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Research article

Design of hybrid nanocomposite solid polymer electrolytes using nano lithium salt for enhanced ionic transport in solid-state lithium batteries

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ABSTRACT

Solid polymer electrolytes with high ionic conductivity, dominant ion transport, and long-term electrochemical stability are essential for next-generation solid-state lithium batteries. In this study, a fully hybrid nanocomposite solid polymer electrolyte based on poly(ethylene oxide) (PEO), POSS-benzyl$_7$(BF_3Li)$_3$ nano lithium salt, and POSSPEG$_{13.3}$ nano plasticizer is developed using solution casting technique, in which both the salt and plasticizer possess organic–inorganic hybrid architectures. The optimized electrolyte containing 40 wt% POSSPEG$_{13.3}$ exhibits a high room-temperature ionic conductivity of 8.64×10^{-4} S cm^{-1} and follows Vogel–Tammann–Fulcher (VTF) behavior. Structural and thermal analyses reveal near-complete suppression of PEO crystallinity (~1%) and good thermal stability up to ~235 °C. The electrolyte shows excellent mechanical flexibility and a near-unity ion transference number ($t_{ion} = 0.99$). A wide electrochemical stability window of ~4.7 V vs. Li/Li$^+$ is obtained. Solid-state $LiFePO_4$/Li cells deliver an initial discharge capacity of 169.3 mAh g^{-1} at 0.1 C with 89.8% capacity retention after 100 cycles. These results demonstrate the effectiveness of the fully hybrid electrolyte design for solid-state lithium batteries.

1. Introduction

The consecutively accelerating development of portable consumer electronics, electric vehicles, and grid-scale energy storage systems has strengthened the worldwide demand for higher-performance electrochemical power sources that offer higher energy density, a long cycle lifetime, and safer operation. Lithium ion batteries (LIBs) currently represent the most successful type of electrochemical power storage systems because of their ability to offer a wide operating voltage associated with a high gravimetric and volumetric energy density as well as a rather convenient cycling behavior [1,2]. Nevertheless, the continued use of liquid electrolytes that consist of a solution of lithium salts and organic solvents that are volatile at the values of typical operating temperatures poses essential challenges associated with the safety of LIB power sources. These organic media are inherently flammable and volatile, so they pose a challenge of leakage during transportation and storage as well as exhibit an increased danger of self-combustion because of the internal heating associated with the possible fractures and discharges within the organic materials during the operation of LIB devices under the possible mechanical, electric, or heating abuse [3]. Thereupon, the development of solid-state materials as a replacement for the existing liquid electrolyte materials represents a most important goal concerning the development of advanced LIB materials.

Among the developed solid-state LIB materials, solid polymer electrolytes (SPEs) exhibit most attractive features concerning safety aspects because of additional flexibility, reduced weight, and possible simple processing of the respective materials [4]. Furthermore, these materials are capable of efficiently inhibiting the growth of Li dendrites that would often lead to the prerequisite of employing a more safety-critical lithium metallic electrodes during the operation of LIB materials. This would further allow the development of LIB materials associated with significantly higher theoretical storage densities [5]. Nevertheless, the major drawback of traditional SPEs is their generally poor room-temperature ionic conductivity (10^{-7}–10^{-6} S cm^{-1}), limiting the use

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of SPEs in power batteries. Such poor conductivity is mainly due to the ionically coupled dynamics between the polymer segments [6]. Although salt-loading modifications of the polymer components of the SPEs by blending with materials using plasticizers or inorganic nanoparticles has garnered great interest for enhancing the conductivity of SPEs. It should be added that the doping of SPEs with liquid plasticizers often causes instability of mechanical properties or thermal conductivity. Moreover, inorganic nanoparticles doping causes particulate-sized aggregates that often impede the uniform ion conduction paths [7]. Such issues reaffirm the need for the development of new materials that combine multiple functions of enhanced ionic conductivity in the same substance.

Poly(ethylene oxide) (PEO) is the most widely researched polymer electrolyte host for solid polymer electrolytes because of its highly efficient ability to solvate lithium salts due to coordination interactions between lithium ions and the oxygen atoms of the ether groups. This allows for highly efficient dissociation of the salts as well as ion mobility, making PEO a gold standard for SPE studies. Additionally, PEO shows excellent film-forming capabilities, low glass transition temperatures, chemical stability, as well as state-of-the-art miscibility with lithium metal electrodes. Among other types of polymer electrolyte hosts such as poly(vinylidene fluoride), poly(methyl methacrylate), poly(acrylonitrile), as well as polycarbonates, PEO demonstrates pronounced ion solvation capabilities in addition to well-known advantages in processing [8,9]. However, the pronounced crystallinity of PEO at room temperatures drastically restricts its mobility at a molecular (polymer chain) level as well as ionic conductivity. While attempts to reduce these crystallinity levels in PEO using conventional lithium salts, liquid plasticizers, as well as ceramic powders have been to a certain extent successful, in some respects, at the cost of tensile strength, interfacial integrity, or electrocyclic stability [10,11].

The lithium salt is a key factor deciding the characteristics of ion transport and stability for polymer electrolytes. Existing lithium salts, including $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, and LiTFSI, which are commonly utilized because of their high solubility and reasonable conductivity, still have inherent limitations making them less suitable for solid-state batteries. In particular, $LiPF_6$ is less thermally stable, decomposing to produce corrosive HF even when a small amount of moisture is absorbed, while $LiClO_4$ is extremely dangerous because of its strong oxidation property. In addition, $LiAsF_6$ is extremely toxic to living organisms, while LiTFSI, despite being stable at high temperatures, is corrosive to aluminum thin film electrodes and poorly compatible with a lithium metal electrode [12,13]. Moreover, these molecular salts still have the disadvantages of incomplete dissociation and appreciable ion pairing at a high concentration, making it difficult to achieve a high lithium transference number and concentration polarization. The need to explore new architectures for lithium salts with improved characteristics for dissocation, thermal stability, and interfacial compatibility is thus clearly indicated.

In this respect, polyhedral oligomeric silsesquioxane (POSS)-lithium salts stand out as a revolutionary leap forward in the design of electrolytes' material components. Specifically, POSS-benzyl$_7$(BF_3Li)$_3$ was the first member of this family synthesized by the Wunder research group and marks a trailblazing category of organic-inorganic hybrids nano lithium salts [14]. In this molecule, there is a rigid Si-O three-dimensional cage with lithium salts of BF_3 groups and organic benzyl groups bonded to it. The unique feature of this material is that it has a dual character as both organic and inorganic molecules with numerous critical advantages compared to traditional salts. In fact, the nanostructure of the POSS molecules improves their dispersion properties throughout the polymer electrolytes' matrix and prevents the salts' aggregation and accumulation at certain sites. In this way, ion dissociation is facilitated. Additionally, the immobilization of the anionic part limits the movement of anionic molecules toward the interface; hence, the transference number of lithium ion transport is increased, and concentration polarization effects diminish accordingly. On the other hand, the rigid inorganic Si-O three-dimensional core provides the molecule with extraordinary thermal and mechanical strength, whereas the organic benzyl groups improve the compatibility of these salts with their hosts composed of macromolecules like PEO [15,16].

Apart from lithium salts, plasticizers, along with fillers, are important for the regulation of dynamics in polymers as well as ionic transfer. Traditional liquid plasticizers enhance ionic conductivity but compromise mechanical and thermal properties, where inorganic fillers often lack effective dispersion with low electrochemical activity. To mitigate these issues, hybrid nano plasticizers based on POSS–PEG have been introduced as effective additives, where plasticization, reinforcement, and nano modification can be achieved using a single compound. POSS-PEG, a hybrid molecule, possesses a sturdy inorganic silsesquioxane backbone with flexible polyethylene glycol moieties, thereby facilitating increased amorphous regions, increased segmental dynamics, and enhanced mechanical strength. For example, unlike liquid plasticizers, POSS-PEG is nonvolatile with an immobilized structure within the polymer matrix, thus no chance of leakage or migration. Also, hybrid molecules like POSS-PEG possess effective dispersion with high interfacial compatibility [17,18]. In this work, we demonstrate a fully hybrid PEO–POSS-benzyl$_7$(BF_3Li)$_3$–POSSPEG$_{13.3}$ nanocomposite solid polymer electrolyte (NSPE), where both the lithium salt and plasticizers are organic-inorganic hybrid nano-materials. The hybrids help present reduced crystalline structures, inhibit ion-pairs, and facilitate nanoscale ionic conductivity channels, thus resulting in an optimized overall ionic conductivity, mechanical strength, and high electrochemical stability. The proposed electrolyte system is an important advancement in establishing safe, high-performance solid-state Li-ion batteries.

2. Materials and methods

2.1. Materials used

Poly(ethylene oxide) (PEO, average molecular weight (Mw) $\approx 4 \times 10^6$ g mol^{-1}), boron trifluoride diethyl etherate ($BF_3{\cdot}O(C_2H_5)_2$), dichloromethane (CH_2Cl_2) and acetonitrile (CH_3CN) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Poly(ethylene glycol)–functionalized polyhedral oligomeric silsesquioxane (POSSPEG$_{13.3}$; average molecular weight = 5576.6 g mol^{-1}; PEG1190) and trisilanol phenyl POSS lithium salt (POSS–benzyl$_7$Li$_3$; $C_{42}H_{35}Li_3O_{12}Si_7$; molecular weight = 949.15 g mol^{-1}) were obtained from Hybrid Plastics (Hattiesburg, MS, USA). All chemicals were used as received without further purification.

2.2. Synthesis of POSS-benzyl$_7$(BF_3Li)$_3$

POSS-benzyl$_7$Li$_3$ was first dried in a vacuum oven at 80 °C for 34 h. After removal of the water, it was dissolved in anhydrous dichloromethane. A stoichiometric equivalent of boron trifluoride diethyl etherate ($BF_3O(C_2H_5)_2$) was then added slowly to the POSS-benzyl$_7$Li$_3$ solution under argon atmosphere at 25 °C. The reaction mixture was stirred for 1 h, whereupon a white precipitate was formed. The precipitate was then filtered, washed with an excess of dichloromethane, and then dried in a vacuum oven at 80 °C for 24 h. However, due to its hygroscopic properties, the synthesized compound, namely, POSS-benzyl$_7$(BF_3Li)$_3$, had to be stored in an argon environment in an argon-filled glovebox. Structural characterization was done with Fourier transform infrared (FTIR) analysis, wherein the spectrum was found to be similar to that previously documented by the Wunder group [14]. Fig. 1 shows the reaction scheme for the synthesis of POSS-benzyl$_7$(BF_3Li)$_3$, along with the FTIR spectrum of the compound.

2.3. Synthesis of PEO:POSS-benzyl$_7$(BF_3Li)$_3$ and PEO:POSS-benzyl$_7$(BF_3Li)$_3$:POSSPEG$_{13.3}$ nanocomposite solid polymer electrolytes

Nanocomposite solid polymer electrolytes based on nanometer-sized particle composites were prepared with solution casting method. Before

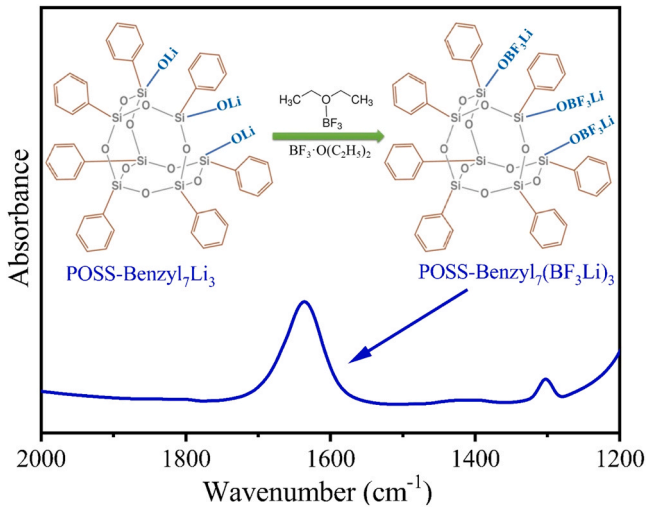

Fig. 1. Schematic illustration of synthesis of POSS-benzyl$_7$(BF$_3$Li)$_3$ lithium salt and its FTIR spectrum.

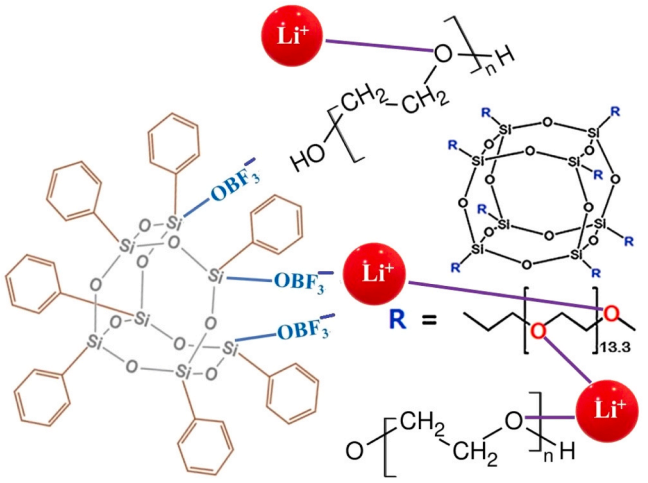

Fig. 2. The interaction among PEO polymer, POSS-benzyl$_7$(BF$_3$Li)$_3$ lithium salt and POSSPEG$_{13.3}$ nano plasticizer.

usage, poly(ethylene oxide) (PEO), POSSPEG$_{13.3}$ hybrid nanoparticle, and POSS-benzyl$_7$(BF$_3$Li)$_3$ lithium salt were subjected to drying under vacuum conditions for 24 h at 50°C, 50°C, and 80°C, respectively, in order to remove the residual moisture. Solid polymer electrolyte films with varying ethylene oxide groups to lithium (EO:Li) molar ratios from 20:1–10:1 were synthesized using binary PEO:POSS-benzyl$_7$(BF$_3$Li)$_3$ system. Certain quantitative proportions of PEO and POSS-benzyl$_7$(BF$_3$Li)$_3$ salt were separately dissolved in anhydrous acetonitrile. These two solutions were then mixed and stirred for 24 h at room temperature to create a homogeneous viscous solution of polymer and salt.

For the preparation of ternary PEO:POSS-benzyl$_7$(BF$_3$Li)$_3$:POSSPEG$_{13.3}$ nanocomposite electrolytes, the EO/Li ratio was fixed at 14:1, based on the molar ratio between the ethylene oxide (EO) units of PEO and the lithium ions of the POSS lithium salt, as the EO/Li = 14 composition exhibited optimum ionic conductivity. Subsequently, various weight percentages (0, 10, 20, 30, 40 wt%) of POSSPEG$_{13.3}$ were added to the binary electrolyte solution. The resulting mixture was stirred continuously for 24 h at 50 °C to ensure uniform dispersion of the hybrid nanoparticle and formation of a homogeneous viscous solution. The prepared solutions were cast onto Teflon plates and allowed to evaporate slowly in a dry box for approximately 24 h. The resulting free-standing films were further dried in a vacuum oven at 40 °C for 24 h and then transferred to a nitrogen-filled glovebox, where they were stored for five days to completely remove residual acetonitrile.

From among the prepared electrolyte films, the one with the concentration of 40 wt% of POSSPEG$_{13.3}$ with good mechanical stability and homogeneity in the film-forming process. It was found that concentrations higher than 40 wt% produced mechanically unstable films which made them impossible to use for any characterizations. Therefore, 40 wt% was chosen as the optimal concentration sample. The interaction among PEO polymer, POSS-benzyl$_7$(BF$_3$Li)$_3$ lithium salt and POSSPEG$_{13.3}$ nano plasticizer is shown in Fig. 2.

2.4. Characterization

The formation of the POSS-benzyl$_7$(BF$_3$Li)$_3$ lithium salt was confirmed by Fourier transform infrared (FTIR) spectroscopy using a Nicolet 380 FT-IR spectrometer (Thermo Electron) in the wavenumber range of 4000–400 cm^{-1} with a spectral resolution of 1 cm^{-1} .

The electrochemical impedance spectroscopy (EIS) measurements were performed with the Iviumstat analyzer (Ivium Technologies, Netherlands) to determine the ionic conductivity of the films of the polymer electrolytes. The Nyquist plots were obtained within a frequency range from 1 Hz to 1 MHz with a temperature range from 23 to 60 °C. The measurements were done by sandwiching the films of the NSPE between gold electrodes with a constant spring pressure. The thickness of the films was determined using the micrometer screw gauge, and accordingly, the ionic conductivity was computed.

The X-ray diffraction (XRD) analysis of the polymer electrolyte films was carried out using a Rigaku D-MAX 2500 X-ray diffractometer with Cu Kα radiation (λ=1.5406 Å). The diffraction data was recorded at room temperature for a 2θ range of 10° to 50°. Thermal analysis was carried out using the differential scanning calorimetry (DSC) technique with a TA Instruments MDSC 2910 calorimeter. About 3–5 mg of the sample was placed in a hermetically sealed aluminum pan in a dry room and heated from 0 to 100 °C at a rate of 10 °C min^{-1} in a nitrogen atmosphere. Thermogravimetric analysis (TGA) was also carried out using a TA Instruments TGA−2950 analyzer. About 7 mg of sample was heated from 25 to 500 °C at a rate of 20 °C min^{-1} in a nitrogen atmosphere. The mechanical strength of the nanocomposite solid polymer electrolyte films was tested with a universal testing machine (Lloyd Instruments, LR5K Plus).

The ion transference number was measured by the chronoamperometric method. The NSPE thin film was positioned between two stainless-steel ion-blocking electrodes, with a 1 V fixed DC bias applied for 1 h. Linear Sweep Voltammetry (LSV) was carried out for the measurement of the electrochemical stability window of the deposited NSPEs with a WonATech WBCS 3000 L battery cycler at a scanning speed of 5 mV/s in a voltage scan limit of 1–7 V vs. Li$^+$/Li with a stainless steel working electrode and a lithium metal counter/reference electrode. Cyclic voltammetric analysis was carried out under the identical setup in a Li/NSPE/Li symmetric cell in a potential window of −1–5 V at a scanning speed of 5 mV/s.

The electrochemical property of the NSPE film with 40 wt% POSSPEG$_{13.3}$ was investigated with CR2032-type coin cells. The cathode slurry consisted of 80 wt% active material LiFePO$_4$, 10 wt% Super P conductive carbon (TIMCAL), and 10 wt% poly(vinylidene difluoride) (PVDF, Kureha KF100) binder in N-methyl−2-pyrrolidone (NMP) solution. After grinding the slurry evenly for 15 min in a mortar, it was deposited on aluminum foil substrates, which were used as current collectors. The resulting electrodes were then dried at 100 °C for 5 h. Metallic lithium foil served as both the counter and reference electrode in the cells. The galvanostatic charge-discharge cycle voltage ranged from 2.4 V to 4.2 V vs. Li/Li$^+$ with a WonATech WBCS 3000 L high-precision battery cycler.

3. Results and discussion

Fig. 3 shows the Cole–Cole (Nyquist) plots of the PEO:POSS-benzyl$_7$(BF$_3$Li)$_3$ solid polymer electrolytes with 0 wt% and 40 wt% POSSPEG$_{13.3}$. These plots clearly show how the hybrid nano plasticizer affects ion transport behavior at an EO/Li ratio of 14. The impedance spectrum for the 0 wt% POSSPEG$_{13.3}$ electrolyte shows a depressed semicircle in the high-to-medium frequency range, followed by an inclined spike in the low frequency range. The semicircle corresponds to the bulk resistance (R_b) arising from ion transport within the polymer matrix, coupled with bulk capacitance. Based on the impedance spectra, the pristine electrolyte (0 wt%) exhibited a bulk resistance of approximately 70 Ω. The presence of a pronounced semicircle and higher Z′ intercept indicates higher bulk resistance, which is mainly attributed to the semi-crystalline nature of PEO and restricted segmental motion of polymer chains. The low-frequency spike shows how the electrode and electrolyte interact with each other, which is common for ion-blocking electrodes [19].

The 40 wt% POSSPEG$_{13.3}$ nanocomposite electrolyte, on the other hand, exhibits a notable leftward shift of the Nyquist plot with a dominant linear spike and a much smaller or almost suppressed semicircle and showed a significantly reduced bulk resistance of approximately 14 Ω. By adding POSSPEG$_{13.3}$, PEO crystallinity is disrupted, amorphous phase content is increased, and flexible PEG chains are produced, which facilitate faster segmental dynamics and better Li ion mobility. Furthermore, POSS's organic–inorganic hybrid structure facilitates continuous ion-conduction pathways and homogeneous salt dissociation [20]. The bulk resistance derived from the Z′-axis intercept is used to calculate the ionic conductivity (σ) of the polymer electrolytes using the following relation:

$$\sigma = \frac{t}{R_b A}$$

Where t is the thickness of the electrolyte film, R_b is the bulk resistance, and A is the electrode–electrolyte contact area. The enhanced ionic conductivity, which confirms the positive effect of the hybrid nano plasticizer in high-performance nanocomposite solid polymer electrolytes, is the direct consequence of the lower R_b for the 40 wt% POSSPEG$_{13.3}$ sample.

The ionic conductivity of PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$ solid polymer electrolytes is represented in Fig. 4 as a function of the concentration of POSS-benzyl$_7$(BF$_3$Li)$_3$ salt at ambient temperature (23 °C). Pure PEO is characterized by a very low ionic conductivity of 3.95×10^{-9} S cm^{-1}, which is indicative of its high crystallinity and low segmental motion at room temperature. When the POSS-benzyl$_7$(BF$_3$Li)$_3$ salt is added, a very pronounced increase in ionic conductivity by almost five orders of magnitude occurs, and the maximum value of 1.34×10^{-4} S cm^{-1} is reached at an EO/Li ratio of 14. This remarkable conductivity increase is a result of both the thorough dissociation of the salt and excellent coordination between Li$^+$ ions and ether oxygen atoms in the PEO chains; the latter facilitates ion movement by a coordination-decoordination mechanism. The first rise in conductivity as the salt content increases is due to the combined effects of higher charge carrier concentration and partial suppression of PEO crystallinity, leading to an expanded amorphous region that is conducive to ion migration. In addition, the presence of the bulky organic–inorganic POSS framework reduces ion pairing and promotes uniform distribution of Li$^+$ ions. On the contrary, when the chosen EO/Li ratio of 14 is exceeded, the ionic conductivity starts to fall again as a result of the overabundant salt which causes strong Li$^+$–anion interaction, ion aggregation, and temporary cross-linking among the polymer chains that result in poor flexibility of the polymer chain [21]. Therefore, EO/Li= 14 signifies an ideal trade-off between the concentration of mobile ions and the dynamics of polymer segments, hence the maximum ionic conductivity.

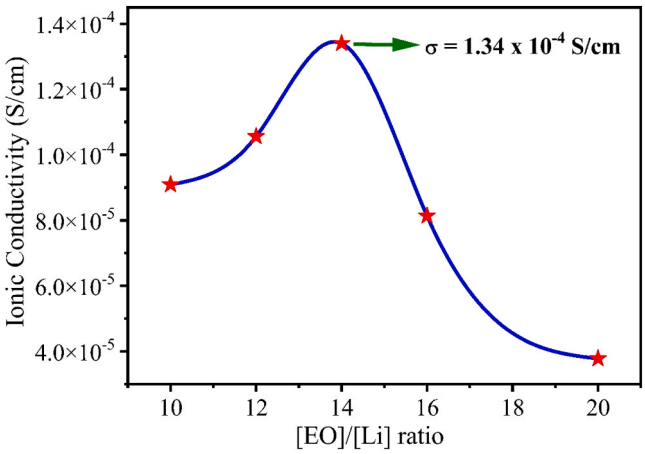

Fig. 4. Variation of ionic conductivity of PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$ solid polymer electrolytes with EO/Li ratio.

In Fig. 5, the dependence of ionic conductivity on the content of the POSSPEG$_{13.3}$ nano plasticizer used in the PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$ salt electrolytes at a fixed EO/Li ratio of 14 at 23 °C is shown. The optimized salt-containing electrolyte without nano plasticizer has an ionic conductivity of 1.34×10^{-4} S cm^{-1}. The increase in the

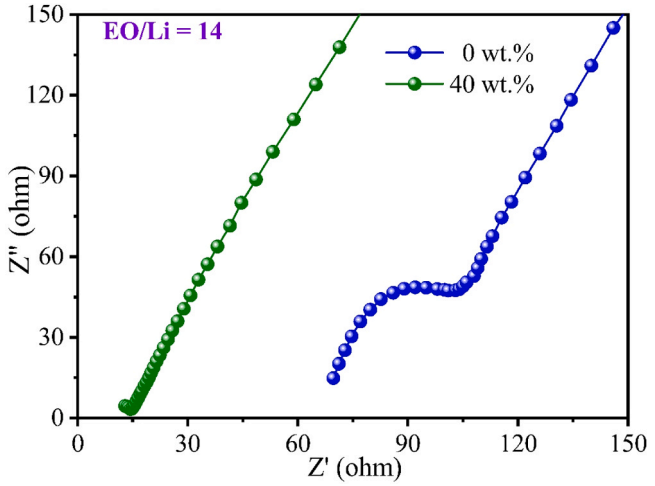

Fig. 3. Cole-Cole plots of PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$ solid polymer electrolytes with 0 wt% and 40 wt% POSSPEG$_{13.3}$.

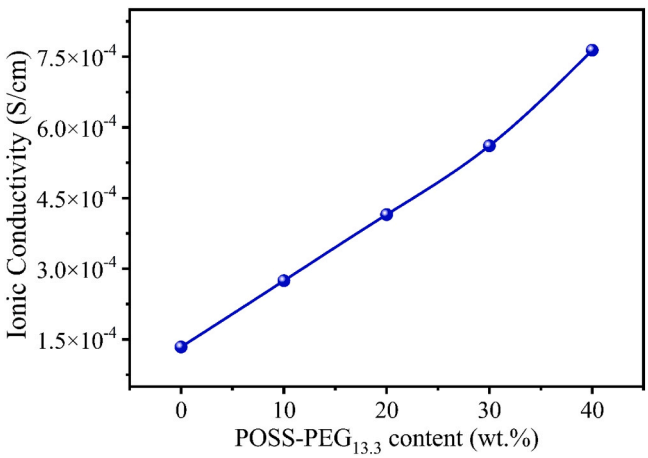

Fig. 5. Variation of Ionic conductivity with POSS-PEG13.3 content at EO/Li = 14.

concentration of $POSSPEG_{13.3}$ resulted in a continuous increase of ionic conductivity, and the maximum ionic conductivity of 8.64×10^{-4} S cm^{-1} was achieved at 40 wt%. This value represents around 6.4 times conductivity improvement over the salt-only system. The obtained ionic conductivity value is higher than those reported for previously studied PEO-based polymer electrolyte systems presented in Table 1. The enormous gain in ionic conductivity is ascribed to the efficient nano plasticizing effect of $POSSPEG_{13.3}$. The soft PEG chains greatly reduce PEO crystallinity, enlarge the free volume, and promote the mobility of polymer segments, which in turn, facilitates Li^+ ion hopping directly. At the same time, the strong inorganic POSS cage guarantees the uniform distribution of the nano plasticizer and the preserving of the structural integrity that would prevent the occurrence of phase separation. The combined organic–inorganic hybrid structure that works in synergy boosts the dissociation of salt and the formation of continuous ion-conduction pathways all over the polymer matrix [21]. Thus, the mobility of Li^+ ions is greatly enhanced, and this proves that utilizing the combination of POSS-benzyl$_7$(BF_3Li)$_3$ salt and $POSSPEG_{13.3}$ nano plasticizer is an excellent way of attaining high ionic conductivity at room temperature.

The plot in Fig. 6 illustrates how the ionic conductivity of PEO–POSS-benzyl$_7$(BF_3Li)$_3$ salt solid polymer electrolytes containing 0, 30, and 40 wt% $POSSPEG_{13.3}$ changes with temperature, with the values being logarithmic (log(σ)) versus the reciprocal of temperature multiplied by 1000 (1000/T) format. It is clearly seen that the temperature sensitivity of ionic conductivity adheres to a typical VTF pattern, the non-linear curve being a hallmark of the situation where the ion transport in amorphous polymer electrolytes is tightly knit with that of the polymer mobility. In PEO systems, the Li^+ ions move through a sequence of coordination–decoordination processes involving the ether oxygen atoms aligned with the polymer backbone. Thus, polymer flexibility becomes the decisive factor in ionic conductivity.

The solid polymer electrolyte made solely from PEO and without any addition of $POSSPEG_{13.3}$ (0 wt%) shows the least ionic conductivity throughout the whole studied temperature range because of PEO's high crystallinity. Such a situation suppresses the segmental motion and, hence, the Li^+ ion mobility. The rising temperature speeds up the melting of the crystalline domains partially, increases the motion of the polymer chains, and thus leads to a continuous rise in ionic conductivity. On the other hand, the electrolytes with 30 wt% and 40 wt% $POSSPEG_{13.3}$ are much more conductive at all temperatures, with the sample containing 40 wt% $POSSPEG_{13.3}$ in particular showing the highest conductivities. The use of $POSSPEG_{13.3}$ renders the PEO crystals effectively inert, creating more free spaces, and increasing the amorphous phase fraction such that the segmental relaxation that involves ion mobility is faster. The less curvature and the higher conductivity that come with increasing $POSSPEG_{13.3}$ content point to a tight coupling between ionic transport and polymer dynamics [22,23].

Table 1
Ionic conductivity values of various PEO based polymer electrolytes.

S. No.	Polymer Electrolyte System	Ionic Conductivity	Reference
1	PEO-LiTFSI-TCE	1.14×10^{-4} S/cm at 25 ∘C.	[8]
2	PEO/PEG-$NaClO_4$- $Na_3Zr_2Si_2PO_{12}$	4.42×10^{-4} S/cm at 60 °C	[9]
3	PEO-$NaClO_4$-$POSSPEG_{13.3}$	1.02×10^{-4} S/cm at 30 ∘C	[16]
4	PEO-LiDFOB-$POSSPEG_4$	1.15×10^{-4} S/cm at 30 °C	[17]
5	PEO-LiDFOB-$POSSPEG_{13.3}$	1.41×10^{-5} S/cm at 30 °C	[18]
6	PEO-LiTFSI-$POSSPEG_{13.3}$	5.05×10^{-5} S/cm at 23 °C	[20]
7	PEO-LiTDI-$POSSPEG_4$	2.23×10^{-5} S/cm at 23 °C	[21]
8	PEO-POSS-benzyl$_7$(BF_3Li)$_3$-$POSSPEG_{13.3}$	8.64×10^{-4} S/cm at 23 °C	Present

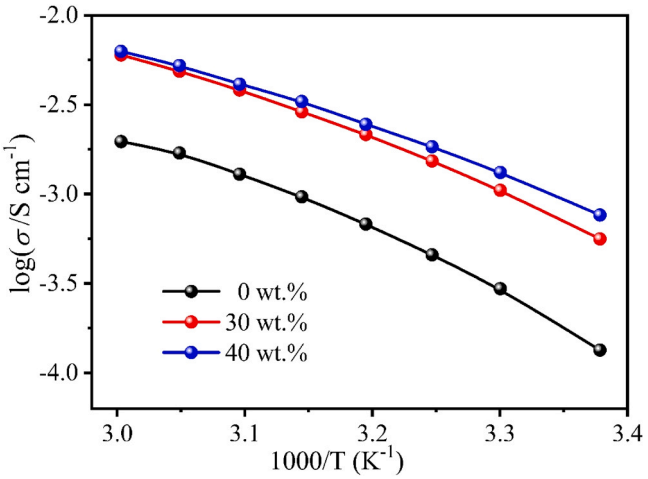

Fig. 6. Logarithm of ionic conductivity vs. reciprocal temperature for PEO: POSS-benzyl$_7$(BF_3Li)$_3$: $POSSPEG_{13.3}$ (EO/Li = 14) nanocomposite electrolytes at 0 wt%, 30 wt% and 40 wt% of $POSSPEG_{13.3}$.

The X-ray diffraction (XRD) patterns of pure PEO, pure POSS-benzyl$_7$(BF_3Li)$_3$ salt, and PEO: POSS-benzyl$_7$(BF_3Li)$_3$ nanocomposite solid polymer electrolytes containing 0, 30, and 40 wt% $POSSPEG_{13.3}$ at an EO/Li ratio of 14 are shown in Fig. 7. Pure PEO shows very sharp and intense diffraction peaks at around $2\theta \approx 19^\circ$ and 23°, which are typical for the semi-crystalline structure. The very strong peaks are evidence of a high degree of crystallinity in pristine PEO, which is known to limit both polymer chain flexibility and ionic transport at room temperature. The XRD pattern of the pure POSS-benzyl$_7$(BF_3Li)$_3$ salt, however, displays several very sharp peaks, which are well-defined throughout the entire scanned range, thus indicating its crystalline nature and confirming that an ordered hybrid inorganic–organic salt structure has been formed.

The intensity of the PEO crystalline peaks decreases significantly and becomes broader upon the incorporation of the POSS-benzyl$_7$(BF_3Li)$_3$ salt into PEO (0 wt% $POSSPEG_{13.3}$) indicating that the crystalline domains are partially disrupted and their content has been increased due to strong coordination between Li^+ ions and PEO ether oxygen atoms. The addition of 30 wt% and 40 wt% $POSSPEG_{13.3}$ further alters the diffraction patterns into broad halos with a substantial reduction in the

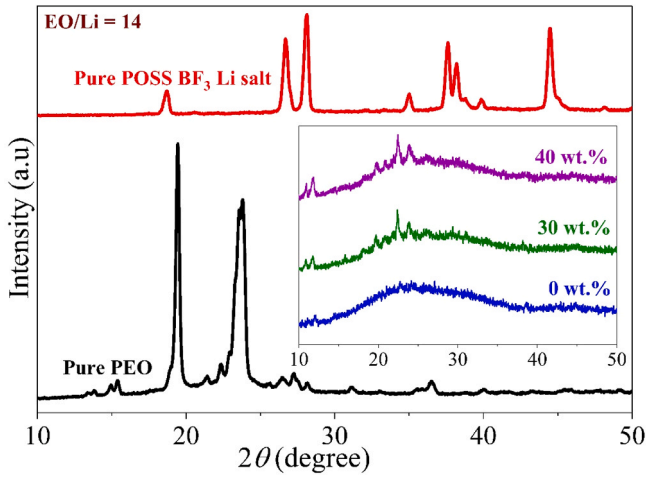

Fig. 7. X-ray diffraction patterns of pure PEO, pure POSS-benzyl$_7$(BF_3Li)$_3$ salt, and PEO: POSS-benzyl$_7$(BF_3Li)$_3$ NSPEs containing 0, 30, and 40 wt% $POSSPEG_{13.3}$ at EO/Li = 14.

intensity of the peaks. Such progressive broadening of the peaks and reduction in their intensity serve to demonstrate crystal growth of the PEO phase being continuously suppressed and at the same time, there is a corresponding increase in the amorphous phase. The hybrid POSSPEG$_{13.3}$ nano plasticizer is acting in two ways: firstly, it introduces flexible PEG chains that support polymer segmental mobility and secondly, the rigid POSS cage guarantees even dispersion and structural stability [24,25]. The 40 wt% POSSPEG$_{13.3}$ electrolyte appears the most amorphous, which is in a perfect match with its highest ionic conductance.

In Fig. 8, the DSC thermograms of the different samples (pure PEO, PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$ (EO/Li=14), and PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$−40 wt% POSSPEG$_{13.3}$) are given, thus showing the impact of the organic–inorganic hybrid components on the melting and crystallinity of the polymer electrolyte system. Pure PEO, as seen in Fig. 8, shows a melting peak that is both sharp and intense and occurs at 72 °C, which is typical for its semicrystalline form. The large enthalpy of melting is related to a high degree of crystallinity (77%), and this is due to the regular arrangement of PEO chains, intermolecular chain interactions and crystalline chain packing within the polymer matrix. The high degree of crystallinity does, however, hinder the motion of the polymer chains and hence it is a barrier to the efficient transport of lithium ions.

The melting endotherm, after the addition of the POSS-benzyl$_7$(BF$_3$Li)$_3$ salt (0 wt% POSSPEG$_{13.3}$), dramatically shifts to the left side at 55 °C and with a great decrease of peak intensity. This displacement points to very strong liaison between Li$^+$ ions and the ether oxygen atoms of PEO, further, the presence of the rigid POSS nanocage causes various steric hindrances. Eventually, these effects lead to the breaking up of the crystalline domains of PEO, thus causing the overall reduction in crystallinity down to ~5% and the establishment of a polymer–salt complex that is mainly amorphous. On top of that, the melting point decreases a little more to 53 °C with the addition of 40 wt% POSSPEG$_{13.3}$, and the endothermal peak becomes so week and wide that it is not too easily observable. The crystallinity is almost completely gone, only ~1% remains, confirming the occurrence of near total amorphization.

The PEG chains disrupting the ordered crystalline domains of PEO, thereby increasing chain flexibility and promoting the formation of an amorphous phase. The enhanced amorphous nature facilitates segmental polymer motion and improves ion mobility, which ultimately contributes to the observed enhancement in ionic conductivity and overall ion transport behavior. Whereas the POSS structure through nanoscale trapping prevents any recrystallization [26]. It is shown as a systematic fall in melting point and crystallinity in the sequence: pure PEO > PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$ > PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$ + POSSPEG$_{13.3}$.

The TGA curves of PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$ nanocomposite solid polymer electrolytes with 0, 30, and 40 wt% POSSPEG$_{13.3}$ are shown in Fig. 9, highlighting the influence of hybrid nano plasticizer content on thermal stability and degradation characteristics. Fig. 9 indicates that all samples undergo minor weight loss (<2–3%) up to around 100 °C, demonstrating the effectiveness of solvent removal and the good thermal stability, being under the normal operating conditions of batteries. The electrolyte with no POSSPEG$_{13.3}$ (0 wt%) has the maximum thermal stability as significant weight loss starts at about 255–260 °C. The reason for this stability is the strong coordination of Li$^+$ ions with PEO ether oxygens and the rigid inorganic POSS cage that limits polymer chain movement. The PEO backbone and other organic components degradation causes the main decomposition step in the 270–360 °C range, leaving a comparatively high residual mass of ~18–19% at 500 °C, which is from the inorganic POSS and boron-containing species.

In the case of using 30 wt% POSSPEG$_{13.3}$, the degradation onset temperature a little bit down to roughly 245–250 °C, thus indicating that the plasticizing effect of the PEG segments is the reason for it. The latter allows the chain to be more flexible and the amorphous content to be greater. The main degradation zone is still at 260–350 °C, and the weight left at 500 °C drops to ~12–13% due to the higher organic fraction. For the electrolyte consisting of 40 wt% POSSPEG$_{13.3}$, a little more change in thermal stability is tracked down to the ≈ 235–240 °C range and the main decomposition step is now 250–340 °C. The remaining mass at 500 °C comes to ~13–14% which indicates a reduction in inorganic content when compared with the 0 wt% sample [27]. The findings thus reveal that even though the thermal decomposition onset is slightly lowered with the increase of the POSSPEG$_{13.3}$ content, all the nanocomposite electrolytes are still thermally stable enough for the use in solid-state lithium battery applications.

The stress–strain behavior of PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$ nanocomposite solid polymer electrolytes is illustrated in Fig. 10, with the addition of 0 wt% and 40 wt% POSSPEG$_{13.3}$ revealing the impact of hybrid nano plasticizing on the mechanical strength and ductility. The 0 wt% POSSPEG$_{13.3}$ electrolyte depicted in Fig. 10 has a very slight linear elastic phase at low strain and then it gets into a plastic deformation phase. The stress gradually continues to grow and reaches its peak at about 4.1 MPa for nearly 572% strain and then breaks at about 600–620% strain. The relatively moderate elongation at the breaking point is suggestive of the rigid hold between the PEO chains and the POSS lithium salt causing limited polymer chain movement along with

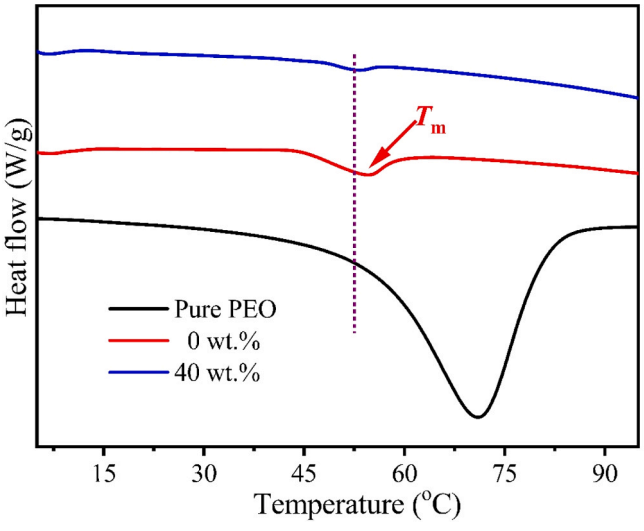

Fig. 8. DSC thermograms of pure PEO, PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$–0 wt% POSSPEG$_{13.3}$, and PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$–40 wt% POSSPEG$_{13.3}$ at EO/Li= 14.

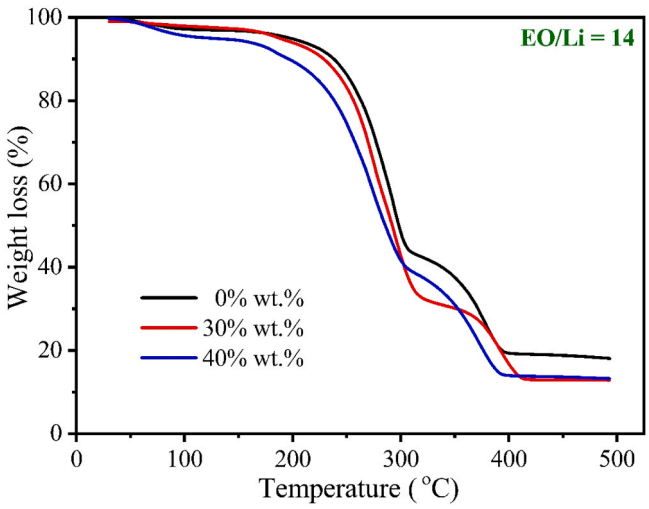

Fig. 9. TGA heating traces 0 wt%, 30 wt% and 40 wt% POSSPEG$_{13.3}$ doped PEO–POSS-benzyl$_7$(BF$_3$Li)$_3$ electrolyte films.

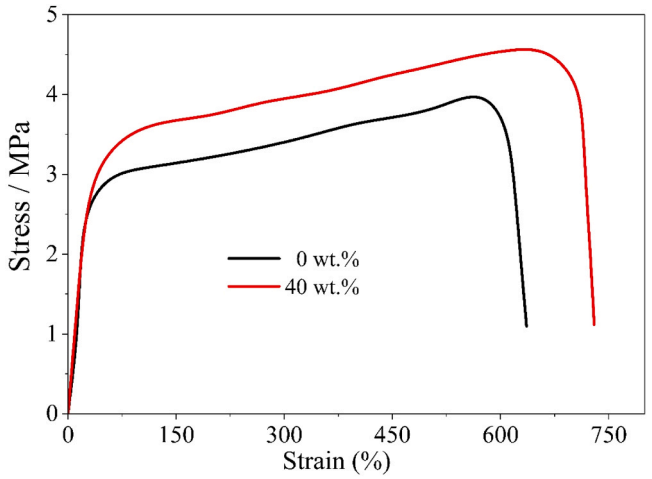

Fig. 10. Stress–strain curves of the PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$: 0 wt% POSSPEG$_{13.3}$ and the PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$: 40 wt% POSSPEG$_{13.3}$ NSPEs at EO/Li = 14.

the remaining crystalline regions acting as stress concentration sites. On the contrary, the mechanical response of the electrolyte with 40 wt% POSSPEG$_{13.3}$ is significantly better. Beyond the elastic region is where an extensive plastic deformation zone is noted, which shows that the polymer has become even more flexible and that stress has been effectively redistributed in the matrix. The maximum tensile stress has been raised to ~4.6 MPa, obtained at a larger strain of about 664%, and the film has undergone deformation up to a strain of ~720–750% before fracture. This development has been ascribed to the plasticizing effect of the PEG parts, which not only make more room for the movement of the polymer but also make it easier for the chains to slide past each other, while the rigid POSS nanocages work like reinforcing fillers that prevent the start and spread of cracks [28]. The addition of 40 wt% POSSPEG$_{13.3}$ brings about an increase of about 12% in tensile strength and a rise of 16% in elongation at break, respectively, compared to the empty electrolyte without POSSPEG$_{13.3}$. The interfacial integrity and mechanical stability during the repeated electrochemical cycling are enhanced by this property, which is indeed very desirable for solid polymer electrolytes to have a combination of mechanical robustness and high ductility.

The DC polarization technique with blocking electrodes was used to measure the ion transference number of the PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$: 0 and 40 wt% POSSPEG$_{13.3}$ nanocomposite solid polymer electrolytes depicted in Fig. 11. The application of a constant DC potential of 1 V across the electrolyte was done for 1 h and the current response was measured over time. The high initial current of the electrolyte seen in Fig. 11 is attributable to the combined effect of mobile lithium ions and a small amount of electronic charge carriers right after the DC bias application. The current drops quickly in the first few hundred seconds due to ion build-up at the electrode–electrolyte interfaces and effective blockage of electronic transport. After that, the current becomes low and unchanging at the steady-state value which reveals very little electronic conduction. The total ion transference number (t_{ion}), calculated with the formula $t_{ion} = \frac{I_i - I_f}{I_i}$, is equal to 0.99, which means that the conduction in these nanocomposite electrolytes are mostly ionic [29]. The almost unity transference number is a proof of the efficient ion conducting through the amorphous PEO matrix which is made possible through the strong coordination between Li$^+$ ions and ether oxygen groups. Besides, the use of POSS-benzyl$_7$(BF$_3$Li)$_3$ and POSSPEG$_{13.3}$ nanostructures in the polymer effectively limits the mobility of anions and lowers the crystallinity of the polymer.

The linear sweep voltammetry (LSV) response of the nanocomposite solid polymer electrolyte PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$: 40 wt% POSSPEG$_{13.3}$ measured at a scan rate of 5 mV s^{-1} in 1–7 V vs. Li/Li$^+$ window is illustrated in Fig. 12. During the interval of 1.0 to around 4.7 V, the current is very low and almost constant, which means there are no significant electrochemical reactions taking place and the electrolyte is oxidatively stable in this voltage region. After 5.0 V vs. Li/Li$^+$ the current shows a slow incline and at the higher voltages the current jumps sharply which indicates that the polymer electrolyte components are starting to oxidatively decompose. The voltage at which this current increase starts to happen is the one that the electrochemical stability window of the electrolyte is defined by. The wide stability window of about 4.7 V indicates that the new nanocomposite electrolyte can operate at high voltages without losing its quality through degradation [30]. The remarkable anodic stability in Fig. 12 is attributed to the hybrid organic–inorganic nature of the POSS-benzyl$_7$(BF$_3$Li)$_3$ lithium salt and the POSSPEG$_{13.3}$ nano plasticizer, which together improve the structural and electrochemical strength of the PEO matrix. The close coordination of Li$^+$ ions with the ether oxygen atoms of PEO, along with the lower polymer crystallinity and stabilized interfacial chemistry brought by POSS nanostructures, effectively extends the time before oxidation happens [31].

In Fig. 13, the cyclic voltammetry (CV) profiles of (a) PEO:POSS-benzyl$_7$(BF$_3$Li)$_3$ for the first cycle and (b) PEO:POSS-benzyl$_7$(BF$_3$Li)$_3$:40 wt% POSSPEG$_{13.3}$ nanocomposite solid polymer electrolyte for the 1st, 5th, and 10th cycles are shown; these were all measured in the potential window of −1–5 V vs. Li/Li$^+$ with a scan rate of 5 mV sec^{-1} . For PEO:POSS-benzyl$_7$(BF$_3$Li)$_3$ (1st cycle), the CV curve displays very

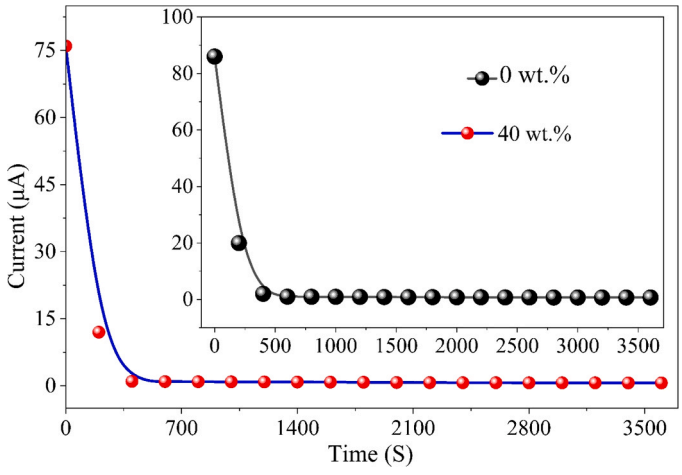

Fig. 11. Ion transference number plot for PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$: 0 and 40 wt% POSSPEG$_{13.3}$ electrolytes with configuration SS/NSPE/SS.

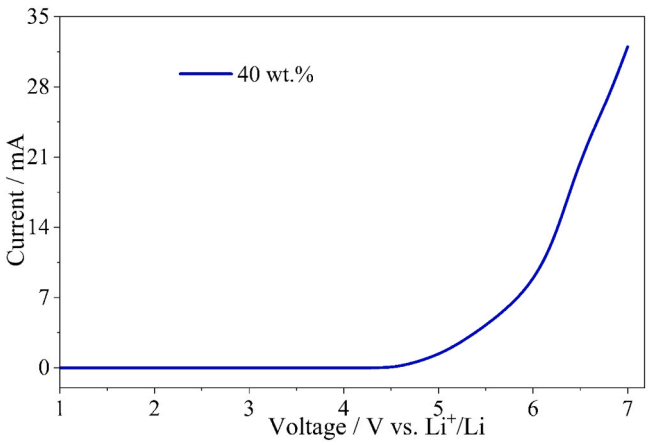

Fig. 12. Linear sweep voltammetry scan of PEO: POSS-benzyl$_7$(BF$_3$Li)$_3$: 40 wt % POSSPEG$_{13.3}$ NSPE at 296 K, 5 mV/s, working electrode stainless steel, counter/reference electrode lithium metal.

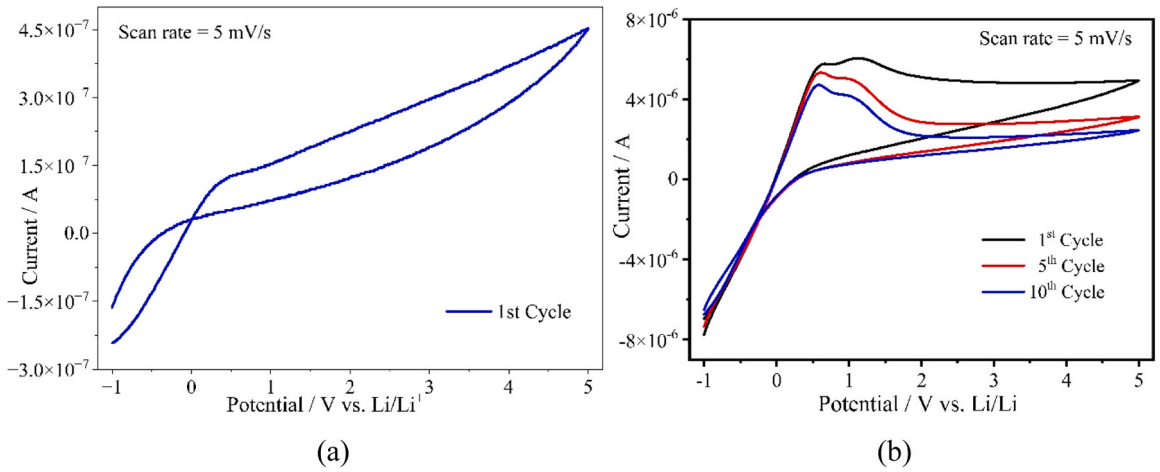

Fig. 13. Cyclic voltammograms of (a) PEO: POSS-benzyl$_7$(BF_3Li)$_3$ and (b) PEO: POSS-benzyl$_7$(BF_3Li)$_3$: 40 wt% POSSPEG$_{13.3}$ NSPEs. Potential sweep rate was 5 mV/s.

low current during the whole potential range with no sharp anodic or cathodic peaks. This reflects the non-existence of considerable faradaic reactions and at the same time affirms the electrochemical inertness of the electrolyte within the aforementioned window. The slight current rise at the higher positive potentials is correlated with the start of the electrolyte oxidation; whereas, the smooth cathodic response at negative potentials represents stable Li^+ plating/stripping without electrolyte decomposition and thus, becoming the cause of the cathodic response. For PEO: POSS-benzyl$_7$(BF_3Li)$_3$: 40 wt% POSSPEG$_{13.3}$, the CV profiles for the 1st, 5th, and 10th cycles are nearly identical and thus, exhibit excellent electrochemical reversibility and interfacial stability during repeated cycling. Compared to the pristine system, the higher current response indicates the enhanced ionic mobility owing to the reduced PEO crystallinity and increased amorphous content brought about by the addition of POSSPEG$_{13.3}$. The broad and featureless humps present in both the cathodic and anodic scans are related to the coordination–decoordination of Li^+ ions rather than to irreversible redox reactions. The scant alteration in the current and the curve shape from the 1st to the 10th cycle is a clear indication of the development of a stable electrolyte–electrode interface and the suppression of parasitic reactions [32].

Fig. 14 presents the voltage profiles obtained from galvanostatic charge-discharge experiments of the $LiFePO_4$ / PEO: POSS-benzyl$_7$(BF_3Li)$_3$: 40 wt% POSSPEG$_{13.3}$ / Li solid-state cell during the first cycle at 0.1 C within the voltage range of 2.4–4.2 V vs. Li/Li^+. The charge and discharge curves show distinct and nearly symmetrical plateaus at approximately 3.5–3.6 V, which are typical for the Fe^{2+}/Fe^{3+} redox couple of the $LiFePO_4$ cathode. This behavior indicates the presence of very reversible lithium intercalation and de-intercalation processes which are enabled by the nanocomposite solid polymer electrolyte. During the first charge cycle, the cell voltage quickly climbs from 2.4 V and levels off at a flat plateau close to 3.6 V, which suggests that the delithiation of $LiFePO_4$ occurs efficiently. A minor voltage rise towards the end of the charging process up to 4.2 V is ascribed to the polarization effects associated with the high states of charge. During discharge, a stable plateau of about 3.45–3.5 V is first seen, then there is a gentle voltage drop close to the cut-off potential, which indicates the controlled lithiation of the cathode and the excellent interfacial contact between the electrolyte and electrodes. The cell has an impressive initial discharge specific capacity of 169.3 mAh g^{-1} , which is almost at par with the theoretical capacity of $LiFePO_4$ and evidences the great utilization of the active material. The minute voltage hysteresis existing between the charge and discharge plateaus points to a low internal resistance and very little polarization losses [33]. The progressive electrochemical performance is primarily due to the electrolyte's high ionic conductivity and near-unity lithium-ion transference number, as well as the reduced crystallinity and increased segmental mobility of PEO that results from the incorporation of POSSPEG$_{13.3}$.

The performance of the $LiFePO_4$ / PEO: POSS-benzyl$_7$(BF_3Li)$_3$: 0 and 40 wt% POSSPEG$_{13.3}$ / Li solid-state cell at 0.1 C for 100 consecutive charge–discharge cycles is shown in Fig. 15. The specific capacity versus cycle number graph indicates a very light and slow capacity evolution,

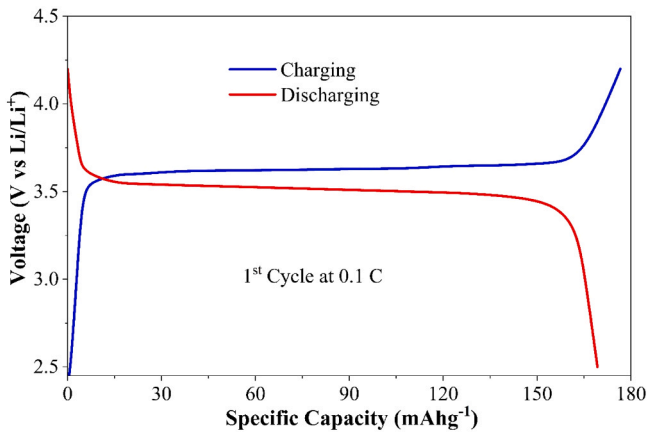

Fig. 14. Charge-discharge profiles of $LiFePO_4$/ PEO: POSS-benzyl$_7$(BF_3Li)$_3$: 40 wt% POSSPEG$_{13.3}$ /Li cell at 0.1 C.

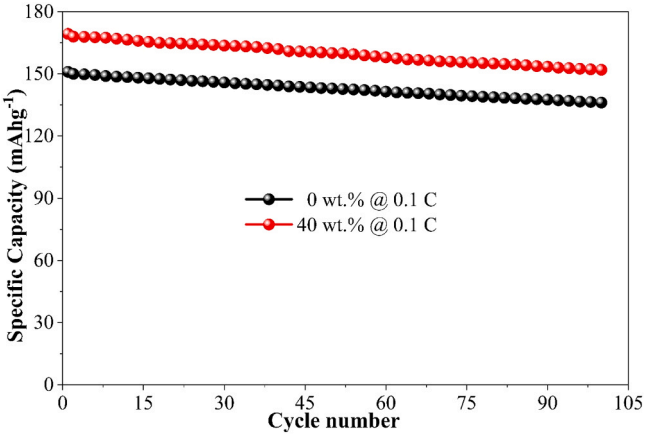

Fig. 15. Cycle performance of $LiFePO_4$/Li cell using 0 and 40 wt% POSSPEG$_{13.3}$ doped solid polymer electrolytes at 0.1 C. Temperature: 23 °C.

revealing the dielectric strength of the nanocomposite solid polymer electrolyte. The 0 wt% sample exhibited an initial charge capacity of 151 mAh g^{-1} , which gradually decreased to approximately 136.2 mAh g^{-1} after 100 cycles. The 40 wt% sample achieved a higher initial charge capacity that reached about 169.3 mAh g^{-1} while maintaining a capacity of approximately 152 mAh g^{-1} after 100 cycles. The specific capacity improvement that follows the addition of 40 wt% $POSSPEG_{13.3}$ shows that this material improves electrochemical performance. The 40 wt% sample maintained 89.8% of its original capacity after 100 cycles, which proved its excellent cycling stability and good compatibility at the electrolyte–electrode interface. The lack of sudden changes in capacity indicates that there is very little electrolyte loss and the contact between lithium anode, polymer electrolyte, and $LiFePO_4$ cathode is stably maintained during cycles [34].

The capacity stability observed is due to the impressive ionic conductivity and almost complete ion transference of the PEO–POSS-based nanocomposite electrolyte, which creates a uniform Li^+ flow and stops the concentration polarization. The introduction of 40 wt% $POSSPEG_{13.3}$ leads to a considerable reduction in PEO's crystallinity and improving the motion of the polymer chain segments, which in turn results in continuous ion transport even if the cycling is prolonged. Besides, the organic–inorganic nature of POSS-benzyl$_7$(BF_3Li)$_3$ and $POSSPEG_{13.3}$ that hybrid promotes mechanical strength and reduces interfacial resistance growth. The little capacity decrease seen after 100 cycles is associated mainly with gradual interfacial evolution and minor polarization effects rather than with the decomposition of the electrolyte. The outcomes obtained affirm that the manufactured nanocomposite solid polymer electrolyte is well-capable of long-term cycling with high retention, thereby verifying its suitability for the application of reliable solid-state lithium batteries.

4. Conclusion

The research and development of a totally hybrid nanocomposite solid polymer electrolyte system comprising PEO, POSS-benzyl$_7$(BF_3Li)$_3$ lithium salt, and $POSSPEG_{13.3}$ nano plasticizer has been successful. The system consisting of organic–inorganic hybrids has the ability to prevent the PEO from crystallizing completely, increase the motion of the polymer segment, and thus make it easier for the lithium ions to move. The optimized electrolyte shows high ionic conductivity at room temperature, very good thermal and mechanical stability, and a nearly complete ion transference number, which corresponds to the case of lithium-ion conduction, no or little polarization. The electrochemical characterization has revealed an extensive stability window and superior interfacial behavior. In the solid-state $LiFePO_4$/Li cells application, the electrolyte is capable of yielding a very high initial discharge capacity and retaining 89.8% of capacity after 100 cycles. The stable cycling performance is interpreted as strong electrolyte–electrode compatibility and little degradation. This fully hybrid electrolyte approach offers a bright and large-scale future for the manufacturing of safe, high-performance solid-state lithium batteries.

CRediT authorship contribution statement

Deepak Kumar: Writing – review & editing, Formal analysis, Data curation. **Obula Reddy Kummitha:** Writing – review & editing, Validation, Methodology. **Anji Reddy Polu:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Amrita Jain:** Writing – review & editing, Formal analysis. **Kuldeep Mishra:** Writing – review & editing, Formal analysis, Data curation.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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None.

Data availability

All data included in this study are available upon request by contacting the corresponding author.

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