

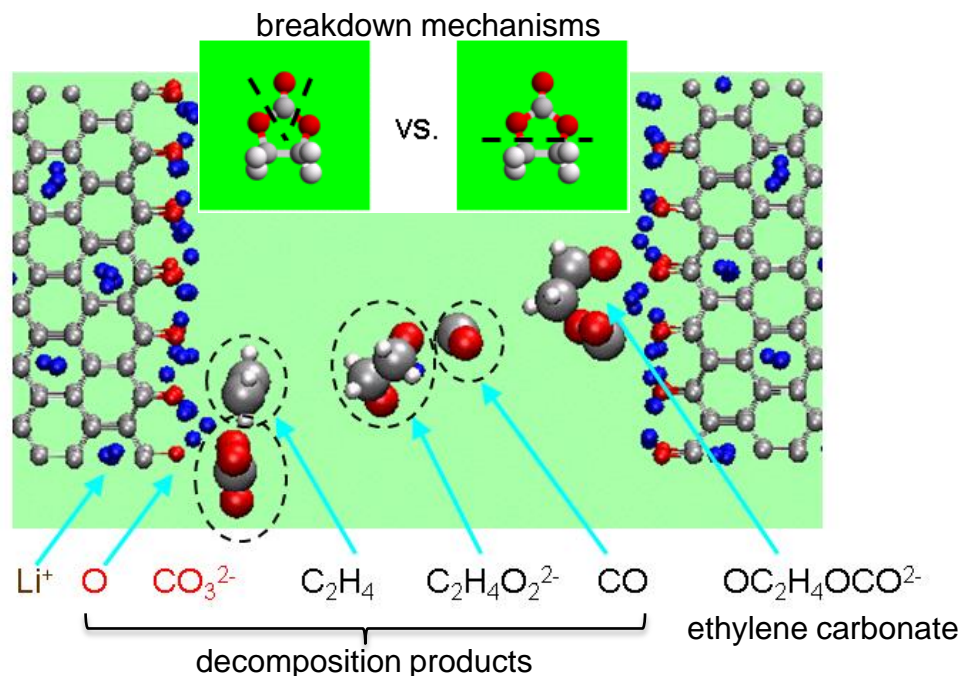
Predictions of Ethylene Carbonate Breakdown & Solid Electrolyte Interphase (SEI) Onset

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 $\text{C}_2\text{H}_4\text{O}_2^{2-}$ reaction products, consistent with experiments¹ but previously unpredicted by computation, as well as expected CO_3^{2-} and C_2H_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.



Collaborators

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Supporting Information

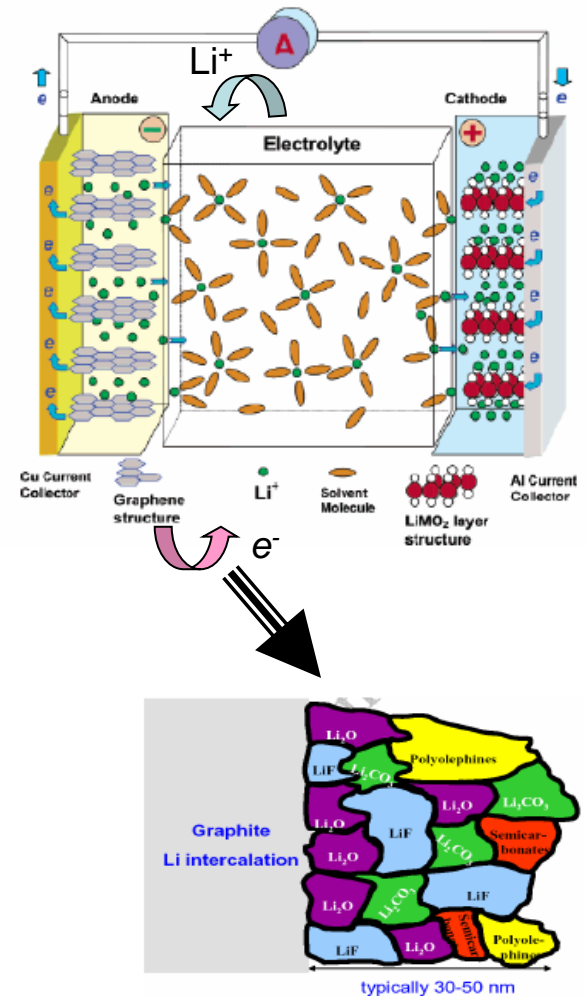
Leung & Budzien, *Phys. Chem. Chem. Phys.* **12**, 6583 (2010)

¹Onuki *et al.*, *J ECS* 155 A794 (2008).

²*Lithium ion batteries: solid electrolyte interface*, ed. Wang & Balbuena (Imperial College, London, 2004)

Notes on SEI films – general introduction

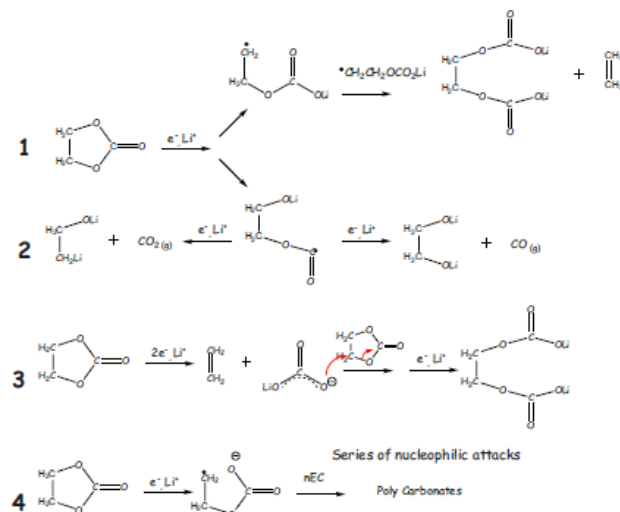
- The term SEI² was coined by Peled to describe the self-limiting solid layer formed by the decomposition of ethylene carbonate, linear carbonate, and Li⁺ salt at the anode surface, mostly during the initial charging of the lithium ion batteries
- SEI films are amorphous, heterogeneous films <50 nm thick 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



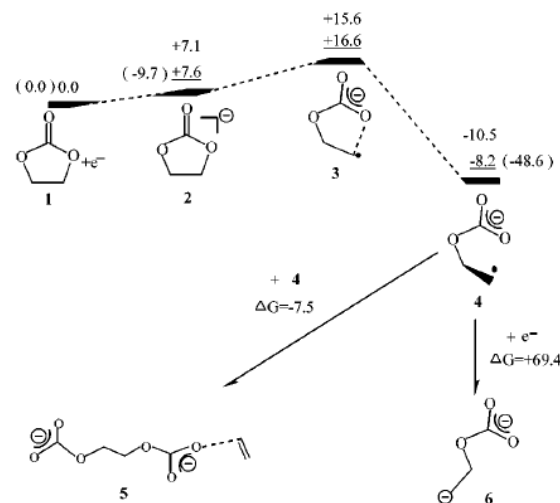
Report of the Basic Energy
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Notes on SEI films – formation mechanisms and modeling

- widely cited (but largely unproven) formation mechanisms¹ 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 J ECS 157 A972 (2010)



- Balbuena *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



[Wang et al., JACS 123:11708 (2001)]