

Toward unveiling structure and property relationships from ionic ordering in Li/S battery electrolytes: Neutron total scattering and Molecular dynamics simulations

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ABSTRACT: With their high energy density and environmental friendliness, lithium/sulfur (Li/S) batteries represent a promising candidate for the post-lithium-ion era. However, complex degradation mechanisms and a lack of microscopic insight into the molecular structure of the polysulfide (PS) and ether-based electrolyte materials have hindered the broad commercialization of this energy storage system so far. Here, neutron scattering experiments combined with electronic-continuum corrected molecular dynamics simulations of typical ether-based electrolytes for lithium/sulfur batteries were used to elucidate the complex electrolyte and PS structure. We find that a delicate balance between ion-ion and ion-solvent interactions steers the ordering and undesired clustering of Li^+ and PS ions at moderate concentrations ($> 1 \text{ M}$). Meanwhile, when NO_3^- ions are added to the electrolyte, they couple with Li^+ ions, screen electrostatic potentials, and frustrate the ionic ordering, thereby preventing PS from forming larger clusters. Consequently, LiNO_3 salt, primarily used for passivation of the lithium anode, also plays a vital role in suppressing the dendrite growth and in higher ionic conductivity. Our study and presented combination of methods are extendable to other electrolytes and compositions and provide a significant step forward in the modeling and understanding of next-generation battery materials.

Introduction

Driven by the ever-growing electric vehicles sales and renewable energy generation, the demand for energy storage systems increases. Highly efficient and economically attractive battery technologies are expected to play a crucial role in transitioning to a sustainable energy system. Lithium-sulfur (Li/S) batteries are a promising candidate for next-generation energy storage systems because of their low cost, safety, and high theoretical specific energy of 2600 Wh kg^{-1} [1].

However, the commercial applications of Li/S batteries are still hindered by several intrinsic problems, such as the dendrite formation and the reactive Li-metal electrode, the significant volume change of the active materials, the insulating properties of S_8 and Li_2S , and the polysulfide (PS) shuttle during the charging. Among these issues, the PS shuttle is considered to be the primary factor causing rapid capacity fading and low Coulombic efficiency [2]. The shuttle effect is caused by highly soluble intermediate PS ions, which escape from the cathode side, and "shuttle" between the cathode and anode during charging,

resulting in parasitic reactions on the Li metal anode. Subsequently, it forms insulating layers on the Li metal surface, leading to fast capacity fading in Li/S batteries.

Various strategies have been attempted to address this shuttle effect. They include the physical confinement of sulfur into a highly ordered porous carbon [3–5], the chemisorption between the host materials and sulfur [6–9], interlayer materials [10,11], or sulfurized-conductive polymers [12,13]. From the electrolyte side, highly concentrated electrolytes [14], ionic liquids [15], restricting the polysulfide solubility, or the use of sparingly solvating electrolytes [16–20] have been explored. Recently, the opposite direction of maximizing the solubility of polysulfides by using high donor solvents or salts is also actively studied in the context of the low electrolyte/sulfur (E/S) ratio [21–24].

The formation of the ionic pairs or aggregates strongly depends on the ionic strength, concentration, polar/non-polar, donor ability, and the shapes of ions and solvents [2,18]. Such ion pairs or aggregates affect ionic conductivity, diffusion, and solubility of Li^+ and PS ions in Li/S electrolytes. The shuttling PS species during charging can be influenced by the $\text{Li}^+\text{-S}_n^{2-}$ association or clustering [25].

Although the properties of electrolytes for Li/S batteries are critical to the electrochemistry [26] and the shuttle effect [15,18,23,27,28], a deeper understanding of the structure of Li/S electrolytes is still controversial. Previously, density functional theory calculations [29,30] revealed that Li/PS clusters or networks are more favorable than simple Li_2S_n . Studies with classical force-field based molecular dynamics (MD) simulations [31,32] also reported aggregated PSs in the solutions. Andersen et al. [32] found that the computationally calculated NMR and X-ray absorption spectroscopies for the aggregated PSs chains agree with experiments. Meanwhile, our previous study [25] showed that the tendency to cluster decreases with PS chain length though single PS units prevail. Up to now, there have been several experimental and theoretical studies investigating the stable PS species in the Li/S battery electrolytes. Nevertheless, the structure of the liquid PS electrolytes is still not fully understood.

In this study, we use a combination of neutron scattering experiments and the electronic continuum corrected (ECC) method [33–40], ‘ECC-MD’ simulations to elucidate the liquid PS electrolyte structure. Neutron scattering experiments can provide a total structure factor for liquid electrolytes, a robust experimental benchmark for solution structure. At the same time, MD simulation trajectories can be used to obtain the total structure factor by Fourier transform of the weighted sum of the radial distribution functions in the system [41]. As shown previously, ECC-MD can provide consistent insight into electrolyte structure and dynamics in organic and aqueous solvents [25,34,39,42], combining neutron experiments and MD simulations provides direct insights into the liquid structural properties of electrolytes for Li/S batteries and elucidates the complex interaction of the lithium salts with the PS.

Experimental Section

All chemicals were used without further purification and were purchased from Sigma Aldrich except for the deuterated dimethoxyethane (d-DME), which was ordered from Eurisotop. Lithium sulfide and sulfur were mixed in the respective ratios to obtain the desired stoichiometric ratio for the different concentrations of PS solutions (0.1 M, 0.5 M, and 1.0 M). The two fully deuterated solvents used are tetrahydrofuran (d-THF) and 1,2-dimethoxyethane (d-DME). THF was used instead of the mainly used 1,3-dioxolane (DOL) because of its more straightforward deuteration procedure and its chemical similarity. The various solutions were mixed with PS, lithium bis(trifluoromethanesulfonyl)imide lithium salt (LiTFSI), and LiNO_3 . The investigated chemical compounds are shown in Figure 1 and their solutions summarized in Table 1 (detailed computational setup is tabulated in Table S1 in the Supporting Information (SI)).

Neutron diffraction data were collected using the Near and Intermediate Range Order Diffractometer (NIMROD) instrument [43] at the ISIS spallation neutron source (Harwell, U.K.). The liquid samples were prepared in a glovebox filled with argon atmosphere, and null scattering $\text{Ti}_{0.68}\text{Zr}_{0.32}$ alloy cells were used, as this avoids potential issues with cell background subtraction from Bragg peaks. These flat sample containers had in-

ternal dimensions of $35 \times 35 \times 1$ mm and were loaded into an automatic sample changer. All measurements were conducted at room temperature, which was around 24°C . The neutron scattering of the samples was measured with a beam size of 30×30 mm for at least 2 hours. The measured neutron scattering was reduced to the differential scattering cross-section $F(q)$ using the program GudrunN [44,45]. This program summarizes the time-of-flight scattering from all detectors to a single q -scale, normalizes to a 3 mm VNb plate calibration standard, subtracts the scattering from the sample container and empty instrument, and applies corrections for beam attenuation, multiple scattering and inelastic scattering.

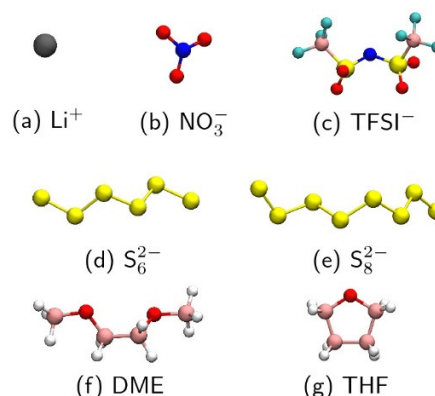


Figure 1 Illustration of the ions (a to e) and solvent molecules (f and g) in the investigated solutions.

Table 1 Investigated solutions in experiments and MD simulations. In the sample name LT x -PS y , x stands for LiTFSI concentration and y for polysulfide concentration.

Sample name	Composition
LT0-PS00	deuterated tetrahydrofuran (D-THF)
LT1-PS00	D-THF + 1 M LiTFSI
LT0-PS05	D-THF + 0.5 M Li_2S_6
LT0-PS10	D-THF + 1 M Li_2S_6
LT0-PS410 ¹	D-THF + 1.0 M Li_2S_4
LT1-PS05	D-THF + 1M LiTFSI + 0.5 M Li_2S_6
LT1-PS10	D-THF + 1M LiTFSI + 1.0 M Li_2S_6
EL	D-THF/d-DME (1:1, v:v) + 0.25 M LiNO_3 + 1 M LiTFSI + 0.1 M Li_2S_8

¹ LT0-PS410 is only investigated with MD simulations.

Molecular dynamics simulations

For atomistic modeling, we used the OPLS-AA force field [46] for the THF and DME solvents, Dang *et al.* parameters for Li^+ ions [47], the DREIDING force field for the S atoms [48], and the CL&P force field for TFSI $^-$ ions [49]. Lennard-Jones interaction parameters (σ_{ij} and ϵ_{ij}) between different species (i and j) were calculated using the geometric combination rules.

The chosen combination of force field parameters has been shown to reproduce very well experimental diffusion coefficients, conductivity, viscosity, and density of similar solutions [25,50]. Notably, the interactions between ions, especially between Li^+ -ions and terminal S atoms, require special attention, as they are the ones responsible for PS clustering and aggregation [25]. Therefore, properly modeling these interactions is crucial to reproduce the experimental results. To that end, we compared two options for ionic interactions: (1) In the conventional approach (termed 'conv'), we used original LJ parameters and formal (integer) ionic charges, as provided by the used force fields. (2) In the second approach (termed 'ECC'), we used the electronic continuum correction (ECC) method [33], in which all ionic charges were reduced by the high-frequency refractive index $n = 1.4$ of THF in order to mimic the electronic polarizability implicitly, which is not included in the classical force field [25,50]. In addition, the LJ size parameter between the Li^+ ion and S atoms was increased from the original $\sigma_{\text{Li-S}} = 0.233$ to 0.275 nm, as rationalized in our previous work [25].

MD simulations were carried out with the GROMACS simulation package using the velocity Verlet algorithm for integrating Newton's equations of motion [51]. Initial simulation structures of ions in the solvent were constructed with the PACKMOL package [52]. The molecules were randomly inserted into the simulation box and then first equilibrated by the energy minimization procedure, followed by an NPT simulation (fixed number of particles, pressure, and temperature) using the Berendsen [53] and Parrinello-Rahman [54] barostats (the equilibrated cubic box size L was ~ 7 nm). The production simulations were carried out with a time step of 2 fs in the NVT ensemble (fixed number of particles, volume, and temperature) at 298 K (see Table S1). The atom positions were stored every 6 ps. The temperature was controlled by the Nosé-Hoover chain thermostat [55] with a time constant of 0.8 ps. The cutoff of the non-bonded interactions was set to 1.2 nm, with a standard dispersion correction for energy and pressure. The particle mesh Ewald method with a Fourier spacing of 0.12 nm and a 1.2 nm real-space cutoff was used for calculating electrostatic interactions [56]. The LINCS algorithm was used for all bond constraints [57]. Periodic boundary conditions were used to approximate infinite bulk behavior. The equilibration was quantified by monitoring the average molecular cluster size $\langle N \rangle$ of PS, see Figure S1 in the SI. A cluster was defined as a group of PS ions whose at least one terminal S atom approaches a terminal S atom of another PS ion within at least 0.53 nm [25].

Radial distribution functions (RDFs) and static structure factors were obtained using a GROMACS utility and the 'DLPUtills' analysis code [51,58]. The total structure factor $F(q)$ in the simulations was obtained by the weighted sum of all of the partial structure factors $S_{ij}(q)$ [45]

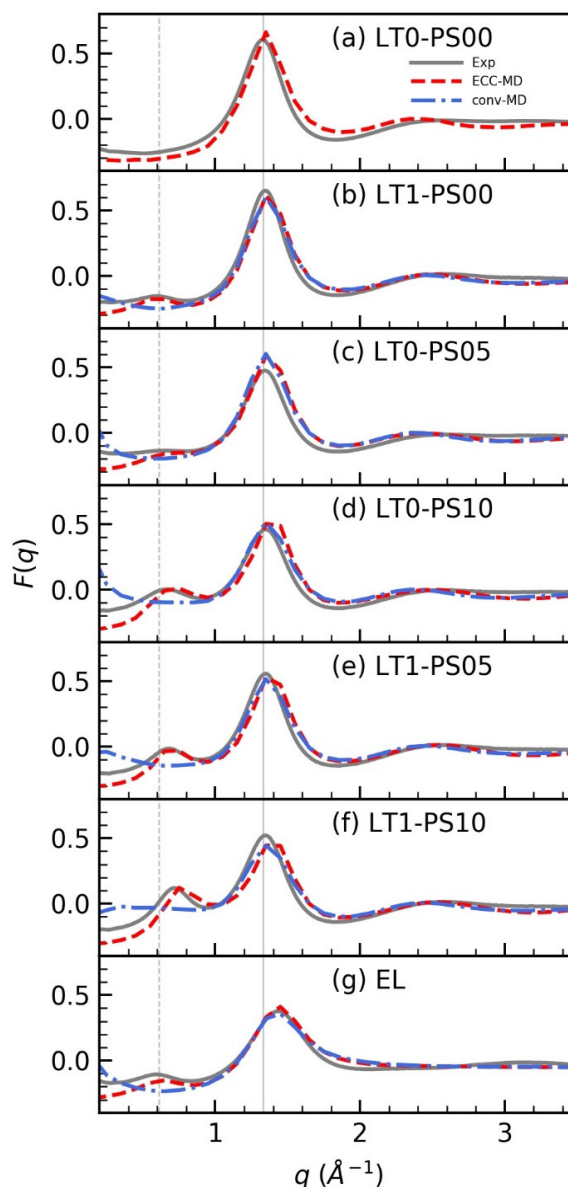


Figure 2. Structure factors $F(q)$ obtained from neutron scattering and MD simulations in different solutions. The neutron scattering data are collected on 100 % deuterated solvents (gray solid lines). MD simulations using the ECC and conventional approaches are shown in red dashed and blue dash-dotted lines, respectively. The solid and dashed vertical lines show the positions of the main peak in LT0-PS00 and the low q peak in LT1-PS00, respectively.

$$F(q) = \sum_{i,j \geq i} (2 - \delta_{ij}) c_i c_j b_i b_j (S_{ij}(q) - 1) \quad (1)$$

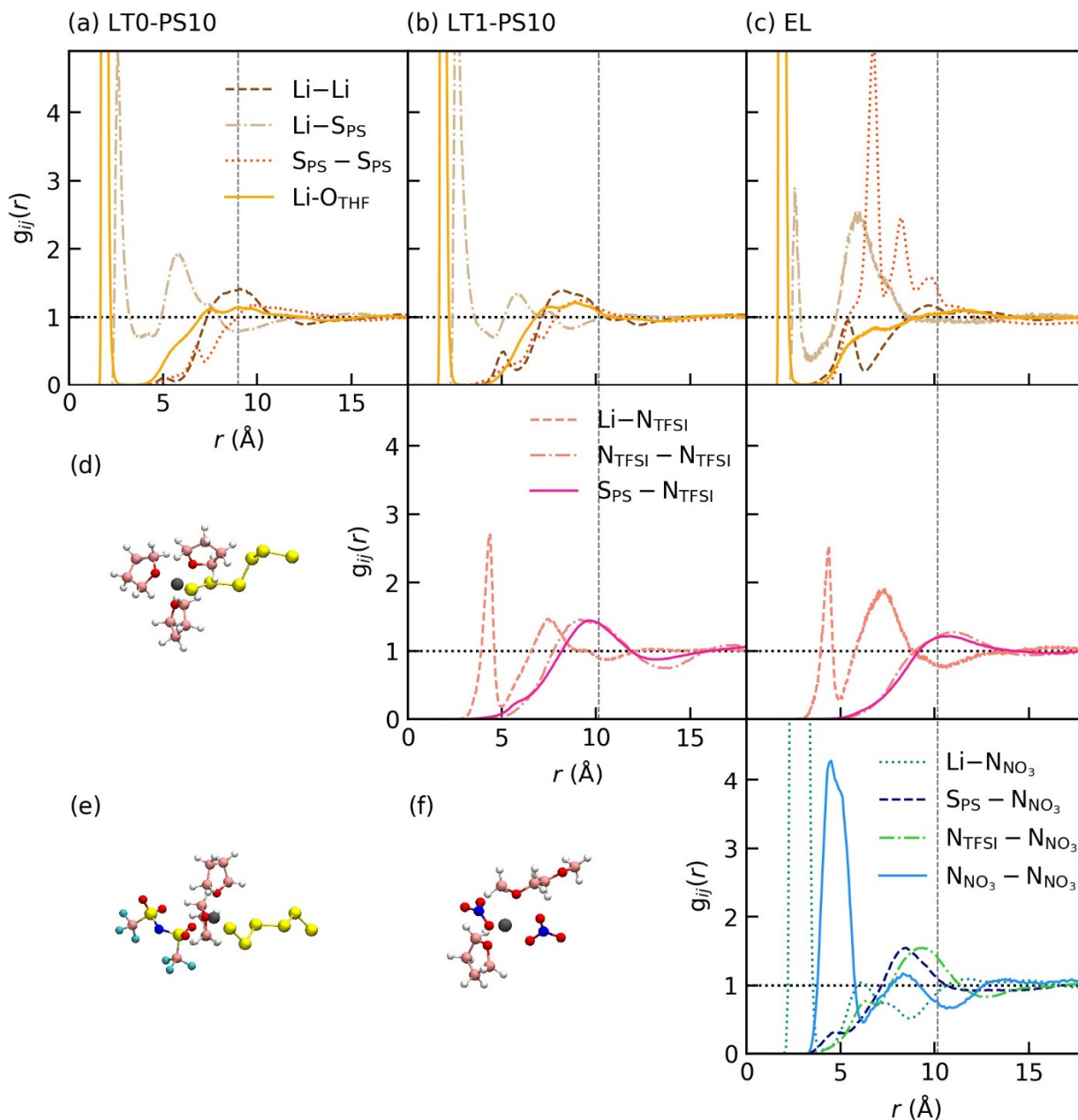


Figure 3: Radial distribution functions (RDFs) derived from ECC-MD simulations for different solutions: (a) LT0-PS10, (b) LT1-PS10, and (c) EL. Representative snapshots of Li^+ solvation shell are shown in (d) for LT0-PS10, (e) for LT1-PS10, and (f) for EL.

where q is the scattering vector of length $4\pi(\sin\theta)/\lambda$ for a neutron of wavelength λ scattered at an angle of 2θ . Here, c_i and b_i are the atomic fraction and the neutron scattering length of atom i , respectively. The partial structure factor $S_{ij}(q)$ was obtained from the RDF, $g_{ij}(r)$, of the atom pair ij by a Fourier transform

$$S_{ij}(q) - 1 = \frac{4\pi\rho_0}{q} \int_0^\infty r[g_{ij}(r) - 1]\sin(qr)dr, \quad (2)$$

where ρ_0 is the atomic number density of the solution. Given that the positions of all atoms in the system are known, the total structure factor $F(q)$ can be calculated and compared to the experimental total structure factor.

Results

Figure 2 shows the total structure factor, $F(q)$, from the neutron scattering data collected on 100 % deuterated THF (solid gray line) and MD simulations using the ECC correction (red dashed line) and the conventional approach (blue dotted dash line). In general, the quality of the structure factor from the ECC approach is found to yield better agreement with the experimental data than the conventional approach. The main peak is located around $1.6 \text{ \AA}^{-1}$, and the tail slightly fluctuates between 2.5 and

4 Å⁻¹. Changing the deuteration percentage in THF has an effect on the magnitude of the main peak and the shape of the tail (see Figure S2 in the SI).

In Figures 2d-g, we observe a distinctive, low q peak between 0.4 Å⁻¹ and 0.9 Å⁻¹ in the scattering data and the ECC simulations. This low q peak increases in intensity with concentrations of PS and LiTFSI. In the EL system (Figure 2g), however, the peak is rather weak. Using shorter PS chains in LT0-PS410 also features the main peak at around 1.4 Å⁻¹ but not the low q peak (Figure S3 in the SI). Note that experimental data for the latter are not available.

Overall, the ECC simulation approach is able to capture the variations of the main peak around 1.6 Å⁻¹ and the low q peak at 0.4–0.9 Å⁻¹ in different solutions. This comparison validates the ECC simulation approach as a suitable model capable of reproducing the experimental results. Therefore, the MD simulation analysis and predictions in the following will be based on the ECC approach.

In general, the structure factor $F(q)$ in Figure 2 features two peaks: the main one at around 1.4 Å⁻¹ and the low q peak between 0.4 and 0.9 Å⁻¹. The main peak can be attributed to the size and packing of the THF molecules and is therefore present in all samples (see the RDF analysis in Figure S4 in the SI). The low q peak develops by adding LiTFSI salt or PS into the THF solvent (LT1-PS00, Figure 2b). Similar observations regarding LiTFSI were reported by Aguilera *et al.* [59], stating that the low q peak between 0.8 and 1.0 Å⁻¹ in LiTFSI/tetraglyme (G4) electrolytes is due to a charge alternation of Li⁺/G4 complexes and TFSI anions. Namely, the long carbon and oxygen chain in G4 embraces (chelates) Li⁺ ions, forming solvent-separated ion pairs. These Li⁺/G4 complexes act as positive ions, and together with TFSI anions, they form alternating structures reminiscent of ionic liquids [59]. Although the chelate effect is not expected to occur in our systems with the THF solvent, we attribute the low q peak in the presence of LiTFSI salt to an alternating structure of Li⁺ and TFSI⁻ ions, which we corroborate by an RDF analysis in Figure S5 in the SI.

Moreover, the low q peak evolves also with an increasing concentration of the PS component (Li₂S₈) alone, that is, even without LiTFSI (LT0-PS10). A significant contribution to the peak in this case stems from the Li-Li pairing, as implied by the RDF results in Figure 3a. In LT0-PS05 (Figure 2c), the concentration of Li₂S₈ is probably too low to engender the peak, even though it features a fairly identical Li-Li RDF as LT0-PS10 (see Figure S6 in the SI).

It is interesting to take a deeper look into the local environment of Li⁺ ions. Li⁺ ions are solvated well by the THF solvent (see Figure 3d), as indicated by a strong of Li-O_{THF} peak in Figure 3a. As follows from the coordination number analysis (Figure S7 in the SI), each Li⁺ in LT0-PS10 is on average surrounded by ~3.4 THF molecules and 0.5 terminal sulfur atoms of PS chains. Similarly to the Li⁺ solvation in LT1-PS00, the solvent-separated Li⁺ ions and PS terminals configure an alternating structure and lead to the long-range correlations that are manifested in the low q peak at 0.4–0.9 Å⁻¹ in Figure 2d.

Figures 2e and f show that the low q peak grows with an increasing concentration of Li₂S₈ particularly strong in the presence of LiTFSI. The position of the low q peak accords with the RDF peaks (via $r = 2\pi/q$) of the Li-Li, S₆-N_{TFSI}, and N_{TFSI}-N_{TFSI} pairs (Figure 3b). The first peak of Li-N_{TFSI} at ~4 Å is contrib-

uted to the TFSI⁻ ions interacting with Li⁺ ions in a monodentate way, whereas the second peak at ~7 Å comes from the TFSI⁻ ions in the second solvation shell of Li⁺ ions. A snapshot of a TFSI⁻ ion in the first solvation shell of Li⁺ is shown in Figure 3e. The coordination number of Li⁺ ions by TFSI⁻ ions increases by ~50 % (from 0.16 to 0.25, see Figure S7d and e in the SI) when going from LT1-PS05 to LT1-PS10. This can be interpreted that adding Li₂S₈ increases the alternating structure of TFSI⁻ ions.

Interestingly, adding 0.25 M LiNO₃ into the 0.1 M Li₂S₈ + 1 M LiTFSI (EL solution) features only a weak low q peak. We also observe that the RDF peak for Li-Li at around 9 Å, which corresponds to the low q peak, in Figures 3a and b is absent in Figure 3c (EL solution). Thus, the low q peak in the EL solution (Figure 2g) does not stem from Li⁺ ions but instead from anion-anion pair correlations involving TFSI: S₆-N_{TFSI}, N_{TFSI}-N_{TFSI}, and N_{TFSI}-N_{NO3}.

Based on our observation described above, Li⁺ ions in LT0-PS10, LT1-PS10, and EL are closely surrounded by O_{THF} and S atoms. NO₃⁻ ions in EL are also able to tightly bound to Li⁺ ions (see a pronounced peak at low r in Figure 3c). Meanwhile, the pair distributions of anion-anion pairs, except N_{NO3}-N_{NO3}, are found at a larger r than Li-O_{THF} and Li-anion.

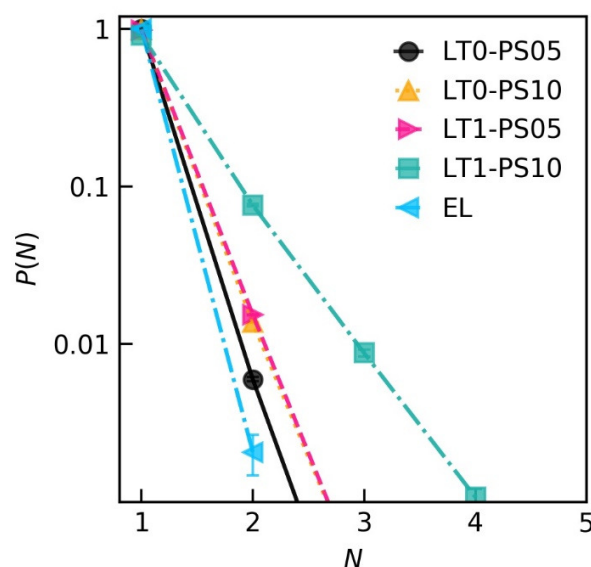


Figure 4: Cluster size distributions in a log-lin representation obtained from ECC-MD simulations for the investigated solutions.

We now take a closer look at how PS molecules in the simulations cluster together. Our previous study showed that PS ions are very inclined to cluster together, especially at higher concentrations [25]. Here, we also observe that the clustering of PS tends to increase with PS and LiTFSI concentration, as shown in Figure 4. Yet, single PS ions still prevail at the investigated concentrations. The most extensive clustering is therefore observed at the highest concentrations of PS and LiTFSI simultaneously, which is in the LT1-PS10 solution, albeit only with around 10% of dimers and 1% of trimers. In contrast, the EL solution forms the fewest PS clusters among all the solutions. The major reason is that S₈ is less prone to clustering than S₆ owing to less localized charges its termini [25]. By the same token, substituting S₆²⁻ by S₄²⁻ increases clustering (see Figure

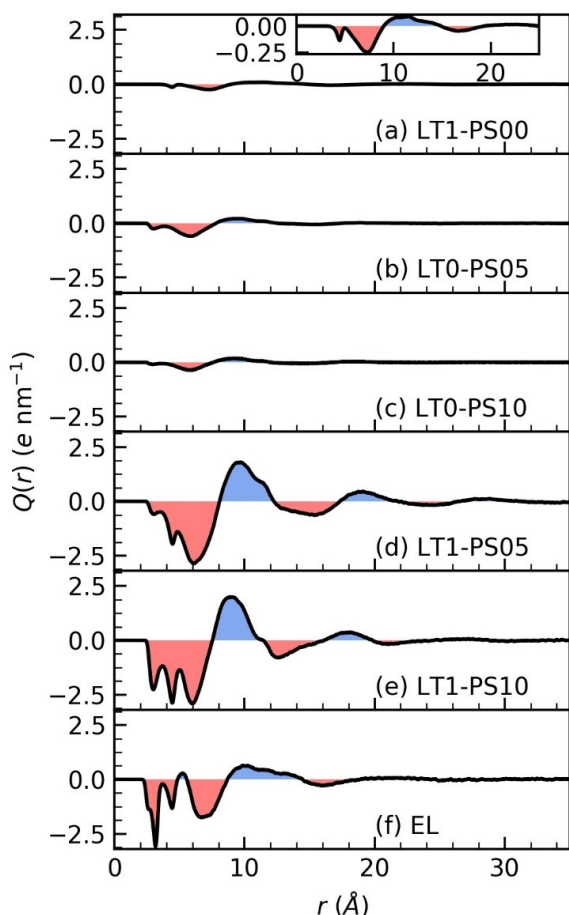


Figure 5: Charge-charge correlations $Q(r)$ referenced with respect to Li^+ ions in (a) LT1-PS00, (b) LT0-PS05, (c) LT0-PS10, (d) LT1-PS05, (e) LT1-PS10, and (f) EL using ECC-MD.

S8 for the LT0-PS410 system). Interestingly, the low q peak does not stem from PS clustering. Namely, conv-MD simulations, which are prone to unrealistically excessive clustering (see Figure S8 in the SI), do not produce the low q peak in Figure S3 in the SI.

To elucidate the relation between the low q peak in $F(q)$ and the alternating charge structure, we further analyze the charge-charge correlations. We define the charge-charge correlations as

$$Q(r) = \sum_{i=\{+,-\}} 4\pi z_i \rho_i g_{\text{Li},i}(r) r dr \quad (3)$$

where z_i , ρ_i , and $g_{\text{Li},i}(r)$ are the valency, the number density of ion i , and the RDF between Li^+ ion and ion i . Evaluated $Q(r)$ for different systems, shown in Figure 5, exhibit asymptotically decaying oscillations, which indicates a long-range ordering of anions and cations around the Li^+ ion.

Notably, the charge oscillations in panels d–f are much stronger than those in panels a–c and exhibit several local minima at small r . Importantly, the ionic strength of the solutions shown in panels a–c is weaker than in the solutions in panels d–f. We suppose that adding a LiTFSI salt into the solution increases the packing of solvent-separated cations and anions, which induces an alternating structure. In the case of EL (panel f), we can find a tiny positive peak at around 5 Å followed by relatively weak

anion/cation oscillations compared with those in panels d and e. According to the RDF for $\text{Li}-\text{NNO}_3$ in Figure 3c, the Li^+ and NO_3^- ions form strong ion pairs or triples (see Figure 3f).

Discussion

We have shown that the main peak and the low q peak in Figure 2 are related to the packing of solvent molecules and the alternating structure of cations and anions. ECC-MD simulations feature that this alternating structure occurs only when ions are separated by solvent molecules. Figure 6 shows representative snapshots of ion distributions in different systems. The dashed lines depict the connectivity of Li^+ ions in the distance 7–12 Å (which corresponds to the low q peak in $F(q)$). In LT0-PS10, Li^+ and S_6^{2-} ions are uniformly distributed over space (Figure 6a), but S_6^{2-} ions are able to contact Li^+ ions via terminal S atoms instead (see Figure 3d), forming weak Li^+-S_6 networks. Although the electrostatic force from Li^+ ions attract anions, Li^+ and S_6^{2-} ion pairs are frequently disrupted by solvent molecules (reflected by the coordination number of the terminal S_6^{2-} in Figure S7c). This is attributed to the relatively lower electron density at terminal S atoms of S_6^{2-} ions compared to shorter PS chains [25].

Adding LiTFSI into the solution (cf. LT0-PS10 and LT1-PS10) increases the packing of ions, and Li^+ ions are more uniformly distributed in LT1-PS10 (Figure 6b) than in LT0-PS10 (Figure 6a). Similar to S_6^{2-} ions in LT0-PS1, the binding affinity of S_6^{2-} and TFSI $^-$ to Li^+ ions is not intense enough to entirely replace solvent molecule in the first solvation shell of Li^+ ions. The delicate balance between the ionic and solvent interactions leads to a regular distance between the ionic species, as shown in the RDFs in Figure 3 and the alternating net charge in Figure 5.

It can be conceived that the peak intensity at the low q peak observed in Figure 2 can be also related to the binding affinity or the donor ability of ions and solvent molecules. Depending on the binding affinity, ionic species can be categorized as a 'solvent-separated ion pair' (SSIP), 'contact ion pair' (CIP), or aggregate. In our previous study [50], we categorize $\text{Li}^+-\text{TFSI}^-$ as a SSIP and $\text{Li}^+-\text{NO}_3^-$ as a CIP or aggregate. Considering the $F(q)$, RDFs, and the coordination number analysis, S_6^{2-} chains also can be categorized as SSIPs. This SSIP of $\text{Li}^+-\text{S}_6^{2-}$ facilitate the dissociated free Li^+ ions, resulting in high conductivity and transference number in the solutions [25].

Meanwhile, the strong ionic interactions alter the solvation structure of Li^+ ions and PS clustering to a large degree, as shown in Figure 6c. The aggregates of $\text{Li}^+-\text{NO}_3^-$ observed in Figure 3c and f impact the Li^+ connectivity and PS clustering. We assume that the NO_3^- ions in the $\text{Li}^+-\text{NO}_3^-$ pairs screen the electrostatic forces induced by Li^+ and repel PS ions with repulsive electrostatic forces. This is well featured in the short decay distance of oscillations (Figure 5f) and in the Li^+ ion connectivity (Figure 6c). It can be assumed that NO_3^- ions cause the geometric frustration of the cation and anion alternations and disturb their ordered sequence shown in Figures 6a and b.

In addition, recent studies show that high donor number solvents and salts can facilitate Li_2S nucleation growth and its kinetics [21,60]. The nucleation and growth of Li_2S are controlled by the diffusion of PS in the solutions. We assume that the repulsive interaction between the high donor anions and PSs can influence the shape of the Li_2S nucleation. Similarly, other high-donor salt anions, such as Br^- , CF_3CO_3^- and I^- ions, are

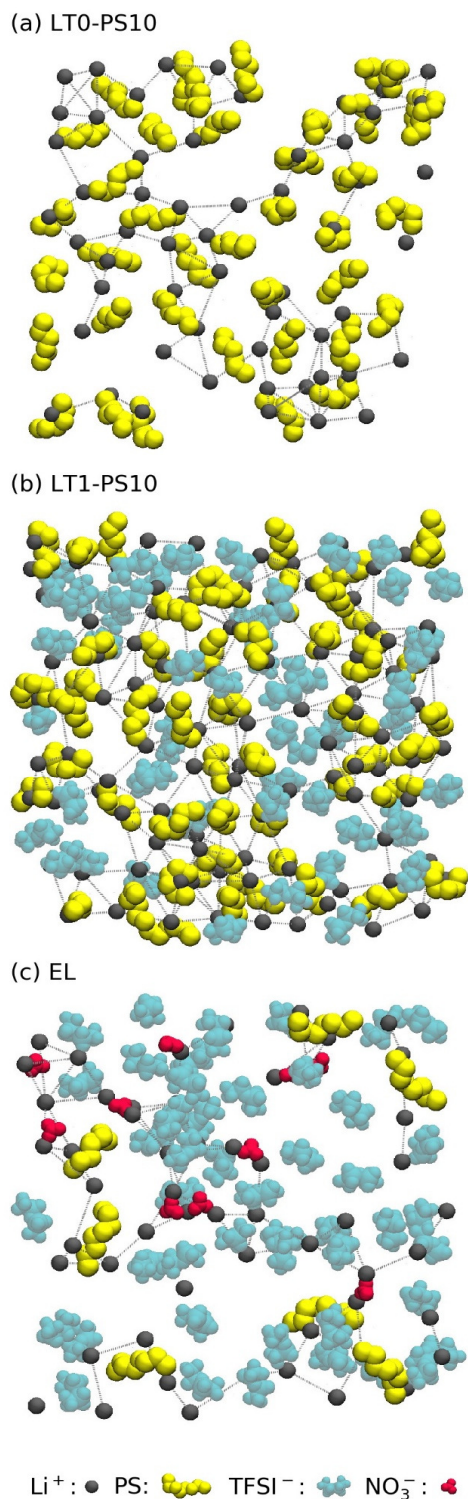


Figure 6: Representative snapshots from ECC-MD of (a) LT0-PS10 (b) LT1-PS10, and (c) EL. The solvent molecules are not shown. The dotted lines connect Li-ions whose distance are between 7 to 12 Å.

expected to exhibit similar solvation structures as Li⁺-NO₃⁻ observed in this study.

This result is surprising because the actual motivation for adding LiNO₃ to the electrolyte is the passivation of the lithium anode. [61] This cluster-breaking effect, therefore, represents a second positive effect against cluster formation. The presence of NO₃⁻ ions increases the transfer number of lithium ions in the electrolyte and thus actively decreases the formation of dendrites on the anode side [62].

Conclusion

By comparing neutron scattering experiments and force-field based electronic-continuum corrected MD simulations, we investigate the structure and clustering behavior of PS in THF solutions. Neutron scattering data show pronounced low q peaks between 0.4 and 0.9 Å⁻¹ in LT0-PS10 and LT1-PS10. MD simulations reproduce the structure factor $F(q)$ very well, along with the low q peak. The latter is attributed to the long-range Li⁺-Li⁺ and anion-anion correlations as an alternating structure of cations and anions in the solutions. The presence of LiNO₃ in the EL solution breaks the geometric ordering and weakens the low q peak in $F(q)$. This observation indicates that the anions with low donor numbers (i.e., TFSI⁻ and S₆²⁻ ions) form SSIPs with Li⁺ ions. SSIPs in moderate concentrations (> 1 M) induce the cation and anion alternating structures. In contrast, the anions with high donor numbers (i.e., NO₃⁻) form CIPs or aggregates. We observe that adding LiNO₃ salt into the PS solutions reduces the clustering of PS. Highly coupled NO₃⁻ and Li⁺ ions prevent PS from forming larger clusters by screening electrostatic potentials.

MD simulations reveal that a delicate balance between ion-ion and ion-solvent interactions influences the ordering and clustering of ions. These ion-ion and ion-solvent interactions are crucial in low E/S ratios in porous environments to control the PS chains' solubility while maximizing the transport of Li⁺ ions.

The combination of neutron scattering experiments and MD simulations is expected to play a vital role also in further studies, e.g., to shed light on atomic-level solvation structures of various donor number salts, or the effects of variations of solvent types and compositions for Li/S battery electrolytes or other energy storage devices.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the website. It contains details on simulation box sizes, duration of the production runs and numbers of ions/molecules in MD simulations; Average polysulfides clustering size; Experimental total structure factor with the different deuteration percentage in THF; Total structure factor computed from MD simulations for LT0-PS410; Radial distribution functions evaluated from ECC-MD simulations for LT0-PS05/PS10 and LT1-PS05/PS10.; Cluster size distributions derived from MD simulations for LT0-PS410; Radial distribution functions derived from MD simulations for a pure THF solvent; Radial distribution functions of all atom combinations derived from ECC-MD simulations for LT1-PS00; Coordination numbers of Li-ions in the investigated solutions.

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Author Contributions

S.R. conceived the idea. S.R., J.D., M.K., and T.Y. designed and supervised the project. S.R., C.P., and T.H. conducted the experiments. S.R. and T.H. analyzed experimental data. C.P. performed MD simulations and analyzed simulation data. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

Lithium/sulfur (Li/S)

Polysulfide (PS)

Molecular dynamics (MD)

Electrolyte/Sulfur (E/S)

Deuterated 1,2-dimethoxyethane (d-DME)

Deuterated tetrahydrofuran (d-THF)

Lithium bis(trifluoromethanesulfonyl)imide lithium salt (LiTFSI)

The Near and Intermediate Range Order Diffractometer (NIMROD)

The electronic continuum correction (ECC)

Radial distribution functions (RDFs)

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