ELUCIDATING ADDITIVE EFFECTS ON EARLY STAGE SOLID-ELECTROLYTE INTERPHASE GROWTH MECHANISMS USING MOLECULAR DYNAMICS

Luke D. Gibson[†*] and Jim Pfaendtner[†‡]
[†]Department of Chemical Engineering, University of Washington, Seattle, WA 98195
[‡]Senior Scientist, Pacific Northwest National Lab, Richland, WA 99354

Abstract

Solid-electrolyte interphase (SEI) formation is one of the major contributors to the loss of capacity over time in lithium-ion batteries (LIBs). SEI forms as the product of reductive decomposition of a battery's electrolyte, which typically consists of a mixture of ethylene carbonate (EC) and dimethyl carbonate in LIBs. Chemical additives are often included in small amounts to improve the cycling lifetime of LIBs, which are variants of EC such as fluoroethylene carbonate (FEC) and vinylene carbonate (VC). Herein, we used molecular dynamics with metadynamics, an enhanced sampling technique, to explore chemical reaction networks for systems containing 3 EC molecules, a Li^+ ion, an extra unpaired electron, and a FEC, VC, or a fourth EC molecule. The reaction networks for the 3 systems show similar initial mechanisms whereby an oxygen in an intact or ring-opened EC attacks the electrophilic carbon in the carbonate group of a neighboring EC, FEC, or VC. However, after the initial reaction, the 3 systems diverge and follow different mechanisms. We report that FEC reduced the overall volume of reactions, whereas VC increased the reactivity of the system when compared to the pure EC system.

Keywords

Chemical reaction networks, solid-electrolyte interphase, lithium-ion batteries, parallel-bias metadynamics.

Introduction

The need for reliable, long-term energy storage is rapidly growing, especially as renewable energy resources such as solar and wind become more and more efficient. The lithium-ion battery (LIB) is an excellent candidate for long-term energy storage due to its high energy density; however, it suffers from irreversible capacity loss over its lifetime. There are many mechanisms that contribute to this capacity loss, but this work is focused on the formation of solid-electrolyte interphase (SEI) and how this phenomenon proceeds in various chemical environments.

SEI growth is driven by the reductive decomposition of electrolyte molecules at the interface of the battery electrodes (Peled 1979; Doron Aurbach 2000; D. Aurbach et al. 1996). Understanding the mechanisms that drive SEI growth can grant insight into how this process can be controlled such that the layer thickness is minimized while still insulating the electrodes from further electrolyte degradation.

Traditionally, a LIB is comprised of a graphitic anode, a metal oxide cathode, a separator, and an electrolyte. The electrolyte includes the Li^+ source and the solvent. Electrolytes are commonly mixtures of ethylene carbonate (EC) and dimethyl carbonate (DMC) with additives that often are also cyclic and linear carbonate species. Popular

---

[*] To whom all correspondence should be addressed

additives are fluoroethylene carbonate (FEC), vinylene carbonate (VC), propylene carbonate, etc., which have been reported to increase cycling lifetime (Ushirogata et al. 2013).

To gain a better insight into how FEC and VC additives affect SEI formation mechanisms, we examined 3 model electrolyte systems which are listed in Table 1.

Table 1: Model Electrolyte Systems

System Name	System Composition
4EC	$4\ EC + 1\ Li^+ + 1\ e^-$
3EC+FEC	$3\ EC + 1\ FEC + 1\ Li^+ + 1\ e^-$
3EC+VC	$3\ EC + 1\ VC + 1\ Li^+ + 1\ e^-$

We have used molecular dynamics (MD) to study SEI formation with molecular-scale resolution. All simulations were run with system temperature set to 300 K in the NVT ensemble and the time step was set to 1 fs. To simulate 1-electron reduction, the multiplicity of each system was set to doublet, i.e., the inclusion of one extra unpaired electron. The systems were described using the semi-empirical PM6 level of theory.

Chemical reactions are rare events that can often occur on time scales much longer than what is typically afforded to MD simulations. We have used parallel-bias metadynamics (PBMetaD) to bias all atomic social permutation invariant (SPRINT) coordinates to enhance the rate at which chemical reactions occur (Pfaendtner and Bonomi 2015; Pietrucci and Andreoni 2011). This method of using PBMetaD+SPRINT has been shown to be an effective tool for reaction network exploration (Fu and Pfaendtner 2018).

The goal of this work is to further elucidate the mechanisms that drive SEI formation across various chemical environments.

Conclusions

Based on current results, we see that when compared to the 4EC system, FEC in the 3EC+FEC system suppressed the depth of reaction networks, whereas VC increased the overall reactivity of the 3EC+VC system.

These changes in system reactivity are consistent with literature (Okuno et al. 2016) and we expect to see stable, oligomeric species being formed through different mechanisms for FEC- and VC-containing systems instead of unstable and inorganic species with pure EC systems.

Acknowledgements

References

Aurbach, D., B. Markovsky, A. Shechter, and Y. Ein-Eli. 1996. "A Comparative Study of Synthetic Graphite and Li Electrodes in Electrolyte Solutions Based on Ethylene Carbonate-Dimethyl Carbonate Mixtures." *Journal of The Electrochemical Society* 143 (12): 3809–20. doi:10.1149/1.1837300.

Aurbach, Doron. 2000. "Review of Selected Electrode-Solution Interactions Which Determine the Performance of Li and Li Ion Batteries." *Journal of Power Sources* 89: 206–18. doi:10.1016/S0378-7753(00)00431-6.

Fu, Christopher D, and Jim Pfaendtner. 2018. "Lifting the Curse of Dimensionality on Enhanced Sampling of Reaction Networks with Parallel Bias Metadynamics." *Journal of Chemical Theory and Computation* 14: 2516–25. doi:10.1021/acs.jctc.7b01289.

Okuno, Yukihiro, Keisuke Ushirogata, Keitaro Sodeyama, and Yoshitaka Tateyama. 2016. "Decomposition of the Fluoroethylene Carbonate Additive and the Glue Effect of Lithium Fluoride Products for the Solid Electrolyte Interphase: An Ab Initio Study." *Phys. Chem. Chem. Phys.* 18 (12). Royal Society of Chemistry: 8643–53. doi:10.1039/C5CP07583A.

Peled, E. 1979. "The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems—The Solid Electrolyte Interphase Model." *Journal of The Electrochemical Society* 126 (12): 2047. doi:10.1149/1.2128859.

Pfaendtner, Jim, and Massimiliano Bonomi. 2015. "Efficient Sampling of High-Dimensional Free-Energy Landscapes with Parallel Bias Metadynamics." *Journal of Chemical Theory and Computation* 11 (11): 5062–67. doi:10.1021/acs.jctc.5b00846.

Pietrucci, Fabio, and Wanda Andreoni. 2011. "Graph Theory Meets Ab Initio Molecular Dynamics: Atomic Structures and Transformations at the Nanoscale." *Physical Review Letters* 107 (8): 1–4. doi:10.1103/PhysRevLett.107.085504.

Ushirogata, Keisuke, Keitaro Sodeyama, Yukihiro Okuno, and Yoshitaka Tateyama. 2013. "Additive Effect on Reductive Decomposition and Binding of Carbonate-Based Solvent toward Solid Electrolyte Interphase Formation in Lithium-Ion Battery." *Journal of the American Chemical Society* 135 (32): 11967–74. doi:10.1021/ja405079s.