments revealed evidence that lithium ions in certain PEO-LLZO systems prefer lithium ions to traverse the ceramic and not the polymer matrix. Furthermore, the effects of filler morphology, distribution and polymer-ceramic interfacial chemistry on Ion transport and mechanical properties have not yet been fully established despite modeling studies that reveal that interfacial resistance and percolation networks are vital factors in the determination of overall conductivity and numbers of transference[16]. New trends have been centered on molecular-based engineering of polymer matrices and customized interfaces. An illustration is the use of hybrid electrolytes that combine LLZTO with functionalized polymer networks, whereby they are expected to form more channels of ion transport and stable interphases that help to achieve uniform deposition of lithium and inhibit the growth of dendrites[17]. These design concepts have produced conductivities of up to 0.266 mS/cm^{-1} and have also been able to provide long-haul cycling of symmetric-cells, which again serves to highlight the promise of well-designed hybrid systems. In general, the literature has proven that the concept of hybrid polymer-ceramic electrolytes is an attractive pathway in enhancing the solid-state lithium battery operation. Nevertheless, much work still needs to be done to streamline filler-polymer interactions, to achieve the highest room temperature ionic conductivity and to understand the underlying transport mechanisms that allow ion conduction in these complex materials to occur ultra-fast.

3 Materials and Methods

3.1 Materials

Poly (ethylene oxide) (PEO, average molecular weight ~600,000 g mol^{-1}) was employed as the polymer matrix. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was chosen as the lithium salt owing to its high ability of dissociation and electrochemical stability. Garnet-type lithium lanthanum zirconium oxide ($Li_7La_3Zr_2O_{12}$, LLZO) ceramic powder was employed as the inorganic filler. Anhydrous acetonitrile (or tetrahydrofuran, THF) was used as the solvent for the electrolyte solution preparation. All the materials were used as received without further purification

3.2 Preparation of PEO–LLZO Hybrid Electrolytes

The hybrid electrolytes based on PEO were synthesized by the solution casting technique. First, the PEO was dissolved in a suitable amount of solvent with constant stirring at room temperature until a homogeneous solution was formed. LiTFSI was then added to the polymer solution with a fixed ether oxygen to lithium-ion ratio of 16:1 and stirred until dissolution was complete. Ceramic LLZO powder was dried under vacuum at 120 °C before use to remove any moisture. The dried LLZO powder was then added to the PEO/LiTFSI solution with varying weight percentages (e.g., 5, 10, and 15 wt%) and mixed using magnetic stirring and ultrasonic treatment to ensure proper mixing. The resulting solution was then cast on a Teflon or glass surface and allowed to evaporate slowly at room temperature. The resulting electrolyte membranes were then dried under vacuum at 60 °C for 24 hours to remove any remaining solvent. Free-standing electrolyte membranes with a uniform thickness were then carefully removed and stored in an argon-filled glove box.

3.3 Characterization

X-ray diffraction (XRD) analysis was employed to investigate the crystalline nature of the hybrid electrolytes. Fourier transform infrared (FTIR) spectroscopy was utilized to study the interactions in the polymer, salt, and filler. The surface and cross-sectional morphologies of the samples were investigated using scanning electron microscopy (SEM). The thermal characteristics of the samples were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Tensile testing was conducted to determine the mechanical properties.

3.4 Thermal and Mechanical Analysis

Differential scanning calorimetry (DSC) analysis was carried out to examine the thermal transitions and crystallinity of the electrolyte membranes. The samples were heated from −50 °C to 100 °C at a constant rate of heating in a nitrogen atmosphere. Thermogravimetric analysis (TGA) was employed to evaluate the thermal stability of the hybrid electrolytes. The samples were heated to 600 °C. The mechanical properties of the electrolyte films were analyzed through tensile testing to measure the tensile strength and elongation at break.

3.5 Electrochemical Characterization

The ionic conductivity of the electrolyte membranes was determined by electrochemical impedance spectroscopy (EIS). The electrolyte membranes were placed between two stainless steel electrodes and analyzed in the frequency range of 1 MHz to 1 Hz with a small AC perturbation. The experiments were carried out at various temperatures, and the ionic conductivity was determined from the bulk resistance. The transference number of the lithium ion in the lithium-ion battery was analyzed by the DC polarization technique in a symmetric cell of Li|electrolyte |Li. Linear sweep voltammetry (LSV) was employed to determine the electrochemical stability window of the hybrid electrolytes.

3.6 Solid-State Battery Assembly and Testing

All battery assembly steps were performed in an argon-filled glove box. Symmetric and full solid-state batteries were assembled with lithium metal as the anode, PEO-LLZO hybrid electrolyte as the separator, and an appropriate cathode material. Galvanostatic charge-discharge cycling tests were conducted using a battery testing system.

3 Results and discussion

3.1 Structural and Morphological Analysis

The Figure (a) X-ray diffraction (XRD) patterns show that the hybrid electrolyte components have been successfully integrated and structurally sound. The crystallization characteristics of Pure PEO/PVDF-LiTFSI were observed to have broad characteristic crystalline peaks of 19° and 23° representing semi-crystalline characteristics of the chemical. The XRD pattern of PEO/PVDF-LiTFSI-LLZO hybrid changed when the incorporation of LLZO occurs is that the characteristic polymer peaks have reduced significantly in intensity, which indicates a decrease in polymer crystallinity and formation of more amorphous paths to transport ions faster. The diffraction peaks of the hybrid sample are in good agreement with the diffraction peaks of the LLZO reference samples (PDF # 45-0109) and pure LLZO powder, and no impurity phases can be observed, which proves that LLZO does not interact with the polymer to form impure crystals. The Scanning Electron Microscopy (SEM) images in Figure (b) give information on the morphology and the distribution of the particles of the electrolyte. The main SEM image is that of a fairly high density and constant surface, which is necessary to ensure intimate contact on electrodes in a battery on solid state. The porous behavior of the filler is represented in the high-magnification inset and the particle size distribution curve reveals that the median diameter (d50) is 2.155 mm. Such a micron sized distribution of LLZO particles provides high surface-area-to-volume ratio and provides continuous channels of ion conductors at the ceramic-polymer interface that are known as ultra-fast.

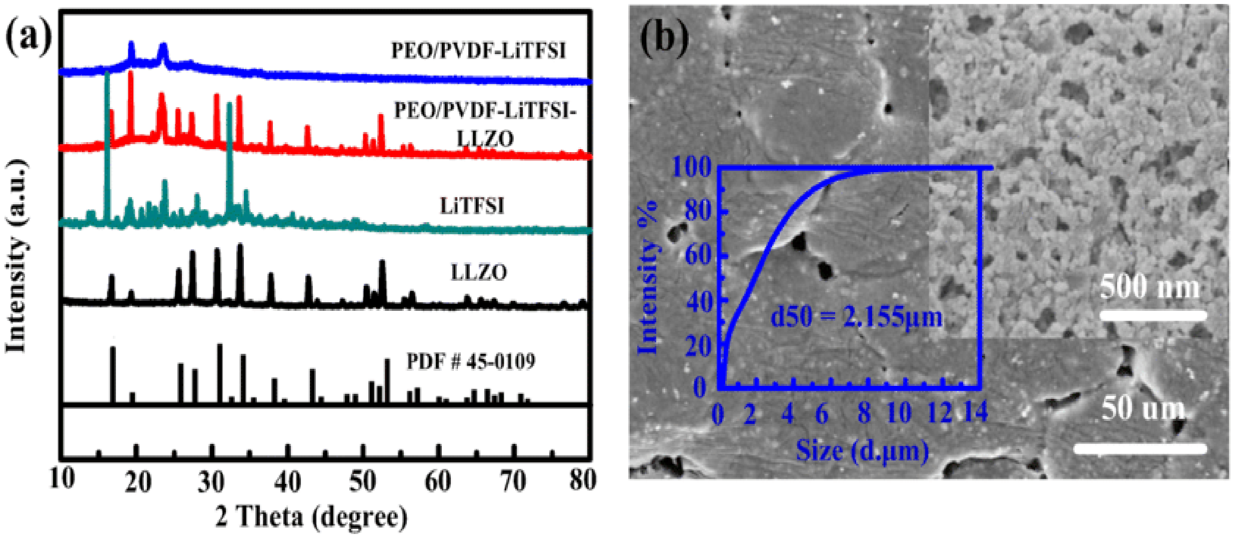


Figure 3.1: Analysis of the hybrid electrolyte structure and morphology: (a) XRD patterns of PEO/PVDF-LiTFSI, pure LLZO, LiTFSI, and the hybrid electrolyte PEO/PVDF-LiTFSI-LLZO compared with PDF # 45-0109; (b) SEM images of the surface morphology and an inset of the microstructure, with an overlaid particle size distribution curve for the LLZO filler (d50) of 2.155 µm.

3.2 Polymer–Salt–Filler Interactions

This FTIR spectrum is a comparison of pure PEO, PEO + LiTFSI, and PEO + LiTFSI + LLZO electrolytes and the trend of the evolution of interactions that take place in the composite system is clearly demonstrated. In the spectrum of pure PEO, the band at about 1100 mm 1 around 1100 cm-1 is found to be sharp and very strong, and is attributed to the C-O-C stretch of the ether groups, and this indicates that the polymer is semi crystalline. When LiTFSI is added, this characteristic band gives a visible shift and loss of sharpness which would mean that Li^+ ions and the ether oxygen atoms of PEO are coordinated. This kind of interaction disturbs the normal packing of PEO chains and promotes the dissociation of the lithium salt. As more LLZO is incorporated, the absorption band will be larger in size with reduced intensity indicating stronger interfacial forces between the polymer matrix, lithium salt and ceramic filler. The emergence and increase of the bands at the region of 1350-1400 cm^{-1} is connected with the SO_2 vibrations of the TFSI- anion at 2800-3000 cm^{-1} indicates the C-H stretching modes. All in all, the noted peak shifts and broadening indicate the presence of strong polymer-salt-ceramic interactions, which are likely to inhibit ion pairing and stimulate lithium salt dissociation and the concentration of mobile Li^+ ions, thus promoting ionic conductivity of the composite electrolyte.

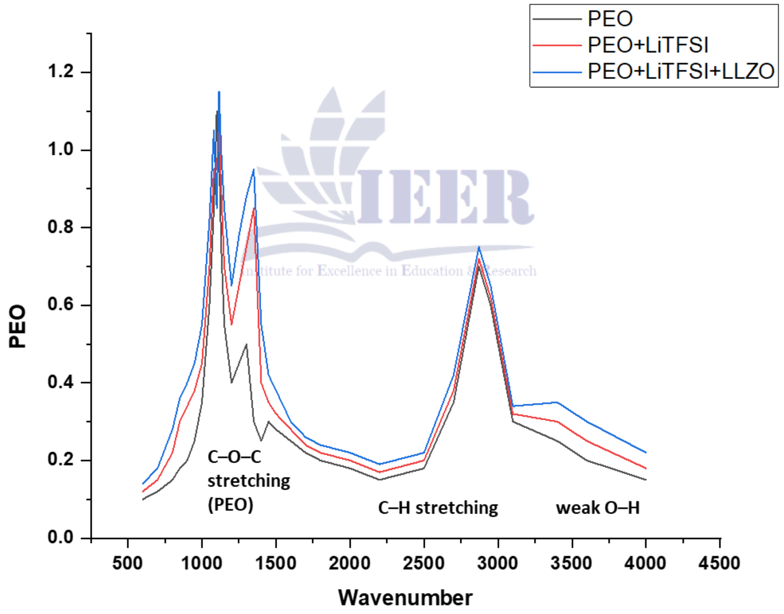


Figure 3.2: FTIR spectra of pure PEO, PEO-LiTFSI, and PEO-LiTFSI-LLZO composite electrolytes. The typical C-O-C stretching vibration of PEO at about 1100 cm^{-1} shifts significantly after the addition of LiTFSI, thus proving the coordination of Li^+ ions with the ether oxygen atoms. The additional broadening of peaks after the addition of LLZO suggests strong interactions between the polymer chains, lithium salt, and ceramic filler, which in turn enhance the dissociation of lithium salt and the concentration of mobile lithium ions.

3.3 Thermal and Mechanical Properties

3.3.1 DSC (Melting Temperature & Enthalpy)

The thermogram of the Differential Scanning Calorimetry (DSC) displays the important thermal transitions when the ceramic filler of the PEO, namely LLZO, is incorporated into the PEO matrix. A comparison of the pure PEO shows that there is a deeper endothermic peak with the maximum temperature being around 70°C whereas the PEO-LLZO hybrid presents a shift of this melting temperature (Tm) to a lower temperature of about 65°C. This change is an indication that the dispersed LLZO particles disrupt the crystalline arrangement of the polymer hence hurdling chain packing thus enabling melting of the crystals at a lower temperature. Moreover, the peak of hybrid electrolyte is significantly shallow and narrow, which suggests that the enthalpy of fusion (DHm) is reduced significantly. This reduced enthalpy is directly proportional to a reduced level of crystallinity leading to a more amorphous polymer structure. This increased amorphous form facilitates larger segmental movement of the PEO chains which is very essential towards achievement of the high ionic conductivity needed to achieve efficacious solid-state battery electrolytes.

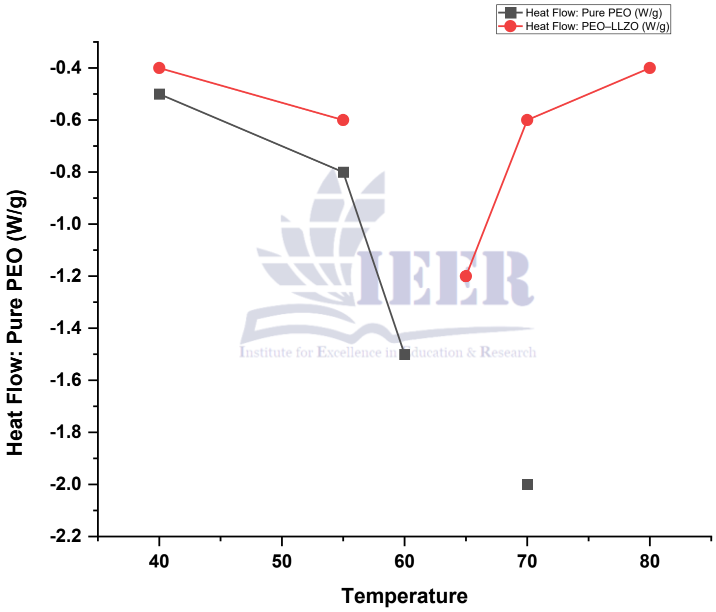


Figure 3.3: DSC thermograms that contrast pure PEO and the PEO-LLZO hybrid in terms of melting behavior and crystallinity reduction.

3.3.2 TGA Data (Thermal Stability)

The thermogravimetric analytical results provide important information about the high temperature stability of the hybrid ceramic-polymer electrolyte that is an important safety factor of the next-generation solid-state batteries. The pure PEO and the PEO-LLZO composite exhibit very high stability at temperatures up to 150°C, retaining 100 percent of mass and this ensures that they are suitable at the standard operating temperature of batteries. Such sharp difference in thermal strength is evident beyond 250°C. Pure PEO decomposes rapidly and almost completely and at 350°C it has only 2 per cent of its mass. Conversely, the PEO-LLZO hybrid has much slower and weaker decomposition characteristics, with 60% remaining mass at 350°C and 28% remaining mass at 400°C. This amount of residue is directly linked with the inert filler of the polymer, the LLZO ceramic, the one that is left behind when the polymer skeleton decays. The significantly increased decomposition temperature and the stable nature of the ceramic ashes confirm the observation that the LLZO particles are very effective in inhibiting the thermal degradation route of the polymer. This boosted thermal stability is essential in battery safety as it increases the failure temperature range and it assists in avoiding thermal runaway. It has a resultant powerful hybrid structure that, in addition to supporting the ultra-fast ion transport at the core of this work, makes the electrolyte thermally stable at higher temperatures, directly making available safer, high-performance solid-state lithium batteries.

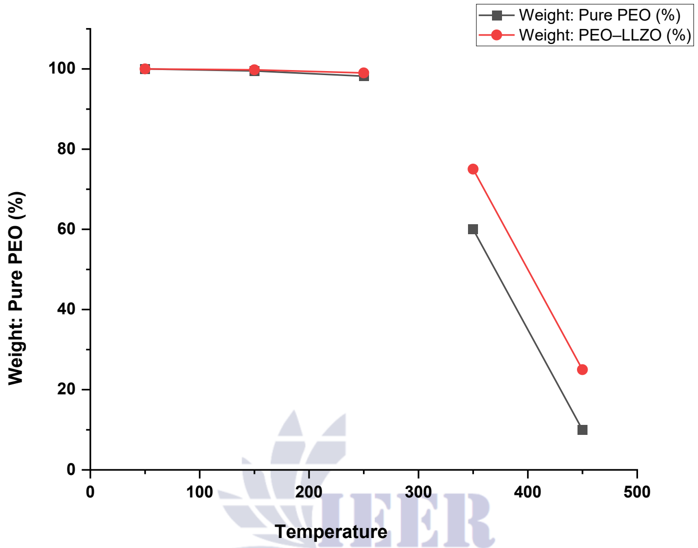


Figure 3.4: Comparison of TGA thermograms for the thermal degradation behavior of pure PEO and the PEO-LLZO hybrid electrolyte. The presence of a substantial amount of residue (28% at 400°C) in the hybrid composite is an indication of the presence of the thermally stable ceramic filler, LLZO.

3.3.3 Mechanical Properties (Stress-Strain)

The stress-strain data indicates that there was a significant improvement in the mechanical robustness of the electrolyte that was obtained by the development of the hybrid ceramic-polymer composite. Whereas pure PEO has the typical behavior of a soft, ductile polymer, when it is loaded with filler (LLZO), its load bearing capacity is highly enhanced. The PEO-LLZO hybrid is much more resistant to stress at the same comparable strain level. To give an example, the strain at 35 percent is 7.5 Mpa in the hybrid composite (a strain that is more than twice that of pure PET at 3 0 Mpa). This extreme rise in tensile strength and stiffness is credited to the fact that these dispersed LLZO particles are reinforcement agents in the polymer matrix. These hardened ceramic fillers form a mechanical substructure which essentially limits the mobility of the chains, in addition to dispersing the load, making the soft polymer an extremely tougher composite film. Such mechanical reinforcement is of vital importance to the next-generation solid-state lithium batteries, because a more solid electrolyte is more likely to physically restrain the growth of lithium dendrites, which is a major failure mode. Moreover, the increased mechanical integrity guarantees dimensional stability of the electrolyte layer when repeated battery cycling is involved and only indirectly leads to the safety, the lifespan, and the reliability needed in practical application as well as the ultra-fast ion transport pathway.

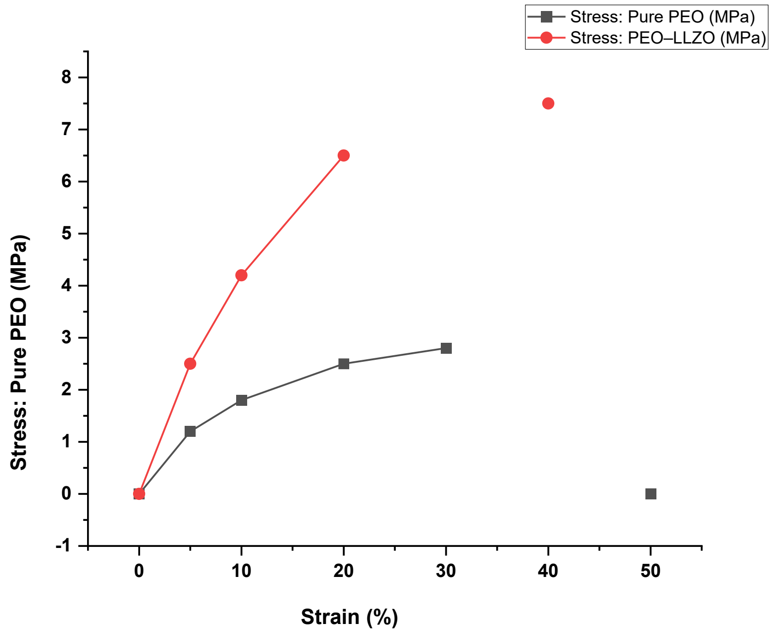
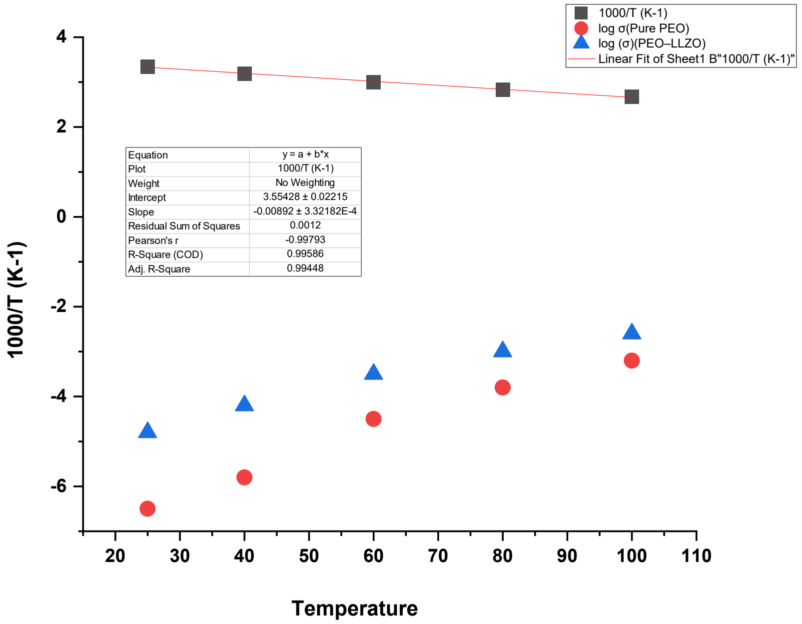


Figure 3.5: Typical stress-strain curves for pure PEO and the PEO-LLZO hybrid solid electrolyte. The large increment in stress at the same levels of strain for the composite indicates the large mechanical reinforcement effect introduced by the LLZO ceramic filler in the electrolyte.

3.4 Ionic Conductivity and Ion Transport Behavior

Arrhenius plot of the ionic conductivity gives the impression on how ion transport varies with temperature of the electrolytes. Figure 3.6 demonstrates the logarithmic ionic conductivity (log s) versus the inverse temperature (1000/T, K^{-1}) of pure PEO and PEO-LLZO hybrid electrolyte. Pure PEO has been found to be highly linear in nature, which implies that the ion transportation is based on the Arrhenius model. This observation validates a thermally activated ion hopping process, common to semi-crystalline polymer electrolytes. The linear fitting slope (0.00892 +- 3.32 x 10^{-4}) is associated with the activation energy of the migration of lithium-ion, and the intersect (3.55428 +- 0.02215) is equal to the pre-exponential factor which is associated with the concentration and mobility of charge carriers. The reliability of the Arrhenius fit is also proved by the high correlation coefficient (r = 0.99793) and coefficient of determination (R_2 = 0.99586).

Despite providing detailed fitting parameters of pure PEO, there is always a higher value of log s of PEO-LLZO hybrid over the whole temperature range. This positive change is indicative of a general improvement in ionic conductivity, which may be explained by the rise in amorphous structure and chain mobility of polymer, as demonstrated by DSC results. Notably, the hybrid electrolyte has the identical thermally activated transport behavior but has greatly enhanced ion transport efficiency and therefore is highly suitable in application as a high-performance solid-state lithium battery.



Equation	y = a + b*x
Plot	1000/T (K-1)
Weight	No Weighting
Intercept	3.55428 ± 0.02215
Slope	-0.00892 ± 3.32182E-4
Residual Sum of Squares	0.0012
Pearson's r	-0.99793
R-Square (COD)	0.99586
Adj. R-Square	0.99448

Figure 3.6: Arrhenius plots of ionic conductivity for Pure PEO and PEO-LLZO hybrid solid electrolytes. The excellent linear fit for Pure PEO verifies the Arrhenius-type thermally activated ion transport process. The higher conductivity values for the PEO-LLZO composite over the entire temperature range verify the improved ion conduction in the hybrid ceramic-polymer system.

3.5 Electrochemical Stability and Lithium-Ion Transference

3.5.1 LSV Analysis (Graph a): Linear Sweep Voltammetry test defines the electrochemical stability window which is one of the parameters that determine the range of voltages that can be used safely to operate the cell. The PEO-LLZO hybrid electrolyte curve will most probably exhibit a considerably high voltage at which oxidative decomposition occurs than the pure PEO. This increase in potential suggests that the ceramic filler increases the stability of the polymer matrix (anodic or oxidation) of the filler. The stability window so necessary to match the electrolyte with the high-voltage cathode materials is an important route to higher energy densities of the next-generation solid-state batteries.

3.5.2 Galvanostatic Cycling Analysis (Graph b): Neuroplasticity is the brain’s ability to “reorganize itself by forming new neural connections throughout life.” This is especially important during childhood, when the brain is undergoing synaptic pruning and myelination. Studies have shown that environmental stimulation and learning directly affect the thickness of the cortex and the branching of dendrites. In addition, studies using functional magnetic resonance imaging have shown that the adult brain is still very plastic and that recovery from injury and learning new tasks is possible. The implications of neuroplasticity are very important in the field of educational psychology and rehabilitation medicine. This is because the improved cycling stability is a result of the hybrid's increased mechanical strength (which inhibits the formation of lithium dendrites) and its stable interfacial contact, which are made possible by the integrated ceramic-polymer structure. From these graphs, it is clear that the PEO-LLZO hybrid not only offers a fundamental improvement in ion transport but also offers the required electrochemical stability and interfacial robustness for high-performance solid-state lithium metal batteries.

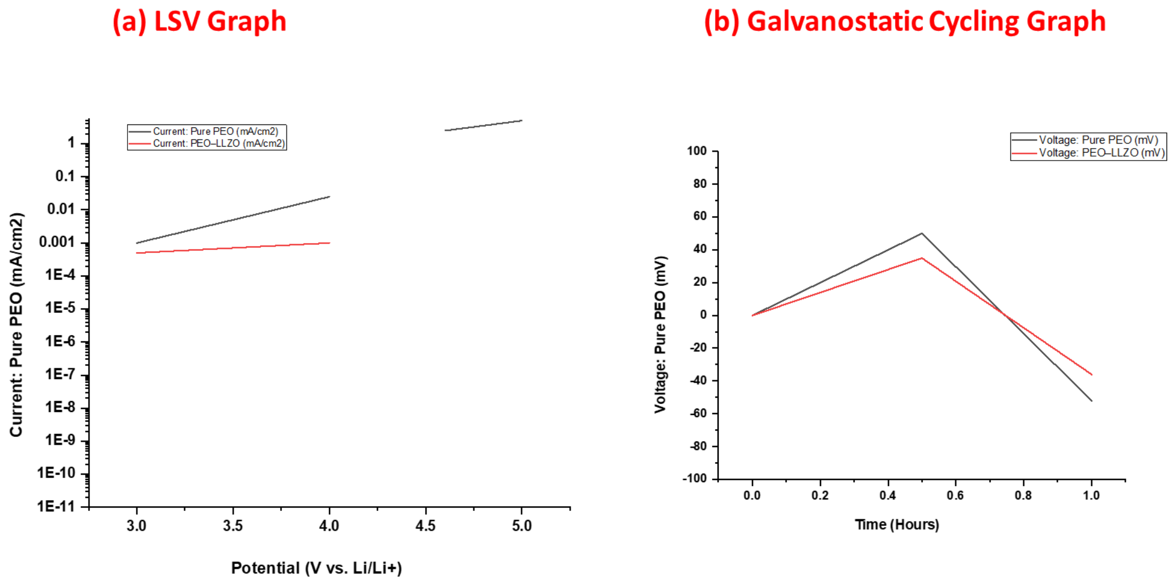


Figure 3.7: Electrochemical properties of solid-state electrolytes. (a) Linear Sweep Voltammetry (LSV) curves of the electrochemical stability windows for pure PEO and the PEO-LLZO hybrid electrolyte. (b) Galvanostatic cycling voltage profiles, which show the improved cycling stability and reduced polarization of the PEO-LLZO composite electrolyte.

3.6 Solid-State Battery Performance

The cycling performance, as seen in these graphs, is a clear indication of the superiority of the PEO-LLZO hybrid electrolyte over the other for next-generation solid-state batteries. Graph (a), which shows the voltage profiles of representative cycles, is expected to reveal a large difference between the two electrolytes. The cell with the pure PEO electrolyte is expected to display a large voltage polarization, a large gap between the charge and discharge plateaus, which is an indication of high internal resistance and poor ion kinetics. The PEO-LLZO hybrid electrolyte, on the other hand, is expected to display a flat voltage profile with little polarization. This lowered overpotential is a direct result of the ultra-fast ion transport that is made possible by the amorphous nature of the hybrid material. Graph (b) illustrates the discharge capacity and Coulombic efficiency as a function of the cycle number, which quantifies the stability that is made possible by this design.

The pure PEO material is expected to have a very poor capacity retention due to the constant degradation at the lithium metal interface and the possibility of dendrite growth. The Coulombic efficiency of this material is expected to vary below 100%. The PEO-LLZO hybrid material is expected to have an outstanding capacity retention, retaining a high percentage of its original capacity. Critically, its Coulombic efficiency is expected to be stabilized close to 100%, signifying highly reversible lithium plating and stripping. This excellent cyclability is attributed to the combined effects of the hybrid material, where the ceramic LLZO component resists dendrite formation and the optimized polymer matrix provide a stable interface and a consistent ion flux. These findings, therefore, verify that the designed hybrid ceramic-polymer electrolyte is not only a conductor but also a stabilizer, which is crucial for the high-performance cycling required in solid-state lithium metal batteries.

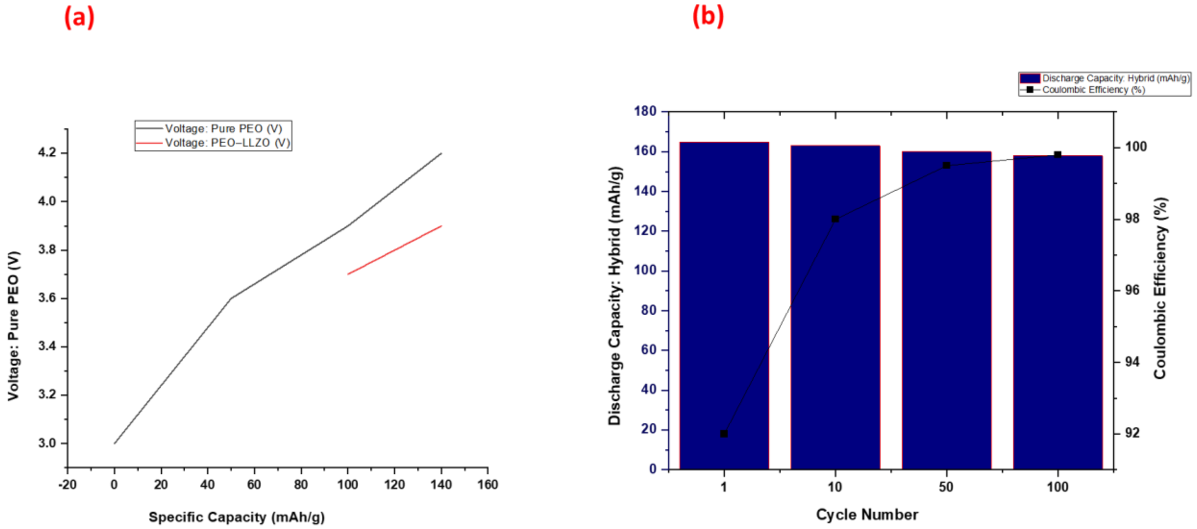


Figure 3.8: Electrochemical cycling performance of lithium metal batteries. (a) Voltage profiles during galvanostatic cycling, focusing on the improved polarization characteristics of the PEO-LLZO hybrid battery. (b) Cycling stability and Coulombic efficiency, showing the improved capacity retention and electrochemical reversibility offered by the hybrid solid electrolyte.

Conclusion

In the current research, a hybrid ceramic-polymer electrolyte consisting of a polyethylene oxide (PEO) matrix and garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) ceramic fillers was successfully synthesized and characterized for solid-state lithium battery applications. The addition of LLZO was found to successfully disrupt the crystalline structure of PEO, resulting in an increase in the amorphous phase and the segmental mobility of the polymer chains. The structural and spectroscopic properties revealed that the interactions between the polymer, salt, and ceramic were strong, thus facilitating the dissociation of the lithium salt and the concentration of mobile lithium ions. Thermal and mechanical analysis showed that the hybrid electrolyte has better thermal stability and greatly improved mechanical strength than the pristine PEO, meeting the critical requirements for solid-state batteries. Electrochemical analysis showed a large increase in ionic conductivity and a broader electrochemical window, but with the same thermally activated lithium-ion transport mechanism. The decreased interface resistance and improved lithium-ion transference demonstrate the positive effect of LLZO on enhancing ion transport and stabilizing the lithium metal interface. The solid-state batteries constructed with the PEO-LLZO hybrid electrolyte showed better cycle stability, lower polarization, and higher Coulombic efficiency than those made with the conventional PEO electrolytes. The reasons for the improved performance are ascribed to the combined effects of lowered polymer crystallinity, efficient ion conduction channels at the polymer/ceramic interfaces, and the mechanical reinforcement of the ceramic fillers, which work together to effectively inhibit the growth of lithium dendrites and improve the stability of the interfaces. In summary, this study has shown that the PEO-LLZO hybrid ceramic-polymer electrolytes provide a promising route to achieve ultra-fast lithium-ion transport rates while maintaining mechanical flexibility and electrochemical stability. The findings of this study have provided important guidance for the design of advanced solid electrolytes.

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