

Li-ion desolvation and transport through model SEI/electrolyte interface

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The understanding of correlations between changes in the Li^+ local environment, the details of interfacial and bulk structure, and the mechanisms of ion transport is one of the crucial fundamental aspects needed for efficient design of solid electrolyte interfaces (SEI) with optimal properties for Li-ion battery applications. Using molecular dynamics (MD) simulation methodologies and high fidelity polarizable force fields^{1,2} we have investigated correlations between the underlying structure and the ion dynamics in bulk SEIs and through the SEI/electrolyte interfaces. Specifically, we focused on investigation of the model SEIs comprised of dilithium ethylene dicarbonate (Li_2EDC) and dilithium butylene dicarbonates (Li_2BDC).

Using APPLE&P quantum chemistry-based polarizable force field MD simulations of bulk dilithium alkyl carbonate SEIs in amorphous and ordered (smectic-like) phases showed an Arrhenius temperature dependence with an activation energy of 60-80 kJ/mol.¹ Extrapolation of MD simulation results to room temperature showed very good agreement with the experimentally measured conductivity of 10^{-9} S/cm for Li_2EDC .¹ Li^+ mobility in bulk SEI was found to be highly heterogeneous and the evidence of correlated motion of neighbouring ions have been observed.

The structure of dilithium alkyl carbonate SEI and $\text{LiPF}_6\text{:EC:DMC}(1:2.3)$ electrolyte interfaces (illustrated in Fig 1) has been investigated in detail and correlated with the ability of Li^+ to transfer through interface. The changes in Li^+ coordination as well as its relative position to the interface have been used to define transition events (as illustrated in Fig. 2) and to determine the rate. It was found that the Li^+ transition through Li_2BDC /electrolyte interface has significantly higher rate compared to Li_2EDC . The activation energy for interfacial transition was found to be on the order of 40-60kJ/mol for Li_2BDC /electrolyte interface. We found that the transition rate has only slight dependence on whether the SEI phase is amorphous or ordered.

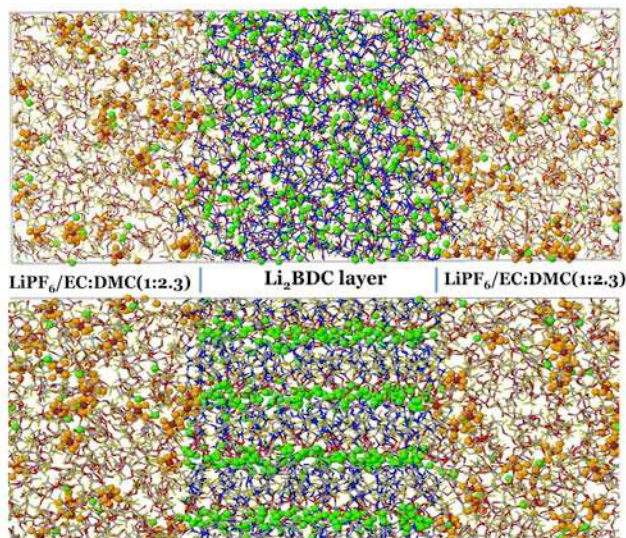


Figure 1. Snapshots of simulated SEI/electrolyte systems: SEI in amorphous phase (top) and SEI in the ordered phase (bottom).

A detailed analysis of atomic distributions and orientation of solvent molecules in the interfacial layer as well as analysis of Li^+ coordination as a function of its position in the system will be presented.

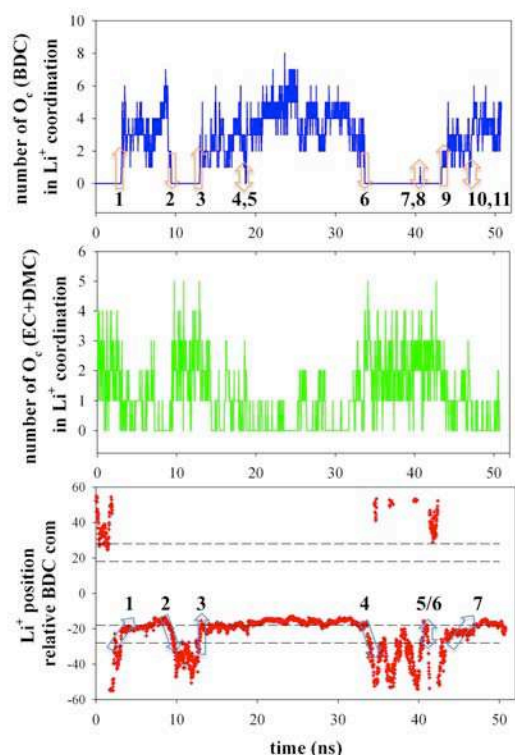


Figure 2. Illustration of the Li^+ evolution that was used to determine the Li^+ transitions through SEI/electrolyte interface. a) evolution of the Li^+ coordination by alkyl carbonate oxygens, b) evolution of the Li^+ coordination by electrolyte oxygens, and c) Li^+ position relative to the center of mass of SEI layer (dashed lines define location of the SEI/electrolyte interfaces).

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References

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