Predictions of Ethylene Carbonate Breakdown & Solid Electrolyte Interphase (SEI) Onset

Accomplishment
- Computational methods predict the electrolyte decomposition products at an electrode-electrolyte interface during charging
- In the *ab initio* molecular dynamics model, two electrons transferring from LiC$_6$ anode to ethylene carbonate-based electrolyte instigates breakdown.
- Results indicate formation of CO and C$_2$H$_4$O$_2$$^2-$ reaction products, consistent with experiments$^1$ but previously unpredicted by computation, as well as expected CO$_3^{2-}$ and C$_2$H$_4$ compounds.

Significance
- The stability and safety of many electrochemical systems for electrical energy storage depend on a critical solid-electrolyte interphase (SEI), which forms from the reaction products and passivates the electrode layer.
- The formation and character of the SEI layer is largely unclear.
- This work is the first theoretical to address the initial chemical mechanisms of electrolyte breakdown at explicit electrode-liquid electrolyte interfaces and therefore SEI formation.

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Supporting Information

The term SEI was coined by Peled to describe the self-limiting solid layer formed by the decomposition of ethylene carbonate, linear carbonate, and Li⁺ salt at the anode surface, mostly during the initial charging of the lithium ion batteries.

SEI films are amorphous, heterogeneous films <50 nm thick on the anode side, containing Li₂CO₃, LiF, and organic components such as lithium dicarbonate. The precise composition is not known and depends on charging conditions, additive molecules, etc.

Cracking, poisoning, and gradual decay/regeneration of SEI are among the main sources of capacity fade, loss of active Li⁺, and lifetime reduction as the battery cycles power.

Thinner SEI films also form on high voltage (>4.2 V) cathode oxide materials.
Notes on SEI films – formation mechanisms and modeling

• widely cited (but largely unproven) formation mechanisms\(^1\) notwithstanding, the multitude and complexity of SEI products means that their chemistry remains important objects of study

• For recently revised proposed mechanisms, see Maron, Haik, Aurbach, Halalay JECS 157 A972 (2010)

• Balbuena \textit{et al.} pioneered modeling of solvent decomposition near anode

• Their quantum chemistry calculations omit electrodes (injection of free electrons)

• NEES modeling of solvent decomposition include explicit graphite anode surfaces with C=O and C-OH edges, liquid electrolyte, and state-of-the-air (if costly) AIMD simulations

• We discover multiple mechanisms depending on stage (thickness) of SEI growth, and stress the importance of electrode/electrolyte $e^-$ transfer

\[\text{[Wang et al., JACS 123:11708 (2001)]}\]