7.1 Introduction

Solid Polymer Electrolytes (SPEs) consisting of alkali salts dissolved in a solid polymer matrix (for example, poly(ethylene oxide), PEO) are of intense research interest due to their unique property of ionic conductivity with mechanical flexibility. PEO-based SPEs find their applications in solid state electrochemical devices such as thin-film batteries, electro-chromic devices, and fuel cells due to their advantages over liquid electrolytes. SPEs may exist in crystalline or amorphous state; the crystalline SPEs are formed at specific cation to ether-oxygen \( (n_o/n_+) \) compositions, while the amorphous SPEs are obtained over a wide range of temperatures and compositions.\(^8-10\)

The mechanism of ion conduction in SPEs is believed to be different from other ceramic and glassy solid ionic conductors in that the segmental motion of the polymer chains facilitates the transport of ions whereas in other solid materials the ion hopping occurs in a rigid host frame.\(^226\) Following the earliest NMR experimental evidence that the ionic transport in SPEs occurs predominantly in the amorphous regions, it was believed that only the amorphous SPEs promote facile ion transport and the crystalline SPEs were generally regarded as insulators.\(^227\) The notion that crystalline SPEs are non-conductors was substantiated by subsequent experimental observations that showed an increase in ionic conductivity upon de-
creasing the degree of crystallinity in SPEs. These experimental observations directed the research towards increasing the amorphous content of SPEs to improve the ionic conductivity of these materials at ambient conditions. However, recent experimental findings reveal that ionic conductivities of some crystalline SPEs, in particular, PEO$_8$:NaAsF$_6$, PEO$_6$:LiPF$_6$, PEO$_6$:LiAsF$_6$, and PEO$_6$:LiSbF$_6$, are higher than their amorphous counterparts. This has opened up new avenues to search for ionic conduction in crystalline SPEs.\textsuperscript{68,111,228}

The present levels of ionic conductivities in crystalline SPEs (i.e., $\sigma < 10^{-4}$ S cm$^{-1}$) are not sufficient for many commercial applications. There is a compelling need to improve the ionic conductivity of the crystalline SPEs. A detailed molecular-level understanding of the interplay between the structure, dynamics, and energetics of SPEs, is essential to better understand and design SPEs with improved ionic conductivity and mechanical stability.

In this chapter, we have used all-atom MD simulation, adaptive biasing force (ABF), method and the nudged-elastic band (NEB) method to characterize the energetics and the minimum energy paths (MEP) for ion transport in crystalline PEO$_6$:LiPF$_6$.\textsuperscript{4,91,93,97} In particular, the free energy profiles associated with the cation transport along the tunnel formed by the host polymer, the activation energy for hopping of a cation between two adjacent energetically-favourable coordination sites, and crucial factors determining the features of the free energy profiles are examined. The minimum energy paths (MEP) and barrier regions along the transport pathway were characterized. The defect-induced structural changes in micro-environment around defect site and polymer flexibility are also investigated.

### 7.2 Simulation Details

The MD simulations were performed on two crystalline PEO$_6$:LiPF$_6$ models: Model-I represents the ideal PEO$_6$:LiPF$_6$ crystal with no point defects and Model-II is a defected crystal with a chosen Li$^+$ and a remote PF$_6^-$ ions were removed from the lattice (Figure 7.2). The experimental crystal structure of PEO$_6$:LiPF$_6$ was used as the starting structure for the MD simulations.\textsuperscript{58} The simulated $6 \times 2 \times 4$ crystal consisted of 48 unit cells (6, 2 and 4 unit cells along the $\vec{a}$, $\vec{b}$ and $\vec{c}$ axes, respectively) with 32 PEO chains, each having 36 monomers and methyl end-caps with a molecular formula $CH_3O-(C_2H_4O)_{36}-CH_3$, oriented parallel to
7.2. Simulation Details

The starting structure of Model-II was identical to that of Model-I except for the missing Li$^+$ and PF$_6^-$ ions. Model-I provides insights into the nature of fluctuations of ions and polymer chains around their equilibrium positions while Model-II is used to probe the mechanism and energetics of defect-induced ion hopping and the coupling between polymer dynamics and ion transport in the crystalline PEO$_6$:LiPF$_6$.

The all-atom MD simulations were carried out in the isothermal-isobaric ensemble using LAMMPS with the force field parameters taken from the works of Neyertz et al. and Smith et al. The anisotropic pressure control was achieved using the Parrinello-Rahman method with a time constant of 1 ps and the temperature was controlled using the Nosé-Hoover chain thermostats with a time constant of 0.1 ps. Three dimensional periodic boundary conditions consistent with the symmetry of the unit cell were applied. The long-range electrostatic interactions were treated using the particle-particle particle-mesh Ewald (PPPM) method with a real space cut-off of 12 Å. The systems were subjected to energy...
minimization using the conjugate gradient method followed by 5 ns equilibration and 20 ns production runs in the NPT ensemble at 300 K and 1 atm pressure with a time step of 1 fs. The distance, $D_{13}$, between a pair of Li$^+$ ions nearest to the cation vacancy was selected as the reaction coordinate to describe the cation transport in Model-II of PEO$_6$:LiPF$_6$. The mean force as a function of $D_{13}$ was accumulated in bins of width 0.1 Å from 100 ns ABF simulations. The collective variables module implemented in LAMMPS was used for performing the ABF calculations. The nudged-elastic band (NEB) calculations on Model-II of PEO$_6$:LiPF$_6$ with 30 replicas were performed to characterize the minimum energy path between the two cation sites adjacent to the vacancy.

7.3 Results and Discussion

7.3.1 Validation of Model

To validate the simulated models, the MD-derived lattice parameters, radial distribution functions (RDFs) and time-averaged structure are compared against the corresponding experimental data obtained from the crystal structure. The time evolution of the MD-derived lattice parameters is shown in Figure 7.3. Table 7.1 compares the calculated lattice parameters against
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Figure 7.3: The time evolution of the lattice parameters obtained from 15 ns MD trajectory is shown for Model-I of crystalline PEO_6:LiPF_6: (a) a, (b) b, (c) c, (d) α, (e) β, and (f) γ.

the experimental data. From the time evolution of the lattice parameters it is evident that the lattice parameters do not drift with time but exhibit smaller fluctuations around the expected average values tabulated in Table 7.1. The time-averaged structure of PEO_6:LiPF_6 is compared against experimental crystal structure in Figure 7.4. The MD-derived lattice parameters and time-averaged structure agree reasonably well with the experimental data indicating that the force field parameters used in the present study realistically represent the crystalline state of PEO_6:LiPF_6.

7.3.2 Radial distribution functions

Figure 7.5 compares the MD-derived RDFs for different pairs of atoms in the simulated crystals with the corresponding experimental RDFs obtained from the crystal structure. The following naming convention is used in this chapter to denote different RDFs computed for
Table 7.1: The time-averaged unit cell parameters for Model-I and Model-II of crystalline PEO$_6$:LiPF$_6$ obtained from 15 ns MD simulation performed at 300K and at 1 atm pressure are compared against the corresponding experimental values.$^{58}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model-I</th>
<th>Model-II</th>
<th>Experimental$^{58}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>13.40 ± 0.02</td>
<td>13.35 ± 0.02</td>
<td>11.7</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.10 ± 0.02</td>
<td>17.08 ± 0.03</td>
<td>17.4</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.70 ± 0.01</td>
<td>8.71 ± 0.01</td>
<td>9.1</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90.30 ± 0.17</td>
<td>90.25 ± 0.17</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>110.00 ± 0.14</td>
<td>110.08 ± 0.14</td>
<td>107.8</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>89.40 ± 0.20</td>
<td>89.36 ± 0.20</td>
<td>90</td>
</tr>
</tbody>
</table>

Figure 7.4: MD-derived structure of crystalline PEO$_6$:LiPF$_6$ is compared with the experimental crystal structure. The carbons (exp:blue, MD:green), oxygen (exp: yellow, MD:red), and phosphorus (exp:magenta, MD:brown) are shown. Hydrogens and fluorines are not shown for clarity.
Figure 7.5: Comparison of the experimental (black) and MD-derived (red) radial distribution functions (RDFs) (a) O-O, (b) C-C, (c) C-O, (d) Li-Li, (e) Li-P, and (f) Li-O.
7.3. Results and Discussion

PEO$_6$-LiPF$_6$ crystals: $g^I_{X-Y}(r)$ denotes the RDF quantifying the radial distribution of Y-type atoms around a central X-type atom in the $J^{th}$ crystalline model of PEO$_6$-LiPF$_6$, $r$ denotes the distance between atoms X and Y and the values of $J$ can be I (Model-I) and J=EXP represents the corresponding RDF computed from the experimental crystal structure. $g^{EXP}_{O-O}(r)$ (Figure 7.5(a)) consists of multiple sharp peaks in the first coordination shell ($r < 4.6$ Å ) with 5 NN O$_{PEO}$ coordinated to each O$_{PEO}$. O$_{PEO}$ atoms from both the coiled polymer chains contribute to the first coordination shell. $g^I_{O-O}(r)$ shows a peak at 3 Å followed by a minimum at 4.5 Å with a coordination number of 5 at $r = 4.5$ Å. The consistency between the calculated and experimental coordination numbers of the first coordination shell suggests that all the sub-peaks observed at $r < 4.5$ Å in $g^{EXP}_{O-O}(r)$ are merged into a single peak in $g^I_{O-O}(r)$ due to thermal fluctuations of atoms about their crystallographic positions.

$g^{EXP}_{C-C}(r)$ exhibits a single peak at $r = 1.6$ Å with a coordination number of 1 and this peak is due to C-C bond. The peak at $r = 2.36$ Å is due to C$_{PEO}$ connected through C-O-C angle. $g^I_{C-C}(r)$ also captures all the features in $g^{EXP}_{C-C}(r)$. $g^{EXP}_{C-O}(r)$ exhibits a peak at $r = 1.45$ Å with a coordination number of 1 and this peak is due to C-O bond. The other peak at $r = 2.4$ Å is due to C-C-O angle. The second coordination shell extends from 3.0 Å $< r < 8$ Å. $g^I_{C-O}(r)$ captures all the essential features in $g^{EXP}_{C-O}(r)$.

$g^{EXP}_{Li-Li}(r)$ shows a peak at $r = 4.4$ Å with coordination number of 1. The first peak in $g^I_{Li-Li}(r)$ extends form $r = 4.3$ to 6.5 Å with coordination number 1 at minimum $r = 6.5$ Å . $g^{EXP}_{Li-P}(r)$ shows first peaks at $r = 5.68$ Å with a coordination number of 2 indicating that each Li$^+$ ion in the crystal is coordinated by two NN PF$_6^-$. The second coordination shell shows two peaks in the range 6.3 Å $< r < 7.0$ Å. The MD-derived $g^I_{Li-P}(r)$ shows a single peak at 6.23 Å with a coordination number of 4 at $r = 7.5$ Å. $g^{EXP}_{Li-O}(r)$ shows a single peak at $r = 2.15$ Å with a coordination number of 5 i.e., each Li$^+$ ion is coordinated by the five O$_{PEO}$ (three from one polymer chain and the remaining two from other polymer chain of a PEO tunnel). The second coordination shell extends form 3.4 Å $< r < 4.3$ Å with two peaks at $r = 3.65$ Å and 4.16 Å. $g^I_{Li-O}(r)$ also shows a single peak at $r = 2.06$ Å with coordination number of 5 at $r = 2.8$ Å.

The detailed analyses based on RDFs reveal that there is a reasonably good agreement
7.3. Results and Discussion

Figure 7.6: (A) The distributions (Model-I (black) and Model-II (red)) of C-O dihedral angles for a few backbone dihedrals (color coded in (B)) in PEO$_D$ proximal to the void.

between the calculated and experimental RDFs. This consistency indicate that the force field parameters used in our simulation realistically stabilize the experimental crystal structure of PEO$_6$:LiPF$_6$.

7.3.3 Dihedral distributions

To probe the conformational response of polymer to the defect formation in Model-II the distributions of backbone dihedral angles of PEO$_D$ were examined. Figures 7.6 and 7.7 compare the distributions of Model-II C-O/O-C dihedral angle for a few C-O/O-C dihedrals near the void with Model-I C-O/O-C dihedral distributions. In Model-II, however, $P(\phi)$ for a few specific dihedrals (color-coded in Figure 7.6(B) and Figure 7.7(B)) are shifted with respect to the corresponding $P(\phi)$ in Model-I while $P(\phi)$ for all other dihedrals are unperturbed upon defect formation. $P(\phi)$ for individual C-C dihedrals in Model-II were almost identical to the corresponding distributions in Model-I indicating that the C-C dihedrals are insensitive to defect formation.
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Figure 7.7: (A) The distributions (Model-I (black) and Model-II (red)) of C-O dihedral angles for a few backbone dihedrals (color coded in (B)) in PEO$_D$ proximal to the void.

7.3.4 Free Energy Profiles

To understand the energetics of defect-induced ion transport in crystalline PEO$_6$:LiPF$_6$, free energy calculations were performed using the ABF method. The distance, $D_{13}$, between a pair of Li$^+$ ions nearest to the cation vacancy is used as collective variable for determining the PMF profile (Figure 7.2(b)). The calculated PMF profile for cation transport in crystalline PEO$_6$:LiPF$_6$ is shown in Figure 7.8(a). The PMF profile consists of two minima at $D_{13} = 7$ and 12 Å corresponding to the most probable crystallographic positions of Li$^+$ ions along the polymer tunnel in the PEO$_6$:LiPF$_6$ crystal. The conformational state at $D_{13} = 7$ Å is $\sim 25$ kcal/mol more stable than the conformational state at 12 Å. The energy barrier for Li$^+$ transition from the conformational state at $D_{13} = 7$ Å to the conformational state at $D_{13} = 12$ Å is 30 kcal/mol, while the barrier for reverse transition is 4 kcal/mol.
7.4. Conclusions

Figure 7.8: ABF-derived free energy profile and NEB-based minimum energy path (MEP) for cation transport in Model-II of PEO$_6$:LiPF$_6$ are shown. The carbons (green), oxygens (red), Li$^+$ (blue) and instantaneous positions of Li$^+$ ions along the MEP (cyan) are shown. PF$_6^-$ ions and hydrogen atoms are not shown for clarity.

### 7.3.5 Minimum Energy Path

The minimum energy path (MEP) for cation transport along the polymer tunnel in Model-II of PEO$_6$:LiPF$_6$ is characterized using the NEB method and is shown in Figure 7.2(b). The MEP reveals that the Li$^+$ ions follow a curvilinear migration path between adjacent cation sites along the polymer tunnels in crystalline PEO$_6$:LiPF$_6$.

### 7.4 Conclusions

The all-atom MD simulations, ABF and NEB calculations are carried out to understand the structure, dynamics and energetics of crystalline PEO$_6$:LiPF$_6$. The calculated lattice parameters, radial distribution functions and time-averaged structure are consistent with the experimental data suggesting that the force field parameters used in the present study realistically represent the crystalline state of PEO$_6$:LiPF$_6$. The free energy profile and activation energy barriers for the cation transport along the polymer tunnels are quantified using the ABF-method. The MEP identified using the NEB calculations for cation transport between adjacent cation sites in the polymer tunnels in crystalline PEO$_6$:LiPF$_6$ reveals a curvilinear migration path for Li$^+$ ions. The conformational response of PEO to ion hopping near the
defect site has also been investigated.