SEI layer formation on Si anodes

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Silicon has been shown as a promising material for anodes of Li-ion batteries due to its enhanced storage capacity, about one order of magnitude higher than that of graphite. However, lithiation causes swelling and amorphization of the electrode structure. Organic solvents such as ethylene carbonate together with a Li-salt are the main constituents of the electrolyte that is usually chemically unstable and becomes reduced in contact with the electrode surface.

The reduction products include a series of organic and inorganic species, which form a polycrystalline solid film deposited on the electrode surface, known as solid-electrolyte interphase (SEI) layer. Since the reduction is driven by electron transfer via quantum tunneling, the SEI layer only grows up to a certain thickness. In some cases the film exerts a protective role providing mechanical stability to the electrode, but its physical and chemical properties are critically dependent on the nature of the electrolyte but also on that of the electrode surface.

In this work, we report results of density functional theory (DFT), ab initio molecular dynamics (AIMD) simulations, and a DFT-Green function approach aimed to elucidate the SEI layer formation due to ethylene carbonate, vinyl carbonate or fluoroethylene carbonate decomposition on Si anodes. We utilize two approaches: in one of them the surface is represented by a cluster emulating lithiated Si (001) surfaces, in the other periodic slabs are used to simulate similar lithiated surfaces. We discuss the reduction mechanism and the effect of surface functional groups as well as the presence of surface oxide films on the reduction. We also show preliminary results of the characterization of electron transfer through model SEI films on functionalized and oxidized surfaces.