

In-depth surface and reactivity investigation of Li – based electrolytes

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Abstract

In an electrochemical device, interfaces between electrolytes and highly reducing/oxidizing electrodes play an important role in governing the overall performance and safety of the systems. Ever since the inception of the SEI layer concept in 1979,^[1] many investigations aiming at mastering the electrified interface at the vicinity of lithiated graphite and electrolyte materials have been conducted. However, the complete understanding and controlling of this passivation layer has remained as the least understood component of the LIB. Besides to its being a legitimate interface for charge transfer, the continuous decomposition and formation of the SEI layer also controls the reactivity of (de-) lithiated electrode materials, owing to the fact that all the cascading reactions in LIBs are initiated by the SEI cracking.^[2,3]

In an effort to better understand the SEI and its accompanying role, a detailed comparative investigation on the reactivity and filming behavior of various new and state – of – the – art Li – based electrolytes was carried out using XPS, DSC and chemical simulation. The electrolytes investigated includes LiX (X = PF₆, TDI, FSI, TFSI and FTFSI), dissolved in EC/DMC (1/2, wt. %). The reactivity and SEI nature of the newly emerging imide (FSI-, and FTFSI-) and imidazole (LiTDI) - based electrolytes are evaluated and compared to the well - researched salts, mainly LiPF₆. Analysis of DSC traces indicates that the salt nature plays an important role in determining the reactivity of the LiX-EC/DMC electrolytes systems. For same state of charge (SOC), the reactivity of lithiated graphite (Li_xC₆) in the different electrolytes was found to be in the order of LiFSI > LiTDI > LiTFSI > LiFTFSI > LiPF₆ and LiTDI < LiTFSI < LiPF₆ < LiFTFSI < LiFSI in terms of increasing onset exothermic temperature and normalized total heat generated, respectively. Chemical simulation tests proved that FSI⁻ and FTFSI⁻ anions readily get reduced by anthracene radical anion (≈ 1.0V vs. Li⁺/Li⁰), resulting in the formation of stable SEI layer components. On the contrary, LiPF₆, LiTDI and LiTFSI were found to be highly stable, even to lower potential reducing agent such as biphenyl (≈ 0.5V vs. Li⁺/Li⁰), enlisting the presence of predominance for salt and solvent reductions in the two categories.

Depth-profiling XPS analysis on both cycled and uncycled binder free half - cells was performed on the above-mentioned electrolyte formulations. The results provided insight into the differences and similarities of the SEI (composition, thickness, evolution etc.), resulting from the structure of the various anions.

References:

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