Multiscale Modeling of Polyether-Based Solid Polymer Electrolytes

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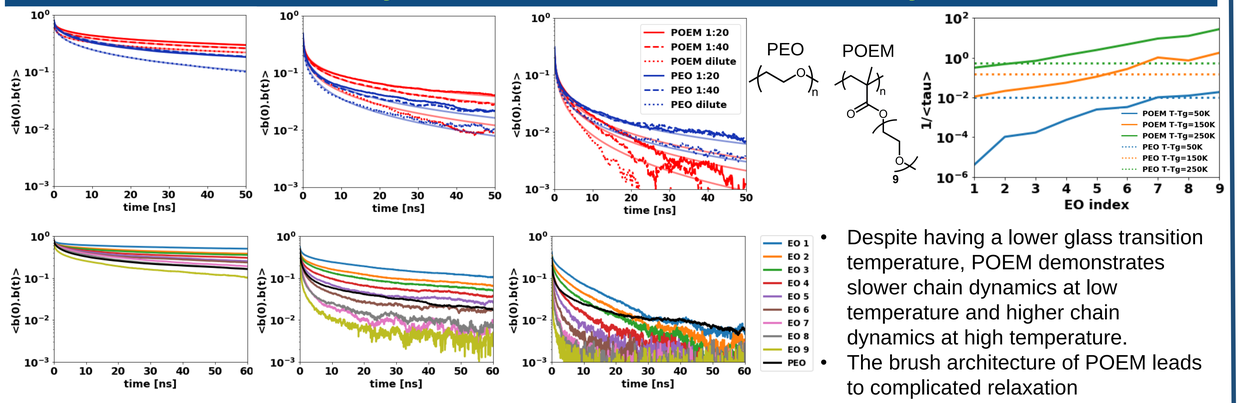
Objectives and Design Goals

Solvent-free polymer electrolytes rise as a new class of electrolyte materials used in Lithium-ion batteries. Compared with conventional electrolytes, polymer electrolytes are safe and mechanically strong. Modeling polymer electrolytes at multiple length-scales is important for understanding the ion transport mechanisms and designing materials that have enhanced room-temperature conductivity. In this study, we aim to understand the effect of polymer architecture on Lithium-ion transport using atomistic simulation. We also aim to develop an effective Brownian dynamics model that reaches large time- and length- scales efficiently, while simultaneously capturing the underlying physics. The final goal is to produce the Electrochemical Impedance Spectrum (EIS) of the system and gain insight about electrochemical phenomena that are happening at different timescales.

Background

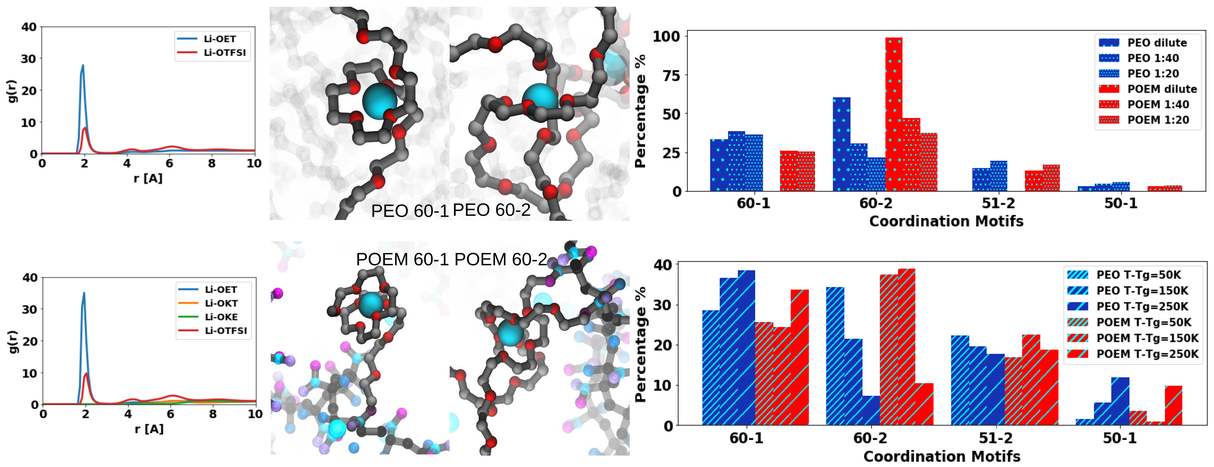
Polymer chain dynamics and solvation site connectivity—the spatial distribution of available coordination sites for Li ion, are two important factors that contribute to ion transport in polymer electrolytes. To understand the effect of polymer architecture on Li ion transport, we used atomistic simulation to study Li ion transport behavior in poly(ethylene oxide) (PEO) and poly[oligo (oxyethylene) methacrylate] (POEM).

Effect of Polymer Architecture on Chain Dynamics



- Despite having a lower glass transition temperature, POEM demonstrates slower chain dynamics at low temperature and higher chain dynamics at high temperature.
- The brush architecture of POEM leads to complicated relaxation

Effect of Polymer Architecture on Ion Solvation Structures



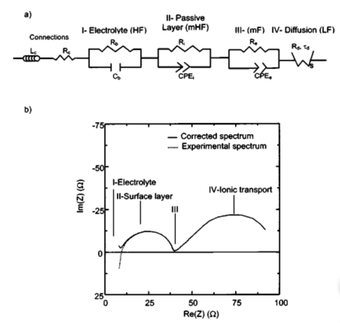
- The Li ion solvation structures in PEO and POEM are similar. Most lithium ions are coordinated by six ether oxygens.
- Due to the brush architecture of POEM, lithium ions in POEM prefer to be coordinated by two chains to a larger extent than in PEO.

C. Deng, M. Webb, P. Bennington, D. Sharon, P. Nealey, S. Patel, and J. de Pablo. *In preparation*

Effective Brownian Dynamics Model

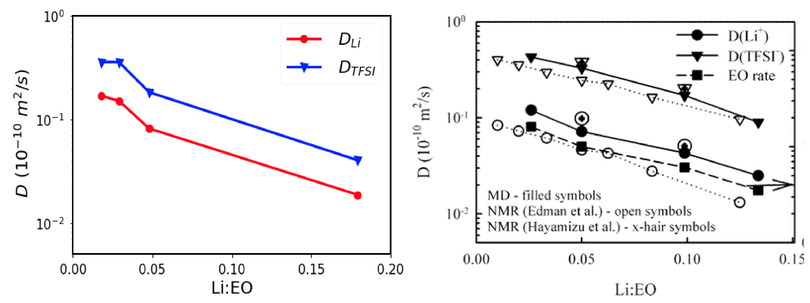
- Coarse-grain all the polymer degrees of freedom into one parameter: the effective global friction γ
- The system is described by charged Brownian particles in an implicit solvent medium

Dielectric constant
Global Friction
→
Model
+
NEMD
→
Conductivity
Impedance Spectrum



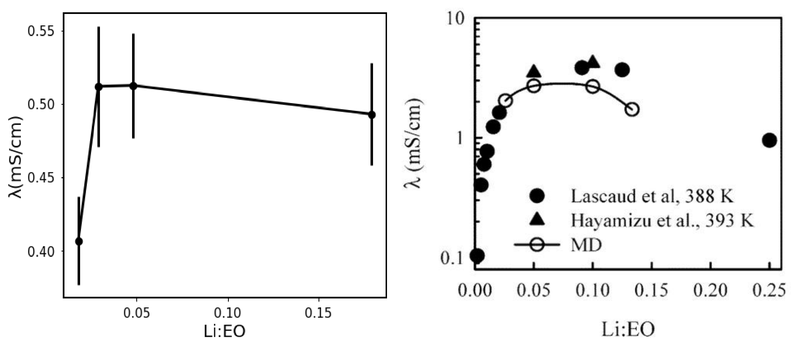
EIS for PEO-LITFSI

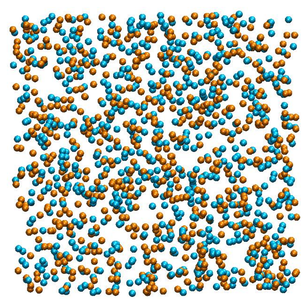
Comparison with Experiment



- The model captures the diffusivity qualitatively.
- Li has lower diffusivity than TFSI, since it interacts strongly with the polymer.
- As the concentration increases the dynamics of the polymer are suppressed and ion pairing becomes significant.
- At higher concentrations the conductivity drop is captured.

$$\sigma_E = \frac{e^2}{Vk_BT} \times \lim_{t'\to\infty} \frac{1}{6t'} \sum_{ij} z_i z_j \langle ((x_i(t+t') - x_i(t)) \times ((x_j(t+t') - x_i(t)) \rangle$$





Snapshot of the system with Li:EO=0.1

O. Borodin, G. D. Smith, Macromolecules 2006,39,4,1620-1629

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