Modeling the effects of additives and oxides on solid electrolyte interphase properties on silicon anode surfaces

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Silicon is a promising anode candidate for lithium ion batteries. The performance of silicon anodes is known to be affected by additives like fluoroethylene carbonate (FEC)[1] and silicon oxide layers[2], most likely through modifications of the solid elecrolyte interphase (SEI) films which allow them to withstand the large volume expansion during lithium intercalation or impact "self-healing" properties. We use both static and dynamic electronic structure computational techniques to examine the interactions of FEC with the surfaces of lithium intercalated silicon[3]. FEC is found to decompose along reaction pathways similar to ethylene carbonate, but the fluoride ion is readily detached after the initial decomposition reactions. The implication for passivating behavior will be discussed. At the initial stages of SEI formation, Si is usually coated with native oxide films, residues of which may react to form lithium silicates[4]. Additives that induce surface siloxane linkages appear to improve Si anode performance[2]. Therefore we also consider the lithium transport properties and electrochemical reactions of silicon dioxide and lithium silicate. Formation of the latter mixed oxide is found to be thermodynamically favorable over some voltage windows. However, surface covalent Si-OH bonds, unlike bare Si surfaces, are found to react slowly with lithium metal.

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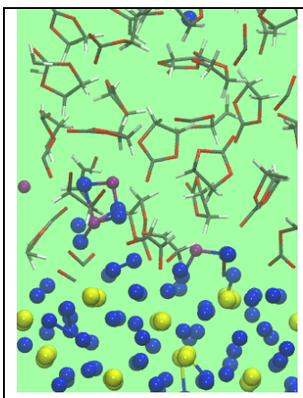

Snapshot of an *ab initio* molecular dynamics trajectory of a FEC/EC mixture on a Li13Si4 surface. Si, Li, and F atoms are show as yellow, blue, and purple spheres. EC and FEC molecules (decomposed or otherwise) are depicted as stick figures.