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Ernest Ahiavi, Priscillia Soudant, Didier Devaux, Renaud Bouchet. Ionic transport properties of lithium polysulfides within poly(ethylene-oxide) homopolymer electrolytes. *Electrochimica Acta*, 2024, 488, pp.144202. 10.1016/j.electacta.2024.144202 . hal-04546068

HAL Id: hal-04546068

<https://hal.science/hal-04546068v1>

Submitted on 15 Apr 2024

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Ionic transport properties of lithium polysulfides within poly(ethylene-oxide) homopolymer electrolytes

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Abstract

Lithium-sulfur (Li-S) batteries are attractive due to their high theoretical specific energy density, nonetheless, their upscaling and widespread adaptation have been hampered by issues such as the dissolution and shuttling of lithium polysulfides species (Li_2S_x , $2 \leq x \leq 8$) from the positive electrode through the electrolyte to the negative electrode. The electrolyte medium is thus a decisive factor in tackling the lithium polysulfide shuttle mechanism. In this study, the thermodynamical, structural, and ionic transport properties of Li_2S_x within poly(ethylene-oxide), PEO, a solid-polymer electrolyte that can potentially be used in all-solid-state Li-S batteries have been investigated. Results from thermodynamical, infrared spectroscopy and XRD characterizations show that Li_2S_8 solubilizes better in PEO homopolymer compared to Li_2S_4 salt. In terms of ionic transport properties, the diffusion measurements via electrochemical methodologies also demonstrate that PEO can slow down the shuttling speed of S_8^{2-} and S_4^{2-} by almost an order of magnitude compared to a conventional liquid electrolyte such as DOL/DME. Long-chain polysulfides in PEO homopolymer show more pronounced shuttling than the short-chain polysulfide. These findings may guide the design of adapted solid polymer electrolytes that can be used as binders or electrolyte separators for all-solid-state Li-S batteries.

Keywords

Solid polymer electrolyte; lithium polysulfides; thermodynamical properties; transference number, diffusion coefficient.

Introduction

The need for batteries in portable electronic devices, stationary storage, and electric mobilities, makes them ubiquitous¹. Despite Li-ion battery's market domination, there is a growing demand for safer², better performing³, affordable, and environmentally friendly batteries which calls for the need to pursue other battery chemistries. Among those, lithium-sulfur (Li-S) batteries can theoretically deliver energy densities ten times higher than what the current Li-ion battery offers⁴. Besides its ability to store high amounts of energy, sulfur is cost-effective, abundant, nontoxic, and environmentally friendly⁵. Lithium is also the lightest of all metals, having the lowest standard potential (-3.05 V vs. Li/Li⁺)⁶, and possesses a very high theoretical specific capacity (3860 mAh.g⁻¹)⁷. Marrying these properties give Li-S batteries a large storage capability of 2500 Wh.kg⁻¹ in theoretical energy density based on the two-electron transfer per S atom⁸.

Despite intense development in the past decade, the scale-up and widespread adaptation of this promising technology is impeded by tremendous challenges; prominent among them is the dissolution and transport of intermediate products (lithium polysulfides, Li₂S_x, 2 ≤ x ≤ 8) within the electrolyte in a redox shuttle process which reduces the faradic efficiency and affects the cycle life⁴. Li₂S_x reacts with the Li negative electrode forming an insulating layer thereby increasing the internal resistance of the cell and eventual capacity fading⁵. One crucial point is that the dynamics of polysulfide driving the rate of shuttling depend on the nature of the electrolyte, usually a mixture of 1, 3-dioxolene (DOL) and 1,2-dimethoxyethane (DME) with a Li salt and its additives (e.g., LiNO₃) when a liquid electrolyte is used⁴.

To improve the performance of the Li-S battery, several strategies have been devised in an attempt to confine Li₂S_x within the positive electrode volume using architected active materials⁹⁻¹², functionalized separators¹³⁻¹⁵ or protective layer on the Li surface¹⁶⁻¹⁸. Some of these approaches may be efficient but are often too complex to be cost-effective in industrial applications. Moreover, the use of high-capacity sulfur-positive active material leads to high current densities even at low battery cycling rates facilitating the onset of dendrite growth on the Li metal electrode. Therefore, to tackle the issues of polysulfide shuttle and dendrite growth, replacing the liquid electrolyte with a dendrite-resistant solid-based electrolyte is of interest as its functionalities can be tailored.

Among the families of solid electrolytes, solid polymer electrolytes (SPEs) based on poly(ethylene oxide) (PEO) are promising thanks to their ionic conductivity (σ), high enough at temperatures (T) above the PEO melt (T_m , typically at 55 – 60 °C), relatively high Gutmann donor number¹⁹ and their electrochemical stability window compatible with sulfur²⁰. In an important piece of work, the group of N. P. Balsara reported on the effect of Li₂S_x (2 ≤ x ≤ 8) chain length on the thermodynamical and electrochemical properties with a specific focus on PEO homopolymers and diblock copolymer electrolytes^{21,22}. The interest of such a study is to mimic Li-S battery failure when Li₂S_x diffuses within the PEO-based electrolyte. To achieve a functional battery system, Armand, and Rodriguez-Martinez *et al.* investigated the dissolution of polysulfides in polyethylene

oxide (PEO)^{23–25}. Their studies also focused on optimizing the cell assembly and its chemistry, particularly using additives. Notably, they successfully documented the cycling behavior of Li metal batteries.

To go further, a comprehensive study of the effect of chain length, and concentration of lithium polysulfides on the ambipolar diffusion coefficient (D_{amb}) and cationic transference number (T^+) would help to fully understand Li polysulfide transport in the PEO homopolymer. Indeed, since lithium polysulfides are ionic, they can be considered as Li salt and their solvation, degree of dissociation and transport in SPEs can be described by the three ionic transport properties (σ , T^+ , and D_{amb}).

Herein, solid polymer electrolytes were formulated in a controlled inert atmosphere to avoid any moisture contamination by filling high molecular weight PEO homopolymer with lithium polysulfides (Li_2S_x , $x = 4, 8$) at different concentrations. The goal is to assess the PEO efficiency to solubilize lithium polysulfide and to understand the resulting ionic transport properties within the PEO matrix. For this, thermodynamical properties are reported using differential scanning calorimetry (DSC) while X-ray diffraction (XRD) sheds light on the PEO crystal structuration and the vibration modes of bonds are analyzed using Fourier transform infrared spectroscopy (FTIR) and finally, the three ionic transport properties (σ , T^+ , and D_{amb}) are investigated by the means of electrochemical methodologies. The results show a strong impact of polysulfides on the transference number compared to PEO mixed with a conventional Li salt (LiTFSI), while the Li^+ diffusion coefficient seems to be independent of the concentration of the lithium polysulfides or the nature of the anion. In addition, FTIR is shown to be an efficient tool to study polysulfide solubility in the PEO matrix.

1 Experimental

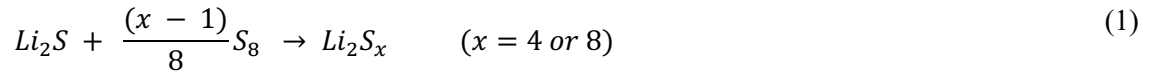
1.1 Materials

High molecular weight (M_n , 100 kg.mol⁻¹) poly(ethylene oxide), (PEO, Alfa Aesar) homopolymer and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Merck) were dried under vacuum for several days at 90 °C and 120 °C respectively and placed in an argon (Ar) glovebox (H_2O and $\text{O}_2 < 1$ ppm). In addition, powders of lithium sulfide (Li_2S , Thermo Scientific, 99.9 %) and sulfur (S_8 , Alfa Aesar, 99.5 %) were also dried in a vacuum chamber (desiccator, Vacuo-Temp) placed directly inside the Ar glove box.

1.2 SPE formulation

As reference solid polymer electrolyte (SPE), PEO/LiTFSI films were formulated by dissolving different mole ratios (EO/Li) of PEO and LiTFSI in acetonitrile (Merck, 99.8 %). The mixtures

were stirred magnetically overnight at 60 °C in an Ar glovebox (H_2O and $O_2 < 1$ ppm) until a homogeneous solution was obtained before casting into a polytetrafluoroethylene Petri dish. The solvent was evaporated at room temperature in the glovebox and finally, the Petri dish containing the semi-dried membrane was placed in a desiccator to be vacuum-dried at 60 °C overnight. A schematic of the SPE formulation process is shown in **Figure S1**. The resulting dry SPEs were peeled off the Petri dish and then transferred into a solvent-free Ar glovebox dedicated to electrochemical cell assembly for at least two weeks before any characterization. Similarly, PEO was formulated with different concentrations of lithium polysulfides. For these, the polymer was first dissolved in acetonitrile at 60 °C and mixed with defined amounts of a prepared solution of Li_2S_x ($x = 4$ or 8) in the same solvent before casting. For the latter solution, Li_2S and S_8 were mixed in stoichiometric amounts in acetonitrile and stirred overnight to obtain a uniform solution. The reaction equation to obtain a known quantity of Li_2S_x is ^{21, 22}:



The lithium polysulfide concentration in the polymer is presented as the molar ratio R , varied between 0 and 0.12 based on the work of Wang *et al.* ^{21, 22}:

$$R = \frac{n(Li_2S_x)}{n(polymer)} \quad (2)$$

1.3 Differential scanning calorimetry (DSC)

The thermodynamical properties of the SPEs with varying salt concentrations (R) were determined using differential scanning calorimetry (DSC 1, Mettler Toledo). The SPE samples were sealed in hermetic Aluminium pans in the glovebox before measurements. All samples were heated up to 130 °C (at 5 °C/min), cooled down to -100 °C (at 10 °C/min) and heated again to 120 °C (at 5 °C/min). The glass transition temperature (T_g), melting temperature (T_m) and the enthalpy of melting ΔH_m were all extracted from the second heating scan. As a typical example, the thermogram of PEO/ Li_2S_8 at $R = 0.008$ is shown in **Figure S2** indicating that the T_g values were extracted from the mid-point of the glass transition and T_m from the intersection of the tangent and the baseline of the heat flow transition (onset of the T_m). Then, the degree of crystallinity (X_c) was calculated according to **eq. 3**.

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} * 100 \% \quad (3)$$

With ΔH_m the enthalpy of melting of the SPE and ΔH_m^0 is the enthalpy of melting of a 100 % crystalline PEO taken as 195 J.g⁻¹ ²⁶.

1.4 Density of PEO/Li₂S_x

The density of the PEO/Li₂S_x electrolyte was measured based on Archimedes principles by using a standard density kit (Mettler Toledo) placed on a balance inside an Ar-filled glovebox. At room temperature, the weight of a PEO/Li₂S_x dry mixture was measured in Argon (density, $\rho_{Ar} = 0.0016$ g.cm³) and heptane ($\rho_{heptane} = 0.6692$ g.cm³). The density of the SPE (ρ_{PEO/Li_2S_x}) was calculated according to **eq. 4**.

$$\rho_{PEO/Li_2S_x} = \frac{\text{weight in Ar}}{\text{weight in Ar} - \text{weight in heptane}} * (\rho_{heptane} - \rho_{Ar}) + \rho_{Ar} \quad (4)$$

For comparison purposes, the theoretical density of the PEO/Li₂S_x electrolyte assuming an ideal mixture was calculated according to:

$$\rho_{PEO/Li_2S_x} = \frac{M_{EO/Li_2S_x}}{V_{EO/Li_2S_x}} = \frac{(M_{EO} + R * M_{Li_2S_x})}{(V_{EO} + R * V_{Li_2S_x})} \quad (5)$$

The molar mass of PEO/Li₂S_x was calculated using a linear combination of the individual molar masses:

$$M_{EO/Li_2S_x} = (n_{EO} * M_{EO}) + (n_{Li_2S_x} * M_{Li_2S_x}) \quad (6)$$

The volume of the mixture was calculated by considering the ratio of masses and molar masses (m/M) for each compound where the partial molar volume of PEO was taken to be 38.5 cm³.mol⁻¹ ²⁷:

$$V_{EO/Li_2S_x} = (n_{EO} * V_{EO}) + (n_{Li_2S_x} * V_{Li_2S_x}) \quad (7)$$

Likewise, the molar mass and volume of the Li₂S_x assuming an ideal mixture, were calculated using **eq. 8** and **eq. 9** respectively.

$$M_{Li_2S_x} = \left(\frac{1-x}{8}\right) * M_{S_8} + M_{Li_2S} \quad (8)$$

$$V_{Li_2S_x} = \left(\frac{1-x}{8}\right) * V_{S_8} + V_{Li_2S} \quad (9)$$

Here the partial molar volumes of S₈ and Li₂S were taken to be 123.9 cm³.mol⁻¹ and 27.7 cm³.mol⁻¹ respectively ^{28, 29}. The molar mass of S₈ (M_{S_8}) and Li₂S (M_{Li_2S}) were taken to be 256.52 g.mol⁻¹ and 44.95 g.mol⁻¹ respectively.

1.5 Fourier transformed Infrared spectroscopy (FTIR)

SPE solutions of polymer/salt dissolved in acetonitrile were coated onto a ZnSe window (PerkinElmer) inside the Ar-filled glovebox. Subsequently, the solvent was evaporated by placing

the sample in a desiccator under vacuum in a similar fashion as used for the SPE formulation. This process resulted in the formation of thin SPE films of about $\leq 1.5 \mu\text{m}$ thick. To ensure airtightness when the samples were taken outside the glovebox for measurement, a parafilm mask was placed on the facing edges of the ZnSe window and firmly pressed together. The FTIR spectra were recorded using PerkinElmer Spectrum 2 FTIR spectrometer in transmission mode, within 800 - 1500 cm^{-1} range with 1 cm^{-1} resolution.

1.6 X-ray diffraction (XRD)

X-ray diffraction was carried out using a diffractometer X'Pert Pro (Malvern PANAnalytical) equipped with a Bragg-Brentano geometry at the Consortium des Moyens Technologiques Communs (CMTC Grenoble INP, France) platform. A Cu-K α anode ($\lambda = 1.5406 \text{ \AA}$) was used with a 2θ angle ranging from 6 ° to 60 ° with 0.05 ° intervals. Inside the Ar-filled glovebox, SPEs were filled into capillaries made of borosilicate glass and sealed using a resin to avoid exposure to air. Phase identification was performed using DIFFRAC.EVA (Bruker) phase indexing software by comparing the diffractograms to a reference database.

1.7 Scanning electron microscopy and energy dispersive X-ray spectroscopy

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to study the particle size and composition of the sulfur powder (S_8) respectively. The measurements were performed at the CMTC platform using a scanning electron microscope (Ultra 55 SEM FEG, Zeiss, Jena, Germany) operated at 5 kV.

1.8 Ionic conductivity

The ionic conductivity (σ) of the SPEs was determined using Li symmetric coin cells (CR2032) by sandwiching the SPE of known thickness (l) within a polypropylene spacer (to maintain a fixed active surface area, A of 10 mm diameter) between two Li foils stacked to stainless steel current collectors. For completeness, impedance was also measured using stainless steel blocking electrodes and compared to non-blocking ones.³⁰ The results for PEO/Li₂S₄ are displayed in **Figure S3** showing a full agreement of the bulk contribution and resulting ionic conductivities for the two types of symmetric cells. In the glove box, the Li/SPE/Li cells were first assembled using a homemade laminating machine held at 80 °C and 3 bars to ensure intimate contact between the layers, before being sealed in the coin cell. The cells were then placed in an oven (Clima Temperature System) and connected to a potentiostat with impedance capability (VMP300, BioLogic). Electrochemical impedance spectroscopy was performed at a given temperature (T) using an excitation signal of 40 mV in the frequency range between 7 MHz and 100 mHz. The temperature program consisted of heat-cool-heat scans from 25 °C to 100 °C by step of 5 °C. Each impedance spectrum was fitted using Z-View software (Scribner Inc.) to extract the bulk electrolyte

(R_{bulk}) and the interface resistances (R_{int}). The electrical equivalent circuit is the sum of the cable and instrument resistances and inductance at high frequencies, followed by the electrolyte response fitted with a resistance in parallel with a pseudo-capacitance for $T > T_m$ and just a resistance for $T < T_m$, followed by another resistance in parallel with a pseudo-capacitance for the Li/SPE interfaces. As an example, the impedance spectrum and its best fit ($\chi^2 > 0.99$) of a Li symmetric cell comprising the PEO/Li₂S₄ ($R = 0.03$) recorded at 90 °C is displayed in **Figure S4**. Then σ was calculated using the usual relationship:

$$\sigma = \frac{l}{A * R_{bulk}} \quad (10)$$

1.9 Transference number

The cationic transference number (T^+) was calculated using the Bruce and Vincent method³¹ by applying the Watanabe equation³². Typically, a Li symmetrical cell is potentiostatically polarized by a constant potential (ΔV vs. Li⁺/Li) at 80 °C and the current (I) response is recorded over time until a steady state (I_s) is reached. An example of such a polarization is provided in **Figure S5a** for the PEO/Li₂S₄ ($R = 0.03$) at 80 °C. The bulk and interface resistances are determined before and after polarization by fitting the impedance spectra exemplified in **Figure S5b** for the same electrolyte. T^+ was calculated using the following equation³²:

$$T^+ = \frac{R_{bulk}}{\left(\frac{\Delta V}{I_s} - R_{int}\right)} \quad (11)$$

1.10 Ambipolar diffusion coefficient

The ambipolar diffusion coefficient (D_{amb}) was determined based on the restricted diffusion technique from Newman and Chapman³³ by allowing the previously polarized Li symmetrical cell to relax while the cell potential (ΔV vs. Li⁺/Li) is recorded over a typical time (t) of 3 hours. **Figure S5c** represents such a relaxation profile in the logarithm scale for the PEO/Li₂S₄ ($R = 0.03$) electrolyte at 80 °C. The slope of the linear part of $-\ln(\Delta V)$ vs. time (t) corresponds to the characteristic diffusion time (τ_d) of the ionic species. Then, D_{amb} was calculated according to **eq. 12**³⁴.

$$D_{amb} = \frac{\tau_d * l^2}{\pi^2} \quad (12)$$

By definition, the ambipolar diffusion coefficient can be written as a function of the cationic (D^+) and anionic (D^-) diffusion coefficients as:

$$D_{amb} = \frac{2D^+D^-}{D^+ + D^-} \quad (13)$$

$$D^+ = \frac{D_{amb}}{2(1 - t^+)} \quad (14)$$

$$D^- = \frac{D_{amb}}{2 * t^+} \quad (15)$$

2 Results and Discussion

2.1 Density of PEO/Li₂S_x

The density (ρ_{PEO/Li_2S_x}) of PEO/Li₂S_x electrolytes first determined in the Ar glovebox using the conventional density kit are displayed as a function of the lithium polysulfide concentration (R) in **Figures 1a** and **1b** for PEO/Li₂S₄ and PEO/Li₂S₈ respectively. In **Figure 1a**, the ρ of PEO/Li₂S₄ is a gradually increasing function of R . As a comparison, the theoretically calculated density based on **eq. 5** assuming an ideal mixture is added in **Figure 1a** as a red line. There is good agreement between the theoretical and the experimental data. In **Figure 1b**, the experimental density, ρ_{PEO/Li_2S_8} also follows the evolution of the theoretical density with the polysulfide concentration. However, the density of PEO/Li₂S₈ has a stronger increase with R compared to the PEO/Li₂S₄ electrolyte. Indeed, the slope of ρ_{PEO/Li_2S_8} is about twice that of ρ_{PEO/Li_2S_4} . Park et. al reported a similar difference in the slope between Li₂S₄ and Li₂S₆ in DOL/DME liquid-based electrolytes using molecular dynamic (MD) simulations³⁵. Depending on the amount of S₈ or Li₂S present in the Li₂S_x, the molar volume and thus the density of the PEO/Li₂S_x change accordingly. The difference between the experimental and theoretical density results from the specific interaction between the solute and the PEO matrix. Herein, the difference is in the error margin. For Li₂S₄, the break in slope in the experimental data around $R = 0.05$ could suggest reaching the limit of solubility. The assumption of an ideal mixture for the calculation of the density of PEO/Li₂S_x is a simplification, and it becomes particularly challenging because the disproportionation reaction results in a polydisperse distribution of species rather than a single Li₂S_x species. However, on average, the lithium polysulfide mixture seems to behave as the as-prepared equivalent Li₂S_x³⁶.

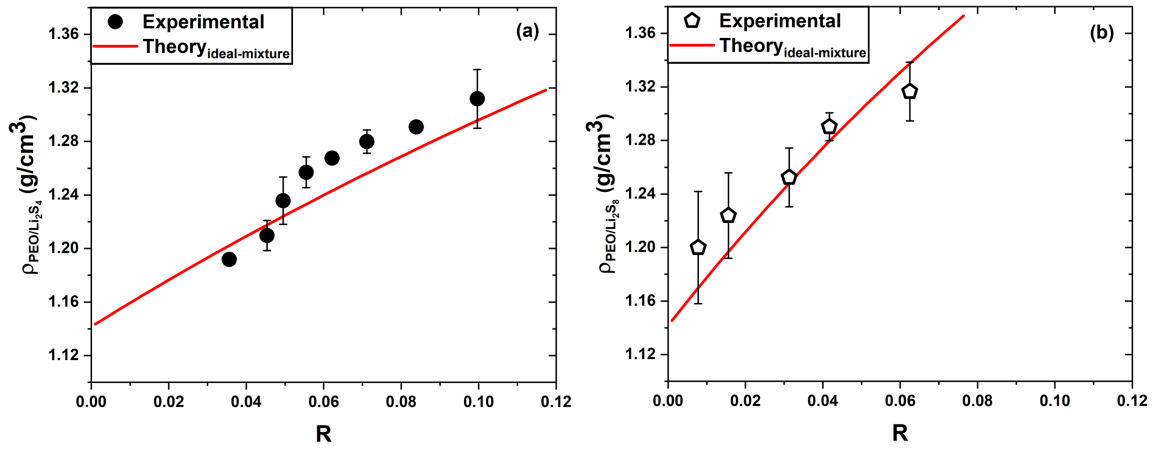


Figure 1. Experimental densities of (a) PEO/Li₂S₄ and (b) PEO/Li₂S₈. Theoretically calculated densities of the PEO/Li₂S_x are shown as a straight line (eq. 5) within the respective Li₂S_x.

2.2 Thermodynamical properties

DSC is a pivotal tool for understanding thermodynamical properties such as glass transition and crystallinity, which have a direct correlation to the ionic conductivity properties of polymer/salt complexes³⁷. In **Figure 2**, the DSC thermograms of PEO/Li₂S₈ at different salt concentrations are shown, highlighting the glass transition temperature (T_g , **Figure 2a**) and the melting temperature (T_m , **Figure 2b**) of the PEO. In **Figure 2a**, compared to the neat PEO ($R = 0$), the T_g shifted to higher temperatures with increasing Li₂S₈ concentration. Such dependency is typical of the physical crosslinking effect of salt solvation resulting in a stiffening of the polymer chains and thus decreasing the segmental motion³⁸. Also, the increasing height of the transition step with concentration suggests an increase in the amorphous content of PEO-Li₂S₈ complexes in the film. In addition, a single T_g is observed for the exemplified SPE in **Figure 2a** as well as for all the other investigated electrolytes irrespective of the nature of the lithium polysulfide and the concentration which indicates uniform composition²². In **Figure 2b**, T_m decreases to lower temperatures with the increase in Li₂S₈ concentration until complete amorphization which correlates to a lowering of the degree of crystallinity as the enthalpy of melting (ΔH_m) is also reduced. For all R values, the elemental sulfur (S₈) melting peak expected at about 118 °C is absent which confirms that there are no S₈ leftovers in the SPE mixtures resulting from the electrolyte formulation process³⁹.

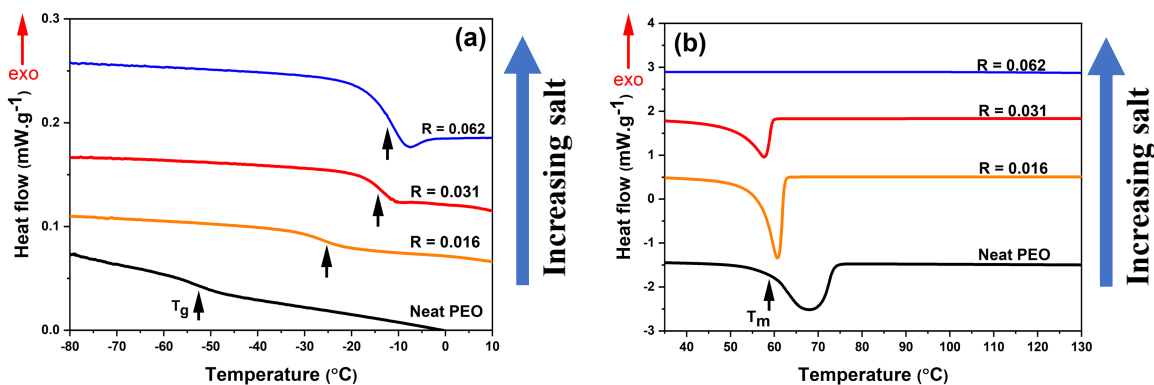


Figure 2. DSC thermograms of PEO/Li₂S₈ for different salt concentrations (R) focusing on the a) T_g and b) T_m regions. To enhance the clarity, the plots are vertically shifted.

The plot of T_g as a function of salt concentration (R) for the SPEs is shown in **Figure 3a**. As expected, the evolution of T_g with the concentration of LiTFSI (R) in PEO homopolymer is a constant increase and consistent with previous literature report⁴⁰. The T_g of PEO/Li₂S₄ versus R is also shown in **Figure 3a**. From this plot, it can be observed that at any given R value, the T_g of PEO/Li₂S₄ is higher than that of PEO/LiTFSI. This implies that when filled with Li₂S₄ salt, the chains of the PEO homopolymer become less mobile as compared to LiTFSI. Meanwhile, the T_g of PEO/Li₂S₄ presents a pseudo-linear increase from $R = 0$ (T_g of -56 °C) until $R \sim 0.056$. After this R value, there is a drop of about 10 °C of the T_g which was verified for several replicas of the PEO doped with Li₂S₄. This drop in T_g is an indication of reaching the limit of solubility of Li₂S₄ into the PEO homopolymer. Meanwhile, the results agree well with those reported by Wang *et al.* on comparable PEO/Li₂S₄ mixtures²². We noted that during the drying process in the desiccator of the highest concentrated electrolytes, some elemental sulfur particles tend to cover the glass dome of the apparatus. The collected particles were analysed by SEM and EDX and the results are shown in **Figures S6a** and **b** confirm the presence of bare sulfur. This indicates that the effective salt concentration of equivalent Li₂S₄ in the polymer for $R > 0.056$ is most probably lower than the reported value and confirms the principle of limit of solubility. On the other hand, the T_g of PEO/Li₂S₈ (**Figure 3a**) also increases continuously from -54 ± 2 °C at $R = 0$ to reach a plateau at $R = 0.063$ (-13 ± 2 °C). For $R \geq 0.013$, the T_g of PEO/Li₂S₈ is slightly lower than that of the PEO/Li₂S₄ counterpart. This translates into a faster dynamic of the PEO chains for Li₂S₈ than Li₂S₄. Also, within the investigated concentration range, there was no limit to the solubility of Li₂S₈ in PEO compared to Li₂S₄. This implies that the long-chain lithium polysulfide (Li₂S₈) is more soluble in PEO homopolymer than the short-chain lithium polysulfide (Li₂S₄). So, within a Li-S battery comprising PEO electrolyte, the thermodynamic and thus the correlated ionic transport properties will evolve during cycling, depending on the state of charge as a function of the polysulfide nature (redox shuttle).

The plot of melting temperature (T_m) versus R for PEO homopolymer doped with different salts is displayed in **Figure 3b**. The T_m of PEO/LiTFSI strongly decreases with increasing R as expected⁴⁰. The T_m of PEO/Li₂S₄ decreases strongly from the neat PEO until $R \approx 0.013$. Above this R value, the decrease in T_m is similar to PEO/LiTFSI but with higher magnitudes. Comparatively, the T_m of PEO/Li₂S₈ also shown in **Figure 3b**, decreases sharply with R until complete amorphization at $R > 0.06$. In general, the abrupt decrease of the T_m s with increasing Li₂S₈ concentration is similar to the seminal work by Balsara's group^{21,22}.

In **Figure 3c**, the plot of the degree of crystallinity (X_c) of the SPEs as a function of the concentration of the lithium salts (R) is displayed. For PEO/LiTFSI, X_c decreases with R due to the reduction in the enthalpy of melting by the presence of the salt⁴¹. For PEO/Li₂S₄, X_c decreases linearly with R from 74 % (neat) down to 0 % (amorphous) at $R = 0.093$. When the PEO homopolymer is doped with Li₂S₈, as also shown in **Figure 3c**, the decrease of X_c with R is more significant, reaching zero at $R = 0.06$. Below $R \leq 0.042$, the magnitude of X_c for PEO/Li₂S₈ is similar to that of PEO/LiTFSI electrolyte.

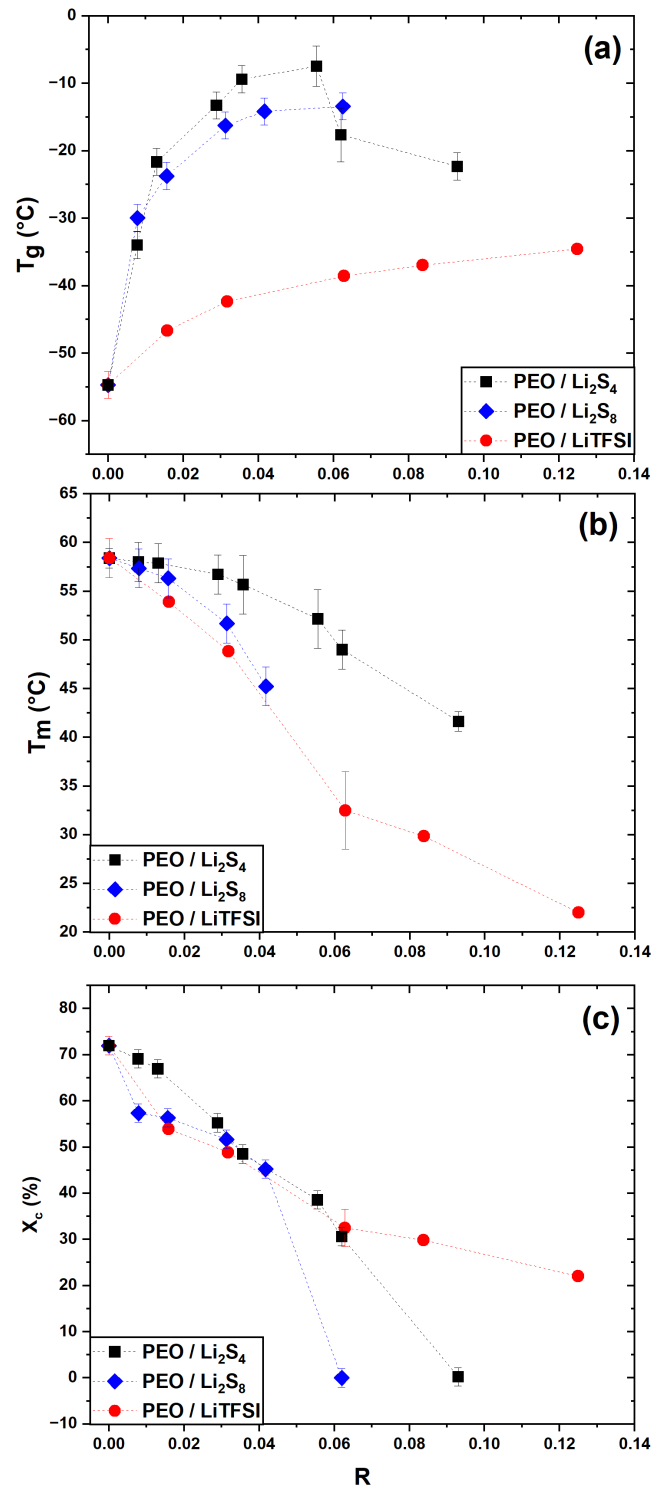


Figure 3. Thermodynamical properties of PEO doped with Li_2S_4 , Li_2S_8 and LiTFSI as a function of the salt concentration (R) for the (a) glass transition temperature (T_g), (b) melting temperature (T_m) and (c) degree of crystallinity (X_c).

2.3 FTIR spectra of PEO/Li₂S_x electrolytes

The interest of performing FTIR measurements is to study the effect of the polysulfide solvation into the PEO homopolymer. But to achieve this, the effect of well-studied LiTFSI on PEO was first investigated and compared. The FTIR spectra of neat PEO bands in the 800 - 1500 cm⁻¹ region, recorded at room temperature, are shown in **Figure 4a**. The vibrational peaks align well with the band positions reported in the literature^{42 43 44, 45}. Specifically, the bands between 1061 and 1147 cm⁻¹, corresponding to the C-O-C stretching vibrations, are reported to be sensitive to complexation with Li⁺ cations. In **Figure 4a**, upon the addition of LiTFSI, the relative intensity of the strong band at 1113 cm⁻¹ changes with salt concentration. In the region of interest (1061 and 1147 cm⁻¹), the vibrational modes of SO₂ and CF₃ from TFSI⁻ anion (reported in **Table 1**) overlap with the vibrations of C-O-C modes of the PEO occurring in the same frequency⁴³. Due to this, it is difficult to specifically quantify the effect of the solvation of the Li⁺ cations from LiTFSI by the PEO homopolymer. Therefore, the effect of Li⁺ cations on the stretching mode of the C-O-C vibration is subtle. Nonetheless, it is clear from **Figure 4a** that the addition of LiTFSI salt to the PEO leads to a reduction in the crystallinity evidenced by the broadening of the peaks between the 1060 and 1148 cm⁻¹.

Assignments	Frequency (cm ⁻¹)
ν_a ·SO ₂	1354, 1333
ν_s ·SO ₂	1136
ν_a ·CF ₃	1193
ν_s ·CF ₃	1240
ν_a ·SNS	1060
C-O-C	1100, 1118, 1147

Table 1. Characteristic frequencies of SO₂² and CF₃ stretching vibrations of TFSI⁻ from references⁴² and ⁴³, and that of the C-O-C band of the PEO. The symbols ν_s and ν_a represent symmetrical and asymmetrical stretching vibrational modes. The measurements were performed on PEO/LiTFSI ($R = 0.06$) at 80 °C.

The infrared absorption of the disulfide (S-S) vibrational band occurs in the 482 - 540 cm^{-1} range^{46 47}. Since the region of interest lies in the range of 1000 – 1200 cm^{-1} , using thin films of PEO/Li₂S_x provides a better way compared to LiTFSI to probe the interaction between Li⁺ and PEO. The molecular interactions of the PEO doped with varying concentrations of Li₂S₄, are shown in **Figure 4b**. Overall, minimal changes are observed in the peak positions of the complexes when compared to the neat PEO. This observation runs counter to the strong broadening and change of peak position, shape and intensity of the C-H bands that was reported by Fang *et al.* when a few concentrations of Li₂S₆ (≤ 5 wt %) were added to PEO⁴⁸. However, a closer examination of the frequency at 1113 cm^{-1} (in **Figure 4b**) reveals that the peak broadens slightly as the concentration of Li₂S₄ increases. This may provide some evidence of salt solubility within the PEO. This also suggests that there is a reduction in the crystallinity of the PEO due to the crosslinking effect of Li₂S₄ as already seen in the DSC measurements.

The vibrational spectra of PEO/Li₂S₈ are shown in **Figure 4c**. At $R \leq 0.03$, there is minimal visible effect of the Li₂S₈ salt on the PEO vibrational modes except for the slight broadening of the 1113 cm^{-1} peak. However, as R increases further, the C-H and C-O-C modes of the PEO become broader and signal a stronger reduction in crystallinity. At $R = 0.06$, the distinct vibrations between 1061 and 1150 cm^{-1} , merge into a single broad peak, shifting to lower frequency. This is an indication of a strong interaction between Li₂S₈ and the PEO at this concentration leading to almost complete amorphization of the PEO. This confirms the argument that Li₂S₈ may solubilize better in PEO compared to Li₂S₄ as demonstrated by the thermodynamical analysis in **Figure 3**.

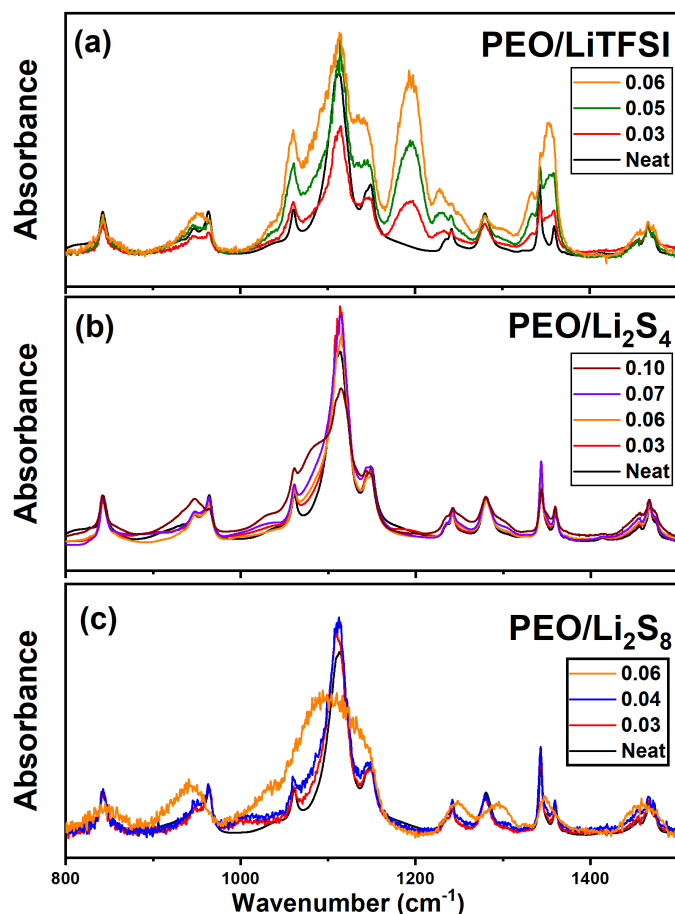


Figure 4. Infrared spectra measured at room temperature covering the region between 800 and 1500 cm^{-1} of PEO doped with (a) LiTFSI, (b) Li_2S_4 and (c) Li_2S_8 are displayed. The spectra are compared to the spectra of the neat PEO and are vertically stacked for easier comparison.

2.4 Microstructure of the PEO/ Li_2S_x mixtures

To assess the impact of Li_2S_x on the microstructure of the PEO, X-ray diffraction (XRD) measurements were conducted on selected samples at room temperature. The XRD patterns of PEO/ Li_2S_4 electrolytes measured at room temperature are shown in **Figure 5a**. Data obtained from neat PEO and Li_2S are given as references. The spectra for the neat PEO present the characteristic peaks of its semi-crystallinity and agree well with those reported in the literature^{49, 50}. As the concentration of Li_2S_4 was increased, the intensity of the crystalline peaks especially the single 120 peak at $2\theta = 19.1^\circ$ and the triple 032 peaks at 23.3° tend to broaden slightly while their intensities slightly decrease. There is a coalescence of the crystalline peaks at $2\theta = 13.1^\circ$ and 13.5° into a single peak at $R = 0.09$ as can be seen clearly in the insert of **Figure 5a**. This signifies a reduction in the PEO crystallinity. However, there are two distinctive peaks (indicated by an arrow) that can be observed at $2\theta = 10.7^\circ$ and 11.3° for $R \geq 0.02$. The presence of these peaks may be linked to a specific PEO: Li_2S_4 complex, similar to those of PEO:LiTFSI when the salt concentration reaches a certain threshold of $R > 0.042$ (*i.e.* $\text{EO}/\text{Li} < 12$)^{51, 40}. For $R = 0.02$, apart from the peaks of the PEO and PEO: Li_2S_4 complexes, there are peaks attributed to Li_2S that are present in the diffraction

pattern whose origin could either be due to (i) trapped unreacted Li_2S_4 from the Li_2S_4 synthesis or (ii) a disproportionation of Li_2S_4 into Li_2S and long chain polysulfides. Nevertheless, if the Li_2S originated from unreacted species, then the DSC spectra should have shown an endothermic peak at 115 °C due to the presence of a stoichiometric amount of S_8 in the polymer structure. In the absence of sulfur evaporation during SPE drying, the DSC spectra in **Figure 2b** do not display peaks attributed to sulfur melting. Therefore, spontaneous disproportionation or limited solubility of Li_2S_4 could explain the presence of Li_2S in the XRD patterns. However, a thorough investigation of this process is beyond the scope of this paper.

X-ray diffraction patterns for PEO/ Li_2S_8 electrolytes are depicted in **Figure 5b**. Again, there is not much difference between the spectra of the Li_2S_8 doped samples and the neat PEO, nonetheless, there is a slight broadening of the peaks. At $R \geq 0.03$, the 110 peak has diminished in intensity and the peaks marked with asterisks (shown in the insert of **Figure 5b**) merged into a single peak. The 112 peak has become so broadened that it appears almost extinct at $R = 0.06$. These observations attest to the amorphization of the PEO/ Li_2S_8 electrolytes as illustrated by both thermal and infrared measurements in **Figure 3c** and **4c** respectively.

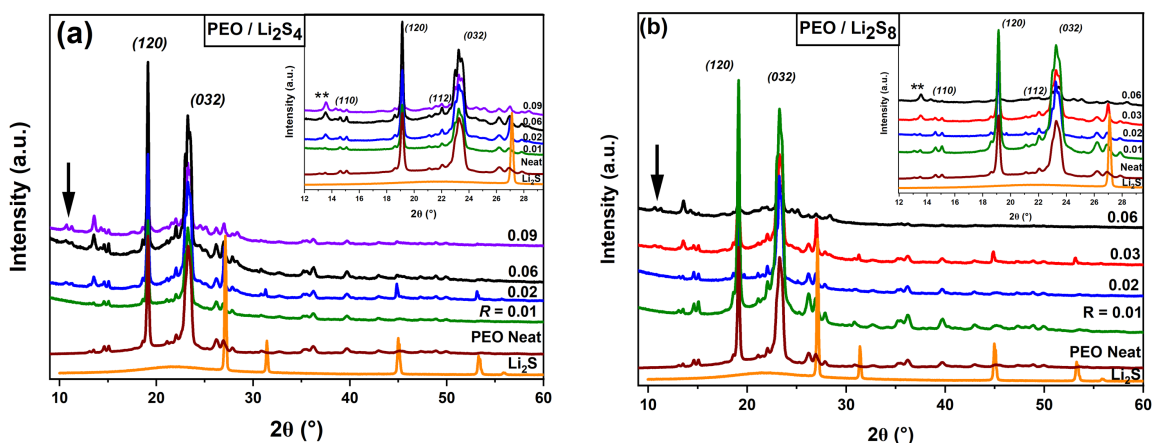


Figure 5. XRD spectra of the PEO doped with (a) Li_2S_4 salt and (b) Li_2S_8 salts. Spectra were recorded at room temperature. For clarity, the plots are vertically shifted.

2.5 Ionic transport of Li_2S_4 in PEO homopolymer

The ionic conductivities (σ) of PEO/LiTFSI and PEO/ Li_2S_4 electrolytes at 80 °C are displayed as a function of salt concentration (R) in **Figure 6a**. Similarly to PEO/LiTFSI, the σ of PEO/ Li_2S_4 , initially increases with R due to the increase in charge carrier concentration then reaches a maximum at $R = 0.05$ before decreasing slightly⁴⁰. The slight drop in σ has been attributed to i) an increase in the viscosity of the amorphous phase caused by the presence of a high concentration of salt and ii) the formation of ion pairs due to the increase in charge carrier concentration⁵². These effects lead to a decrease in both free ions and ionic mobility within the PEO chains. We observed that the reported ionic conductivity (σ) as well as the other ionic transport properties, transference number (T^+) and ambipolar diffusion coefficient (D_{amb}), for a 100 $\text{kg}\cdot\text{mol}^{-1}$ PEO/LiTFSI (see **Figure**

S8) are consistent with those reported in literature^{40, 53–56}, which validates our electrolyte formulation methodology. In **Figure 6a**, the slope of the plot of $\log(\sigma)$ versus $\log(R)$ for low salt concentrations, shown as a straight dotted line, presents a factor of +1, indicating full dissociation of the ionic species in the PEO homopolymer. Indeed, the degree of dissociation for both PEO/LiTFSI and PEO/Li₂S₄ electrolytes at low R is close to unity. This implies that at low salt concentrations, both salts solubilize in PEO to release Li⁺. However, remarkably for the same PEO homopolymer, there is about a factor of 4x reduction in the σ of Li₂S₄ compared to LiTFSI salt. This may indicate slower mobility of ions in general in PEO/Li₂S₄ complexes as compared to PEO/LiTFSI and/or a change in the transport number due to disulfide anion interactions with the PEO matrix. The lithium transference number (T^+) of PEO/Li₂S₄ complexes was investigated and the results compared to the T^+ of PEO/LiTFSI are displayed in **Figure 6b**. The T^+ of PEO/Li₂S₄ (average T^+ of 0.5) is also about a factor of 4x higher than the PEO/LiTFSI (average T^+ of 0.12) counterpart. In the PEO/LiTFSI electrolyte system, it has been shown by molecular dynamics (MD) simulations that the Li⁺ have a strong association with the ether oxygen of the PEO chains while the TFSI anion has less intimacy if any, and therefore moves more freely in the volume of the polymer⁵⁷. Therefore, the increased T^+ of Li₂S₄ means that on average the S₄²⁻ anion is slowed down as compared to the Li⁺. If this assertion is true, then the mobility of the free Li⁺ cations in both systems should be similar. In **Figure 6c**, the contribution of the Li⁺ cations (σ^+) to the overall conductivity of the PEO/Li₂S₄ and the PEO/LiTFSI electrolytes are compared. As expected, the σ^+ of PEO/Li₂S₄ and PEO/LiTFSI electrolytes are similar. This implies that the Li⁺ cations in the respective electrolyte systems, have similar mobilities and the variation in σ is only due to the reduction in anion dynamics (S₄²⁻ vs. TFSI). The S₄²⁻ anions interact with the ether of the PEO which slows down their local dynamics compared to TFSI. This could also mean that the solvation of anions and cations can be more complex with the formation of clusters which further reduces their dynamics and mobility. In that case, the Li⁺ cation could either interact partially with the PEO and the S₄²⁻ anion or the Li⁺ can be linked to two anions. To investigate further the origin of the variation in σ , restricted diffusion measurement was used to calculate the ambipolar diffusion coefficient (D_{amb}) of the ionic species; Li₂S₄ and LiTFSI in the PEO and the results are displayed in **Figure 6d**. Within the investigated concentration range, the D_{amb} is constant and independent of R for both ionic species. However, the diffusion of Li₂S₄ in the PEO is reduced by several factors compared to the LiTFSI. To go further in investigating the contribution of each ionic species to the overall D_{amb} , **Eq. 14** and **15** were used to calculate the cationic (D^+) and anionic (D^-) diffusion coefficients respectively. The plot of D^+ with R in **Figure 6f**, shows that indeed the dissociated Li⁺ in both Li₂S₄ and LiTFSI salts diffuse at the same speed and this speed is constant irrespective of the salt concentration. On the other hand, the plot of D^- vs. R in **Figure 6e**, expectedly displays close to an order of magnitude reduction in the diffusion of the S₄²⁻ anion in comparison to the TFSI. This is evidence that PEO homopolymer can reduce the shuttling of short-chain polysulfides

(S_4^{2-}) by two orders of magnitude ($10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$) relative to conventional liquid electrolytes such as DOL/DME ($10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$) used in Li-S battery⁵⁸.

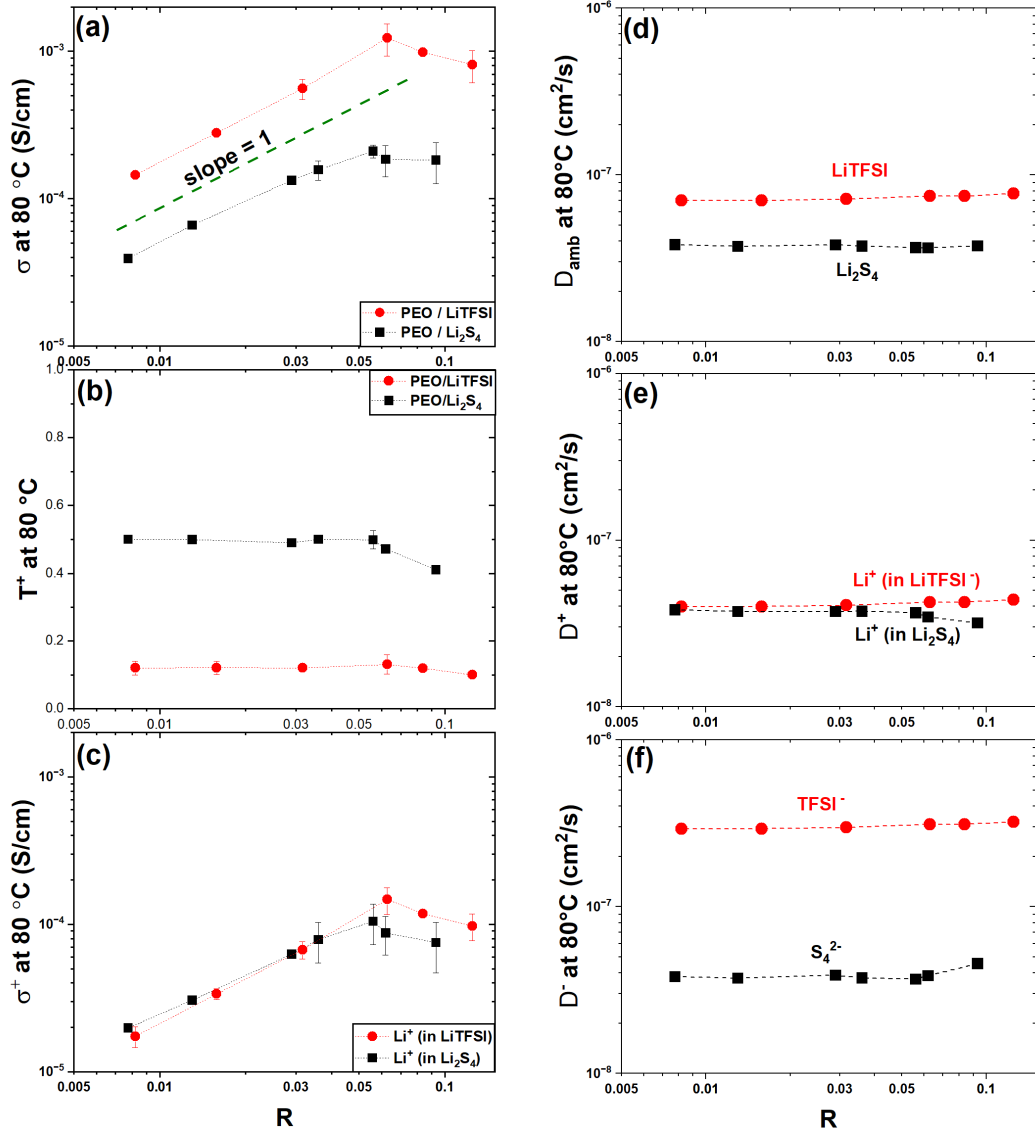


Figure 6. The plot of the (a) ionic conductivity (σ) at 80 °C, (b) Li^+ transference number (T^+) and (c) Li^+ conductivity (σ^+) of Li_2S_4 . The straight dotted lines (green) in (a) represent the full dissociation (slope = 1) of Li^+ at low R . Also shown are the (d) ambipolar diffusion coefficient (D_{amb}), (e) Li^+ diffusion coefficient (D^+) and S_4^{2-} diffusion coefficient (D^-) in PEO.

2.6 Ionic transport of Li_2S_8 in PEO homopolymer

The ionic transport properties of Li_2S_8 in PEO homopolymer were also investigated to analyse the polymer's efficiency in mitigating the shuttling of the long-chain polysulfide. The plot of conductivity σ as a function of Li_2S_8 concentration (R) is shown in **Figure 7a**. Like PEO/LiTFSI, σ of the PEO/ Li_2S_8 electrolyte increases with R until reaching a plateau at $R = 0.03$. But at $R \leq 0.03$, σ the PEO/ Li_2S_8 is more than a factor of 2 lower than that of PEO/LiTFSI, nevertheless higher than that of PEO/ Li_2S_4 . This is in good agreement with the results of the T_g in **Figure 3a**. At $R > 0.03$, σ

of PEO/Li₂S₈ decreases sharply to more than an order of magnitude lower than that of PEO/LiTFSI. This could be a result of increased ion-ion cluster formation leading to high viscosity owing to the full dissociation of 2Li⁺ from the S₈²⁻ as in the equation $\text{Li}_2\text{S}_8 \rightarrow 2\text{Li}^+ + \text{S}_8^{2-}$. The contribution of the transference number of the ionic species to the overall conductivity was investigated by measuring the T^+ of the PEO/Li₂S₈ electrolyte and the result is shown in **Figure 7b**. In the PEO homopolymer, the Li⁺ transference number from Li₂S₈ is more than 4x higher than that from LiTFSI and slightly higher than that of Li₂S₄. This means reduced mobility of S₄²⁻ as compared to S₈²⁻ anions.

A comparison of the σ of PEO/Li₂S₈ and PEO/Li₂S₄ shows a difference of about a factor of 2. This difference could originate from the transference number or the degree of dissociation of the two salts in PEO. Since the transference number of both salts in PEO is similar, the difference in dissociation of the salts in PEO may give rise to different σ . Indeed, from the T_m analysis, we see that Li₂S₈ is more soluble than Li₂S₄. We can therefore assume that the dissociation of Li₂S₄ in PEO will proceed by $\text{Li}_2\text{S}_4 \rightarrow \text{Li}^+ + \text{LiS}_4^-$. On the other hand, Li₂S₈ may fully solubilize in PEO to release 2Li⁺ cations according to the equation: $\text{Li}_2\text{S}_8 \rightarrow 2\text{Li}^+ + \text{S}_8^{2-}$. Overall, for LiS₄⁻ (in Li₂S₄), we can imagine a charge of -1 which is distributed over four sulfur atoms whereas for S₈²⁻ (in Li₂S₈), we would have a charge of -2 distributed over eight sulfur atoms. Therefore, the true equivalent concentration of Li⁺ in Li₂S₈ will be $2R$. In **Figure 7c**, the plot of σ^+ versus R is shown, where the concentration of Li⁺ cations in Li₂S₈ has been taken to be $2R$. At $R \leq 0.06$, the σ^+ of Li⁺ in Li₂S₈ is similar to that of LiTFSI. This translates to similar Li⁺ mobility in both systems. At higher R however, there is a deviation in the Li⁺ for the two systems. To verify this, the D_{amb} of Li₂S₈ in PEO was measured using the restricted diffusion method and the results are presented in **Figure 7d**. The D_{amb} of Li₂S₈ is lower than that of LiTFSI as expected but it is also slightly lower than that of Li₂S₄. This means that despite the higher solubility of Li₂S₈ in PEO compared to Li₂S₄, its mobility is slightly reduced. The result of the calculation of the cationic diffusion coefficient (D^+) using **eq. 14** is shown in **Figure 7e**. The plot shows that the dissociated Li⁺ from Li₂S₈ diffuse slightly slower when compared to those from LiTFSI. The evolution of D^- versus R displayed in **Figure 5e** shows that the diffusion of S₈²⁻ is slightly lower than S₄²⁻. This could stem from both the slightly higher viscosity of the PEO/Li₂S₈ electrolyte due to higher solubility and the bulky nature of the anion (8 sulfur atoms) as compared to S₄²⁻ (4 sulfur atoms). Overall, the difference between σ of Li₂S₈ (factor 2 lower) and Li₂S₄ (factor 4 lower) as compared to LiTFSI in PEO, could stem from the difference in the degree of dissociation between the two lithium polysulfides. Thus, Li⁺ for Li₂S₄ versus 2Li⁺ for Li₂S₈.

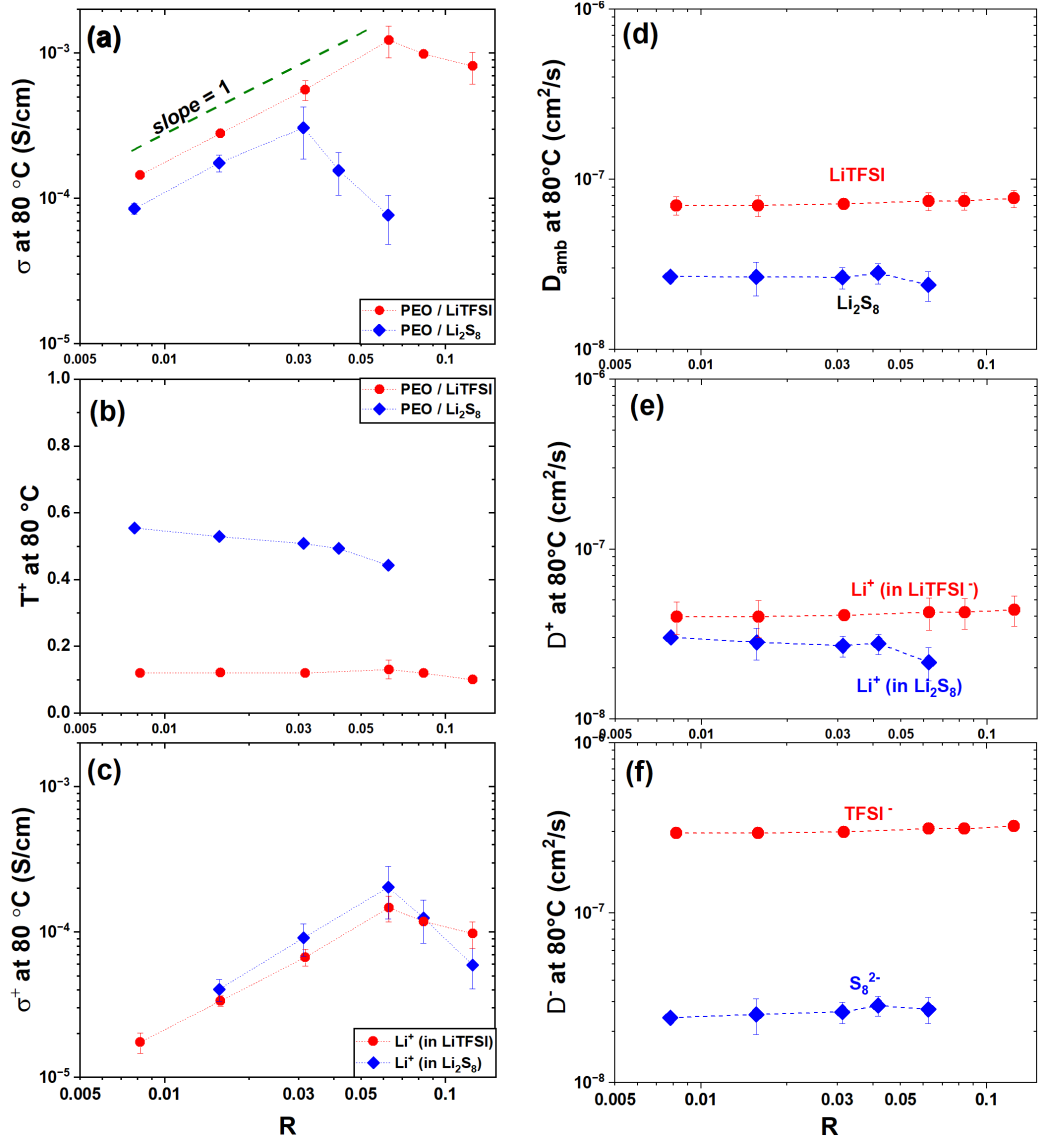


Figure 7. The plot of the (a) ionic conductivity (σ) at 80 °C, (b) Li⁺ transport number (T^+) at 80 °C and (c) Li⁺ conductivity (σ^+) of Li₂S₈. The straight dotted lines (green) in (a) represent the full dissociation (slope = 1) of Li⁺ at low R . Also shown are the (d) ambipolar diffusion coefficient (D_{amb}) measured at 80 °C, (e) Li⁺ diffusion coefficient (D^+) and S₈²⁻ diffusion coefficient (D^-) in PEO.

3 Conclusion

The thermodynamical properties of lithium polysulfides in PEO homopolymer were investigated via differential scanning calorimetry (DSC). The glass transition temperature (T_g) of the PEO/Li₂S₄ electrolytes showed a linear increase with salt concentration until a plateau at $R = 0.04$, indicative of the limit of solubility of Li₂S₄ into the PEO. On the contrary, the T_g of PEO/Li₂S₈ blends

increased continuously with R . This observation was further supported by the melting temperature (T_m), FTIR, density and XRD measurements of the PEO/Li₂S_x electrolytes revealing that the solubility of Li₂S₈ into PEO is higher than Li₂S₄. The electrochemical characterization of the PEO/Li₂S_x electrolytes indicates that Li₂S₄ may dissociate partially in PEO to form Li⁺ and LiS₄⁻ species because of the limited solubility of the polysulfide into the homopolymer whereas the Li₂S₈ tends to fully dissociate. Furthermore, it was demonstrated that PEO can slow down the mobility of short-chain polysulfide (S₄²⁻) anion by an order of magnitude relative to TFSI⁻ anion while the Li⁺ in both systems diffuse at the same speed. Due to the higher solvation of Li₂S₈ by PEO, the long-chain polysulfide can dissociate into 2Li⁺ cations and S₈²⁻ anion resulting in higher ionic conduction in the PEO/Li₂S₈ electrolyte compared to the PEO/Li₂S₄ system. The diffusion of S₈²⁻ ($2 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$) in PEO at 80 °C was found to be slightly slower than that of the S₄²⁻ ($3 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$). These results are intended to guide the design of SPEs used as binders or electrolyte layers to mitigate the transport of Li₂S_x in all solid-state Li-S batteries.

4 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.

5 Data availability

Data will be made available on request.

6 Acknowledgments

This work was supported by the French Agence Nationale de la Recherche ANR grant SHUTTLE (ANR19-CE05-0023).

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