

Article

Systematic Investigation of the Solvation Structure in THF-Based Localized High-Concentration Electrolytes

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Abstract

Understanding Li^+ solvation structure is critical for the rational design of high- and localized high-concentration electrolytes. Here, we present a systematic investigation of tetrahydrofuran (THF)-based electrolytes with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) using Raman spectroscopy and ^7Li nuclear magnetic resonance to investigate the local solvation structures. By varying the THF:LiTFSI molar ratio, we observed a transition of Li^+ solvation from solvent-separated ion pairs to contact ion pairs and aggregates, accompanied by increased structural heterogeneity and constrained local dynamics. Raman spectroscopy captures the evolution of Li^+ -anion coordination with increasing salt concentration, while ^7Li NMR chemical shifts, line widths, and relaxation times provide complementary insight into changes in the electronic environment and symmetry of Li^+ coordination. Electrolyte structure is further examined by introducing a hydrofluoroether co-solvent into a concentrated $(\text{THF})_2\text{-LiTFSI}$ electrolyte. Raman results show that the local $\text{Li}^+\text{-TFSI}^-$ coordination structure is preserved upon 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) addition, whereas NMR reveals subtle modifications of the ion-rich solvation clusters. These results provide fundamental insight into Li^+ solvation and electrolyte localization, offering general design principles for advanced electrolyte systems.

Keywords: Li^+ solvation structure; high-concentration electrolytes; localized high-concentration electrolytes; hydrofluoroether cosolvents



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1. Introduction

High- and localized high-concentration electrolytes (HCEs and LHCEs) have been widely investigated as an effective electrolyte design strategy to regulate solvation structures and interfacial chemistry in lithium-based battery systems [1–4]. In contrast to conventional dilute electrolytes, increasing the Li salt concentration fundamentally reconstructs the local coordination environment of Li^+ , shifting it from solvent-dominated solvation to ion-pair-rich structures involving contact ion pairs (CIPs) and aggregates (AGGs) [5–9]. This restructuring substantially reduces the population of free solvent molecules and has been shown to promote preferential anion reduction during initial interfacial reactions [10–13]. As a result, HCE-based electrolytes typically form stable, inorganic-rich solid electrolyte interphases (SEIs), which suppress parasitic solvent decomposition and

enhance the stability of lithium metal electrodes [13–17]. Building on this concept, LHCEs introduce non-coordinating or weakly coordinating diluents as co-solvents to preserve the localized high-concentration solvation environment while mitigating the high viscosity and limited ion transport commonly associated with HCEs. To date, most LHCE studies have focused primarily on linear ether-based solvent systems, such as dimethoxyethane (DME), dioxolane (DOL), and glymes [18–21].

THF is a small heterocyclic ether solvent containing a single ethereal oxygen atom per molecule, which inherently requires a smaller amount of lithium salt to form stoichiometric coordination complexes. Moreover, THF exhibits higher stability against lithium metal than other mono-donor oxygen- or nitrogen-containing solvents, such as acetonitrile [22–24]. Recently, THF–LiTFSI-based electrolytes combined with aromatic diluents have been demonstrated to enable quasi-solid-state reaction pathways in lithium–sulfur batteries, highlighting the promise of THF-based concentrated electrolytes [25]. To extend this electrolyte concept beyond lithium–sulfur systems to a broader range of lithium-based battery chemistries, a systematic understanding of how Li^+ coordination evolves with electrolyte composition and localization is essential. Accordingly, a systematic investigation of the solvation structure in THF-based high- and localized high-concentration electrolytes is required to establish clear structure–property–performance relationships beyond application-specific observations.

In addition, the small molecular size and single donor site of THF enable access to near-stoichiometric solvation regimes, allowing the continuous evolution of Li^+ coordination from solvent-separated ion pairs to contact ion pairs and aggregates to be resolved. The reduced conformational flexibility of THF further simplifies the solvation landscape, making changes in Li^+ –anion interactions directly observable by complementary Raman and ^7Li NMR spectroscopy.

In THF-based HCE and LHCE systems, the solvation environment of Li^+ , and the overall electrolyte structure evolve continuously with electrolyte composition. This evolution encompasses changes in the primary coordination shell of Li^+ as well as transitions in ion-pairing states, ranging from solvent-separated ion pairs (SSIPs) to contact ion pairs and aggregates. At higher levels of electrolyte localization, these local coordination changes further give rise to mesoscopic structural organization within the liquid phase. Together, these hierarchical solvation features govern ion transport behavior and interfacial reactions at electrode surfaces, thereby influencing electrochemical performance. Without a systematic framework that separates composition-driven solvation effects from localization-induced structural heterogeneity, establishing clear structure–performance relationships remains challenging.

In this work, we present a systematic investigation of the solvation structure in THF-based high- and localized high-concentration electrolytes. A series of THF–LiTFSI electrolytes with precisely controlled molar ratios, $(\text{THF})_n\text{–LiTFSI}$ ($n = 21.49, 9.79, 5.90, 3.95, 2.78, 2.00$, and 1.60), were first prepared to capture the continuous evolution of Li^+ coordination from dilute to highly concentrated regimes. Localized high-concentration electrolytes were subsequently constructed by introducing a hydrofluoroether diluent, 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE), into the concentrated $(\text{THF})_2\text{–LiTFSI}$ electrolyte at controlled volume ratios. The resulting solvation structures were systematically characterized using complementary spectroscopic techniques, including Raman spectroscopy and ^7Li nuclear magnetic resonance (NMR), which are particularly sensitive to coordination-induced changes in anion, solvent, and Li^+ environments. Through this multi-dimensional analysis, we directly correlate local Li^+ solvation structures with electrolyte microdomain formation upon electrolyte localization. This work provides a

unified framework to understand how local solvation structures propagate into mesoscopic electrolyte organization in THF-based localized high-concentration electrolytes.

2. Materials and Methods

2.1. Electrolyte Preparation

Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99.95% trace metal basis) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and dried in a vacuum at 130 °C for 8 h prior to use. Anhydrous tetrahydrofuran (THF) was obtained from a solvent-dispensing system, and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE, 99%, Synquest Laboratories, Alachua, Florida, USA) was dried over activated alumina for at least 7 days. The (THF)_n–LiTFSI electrolytes were prepared by mixing THF and LiTFSI at stoichiometric ratios corresponding to *n* moles of THF per mole of LiTFSI (*n* = 21.49, 9.79, 5.90, 3.95, 2.78, 2.00, and 1.60). The resulting electrolyte solutions were stirred overnight until complete dissolution was achieved, with no visible residual solids observed. Localized high-concentration electrolytes were prepared by diluting the concentrated (THF)₂–LiTFSI electrolyte with TTE to obtain (THF)₂–LiTFSI:TTE mixtures at volume ratios of 2:1, 1:1, and 1:2. Among the investigated concentrated electrolytes, (THF)₂–LiTFSI was selected for the electrolyte localization study because further dilution of the more concentrated (THF)_{1.6}–LiTFSI composition with TTE led to partial precipitation and phase separation, whereas (THF)₂–LiTFSI remained single-phase over the investigated dilution range. All electrolyte preparation steps were carried out in an argon-filled glovebox.

2.2. Electrolyte Characterizations

Raman measurements were performed using a DXR Raman Microscope (Thermo Scientific, Waltham, MA, USA). Electrolyte samples were prepared inside an argon-filled glovebox and loaded into sealed glass capillaries with an inner diameter of 2.5 mm. Raman spectra were collected with an acquisition time of 2 s per scan and accumulated over 240 scans to achieve a good signal-to-noise (S/N) ratio. Spectral deconvolution was carried out using Gaussian line-shape functions to quantitatively determine peak areas. ⁷Li NMR spectra were acquired on a 600 MHz Varian spectrometer using 5 mm screw-cap NMR tubes. An external reference was introduced into each sample in the form of a sealed coaxial capillary containing 10 M LiCl in D₂O. The resonance of the 10 M LiCl in D₂O was calibrated against 1 M LiCl in D₂O, and all reported ⁷Li chemical shifts were referenced to 1 M LiCl. The 90° pulse width was determined individually for each sample. The ⁷Li longitudinal relaxation time (*T*₁) was measured using a standard inversion–recovery pulse sequence. The *T*₁ values were obtained by fitting the peak intensities as a function of relaxation delay using an exponential function. Following *T*₁ determination, ⁷Li NMR spectra were collected using the calibrated 90° pulse, a relaxation delay set to five times the measured *T*₁.

3. Results and Discussion

3.1. Raman Spectroscopy

To examine the evolution of the Li⁺ coordination environment with electrolyte composition, a series of electrolyte solutions with systematically varied THF:LiTFSI molar ratios were analyzed by Raman spectroscopy. Figure 1 presents the Raman spectra of (THF)_n–LiTFSI electrolytes with different amounts of THF per mole of LiTFSI, together with that of neat THF. The vibrational features associated with the TFSI[−] anion and THF solvent are shown in Figures 1a and 1b, respectively, both of which are highly sensitive to changes in Li⁺ coordination. The coordination behavior of the TFSI[−] anion is discussed first.

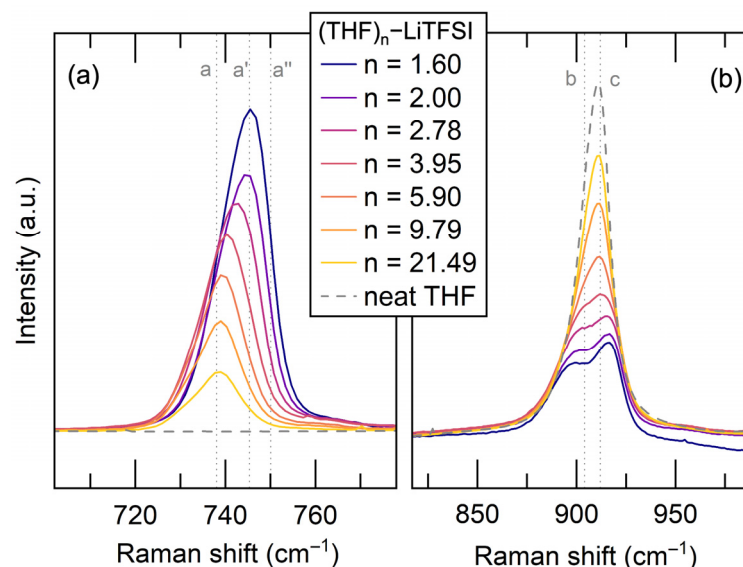


Figure 1. Raman spectra of $(\text{THF})_n\text{-LiTFSI}$ electrolytes with varying numbers of THF molecules per LiTFSI. (a) Symmetric stretching mode of the TFSI^- anion. (b) Spectral region associated with THF vibrational modes.

The TFSI^- anion exhibits a prominent vibrational band in the range of $720\text{--}770\text{ cm}^{-1}$, corresponding to the collective expansion and contraction of the anion framework, which is particularly sensitive to ionic interactions with cations [26,27]. In the absence of direct coordination, the TFSI^- band appears at approximately 738 cm^{-1} (mode a). Upon coordination to Li^+ , this mode shifts to higher wavenumbers, giving rise to a new peak at higher wavenumbers (mode a' and a''), which is associated with the formation of contact ion pairs and aggregates (Figure 1a) [27,28]. At low LiTFSI concentrations, where excess THF is present, the TFSI^- spectrum is dominated by mode a, indicating that the majority of TFSI^- anions exist as solvent-separated ion pairs. As the LiTFSI concentration increases, corresponding to a decrease in the THF:LiTFSI ratio, the Raman band progressively shifts toward higher wavenumbers due to the increasing contribution of mode a' and a'' at the expense of mode a. These observations indicate that highly concentrated THF-based electrolytes are characterized by the predominance of contact ion pairs or aggregated species, in which TFSI^- anions are directly coordinated to Li^+ rather than being separated by solvent molecules. Notably, the Raman band of $(\text{THF})_{1.6}\text{-LiTFSI}$ is further shifted to higher wavenumbers compared to that of $(\text{THF})_2\text{-LiTFSI}$, suggesting a higher degree of TFSI^- coordination to Li^+ at the lowest THF content investigated.

The coordination behavior of THF was analyzed by focusing on the most intense THF-related Raman feature centered near 910 cm^{-1} , as shown in Figure 1b. The Raman spectrum of neat THF displays a strong band composed of two overlapping vibrational modes at 904 cm^{-1} (mode b) and 912 cm^{-1} (mode c), which correspond to C–O stretching and C–C stretching vibrations, respectively [29]. These modes are known to be sensitive to ionic interactions and therefore serve as useful probes of THF coordination [30]. Coordination of THF to Li^+ occurs through the ether oxygen atom, leading to elongation of the C–O bond and contraction of the C–C bond. As a result, mode b undergoes a red shift, while mode c shifts to higher wavenumbers (Figure 1b). Previous studies have shown that coordination of THF to highly charged cations, such as Al^{3+} , induces the appearance of new vibrational modes with large wavenumber shifts relative to neat THF [29]. In contrast, coordination to Li^+ results in relatively modest shifts of approximately $4\text{--}5\text{ cm}^{-1}$ for both modes b and c, rendering the deconvolution of coordinated and uncoordinated THF contributions more challenging. Nevertheless, Figure 1b clearly demonstrates that decreasing the THF:LiTFSI

ratio leads to systematic shifts of mode b toward lower wavenumbers and mode c toward higher wavenumbers, accompanied by increased splitting of the two modes. These spectral changes indicate an increasing fraction of THF molecules coordinated to Li^+ at higher salt concentrations, concomitantly reducing the proportion of free THF in the electrolyte.

While the systematic shifts observed in the TFSI^- vibrational bands in Figure 1 qualitatively indicate an evolution of ion-pairing with electrolyte composition, a quantitative assessment of the relative populations of uncoordinated and Li^+ -coordinated TFSI^- species is required to elucidate the underlying solvation structure. To this end, the TFSI^- symmetric stretching region was deconvoluted into distinct spectral components, and the corresponding fitting results are summarized in Figure 2. A representative example of the Raman band deconvolution is provided in Figure S1.

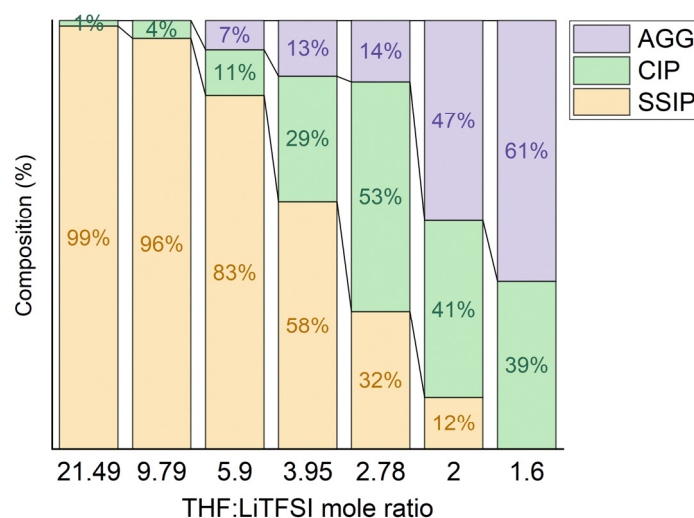


Figure 2. Relative proportions of SSIPs, CIPs, and AGGs in $(\text{THF})_n\text{-LiTFSI}$ electrolytes, quantified from Raman spectral deconvolution of the TFSI^- symmetric stretching region. The fractions were extracted from the fitted peak areas corresponding to each coordination state.

Figure 2 summarizes the relative populations of SSIPs, CIPs, and AGGs in $(\text{THF})_n\text{-LiTFSI}$ electrolytes, as determined from Raman spectral deconvolution of the TFSI^- mode. At the lowest salt concentration investigated ($n = 21.49$), the solvation structure is dominated by SSIP species, which account for 98.8% of the total population, while the combined fraction of CIPs and AGGs remains limited to 1.2%. As the THF content decreases with increasing salt concentration, the fraction of SSIP species progressively decreases, accompanied by a corresponding increase in $\text{Li}^+\text{-TFSI}^-$ contact species. At the highest salt concentration ($n = 1.6$), the electrolyte exhibits a markedly different solvation environment, with CIP and AGG species accounting for 39.4%, and 60.6%, respectively. These results quantitatively demonstrate a continuous shift from an SSIP-dominated regime to one characterized by an increased prevalence of contact ion pairs and aggregates. The increasing degree of $\text{Li}^+\text{-TFSI}^-$ ion pairing promotes the formation of clustered, ion-rich local electrolyte structures as the salt concentration increases.

3.2. NMR Spectroscopy

To gain further insight into how the ion-pairing evolution revealed by Raman analysis influences the local Li^+ environment, ^7Li NMR spectroscopy was employed. While Raman spectroscopy provides insights into anion coordination and ion-pair populations, ^7Li NMR directly reflects changes in the electronic and dynamic environment surrounding Li^+ . Accordingly, systematic variations in the ^7Li chemical shift, line width, and longitudinal

relaxation behavior were analyzed as a function of electrolyte composition, as shown in Figures 3 and 4.

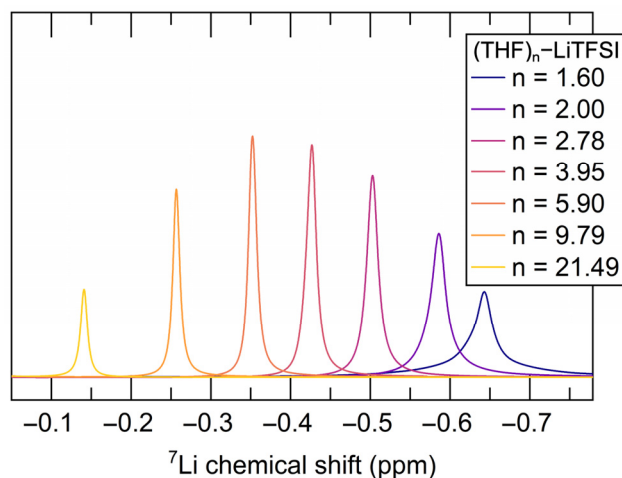


Figure 3. ^7Li NMR spectra of $(\text{THF})_n\text{-LiTFSI}$ electrolytes with varying numbers of THF molecules per LiTFSI.

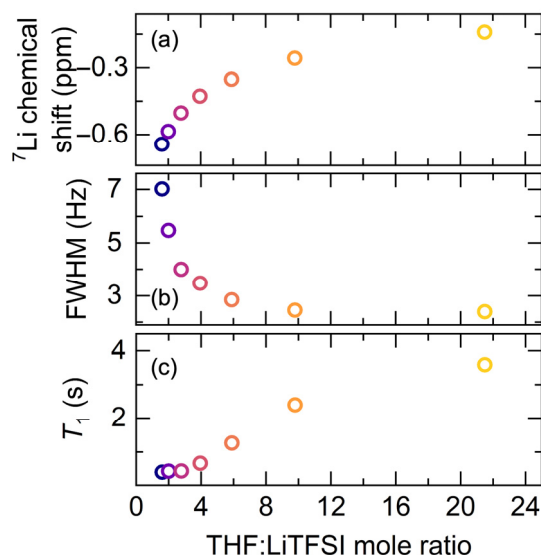


Figure 4. (a) ^7Li chemical shift, (b) full width at half-maximum (FWHM), and (c) longitudinal relaxation time (T_1) plotted as a function of the THF:LiTFSI molar ratio.

Figure 3 shows the ^7Li NMR spectra of $(\text{THF})_n\text{-LiTFSI}$ electrolytes with varying THF contents. As n decreases, corresponding to an increase in Li salt concentration, the ^7Li resonance exhibits a systematic upfield shift. This behavior indicates increased electronic shielding around Li^+ , which arises from enhanced $\text{Li}^+\text{-TFSI}^-$ ion pairing at higher salt concentrations. As the solvation structure evolves from solvent-separated ion pairs toward contact ion pairs and aggregates, negatively charged TFSI $^-$ anions are positioned in closer proximity to Li^+ , increasing the local electron density surrounding the Li^+ nucleus. The resulting enhancement in electronic shielding leads to the observed upfield shift of the ^7Li chemical shift. These results demonstrate that the progressive increase in ion pairing inferred from Raman analysis directly manifests in the local electronic environment of Li^+ . This systematic dependence of the ^7Li chemical shift on the THF:LiTFSI molar ratio is further illustrated in the plot shown in Figure 4a.

Beyond the average electronic environment, the line width of the ^7Li resonance provides information on the local structural heterogeneity surrounding Li^+ . Because ^7Li is

a quadrupolar nucleus with spin $I = 3/2$, its resonance line width is highly sensitive to the symmetry of the local bonding environment. Highly symmetric and dynamically averaged solvation environments result in relatively narrow resonances, whereas locally defined and anisotropic coordination structures lead to significant line broadening. As shown in Figures 3 and 4b, the full width at half-maximum (FWHM) of the ^7Li signal increases markedly with decreasing THF:LiTFSI ratio. This progressive broadening reflects the emergence of contact ion pairs and aggregates at higher salt concentrations, which restrict the rotational and translational freedom of species within the first solvation shell and give rise to a distribution of non-equivalent Li^+ environments.

Additional insight into the local symmetry and dynamics of Li^+ coordination is provided by the longitudinal relaxation time (T_1). For quadrupolar nuclei such as ^7Li , nuclear relaxation is dominated by quadrupolar mechanisms that are particularly sensitive to fluctuations in the local electric field gradient [31,32]. Consequently, T_1 serves as an effective probe of the symmetry of the Li^+ bonding environment. As shown in Figure 4c, T_1 decreases systematically with decreasing THF:LiTFSI ratio, indicating that the Li^+ environment becomes increasingly asymmetric and locally constrained in more concentrated electrolytes. Together with the observed changes in chemical shift and line width, the T_1 trend supports a picture in which increasing salt concentration drives the formation of clustered, ion-rich solvation structures characterized by strong ion pairing and reduced dynamic averaging.

Taken together, the Raman and ^7Li NMR results consistently reveal a continuous evolution of the Li^+ solvation structure with electrolyte concentration in the $(\text{THF})_n\text{-LiTFSI}$ series. Raman analysis demonstrates a progressive shift from solvent-separated ion pairs to contact ion pairs and aggregates as the THF content decreases, indicating enhanced $\text{Li}^+\text{-TFSI}^-$ ion pairing and the development of clustered, ion-rich local structures. These structural changes are directly reflected in the ^7Li NMR response, where decreasing THF:LiTFSI ratios lead to an upfield shift of the ^7Li resonance, increased line broadening, and shortened T_1 values. Collectively, these trends indicate that increasing salt concentration drives a transition toward more asymmetric, locally defined, and dynamically constrained Li^+ environments.

Having established how Li^+ solvation structure and local dynamics evolve with electrolyte concentration in the $(\text{THF})_n\text{-LiTFSI}$ system, we next examine the effect of electrolyte localization induced by the addition of a non-coordinating diluent. Specifically, hydrofluoroether TTE is introduced into the concentrated $(\text{THF})_2\text{-LiTFSI}$ electrolyte to form localized high-concentration electrolytes, and the resulting changes in solvation structure are discussed in Figure 5.

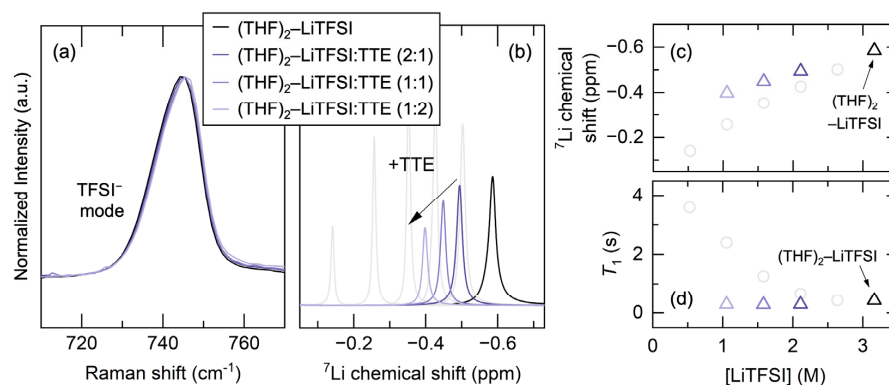


Figure 5. Raman and ^7Li NMR characterization of TTE-added electrolytes based on the concentrated $(\text{THF})_2\text{-LiTFSI}$ system. (a) Normalized Raman spectra of the TFSI^- vibrational mode, (b) ^7Li NMR spectra, (c) ^7Li chemical shift values, and (d) longitudinal relaxation times (T_1) plotted as a function of LiTFSI concentration. Gray curves and symbols denote THF-only electrolytes without TTE, which are included for comparison.

3.3. Effect of Electrolyte Localization via TTE Addition

Figure 5a compares the normalized Raman spectra of the TFSI[−] vibrational mode for the concentrated (THF)₂–LiTFSI electrolyte and its TTE-added counterparts with volume ratios of 2:1, 1:1, and 1:2. Although the absolute Raman intensity decreases with increasing TTE content due to dilution of LiTFSI, normalization of the spectra reveals that the overall band shape and peak position of the TFSI[−] mode remain essentially unchanged across all compositions. In particular, no discernible shift or redistribution of the TFSI[−] vibrational features are observed upon TTE addition.

The invariance of the normalized TFSI[−] Raman spectra indicates that the local Li⁺–TFSI[−] coordination environment characteristic of the highly concentrated (THF)₂–LiTFSI electrolyte is preserved despite the introduction of TTE. This observation suggests that TTE does not directly participate in Li⁺ coordination and instead acts as a non-coordinating diluent, spatially separating pre-existing Li⁺–TFSI[−] solvation clusters without disrupting their internal structure. Consequently, the fundamental Li⁺–TFSI[−] coordination structures established in the concentrated electrolyte are preserved, providing spectroscopic evidence for electrolyte localization rather than simple dilution upon TTE addition.

As shown in Figure 5b, the ⁷Li NMR spectra of TTE-added electrolytes exhibit a gradual downfield (deshielding) shift with increasing TTE content. This trend is confirmed in Figure 5c, where the ⁷Li chemical shift is plotted as a function of LiTFSI concentration in the presence of TTE. Importantly, this deshielding behavior occurs despite the invariance of the TFSI[−] Raman spectral features upon TTE addition (Figure 5a), indicating that the primary Li⁺–TFSI[−] coordination structure characteristic of the highly concentrated electrolyte is largely preserved. The observed chemical shift therefore suggests that the changes in the ⁷Li NMR response are not driven by disruption of local ion pairing, but rather by modifications to the average electronic environment surrounding Li⁺, such as changes in the local dielectric environment and spatial organization of Li⁺–TFSI[−]-rich solvation clusters induced by electrolyte localization.

By contrast, when compared at comparable LiTFSI concentrations, TTE-added electrolytes exhibit more upfield ⁷Li chemical shifts than their THF-only counterparts (shown in gray circles), indicating enhanced electronic shielding around Li⁺. This observation suggests that electrolyte localization induced by TTE promotes a more anion-rich local solvation environment, even at similar bulk salt concentrations.

The effect of TTE addition on the local symmetry and dynamics of the Li⁺ environment is further reflected in the ⁷Li *T*₁ measurements, as shown in Figure 5d. Overall, the *T*₁ values remain within a similar range across the investigated compositions, indicating that the primary Li⁺ solvation structure is largely preserved upon TTE addition. Nevertheless, a modest decrease in *T*₁ is observed, with *T*₁ decreasing from 0.43 s for (THF)₂–LiTFSI electrolyte to 0.29 s for (THF)₂–LiTFSI:TTE (1:2). This reduction in *T*₁ suggests a slight increase in local asymmetry around Li⁺ upon TTE addition, likely arising from subtle reorganization of the solvation environment, including changes in the local cluster surroundings and the formation of spatially segregated subdomains. Overall, Figure 5 shows that TTE induces electrolyte localization by maintaining local Li⁺–TFSI[−] coordination while subtly reorganizing the surrounding solvation environment.

4. Conclusions

In this work, we systematically investigated the solvation structure of THF-based high- and localized high-concentration electrolytes using Raman spectroscopy and ⁷Li NMR. By systematically decreasing the THF:LiTFSI molar ratio, we observed a progressive change in Li⁺ solvation from solvent-separated ion pairs to contact ion pairs and aggregates, accompanied by increased structural heterogeneity. Introduction of the non-coordinating

diluent TTE enabled electrolyte localization, preserving the local Li^+ – TFSI^- coordination structure characteristic of concentrated electrolytes while inducing subtle reorganization of the surrounding solvation environment. Together, these results establish a unified structural framework describing how Li^+ solvation and electrolyte organization evolve in THF-based localized high-concentration electrolytes.

The insights obtained in this study also have direct implications for practical electrolyte design in lithium-based batteries. By controlling Li^+ solvation and ion pairing through concentration and electrolyte localization, the local electrolyte structure can be tuned in ways that influence interfacial chemistry and the speciation of electrochemically active species. Establishing direct correlations between these structural regimes and electrochemical responses will be an important direction for future electrochemical investigations.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/org7010010/s1>. Figure S1: Deconvolution of the TFSI^- Raman band for the $(\text{THF})_{3.95}$ – LiTFSI electrolyte, illustrating the contributions of SSIP, CIP, and AGG species.

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Conflicts of Interest: The authors declare no conflicts of interest.

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