Molecular dynamics study on lithium-ion transport in PEO branched nanopores with PYR$_{14}$TFSI ionic liquid

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Abstract
Lithium ion transport in a poly-(ethylene oxide) (PEO) branched nanopore filled with a solution of [lithium][bis(trifluoromethanesulfonyl)imide]/[1-butyl-1-methylpyrrolidinium][bis(trifluoromethanesulfonyl)imide] (LiTFSI/PYR$_{14}$TFSI) was investigated by molecular dynamics using many-body polarizable force field. The structural and dynamic properties of lithium ions in the nanopores with different sizes and ratios of ions to PEO chains were examined. The first coordination shell of the lithium ions had a lower intensity in the longitudinal direction than in the radial direction. Cluster analysis of [Li$_x$(TFSI)$_n$]$^{-(n-x)}$ showed the absence of large lithium clusters ($x \geq 2$) as a result of the enhanced suppression of monodentate structures compared with binary electrolytes (i.e., LiTFSI/PYR$_{14}$TFSI without PEO chains). The emergence of [Li(TFSI)$_2$]$^-$ and its relatively small hydrodynamic radius facilitated rapid dynamics compared with binary electrolytes. The diffusion coefficients and ionic conductivities of the lithium ions in the longitudinal direction increased with an increase in the ratio of the ions to PEO chains and a decrease in the pore size. It was noted that the lithium-ion transport was mainly governed by structural diffusion based on a shorter residual time for anions compared with binary electrolytes. In addition, single ion trajectory analysis was performed and more frequent anion exchanges were observed when PEO chains were introduced.

KEYWORDS
ionic liquid, lithium-ion transport mechanism, many-body polarizable force field, molecular dynamics, polyelectrolyte
1  |  INTRODUCTION

Lithium-ion secondary batteries (LIBs) have been adopted for many applications ranging from portable electronic devices to electric vehicles, which is why they have been extensively and intensively investigated in recent decades. The electrolyte is one of the key components of a battery system, because the choice of electrolyte affects various properties such as the electrical conductivity, cationic transference number, and stability near electrodes. As the first commercial Li-ion battery was fabricated with LiPF₆ salt and ethylene carbonate (EC), the use of fluorene-based counter anions and carbonate solvents has been common. However, stability issues with carbonate-based electrolytes have prompted extensive studies in a search for solutions. Room temperature ionic liquids (RTILs) are one solution because of their properties; nonvolatile and nonflammable, even though their electrical conductivities are lower than those of EC as a result of their high viscosities. Polyelectrolytes, especially those based on poly-(ethylene oxide) (PEO), have been widely used to replace previous liquid electrolytes because of their good mechanical properties, which produce stable battery operations compared with liquid electrolytes. As polyelectrolytes have relatively low electrical conductivities, researchers introduced various treatments to improve battery performance. Passerini and colleagues added an RTIL to PEO electrolyte, which assisted in accelerating the dynamics of the ethylene oxide as a plasticizer, without changing the transport mechanism or interaction with Li⁺. Yang and colleagues also used ceramic fillers in their battery, which was based on PEO doped with [lithium][bis(trifluoromethanesulfonyl)imide] (LiTFSI), salt, to increase both ionic conductivity and electrochemical stability window. Recently, polyelectrolytes prepared using microphase separation have been suggested to enhance both ionic conductivity and mechanical properties. Anh and Kim developed a thermally and mechanically stable polyelectrolyte membrane as an example, where polyelectrolytes were placed in a matrix domain. The matrix maintained its structural strength, and ion channels allowed fast Li-ion transport. However, the transport mechanism they suggested was not supported by detailed data.

Molecular dynamics (MD) simulations have been extensively used to understand the molecular behaviors of electrolyte systems. However, the classical MD method should be carefully applied, especially for high dielectric constant materials because of the intrinsic limit, which is related to the treatment of electrons. In classical MD simulations, the electrostatic potential is described as a Coulombic interaction between fixed point charges without considering polarization. This results in the dynamics of the system being one to two orders of magnitude lower than reality. Many techniques have been developed to solve this problem. A recent review paper introduced various methods, including both nonpolarizable and polarizable methods. Previous studies have shown great results using a nonpolarizable method in a system with two to three components, but in the case of multicomponent systems, the method showed poor performance. Various models based on polarizable force field have been suggested as fundamental solutions to this problem. The induced point dipole (IPD) model with APPLE&P force fields is one of these and is known to be a very accurate polarizable force field for describing experimental results. The model features the dipole interaction by point dipoles induced by many-body polarization effects to describe electrostatic potential in addition to the Coulombic interaction. Using the force fields, Borodin and Smith explained the Li ion transport mechanism in many different types of electrolytes, including RTILs and polyelectrolytes. Maitra and Heuer suggested a quantitative Li ion transport model in PEO electrolyte, whereas Diddens et al. extended the research with various additives.

In the present study, we also used the IPD model with APPLE&P force fields to elucidate the Li ion transport mechanism in nanopores. The objective was to use a MD simulation with the many-body polarizable force field to understand the mechanism of Li⁺ transport in a LiTFSI/[1-butyl-1-methylpyrrolidinium][bis(trifluoromethanesulfonyl)imide] (PYR₁₄TFSI) solution in PEO branched nanopores, which seem to be similar to the ion channels designed by Anh and Kim. The effects of pore size and ratios of Li⁺ to the PEO chains were examined at various temperatures. The local environment and transport properties were investigated to elucidate the Li ion dynamics. Single ion trajectory analysis, which is an imperative procedure for revealing the atomistic behaviors of various systems, was also performed to determine the transport mechanism from the perspective of thermodynamics and kinetics.

2  |  METHODS

MD simulations with the many-body polarizable force field based on the IPD moment model were conducted for the LiTFSI/PYR₁₄TFSI solution in PEO-branched nanopores, where APPLE&P force-field parameters were used. The nanopores were modeled as zigzag carbon nanotubes (CNTs) with positional constraints and hexagonally branched 12 or 6 PEO chains with 25 repeat units. The CNTs were placed at the center of each simulation box with periodic boundary conditions, which
had a length of 200 Å in the radial (χ−) direction. LiTFSI/ PYR14TFSI solutions with a composition of LiTFSI: PYR14TFSI = 1:6 were introduced to CNTs with different ratios of Li⁺ to PEO chains, denoted as PEOₓLiᵧ; (x, y) = (12, 60), (12, 40), (6, 30), and (6, 20). PEO₁₂Li₆₀ and PEO₁₂Li₄₀ had twice the total number of atoms and longer diameters for the CNT channels (denoted as the “large” systems) than PEO₆Li₃₀ and PEO₆Li₂₀ (denoted as the “small” systems), respectively. Before performing simulations for the PEOₓLiᵧ systems, simulations of bulk solutions with the same composition as the corresponding confined systems were performed at each temperature to obtain density values and determine the dimensions of the nanopores. The detailed information for each system is presented in Table 1.

The long-range electrostatic interactions were evaluated using the Ewald summation method for charge–charge and charge–induced dipole interactions, and the tapering function with a reaction-field approximation for induced dipole–induced dipole interactions. The reversible reference system propagator algorithm (rESPA) was employed to perform time integration. Three different timescales were adopted for the integrator: short, with a timestep of 0.5 fs for bonding and bending motions; medium, with a timestep of 1.5 fs for torsions and nonbonded interactions within 7.0 Å; and long, with a timestep of 3.0 fs for nonbonded interactions between 7.0 and 11.0 Å and long-range electrostatics.

The Packmol software package was used to locate molecules initially in the CNTs. Then, the steepest descent algorithm was used to perform energy minimization. To avoid overlapping atoms within the confined systems, short NVT simulations with a Nosé–Hoover thermostat were performed at a high temperature of 600 K. Subsequently, at least 50 ns NVT simulations were performed to produce data at 423, 393, and 363 K, respectively. To estimate the equilibrium properties, the first few nanoseconds of data were truncated, the details of which are also presented in Table 1. All the simulations were performed using the WMI-MD software package, which was modified to enable energy minimization, remove the rotational momentum of the center of mass, and apply positional constraints.

## 3 RESULTS AND DISCUSSION

### 3.1 Structural properties

Li⁺ ions are transported in form of complexes in electrolytes. Therefore, understanding the local environment of Li⁺ is crucial for understanding the transport mechanism. Li⁺ ions are coordinated with the oxygen atoms of the PEO chains (OPEO) and TFSI⁻ anions (OTFSI), which constitute the first coordination shell of Li⁺.

A quantitative analysis of Li⁺ ion complexes was conducted via angle-dependent radial distribution functions (ARDFs) and cluster analysis. In addition, a comparison with binary electrolytes (LiTFSI/PYR14TFSI) was performed to determine the effect of the PEO chains in the solutions.

#### 3.1.1 First coordination shell of Li⁺

To investigate the molecular structure of the solutions in PEO-branched nanopores, ARDFs (g(r, θ)) for each pair of molecules or atoms were calculated as follows:

$$g(r, \theta) = \frac{1}{<\rho>_{\text{local}, \theta}} \sum_i \sum_j \frac{\delta(r_i - r)\delta(\theta_i - \theta)}{2\pi r^2 \sin(\theta)},$$

where θ is the angle between the given axis (z-axis) and a pair vector (i.e., θ = 0 means the pair vector is aligned in the longitudinal direction and θ = 90° indicates the radial direction), and <ρ>_{local, θ} denotes the ensemble averaged local density for all θ within the maximal distance, r_max. The ARDFs were renormalized by uniform

| System        | Nₓ⁺ | Nᵧ⁻ | NᵧPR | NᵧPEO | d_CNT (Å) | h_CNT (Å) | Simulation time (ns) | Equilibration time (ns) |
|---------------|-----|-----|------|-------|-----------|------------|----------------------|-------------------------|
| PEO₁₂Li₆₀    | 60  | 420 | 360  | 12    | 87.965 (115) | 41.622, 40.840, 40.218 | 56, 60, 90              | 9, 12, 15               |
| PEO₁₂Li₄₀    | 40  | 280 | 240  | 12    | 74.197 (97)   | 41.622, 41.0264, 40.236  | 60, 60, 90              | 9, 10.5, 9              |
| PEO₆Li₃₀     | 30  | 210 | 180  | 6     | 63.488 (83)   | 41.622, 40.840, 40.218   | 60, 60, 90              | 9, 12, 12               |
| PEO₆Li₂₀     | 20  | 140 | 120  | 6     | 53.544 (70)   | 41.622, 41.0264, 40.236  | 60, 60, 60              | 9, 10.5, 18             |

Abbreviations: CNT, carbon nanotube; ns, nanoseconds; PEO, poly-(ethylene oxide).

*Considered the effective diameter d_CNT = 3.328 Å. Indices n of the zigzag CNTs presented in parentheses.

* Determined by the density values of each corresponding bulk solution.

* In order of 423, 393, and 363 K.
fluid distribution \( g_r(\theta) \), which was obtained from a Monte Carlo simulation (Figure S1), as in the previous work.\textsuperscript{38} The details are provided in the Supporting Information.

Figures 1 and S2 show the ARDFs for the Li\(^+\)-NTFSI\(^-\) and Li\(^+\)-Li\(^+\) pairs at all temperatures, and Figure S3a–c show the ARDFs for the Li\(^+\)-OPEO pair. As the first coordination shell of Li\(^+\) consists of TFSI\(^-\) and PEO chains, \( g_{Li^+-NTFSI^-}(r, \theta) \) and \( g_{Li^+-OPEO}(r, \theta) \) exhibit distinct peaks near 3.5 Å and 2.5 Å, respectively. As shown in Figure 1A,C, the magnitude of the first peak of \( g_{Li^+-NTFSI^-}(r, \theta) \) decreases with the angle. This indicates that the coordination energy between Li\(^+\) and TFSI\(^-\) in the longitudinal direction is lower than in the radial direction, which means that Li\(^+\) ions have a preferential direction for its movement. Compared with the PEO\(_{12}\)Li\(_{40}\) systems, the PEO\(_{12}\)Li\(_{60}\) have higher peak intensities for \( g_{Li^+-NTFSI^-}(r, \theta) \) because of the high ratio of TFSI\(^-\) anions to PEO chains. From the fact that the small systems (PEO\(_6\)Li\(_{30}\) and PEO\(_6\)Li\(_{20}\)) show the similar tendency with the large systems, it is noted that the effect of the pore size is limited. The opposite trend can be expected for \( g_{Li^+-OPEO}(r, \theta) \) as well. However, it is not trivial to directly compare the ARDFs, because the peak intensities are not dependent on the direction of the pairs (Figure S3d), so further calculation should be accompanied.

The average number of atoms in the first coordination shell of Li\(^+\) was calculated through the volume integration of the ARDF and defined as the running coordination number (CN). \( n_{Li^+}(O_{PEO}), n_{Li^+}(NTFSI^-), \) and \( n_{Li^+}(O_{TFSI}) \) are listed in Table 2. As expected previously, \( n_{Li^+}(O_{PEO}) \) of PEO\(_{12}\)Li\(_{60}\) is smaller than that of PEO\(_{12}\)Li\(_{40}\) which is same for the small systems as well. According to CNs for Li\(^+\) with O\(_{PEO}\) and O\(_{TFSI}\), a total of four to five oxygen atoms are located near Li\(^+\), of which two to three are O\(_{PEO}\) and the others are O\(_{TFSI}\). However, these values are underestimated compared with the actual numbers of each oxygen binding to a Li\(^+\), because their coordination structures are not homogeneously (i.e., there are Li\(^+\) ions binding to PEO or TFSI\(^-\) solely), so the values should be normalized with the fraction of each structure, which is discussed in Section 3.1.2. The values of \( n_{Li^+}(NTFSI^-) \) indicate that there are one to two TFSI\(^-\) anions near Li\(^+\). In addition, it is noted that ~1.7 O\(_{TFSI}\) are coordinated with Li\(^+\) within a single TFSI\(^-\) anion for all the solutions based on the ratio of \( n_{Li^+}(O_{TFSI}) \) to \( n_{Li^+}(NTFSI^-) \). This suggests that Li\(^+\) with two O\(_{TFSI}\) of a TFSI\(^-\) anion (bidentate) is more prevalent than Li\(^+\) with one O\(_{TFSI}\) of a TFSI\(^-\) anion (monodentate), the structures of which are shown in Figure 2A.

The predominance of the bidentate structure is also confirmed by the fact that \( g_{Li^+-NTFSI^-}(r, \theta) \) exhibits a marginal increment at 4.5 Å, which refers to a...
monodentate structure, whereas the first peak refers to a bidentate structure. This would be favorable for Li ion transport, because the monodentate structure may provide an advantage for the Li\(^+\) to coordinate with more other TFSI\(^-\) anions. The absence of a distinct peak (>1.0) for \(g_{\text{Li}^+}^{\text{TFSI}^-}(r, \theta)\) also supports this argument (Figure 1B,D). According to the previous work involving the simulation of the binary electrolytes (LiTFSI/PYR14TFSI) with relatively high salt concentrations, pair distribution of Li\(^+\)–Li\(^+\) pair exhibited significant peaks near 5.0 Å, which indicated that large Li clusters were formed (i.e., the clusters with more than two Li\(^+\) ions). Therefore, it may be thought that the formation of large Li clusters is suppressed by the existence of PEO chains and Li–TFSI complexes can be transported faster in the present systems.

### 3.1.2 Li–TFSI complex

Li\(^+\) ions in RTIL electrolytes are transported in the form of \([\text{Li}_x(X)_n]^{-(n-x)}\) complexes. As the average size of the complexes increases, the ion conductivity of the system decreases as a result of the large hydrodynamic radius of the complexes. Therefore, identifying the states of Li–anion complexes in a system assists in understanding the ion transport mechanism. The Li\(^+\) ions are classified into two major groups (bonded to the PEO chains or not). Cluster analysis was performed to quantify the amounts of \([\text{Li}_x(\text{TFSI})_n]^{-(n-x)}\) complexes in each group, which was performed using NetworkX 2.5. Figures 3 and S5 show the results of the cluster analysis and their representative conformations, respectively. Approximately half of the Li\(^+\) ions are attached to the PEO chains in the PEO\(_{12}\)Li\(_{60}\) and PEO\(_6\)Li\(_{30}\) systems, and two-thirds of the Li\(^+\) ions are attached to the PEO chains of the PEO\(_{12}\)Li\(_{40}\) and PEO\(_6\)Li\(_{20}\) systems. Interestingly, the fraction of Li\(^+\) bound to the PEO chains is equivalent to the ratio of the number of O\(_{\text{PEO}}\) to the number of oxygen...
atoms in each system, which means there is no energy-preferred binding site for Li+. Considering the fraction of Li⁺ bound to PEO chains and $n^{\text{Li}^+}(\text{O}_{\text{PEO}})$, it could be found that approximately four ethylene oxides (EOs) surrounded a single Li⁺ ion. This result is reasonable, because over a half of the Li⁺ ions bound to the PEO chains are coordinated to EOs only (five to six O$_{\text{PEO}}$ per Li⁺). Other ions in that group form complexes with one or two TFSI⁻ anions. Thus, the ions could hop from the PEO chain to TFSI⁻.

Once the Li⁺ ions are completely detached from the PEO chains, they form [Li(TFSI)$_n$]$^{-(n-1)}$ complexes, of
which [Li(TFSI)2]− is the most. According to the previous studies,39,40 this phase emerged when the solution was sufficiently dilute, whereas the [Li(TFSI)3]−2 phase was dominant at a practical salt concentration (x = 0.1−0.3). The emergence of [Li(TFSI)2]− in the present systems is due to the PEO chains contributing to the coordination with Li+, which causes the effective salt concentration of the electrolyte to become low. It is interesting that the fractions of complexed TFSI− within the groups show similar trends regardless of the pore size and the ratios of Li+ to the PEO chains of the systems, except for the fraction of Li+ bound to two PEO chains as a result of the shorter distance between adjacent branched chains in the large systems than in the small systems.

Figure 2B indicates that there are few monodentate structures in accordance with the ARDFs. This suggests that bidentate structure is more stable than monodentate structure, which is consistent with the previous study.45 Hence, [Li(TFSI)2]− complexes consist of two bidentate structures with four OTFSI− of a Li+ ion, whereas [Li(TFSI)3]−2 complexes inevitably form at least one or more monodentate structures. Once a TFSI− anion forms a monodentate structure with one Li+ ion by one of its −(SO2CF3) functional groups, the other group can form another monodentate structure, resulting in the formation of large Li-clusters.46 Compared with the result of the binary electrolyte, a much smaller large Li-cluster phase is observed for the PEOxLiy systems. In this regard, PEO chains are considered to suppress Li ion aggregation and provide better performance in terms of dynamics.

3.2 | Transport properties

We evaluated transport properties, which are directly related to the performance of LIBs. Specifically, the diffusion coefficients and ionic conductivities of the solutions were estimated, and how the system conditions influenced the dynamic properties was studied. Similar to the structural properties, a comparison with the binary electrolytes was also performed.

3.2.1 | Diffusion coefficient

Self-diffusion coefficient $D_i$ of molecules $i$ can be calculated using the Einstein relation:

$$D_i = \lim_{t \to \infty} D_i^{app} = \lim_{t \to \infty} \frac{1}{2n t} \sum_i <[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 >,$$

where $D_i^{app}$ denotes the time-dependent apparent diffusion coefficient, $\mathbf{r}_i(t)$ denotes the center of mass position at time $t$, $n$ denotes the number of dimensions, and $<>$ denotes the ensemble average. Here, $<[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2>$ is the mean square displacement of each component. Diffusion coefficients in the longitudinal direction of the channel ($D_z$) were only considered because of the confinement in the radial direction. Figure 4 reports the diffusion coefficients according to the temperature for all systems, including binary electrolyte systems, for reference. $D_{Li, Li}$ shows the following order: PEO6Li30 ≥ PEO12Li60 > PEO6Li20 ≥ PEO12Li40 > Binary. With an increase in the ratios of Li+ to the PEO chains, the diffusion coefficients tend to be higher. This result may be related to the Li+ coordination. As mentioned in Section 3.1.2, the Li+ ions in the systems were classified by depending on whether they were bound to the PEO chains. Li+ without PEO chains are transported by the surrounding TFSI−, whereas Li+ with PEO chains travel along the chains and in the segmental motion of the chains.29 Because of the fixed endpoint and high molecular weight of the PEO chains, the Li+ ions linked to the PEO chains are relatively slower than other ions. As the number of Li+ bound to the PEO chains increases with a decrease in the ratio of OTFSI− to OPEO, it is reasonable that the PEO12Li60 and PEO6Li20 have smaller diffusion coefficients than the PEO12Li40 and PEO6Li30, respectively. The Li+ ions in the small systems are slightly faster than those in the large systems, which is attributed to the existence of Li-PEO2 complexes in the PEO12Li60 and PEO12Li40. All the diffusion coefficients for the PEOxLiy systems are greater than those for the binary electrolytes by a factor of ~1−2. This is attributed to the high friction induced by the large hydrodynamic diameters of the [Li,TFSI]x−(x−y) (x ≥ 2) complexes, which are almost absent when the PEO chains are introduced.

The magnitudes of the diffusion coefficients for each ion are in order of $D_{Li, PYR}$ ≥ $D_{Li, TFSI}$ > $D_{Li, Li}$. Interestingly, although $D_{Li, Li}$ is increased in the small systems, $D_{Li, PYR}$ and $D_{Li, TFSI}$ are decreased. This may be attributed to the confinement effects from smaller pore sizes in the small systems on the relatively bulky PYR+ and TFSI−, but not on Li+, than in the large systems. This corresponds to the results of higher magnitudes of ARDFs for the PYR+·TFSI− pair in the small systems compared with those of the large systems (Figure S4). Consequently, this results in an increase in the proportion of $D_{Li, Li}$ over all types of molecules. Hence, the enhanced charge and discharge performances could be expected for the electrolyte with a decrease in the size of the ion transport channel.44
3.2.2 | Ionic conductivity

One of the most important properties of LIBs is their ionic conductivity. The ionic conductivities were calculated from the MD simulation results using the following equation, which is based on the Einstein relationship as follows:

\[
\lambda = \lim_{t \to \infty} \lambda^{app} = \lim_{t \to \infty} \frac{e^2}{6k_BT} \sum_{ij} z_i z_j \langle [\eta(t) - \eta(0)] [r_j(t) - r_j(0)] \rangle,
\]

(3)

where \( \lambda^{app} \) is the apparent time-dependent conductivity, \( e \) is the electron charge, \( V \) is the system volume, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, \( i \) and \( j \) are all the charged molecules, \( z_i \) and \( z_j \) are the charges for molecules \( i \) and \( j \), respectively, and \( \eta \) is the Cartesian coordinate along the trajectory of molecule \( i \). However, because \( \lambda^{app} \) considers correlations between all ion pairs, this value has poor statistics. Thus, it cannot be determined accurately for the long-time limit. Instead, the ionic conductivity can be calculated from the diffusion coefficients under conditions where the ions in the system are sufficiently dissociated. The degree of ion dissociation, \( \alpha \), which is also called the degree of uncorrelated ion motion, is defined by the following equation:

\[
\alpha = \frac{\lambda}{\lambda_{ideal}} = \lim_{t \to \infty} \frac{\sum_{ij} z_i z_j \langle [\eta(t) - \eta(0)]^2 \rangle}{\sum_{ij} z_i^2 \langle [\eta(t) - \eta(0)]^2 \rangle},
\]

(4)

where the calculation of ideal conductivity \( \lambda_{ideal} \) corresponds to the Nernst–Einstein equation. Here, \( \alpha = 1 \) means that all the ion pairs move independently, whereas \( \alpha = 0 \) means that all the ions move collectively. The values listed in Table 3 for \( \alpha_z \), which is the degree of ion dissociation along the longitudinal direction of the nanopores, are in the range of 0.6–0.8 at various temperatures. As the values of \( \alpha_z \) are high enough for an ionic liquid electrolyte, the ionic conductivities of each system could be calculated by combining Equation (4) and the following equation:

\[
\lambda_{ideal} = \frac{e^2}{V k_B T} \left( n_{Li^+} D_{Li^+} + n_{PYR} D_{PYR} + n_{TFSI} D_{TFSI} \right).
\]

(5)
Figure 5 shows the temperature-dependent ionic conductivities, $\lambda_z$, for each electrolyte, as well as $\lambda_z^{Li^+}$. As all the ions within the systems were considered, the values of $\lambda_z$ are equivalent for all cases, except PEO$_6$Li$_{20}$ as a result of the abnormally low values for $D_z^{Li^+, TFSI^-}$ and $D_z^{Li^+, PYR^+}$, which are attributed to the reinforced confinement effect from the reduced pore sizes on bulky RTIL molecules. Nevertheless, the preferential movement to the longitudinal direction in nanopores facilitates higher $\lambda$ values than those of binary electrolytes. $\lambda^{Li^+}$ is as important as $\lambda$ for electrolytes in terms of the battery cycle, as previously mentioned. The temperature dependencies are similar to those of the diffusion coefficients, increase according to the ratios of Li$^+$ to the PEO chains and the reduction of pore sizes, exceeding the values for binary electrolytes.

3.3 | Li ion transport mechanism

It is known that Li$^+$ ions are transported by two kinds of diffusion mechanisms in ionic liquid electrolytes: structural diffusion and vehicular diffusion. Structural diffusion is governed by the anion exchange of Li$^+$ ions during transport. In contrast, vehicular diffusion refers to the transportation of Li complexes without anion exchange. In general, structural diffusion is a faster mechanism than vehicular diffusion. The residual times at each molecule could be obtained from the result of MD simulations, which made it possible to compare the transport mechanisms of the PEO$_x$Li$_y$ systems and the binary electrolytes. In addition, single ion trajectory analysis was conducted to investigate how the Li$^+$ ions changed their coordination sites during the simulation.

3.3.1 | Residual time of Li$^+$ ions

The values of residual time $\tau$ of Li$^+$ ions for the PEO chains and TFSI$^-$ were calculated, which was defined as the mean lifetime of each individual coordinate, to investigate the transport mechanism of Li$^+$ ions. The residual time could be calculated by fitting the autocorrelation function of the neighbor function, $H(r_{ij}, t)$:

$$H(r_{ij}, t) = \begin{cases} 0, & \text{if } r_{ij} \geq r_{ij}^f \\ 1, & \text{if } r_{ij} < r_{ij}^f \end{cases}$$  \hspace{1cm} (6)

where $r_{ij}$ is the pair distance between $i$ and $j$, and $r_{ij}^f$ indicates the cutoff distances, which were determined to be 3.0 Å (O$_{PEO}$) and 5.0 Å (N$_{TFSI^-}$) using the endpoints of the first peaks of $g^{Li^+ - OPEO}$ and $g^{Li^+ - N_{TFSI^-}}$, respectively. The autocorrelation of the neighbor function is found as follows:

$$C(t) = \frac{\sum_{ij} < H(r_{ij}, t)H(r_{ij}, 0)>}{\sum_{ij} < H(r_{ij}, 0)H(r_{ij}, 0)>}.$$  \hspace{1cm} (7)

As the Li$^+$ ions transit from one binding site to another within the simulation time, the autocorrelation function decays from 1 to 0, which can be fitted to a stretched exponential function, $A_{\exp}[(t/\tau_{\text{CWW}})^{\beta}]$ (Figure S6), and residual time $\tau$ can be calculated by integrating this function. Figure 6 shows $\tau_{\text{PEO}}$ and $\tau_{\text{TFSI^-}}$ as functions of the temperature in each system. It is noteworthy that $\tau_{\text{PEO}}$ is the average time needed for Li$^+$ to completely detach from the PEO chain, not limited to the oxygen atoms. The magnitudes of $\tau_{\text{PEO}}$ increase with the ratio of Li$^+$ to the PEO chains, whereas $\tau_{\text{TFSI^-}}$ decrease. However, the $\tau_{\text{TFSI^-}}$ values for all the systems are smaller than the $\tau_{\text{TFSI^-}}$ values for the binary electrolytes by a factor of 2. This suggests that the structural diffusion mechanism contributes more to Li$^+$ in the nanopores than the binary electrolytes. The magnitudes of $\tau_{\text{PEO}}$ are greater than those of $\tau_{\text{TFSI^-}}$ for the binary electrolytes. More details are provided in the next section.
3.3.2 | Single ion trajectory analysis

Single ion trajectory analysis was conducted on Li⁺ by tracing the indices of the coordinated species at each frame. According to Brownian dynamics, the probability distribution of the jump displacements over one dimension follows a Gaussian distribution. The distributions of the longitudinal displacements of Li⁺ at Δt = 150 ps also follow a normal distribution (Figure S7), which indicates that the Li ion dynamics is governed by a single transport mechanism. It is also noteworthy that the Li ion hopping from one molecule to another is a refreshing process in terms of dynamics because of the consistency of the ensemble averaged displacements. Figure 7A,B show coordination maps for each representative of fast and slow Li⁺ ions that indicate which sites the Li⁺ ions are bound to during the simulation at 423 K, where “binding” was defined as coordination lasting at least 150 ps. Both fast and slow ions pass through several PEO chains, as well as TFSI⁻ anions. Specifically, the fast ion in Figure 7A migrates as follows: (i) transported with two TFSI⁻ anions for 2 ns, (ii) totally attached to a single PEO chain for 7 ns, (iii) frequently exchanging many TFSI⁻ anions over 20 ns, (iv) totally attached to another single PEO chain for 5 ns, and (v) exchanging many TFSI⁻ anions until the end of the simulation. The slow ion is transported in a similar manner, but the residual time of each segment is longer than that of the fast ion. In particular, more frequent anion exchanges occur before and after binding to the PEO chains. A comparison of the results showed that the Li⁺ ions in the binary electrolyte are
bound to TFSI\(^{-}\) for a longer time, despite for the fastest ion in the electrolyte (Figure 7C). In fact, the average number of TFSI\(^{-}\) anions encountered by Li\(^{+}\) for a unit time at 423 K is greater in the nanopore systems than in the binary electrolyte, with 1.79, 3.08, 2.08, and 2.71 anions for 1 ns for PEO\(_{12}\)Li\(_{60}\), PEO\(_{12}\)Li\(_{40}\), PEO\(_{6}\)Li\(_{30}\), and PEO\(_{6}\)Li\(_{20}\), respectively, and 1.18 anions for 1 ns (binary). Based on the results of the single ion trajectory analysis, two distinct features of Li ion transport in nanopores are identified. One is that the Li\(^{+}\) ions are completely separated into PEO chains or TFSI\(^{-}\), except when they undergo a transition from PEO chains to TFSI\(^{-}\), and vice versa. The other is that Li\(^{+}\) ions are transported by more frequent anion exchanges in the nanopores than in the binary electrolytes, which is called structural diffusion.

An interesting feature was also observed—positional dependency. Figure 8 shows the probability distributions of the radial density for fast and slow Li\(^{+}\) ions. Both profiles exhibit a distinct peak at a few angstroms from the interface between the nanopores and electrolytes, related to the formation of an electric double layer near the surface. In contrast to slow ions, fast ions can be located at the center of nanopores. This means that anion exchanges frequently occur near the center of the channels, which is favorable in terms of Li\(^{+}\) transport. A distinct difference in the distributions between the fast and slow ions is observed for PEO\(_{12}\)Li\(_{60}\) and PEO\(_{6}\)Li\(_{30}\) compared with PEO\(_{12}\)Li\(_{40}\) and PEO\(_{6}\)Li\(_{20}\), because many Li\(^{+}\) ions could be present without the PEO chains in the large systems as a result of the higher ratios of Li\(^{+}\) to the PEO chains.

4 | CONCLUSION

In the present study, we have performed many-body polarizable MD simulation of a LiTFSI/PYR\(_{14}\)TFSI solution in a nanopore where PEO chains were branched and investigated the local environment and transport mechanism of Li\(^{+}\). The first coordination shell structure of Li\(^{+}\) consisted of TFSI\(^{-}\) anions and PEO chains. The strength of the Li\(^{+}\)-TFSI binding directionally depended on the geometry of the nanopores, whereas it did not for Li-PEO. Smaller magnitudes of the peaks of \(g_{\text{Li}^{+}-\text{TFSI}}(r, \theta)\) were observed in the longitudinal direction than in the radial direction. The high values for \(g_{\text{Li}^{+}-\text{TFSI}}(r, \theta)\) peaks at 3.5 Å suggested the dominant existence of bidentate structures in the Li-TFSI complexes rather than monodentate structures. Therefore, the number of large Li clusters comprising two or more Li\(^{+}\) ions was suppressed compared with the binary electrolytes, which was confirmed by cluster analysis of [Li\(_{x}\)(TFSI)\(_{n}\)]\(^{-}(n-x)\) complexes. In addition, the amount of [Li(TFSI)\(_{2}\)]\(^{-}\) complex was greater than that of [Li(TFSI)\(_{3}\)]\(^{-}\). Thus, the smaller hydrodynamic radius facilitated the fast Li ion transport. A sufficiently high ion dissociation in the longitudinal direction allowed for selective charge transfer. Although the ionic conductivities of the solutions, \(\lambda_{z}\), were similar, with the exception of PEO\(_{6}\)Li\(_{20}\), the Li ion conductivities, \(\lambda_{z}^{Li}\), showed differences. With an increase in the ratios of Li\(^{+}\) to the PEO chains and a decrease in the pore sizes, the Li ion...
conductivity, $\lambda_z^{Li^+}$, increased. An examination of residual times $\tau_{PEO}$ and $\tau_{TFSI}$ showed that more frequent anion exchanges occurred than in the binary electrolytes, which corresponded to the structural diffusion mechanism. The details of this mechanism were confirmed using single ion trajectory analysis. Finally, the Li$^+$ ions near the center of nanopores were faster than the ions stuck to the electric double layer formed at the surface of nanopores.

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CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests.

AUTHOR CONTRIBUTIONS
Seulwoo Kim, Minhwan Lee, and Won Bo Lee designed the systems for simulations. Seulwoo Kim, Chanui Park, and Anseong Park modified the software package. Seulwoo Kim, Minhwan Lee, Chanui Park, Anseong Park, and Sebin Kim conducted the molecular dynamics simulation. Seulwoo Kim, Minhwan Lee, Sangwoo Kwon, JunBeom Cho, and Seunghyok Rho calculated structure and transport properties. Seulwoo Kim drew the figures. Seulwoo Kim, Minhwan Lee, and Won Bo Lee cowrote the paper.

DATA AVAILABILITY STATEMENT
Data available on request from the authors.

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