

List of Figures

1.1	Battery configurations. (a) cylindrical, (b) coin, (c) prismatic, and (d) thin and flat (solid polymer).	2
1.2	Gravimetric power and energy densities (ragone plot) for different rechargeable batteries. ¹	3
1.3	carbonate solvents used in rechargeable batteries	4
1.4	Schematic of the electrochemical cell of a solid polymer battery.	6
1.5	The external and internal structure of a commercial solid polymer battery introduced by AVESTOR TM	6
1.6	Cation motion in SPEs (a) and (b) intrachain hopping, (c) interchain hopping, and (d) intercluster hopping. ²	10
2.1	Length- and time-scales of computer simulations.	17
2.2	A flowchart of molecular dynamics simulation.	18
2.3	Two dimensional schematic of the periodic boundary conditions.	22
2.4	Schematic depiction of the potential energy surface of a complex system. . .	23
2.5	Reconstruction of the free energy surface (FES) along a reaction coordinate using matadynamics. ³	25
2.6	Schematic representation of force decomposition and minimum energy path (MEP) in nudged elastic band (NEB) method. ⁴	25
2.7	A schematic representation of the PSCP thermodynamic cycle for a monoatomic crystal.	27
3.1	Structures of different PEO-based SPEs investigated. (a) PEO, (b) PEO ₃ :NaI, (c) PEO ₃ :LiBF ₄ , (d) PEO ₆ :LiPF ₆ , (e) PEO ₈ :NaAsF ₆ and (f) amorphous PEO. The carbons (green), oxygens (red), Na ⁺ /Li ⁺ (blue) and one atom of anion (purple) are shown. Hydrogens are not shown for clarity.	30

3.2	Polymer conformations in different crystalline PEO-based SPEs. (a) PEO, (b) PEO ₃ :NaI, (c) PEO ₃ :LiBF ₄ , (d) PEO ₆ :LiPF ₆ , and (e) PEO ₈ :NaAsF ₆ . The carbons (green), oxygens (red), Na ⁺ /Li ⁺ (blue) and one atom of anion (purple) are shown. Hydrogens are not shown for clarity.	31
3.3	A schematic representation of the crystalline PEO unit cell along (a) and perpendicular (b) to the chain axis. Hydrogen atoms are not shown for clarity. . .	33
3.4	A schematic representation of the crystalline PEO ₃ :NaI unit cell along (a) and perpendicular (b) to the chain axis. Hydrogen atoms are not shown for clarity.	34
3.5	A schematic representation of the unit cell of PEO ₆ :LiPF ₆ along (a) and perpendicular (b) to the chain axis. Hydrogen atoms are not shown for clarity. . .	35
3.6	A schematic representation of the unit cell of PEO ₈ :NaAsF ₆ along (a) and perpendicular (b) to the chain axis. Hydrogen atoms are not shown for clarity.	36
3.7	Schematic representation of the interactions used in classical force fields to represent the total potential energy of the system.	39
3.8	A schematic representation of the Lennard-Jones (6-12 interaction) potential.	40
4.1	Schematic representation of crystalline PEO-4×2×4 system. Hydrogen atoms are not shown for clarity. Carbons (green) and oxygens (red) are shown. . . .	53
4.2	Lattice parameters of crystal as a function of simulation time at 300 K : (a) a, (b) b, (c) c, (d) α , (e) β , and (f) γ as a function of simulation time.	55
4.3	Temperature evolution of the volume (black) and density (red) of the simulated PEO-4×2×4 crystal.	55
4.4	Temperature dependence of the (a) intra-molecular and (b) intermolecular potential energies of the simulated PEO-4×2×4 crystal.	56
4.5	Temperature dependence of the (a) C-O torsional distributions and (b) percentage of Gauche population around C-O torsions in the simulated PEO-4×2×4 crystal.	57
4.6	Temperature dependence of the (a) helical correlation function (HCF(n)) and (b) helical order parameter (HOP).	58

4.7	The variation of (a) intra-molecular $g_{CC}(r)$ and (b) intra-molecular $g_{OO}(r)$ are shown as a function of temperature.	59
4.8	Temperature dependence of the intra-molecular $g_{CO}(r)$	60
4.9	Intermolecular radial distribution functions (a) $g_{C-C}(r)$ and (b) $g_{O-O}(r)$ across premelting transition.	61
4.10	Behavior of the $P(\cos\eta)$ at room temperature and premelting regime.	62
4.11	Behavior of the $P(\cos\eta)$ in melting regime.	63
4.12	Thermal evolution of (a) inter-chain orientational order parameter (ICOOP) and (b) $\langle \cos\theta \rangle_{\frac{1}{2}}$	63
4.13	The anisotropic diffusion of polymer chains in PEO at (a) 300 K and (b) 600 K. Carbons (green) and oxygens (red) are shown. Hydrogens are not shown for clarity.	66
4.14	Temperature evolution of the time-averaged mean square displacement (MSD) parallel (MSD^{\parallel}) (black) and perpendicular (MSD^{\perp}) (red) to the \vec{c} -axis. The inset shows on an expanded scale the region around 580 K.	67
5.1	A schematic representation of the PSCP thermodynamic cycle.	75
5.2	Schematic representation of crystalline PEO- $4 \times 2 \times 4$ system. Hydrogen atoms are not shown for clarity. Carbons (green) and oxygens (red) are shown.	80
5.3	The probability distribution for the PEO chains center of mass fluctuations at 450 K. Open circles represent the distribution obtained from the simulation and the solid line represents the fit using a harmonic oscillator model.	82
5.4	MD-derived temperature dependence of (a) Density (ρ) and (b) enthalpy (H) of the PEO crystal.	83
5.5	Temperature dependence of (a) enthalpy ($-\frac{H}{RT^2}$) and (b) free energy ($\frac{G}{RT} - < \frac{G}{RT} >$) for solid (black) and liquid (red) phases of PEO.	84
5.6	The thermodynamic integration (TI) for the $C \rightarrow WC$ step of PSCP cycle. Variation of (a) non-bonded interactions and (b) tethering (gauss) potential as a function of λ	84

- 5.7 The thermodynamic integrations for the (a) WC \rightarrow DWF and (b) WL \rightarrow L steps of the PSCP cycle. Plots shows the variation of (a) gauss potential and (b) intermolecular interactions as a function of λ 85
- 5.8 (a) The free energy difference (ΔG) between solid and liquid phases of PEO computed from the PSCP method is shown as a function of temperature. $\Delta G = 0$ at $T = 346$ K, which is the T_m of the crystal predicted by the PSCP method. (b) The free energy difference (in kcal/mol) between states along the PSCP path. 85
- 6.1 A schematic representation of the structure of PEO₃:NaI crystal with 64 unit cells ($2 \times 4 \times 8$ system) (a) view perpendicular to the chain axis and (b) view along the chain axis. The polymer chain that wraps around the cation vacancy (labelled as Na₂) and anion vacancy (labelled as I₃) in the (c) undefected (Model-I) and (d) defected (Model-II) models of $2 \times 4 \times 8$ PEO₃:NaI crystal is shown together with the coordinated ions. The carbons (green), oxygens (red), Na⁺ (blue) and I⁻ (purple) are shown. Hydrogens are not shown for clarity. 89
- 6.2 A schematic representation of the cation transport pathway, which starts from Na₁ to Na₃ via Na₂, along which the adiabatic energies were calculated. The small blue spheres represent the instantaneous positions of the diffusing cation along the transport pathway. 91
- 6.3 The time evolution of the lattice parameters obtained from 10 ns MD trajectories is shown for Model-I (black) and Model-II (red): (a) a (b) b (c) c (d) α (e) β (f) γ . The dashed lines (blue) represent the corresponding experimental values. In all these panels, the data for Model-II are shifted along Y-axis for clarity and the degree of shift is as follows: (a) $y=y-0.3\text{\AA}$; (b) $y=y-0.16\text{\AA}$; (c) $y=y-0.04\text{\AA}$; (d-f) $y=y-0.6^\circ$ 94

- 6.4 The backbone dihedral distributions of PEO obtained from MD simulations of different models of $\text{PEO}_3\text{:NaI}$ crystal: Model-I (blue) and Model-II (magenta). The corresponding dihedral distributions obtained from the experimental crystal structures of $\text{PEO}_3\text{:NaI}$ (red) and PEO (black) are also shown. (a) C-O dihedral distributions; (b) C-C dihedral distributions around the g^- conformational state; (c) C-C dihedral distributions around the g conformational state. PEO crystal MD data is shown in green colour. 96
- 6.5 Radial distribution functions (solid lines) and running coordination numbers (dashed lines) in Model-I (red), Model-II (green), and the experimental crystal structure (black). (a) Na-O (b) Na-C (c) Na-I (d) Na-Na (e) I-C (f) I-O. 99
- 6.6 Radial distribution functions (solid lines) and running coordination numbers (dashed lines) in Model-I (red), Model-II (green), and the experimental crystal structure (black). (d) O-O (e) C-C (f) C-O and the corresponding intramolecular distributions (a) O-O (b) C-C (c) C-O. 100
- 6.7 The MD-derived diffusion pathways of the (a) cations and (b) anions in Model-II. The entire crystal is not shown for clarity. The polymer chain that wraps around the cation vacancy (labelled as Na_2) and anion vacancy (labelled as I_3) is only shown. The carbons (green), oxygens (red), Na^+ (blue) and I^- (purple) are also shown. Hydrogens are not shown for clarity. The crystallographic positions of different (a) Na^+ (small spheres of different colors) (b) I^- (large spheres of different colors) and their corresponding instantaneous positions (points) during MD simulations are shown with (a) I^- (purple) and (b) Na^+ (blue) counter ions. The ellipses denote the location of the vacancy in the initial structure. The fluctuations of the polymer atoms are not shown for clarity. 103
- 6.8 Time evolution of (a) D_{13} , (b) D_{24} , (c) helical pitch (P_h), and (d) radius of gyration (R_g) of PEO in Model-I. 104

6.9	Time evolution of (a) D_{13} (e) D_{24} (d) the helical pitch (P_h) of PEO_D (h) the radius of gyration (R_g) of PEO_D and the van der Waals (red) and electrostatic (black) potential energies of (b) Na_1 (c) Na_3 (f) I_2 and (g) I_4 in Model-II.	104
6.10	Time evolution of the displacement of Na_1 (black) and Na_3 (red) from their initial positions in Model-II obtained during the equilibration phase of the MD simulation performed at 300K.	105
6.11	Ion conduction pathways in Model-II of crystalline $PEO_3:NaI$ with different molecular weights (chain lengths).	106
6.12	The ABF-derived free energy profiles for the (a) cation ($F(D_{13})$) and (b) anion ($F(D_{24})$) hopping and (c) accompanying structural changes in Model-II.	108
6.13	Time evolution of D_{13} in Model-II at different temperatures during the equilibration (black) and production (red) phases of the simulation.	109
6.14	Time evolution of D_{24} in Model-II at different temperatures during the equilibration (black) and production (red) phases of the simulation.	110
6.15	The temperature dependence of (a) $\langle \Delta D_{13}^2 \rangle$ and (b) $\langle \Delta D_{24}^2 \rangle$ obtained from the MD trajectories generated at different temperatures.	111
6.16	Comparison of ABF-derived free energy profiles (black) with the MD-derived harmonic wells (red) obtained from the temperature dependence of $\langle \Delta D_{13}^2 \rangle$ and $\langle \Delta D_{24}^2 \rangle$	112
6.17	The interaction energies (potential energy (black), van der Waals (green) and electrostatic (red) energies) of a sodium ion moving along the adiabatic pathway in Model-I (solid lines), and Model-II (symbols): (a) $Na-O_{PEO}$ (b) $Na-C_{PEO}$ (c) $Na-H_{PEO}$ (d) $Na-Na$ (e) $Na-I$ (f) $Na-All$. All the energy profiles are shifted arbitrarily to set the minimum energy at zero.	113
6.18	(A) (a-d) Time evolution and (e-h) the distributions (Model-I (black) and Model-II (red)) of C-O/O-C dihedral angles for a few backbone dihedrals (color coded in (B)) in PEO_D that are sensitive to defect formation and ion hopping.	117

6.19	(A) The distributions (Model-I (black) and Model-II (red)) of C-C dihedral angles for a few backbone dihedrals (color coded in (B)) in PEO _D proximal to the void.	118
6.20	Dihedral energy $U(\phi)$ profiles for the C-C and C-O torsions in PEO ₃ :NaI. . .	119
7.1	Schematic representation of the crystalline PEO ₆ :LiPF ₆ . The carbons (green), oxygen (red), phosphorus (magenta) and fluorine (cyan) are shown. Hydrogen atoms are not shown for clarity.	123
7.2	Models of PEO ₆ :LiPF ₆ (a) Model-I and (b) Model-II.	124
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	125
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.	126
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.	127
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.	129
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.	130

- 7.8 ABF-derived free energy profile and NEB-based minimum energy path (MEP) for cation transport in Model-II of $\text{PEO}_6:\text{LiPF}_6$ 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. 131
- 8.1 Schematic representation of crystalline $\text{PEO}_8:\text{NaAsF}_6$. Hydrogen atoms are not shown for clarity. Carbon (green), oxygen (red), arsenic (magenta), and fluorine (cyan) atoms are shown. 135
- 8.2 Schematic representation of the models of crystalline $\text{PEO}_8:\text{NaAsF}_6$ (a) Model-I and (b) Model-II. Carbons (green), oxygens (red), sodiums (blue), and arsenic (magenta) are shown. Entire crystal structure and hydrogens are not shown for clarity. 137
- 8.3 The time evolution of the lattice parameters obtained from 10 ns MD trajectories is shown for Model-I of crystalline $\text{PEO}_8:\text{NaAsF}_6$: (a) a, (b) b, (c) c, (d) α , (e) β , and (f) γ 138
- 8.4 MD-derived and experimental structures of crystalline $\text{PEO}_8:\text{NaAsF}_6$ are compared. Hydrogen and fluorine atoms are not shown for clarity. PEO (Exp:blue and MD:cyan), Na^+ (EXP:red and MD:yellow), and arsenic (EXP:green and MD:silver). 139
- 8.5 The backbone dihedral distributions of PEO obtained from MD simulations of $\text{PEO}_8:\text{NaAsF}_6$ crystal. The corresponding dihedral distributions obtained from the experimental crystal structures of $\text{PEO}_8:\text{NaAsF}_6$ (black) are also shown. (a) C-O dihedral distributions; (b) C-C dihedral distributions around the g^- conformational state; (c) C-C dihedral distributions around the g conformational state. 140
- 8.6 Comparison of the experimental and MD-derived radial distribution functions (RDFs) (a) Na-O, (b) Na-C, (c) As-C, (d) Na-Na, (e) Na-As, and (f) As-O. . . 141

-
- 8.7 Comparison of the experimental and MD-derived radial distribution function (rdf) (a) C-O, (b) C-C, (c) O-O, (d) intra C-O, (e) intra C-C, and (f) intra O-O. 143
- 8.8 Projections of AsF_6^- rotations in (a) xy -, (b) xz -, and (c) yz -planes. 144
- 8.9 Distributions of Na-Na distances in Model-I (black) and Model-II (red) (a) D_{12} and (b) D_{13} 145
- 8.10 Time evolutions of Na-Na distances in Model-I (black) and Model-II (red) (a) D_{12} and (b) D_{13} 146
- 8.11 (A) Comparison of MD-derived Na- O_{PEO} distances of Model-I (black) with Model-II (red). Dashed line represent the experimental Na- O_{PEO} distances obtained from crystal structure. (a) Na-O1, (b) Na-O2, (c) Na-O3, (d) Na-O4, (e) Na-O5, (f) Na-O6, (g) Na-O7, and (h) Na-O8. (B) coordination around Na^+ -ion near anion vacancy. The oxygens with in the first coordination shell of Na^+ are shown as van der Waals spheres. Carbons (green), oxygens (red), and Na^+ blue are shown. Hydrogens and anions are not shown for clarity. . . 147
- 8.12 (A) Time evolutions of Na_1 - Na_3 distance and defect sensitive torsions in model-II at 650 K. (B) color coded defect sensitive torsions of PEO_D in Model-II of $\text{PEO}_8:\text{NaAsF}_6$ 149
- 8.13 (A) Time evolutions of Na_1 - Na_3 distance and defect sensitive torsions in model-II at 700 K. (B) color coded defect sensitive torsions of PEO_D in Model-II of $\text{PEO}_8:\text{NaAsF}_6$ 149
- 8.14 (A) Time evolutions of Na_1 - Na_3 distance and defect sensitive torsions in model-II at 750 K. (B) color coded defect sensitive torsions of PEO_D in Model-II of $\text{PEO}_8:\text{NaAsF}_6$ 150
- 8.15 ABF-derived free energy profiles for (a) cation and (b) anion hopping in crystalline $\text{PEO}_8:\text{NaAsF}_6$ 151
- 8.16 Cation transport pathway at temperatures (a) 650 K, (b) 700 K, and (c) 750 K. 152

-
- 9.1 Vibrational density of states obtained from NMA of crystalline (black) and amorphous (red) (a) PEO and (b) PEO₃:NaI are shown with the VACF-based power spectrum (green (a) amorphous PEO and (b) crystalline PEO₃:NaI). 156
- 9.2 Comparison of polymer alone VDOS of PEO₃:NaI with the pristine PEO (a) crystalline PEO (black) and PEO₃:NaI (red), (b) amorphous PEO (black) and PEO₃:NaI (red), and (c) crystalline (black) and amorphous (red) PEO₃:NaI. 157
- 9.3 Local character indicator, L_j , for normal modes of crystalline phases PEO (black) and PEO₃:NaI (red) 158
- 9.4 The maximum of (a) helical pitch (P_h), (b) D_{13} , and D_{24} of crystalline PEO₃:NaI as a function of frequency. 159
- 9.5 Atomic displacements of low-frequency ($< 200 \text{ cm}^{-1}$) vibrational modes of the PEO₃:NaI crystal. For each mode, one of the chains that exhibit significant atomic displacement is shown. Green spheres denote carbon atoms and red spheres denote oxygens. Sodium and Iodide ions and Hydrogen atoms are not shown for clarity. Arrows denote the directions of atomic displacements and their lengths are scaled up for better visualization. The mode at (a) 50 cm^{-1} , (b) 100 cm^{-1} , and (c) 150 cm^{-1} are shown. 160
- 9.6 Vibrational density of states obtained from NMA of crystalline (black) and amorphous (red) (a) PEO₃:LiBF₄ and (b) PEO₆:LiPF₆. 161
- 10.1 The structural hierarchy in solid polymer electrolytes. 164
- 10.2 Schematic representation of crystalline and amorphous PEO₃:NaI systems. Hydrogen atoms are not shown for clarity. Carbons (green), oxygens (red), Na⁺ (blue) and I⁻ (magenta) are shown. 166
- 10.3 Radial distribution functions (solid lines) and running coordination numbers (dashed lines) in crystalline (black) and amorphous (red) PEO₃:NaI. (a) Na-O (b) Na-C (c) Na-I (d) Na-Na (e) I-I (f) I-C. 169

10.4	The coordination numbers distribution (c) and coordination environment around Na^+ ions in (a) amorphous and (b) crystalline $\text{PEO}_3:\text{NaI}$. Hydrogens and iodides are not shown for clarity. The carbons (green), oxygens (red), and Na^+ ions (blue) are shown. The red colour spheres around a Na^+ ion (blue sphere) denote the oxygens coordinated to that particular Na^+ ion.	171
10.5	The distributions of (a) C-O and (b) C-C dihedrals of the crystalline (black) and amorphous (red) $\text{PEO}_3:\text{NaI}$	172
10.6	Time evolution of the selected C-O dihedrals at the Na^+ uncoordinated sites in amorphous $\text{PEO}_3:\text{NaI}$	173
10.7	Time evolution of the selected C-O dihedrals at the Na^+ coordinated sites in amorphous $\text{PEO}_3:\text{NaI}$	174
10.8	Time evolution of the selected C-C dihedrals at the cation uncoordinated sites in amorphous $\text{PEO}_3:\text{NaI}$	175
10.9	Time evolution of the selected C-C dihedrals at the coordinated cation sites in amorphous $\text{PEO}_3:\text{NaI}$	176
10.10	Coupling between ion hopping and polymer dynamics in amorphous $\text{PEO}_3:\text{NaI}$. (a) the distance (D) between Na^+ ions and (b) C-O dihedral time evolution in the vicinity of the cation hopping.	177
10.11	Crystal-like cation coordination environment in amorphous $\text{PEO}_3:\text{NaI}$. Carbons (green), oxygens (red), Na^+ (blue), and I^- (magenta) are shown. Hydrogens are not shown for clarity.	177
10.12	The free energy profiles ($F_C(n)$ and $F_A(n)$) as a function of the coordination of NN O_{PEO} obtained from 200 ns well-tempered metadynamics (WTmetaD) runs for the (a) crystalline and (b) amorphous $\text{PEO}_3:\text{NaI}$	178
10.13(a)	The free energy profile ($F_A(n)$) as a function of the coordination of both NN O_{PEO} and iodides obtained from 200 ns WTmetaD runs performed on amorphous $\text{PEO}_3:\text{NaI}$ and (b) convergence plots for the free energy profiles in Figures 10.12(a) (black), 10.12(b) (red), and 10.13(a) (green).	179