

# Pressure and salt concentration effects on the ionic conductivity of crosslinked thin-film $\text{LiPF}_6$ /poly(ethylene glycol) electrolytes: A molecular dynamics simulation study

## MSc thesis proposal

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May 17, 2017

Many computational studies on electrochemical properties and structure of solid polymer electrolytes (SPEs) have been performed to elucidate the atomistic mechanisms that contribute to the macroscopically observed ionic transport properties, including conductivity. According to these studies, the dominant mechanisms for Li ions predominantly consist in solvent exchange by migrating from one polymer segment to a neighboring one, migration along a single segment or branch, and transport due to segmental mobility. To facilitate these mechanisms, the approach of comb-branched topology will be pursued in the proposed study. The approach offers an additional advantage due to a higher ultimate stress.

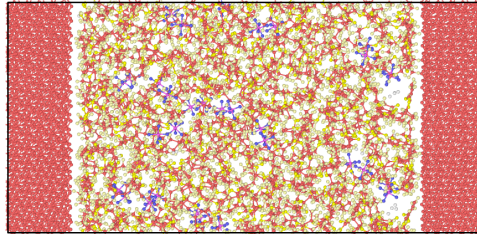
Furthermore, a number of experimental studies have investigated SPE conductivity dependence on hydrostatic pressure. The studies suggest that both large-scale segmental motions of the polymer chain, changes in available free volume, and a combination of free volume and dynamic effects may account for the pressure dependence. In view of these, further studies of SPE atomistic configuration changes at different pressure levels, in particular at compression/expansion transition states, seem relevant, since experimental data do not provide conclusive information regarding suggested nanoscale processes.

**Objectives** Ion diffusivity comparison is performed for crosslinked, PEO or PPGDA-based SPEs at different hydrostatic pressure levels and  $\text{LiPF}_6$  dopant concentrations using classical molecular dynamics (MD). To account for relaxation effects, the relation between polymer segmental dynamics and Li ion diffusivity is considered. To evaluate the SPE film size effects, differences in ion transport properties at the graphitic carbon (GC) interface of SPE films of different thicknesses and bulk-SPEs are studied. Subsequently, optimum SPE film thickness and salt concentration ranges w.r.t. ionic conductivity are determined.

**Why are the answers scientifically relevant or interesting?** The computational study is expected to reveal structural change details and, possibly, changes in ionic transport mechanisms that result from the deformation of the SPE structures, which we consider important for understanding and modeling the material behavior. Reliable analogous information may be difficult, if at all possible, to obtain from experimental

data. A comparison with the mechanical properties of bulk  $\text{LiPF}_6$ -PPGDA and GC-confined-film  $\text{LiPF}_6$ -PPGDA SPEs is of interest for structural battery applications.

**Method** The study is performed using the MD package LAMMPS with a nonreactive force field. A validation of a LAMMPS-based implementation of the force field has been performed. A preliminary study, performed using a reactive force field, could be used as a reference for simulation setup.



60 Å-thick SPE/graphitic carbon film structure (C ●, H ●, O ●, Li ●, P ●, F ●)