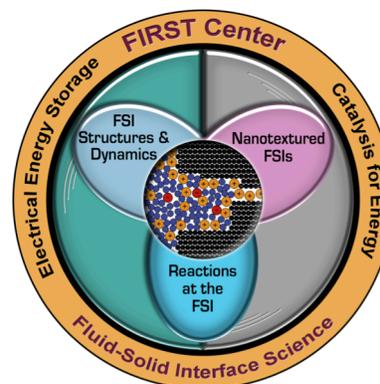


FIRST Center Research Perspective:

AIMD Simulations of Li-ion Battery Electrolytes and Incipient SEI formation

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Research Summary: Using ab initio molecular dynamics (AIMD) techniques we have (i) obtained accurate properties of lithium-ion battery electrolytes, and (ii) performed the first studies of solid-electrolyte interphase (SEI) formation at realistic electrodes. Our studies used the common cyclic carbonate electrolytes ethylene and propylene carbonate, LiPF₆ salt, and realistic graphite carbon anodes. We demonstrated that different graphite terminations show strongly differing effects on the reducibility of the electrolyte, and orientational ordering of electrolyte near the interface precedes reduction. LiF was observed to form and migrate to the surface. Our research demonstrates the importance of studies of the solid-electrolyte interface and indicates routes to improved battery performance via controlled passivation or use of artificial SEI.

Technical Details: Fundamental to the improvement of Li-ion battery science and technology is an improved understanding of the solid electrolyte interphase (SEI). The SEI results from the reduction of commonly-used cyclic carbonate electrolytes at the carbon anode, and at high voltages, also on the cathode side. Formation of the SEI results in capacity loss and an increase in cell resistance, but paradoxically the passivating nature of the SEI also serves to protect the carbon anode. Thus improvements in our understanding of the SEI formation, composition, and transport properties can aid in designing cells with increased lifetime, voltage or temperature range.

Very little is known about the SEI due to the difficulty of performing in-situ characterization, making this an ideal area for complementary simulation and experiment. We performed systematic simulations of the properties of this system, commencing with the properties of bulk electrolytes – where unambiguous experimental validation is available – and then studying the interfacial system.

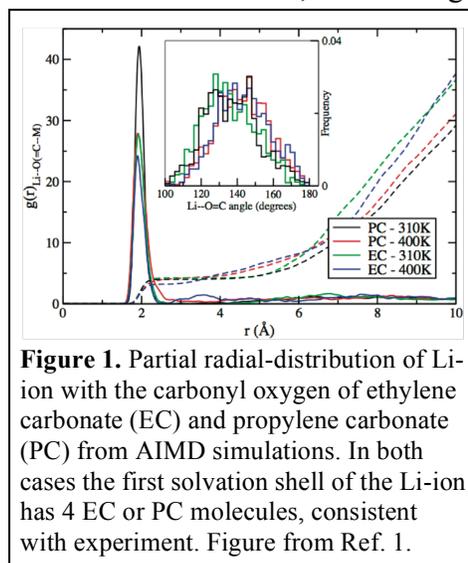
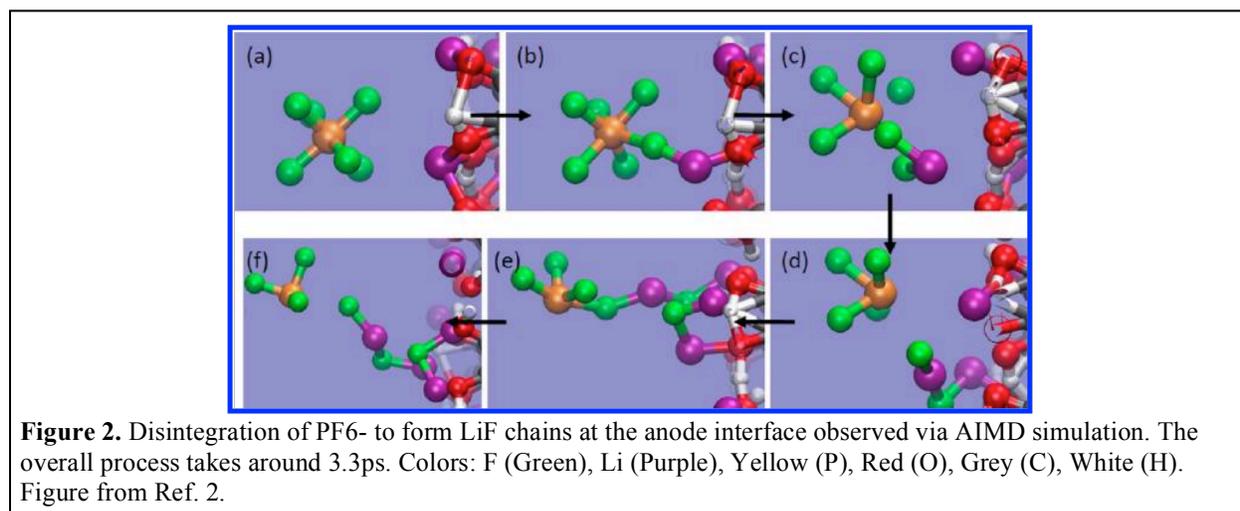


Figure 1. Partial radial-distribution of Li-ion with the carbonyl oxygen of ethylene carbonate (EC) and propylene carbonate (PC) from AIMD simulations. In both cases the first solvation shell of the Li-ion has 4 EC or PC molecules, consistent with experiment. Figure from Ref. 1.

Although numerous classical molecular dynamics studies for electrolytes have been performed and are well justified, our ab initio calculations are nearly parameter free, and permit chemistry to be studied. Our simulations give accurate structures and solvation models that agree well with existing neutron scattering experiments. In **Figure 1** we show the computed radial distribution function for the Li ions. We found that the solvation shells contained either four ethylene carbonate (EC) or propylene carbonate (PC) molecules, at similar distances ($\sim 2\text{\AA}$) to time of

flight neutron scattering experiments. Furthermore, the computed diffusion constants also agree well with measured values at room temperature, giving strong confidence that the ab initio methods are able to accurately capture the structure and dynamics of LiPF_6 in carbonate-based electrolytes.

To study the initial stages of SEI formation we performed simulations with supercells containing EC and PC electrolyte, and LiPF_6 salts, and carbon graphite electrodes with different termination groups. Although our simulation are restricted to short timescales (few 10s ps), we found multiple accessible reduction pathways. The reduction products are consistent with existing literature but are not deterministic; i.e., small changes in our simulation parameters lead to different pathways, possibly due to the large driving force for electrolyte reduction in our simulations. Our results suggest that reduction of cyclic carbonate electrolytes occur via a 2e process, and Li_2CO_3 should be expected to form a vital SEI component near the anode surface. LiF forms via salt decomposition and agglomerates at the anode interface, forming an important component of the SEI. **Figure 2** shows snapshots from an AIMD simulation in which a PF_6^- ion reacts, forming a LiF molecule. This molecule then diffuses to the surface and begins to form LiF chains, i.e. the beginning of a LiF rich SEI layer. The facile formation of these products, even within the short time frame of our simulations, highlights the importance of reducing fluorine chemistry, e.g., via alternative non-fluorinated salts, for Li-ion battery applications. Given the importance of inorganic species such as LiF and Li_2CO_3 naturally formed near the electrode upon electrolyte reduction, engineering thin layers of similar inorganic materials, either crystalline or amorphous, to act as an electronically insulating barriers while allowing ionic transport is an interesting pathway to design artificial SEI. We also find that the electrolyte reduction is strongly influenced by anode surface functionalization and presence of reduced species. Passivated surfaces are seen to be less reactive, suggesting a route to modifying the SEI.



Significant Impacts on Science and Technology: We have demonstrated the feasibility of using ab initio molecular dynamics to study Li-ion battery electrolytes and the initial stages of solid electrolyte interphase formation. We have observed reactions and structural changes that are unique to, and facilitated by, the fluid-solid interface region and therefore can not be obtained by

simulations or experiment that focus on either the electrolyte or electrode in isolation, e.g. via high throughput studies of bulk properties. Our results indicate the feasibility of influencing the SEI via improved passivation of synthesized materials or via the use of “artificial SEI” layers to minimize reactivity at the electrode-electrolyte interface. This could result in enhanced rate performance, longer lifetime, or the feasibility of wider voltage windows for increased energy density.

Publications and Manuscripts:

1. “*Accurate static and dynamic properties of liquid electrolytes for Li-ion batteries from ab initio molecular dynamics*”. P. Ganesh, D. Jiang, P. R. C. Kent. *Journal of Physical Chemistry B* **115** 3085 (2011). <http://dx.doi.org/10.1021/jp2003529>
2. “*Solid electrolyte interphase formation and electrolyte reduction at Li-ion battery graphite anodes: a first-principles molecular dynamics study*”. P. Ganesh, P. R. C. Kent, and D. Jiang. *Journal of Physical Chemistry C* **116** 24476 (2012). <http://dx.doi.org/10.1021/jp3086304>