Understanding the surface modification mechanism of electrolyte additives on silicon anodes in Li-ion batteries

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Silicon has been widely considered as the next generation anode material for lithium-ion batteries, due to its substantially higher capacity compared to conventionally used graphite. However, silicon-based electrodes suffer from problems such as poor capacity retention and low coulombic efficiency.[1-3] Significant amount of work has been devoted to improve the performance of silicon electrodes. Among all the efforts, electrolyte additives, fluoroethylene carbonate (FEC) and vinylene carbonate (VC) particularly, are found to be able to dramatically improve the electrochemical performance. In the present work, the decomposition mechanism of FEC as well as the surface modification of Si electrodes were investigated.[4] The FEC additive degrades prior to the other carbonate solvents at a higher reduction potential, and instantaneously a conformal solid electrolyte interphase (SEI) is formed on the silicon electrode. This stable SEI layer, which mainly consists of the decomposition products of FEC, sufficiently limits the emergence of large cracks and suppresses the additional SEI formation from the decomposition of other electrolyte components. These differences in SEI layer, formed with or without the presence of FEC, are schematically demonstrated in Fig 1. Besides, it was observed that the $LiPF_6$ decomposition can be influenced by the FEC additive, and this effect was further studied with a combination of X-ray photoelectron spectroscopy (XPS) and solid-state nuclear magnetic resonance (NMR) techniques.

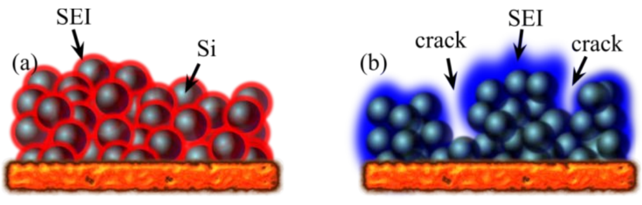

Fig 1. Schematic representation of the SEI formation on silicon anode with different electrolytes FEC/LP40 (a) and LP40 (b), respectively. The two SEI layers are different in compositions and highlighted with different colors. Reprinted with permission from ref4.

Moreover, we also demonstrated that by forming an effective SEI layer with the FEC and VC additives, the silicon electrodes with lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide (LiTDI)-based electrolyte can be well functioning as the state-of-art $LiPF_6$-based electrolyte.

References:

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