

Solid-State NMR Characterization of an Additive-Derived Solid-Electrolyte Interphase

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To further progress the adoption of electric vehicles and other high power energy storage applications, it is desirable to develop lithium-ion cell chemistries that offer longer lifetimes at high temperatures and cell voltages, without significantly increasing the cost. The introduction of sacrificial electrolyte additives on the order of a few weight percent is a practical method to form protective solid-electrolyte interphase (SEI) layers that limit electrolyte decomposition during cell storage and operation. In recent years, significant efforts have provided new understanding of the underlying chemistry of several such additives, including compounds containing a Lewis acid-base adduct [1-2]. The present work focuses on the SEI that is formed from pyridine pentafluorophosphate (PPF), which has been shown to improve charge capacity retention after cycling at high temperature and high cell voltage [3].

This work will present how solid-state NMR spectroscopy (ssNMR) has been used to characterize the SEI formed on a graphite electrode surface from the PPF additive. The PPF-derived SEI was prepared in a full Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O₂/graphite cell, rather than in a coin cell or using a bench-top synthesis approach. ¹⁹F and ¹⁹F → ³¹P cross-polarization measurements offer direct evidence that F atoms and P-F bonds are present in the SEI. By comparing rinsed and unrinsed samples, an insoluble SEI component was differentiated from residual LiPF₆ from the dried electrolyte. The SEI species contains F and P chemical environments that are similar to, but distinct from, the additive starting material and the LiPF₆ electrolyte salt used in this work. The results are consistent with the previously proposed formation of a dilithium 4,4'-bipyridine-N,N'-bis(pentafluorophosphate) salt [1]. LiF was also observed and is attributed to decomposition of the PPF-derived surface layer and/or the LiPF₆ electrolyte salt.

In general, the results in this work confirm previous recommendations that a wide variety of experimental techniques, coupled with computational methods such as density functional theory, can offer new insights into the underlying chemistry of SEI formation in lithium-ion cells. The present work demonstrates that for additives with suitable nuclei, ssNMR is a valuable complement to explore these chemical pathways.

References:

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