

**NMR Studies of SEI Formation in Cycled and Stored LiCo<sub>2</sub> Cathodes and MCMB Anodes.**

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One of the life-time limiting factors to long lasting lithium ion rechargeable batteries is the growth of an electrically insulating interface termed as Solid Electrolyte Interphase (SEI). SEI forms during battery cycling and is a byproduct of the reaction between the electrolyte and battery electrodes.<sup>1,2</sup> While this layer initially protects the electrodes from degradation, continued growth of the SEI increases the internal resistance and reduces the capacity of the battery.

The goal of this work is to identify the different chemical species, both organic and inorganic, that comprise the SEI and to quantify the amounts present under the various cycling conditions. While other techniques have qualitatively described the SEI,<sup>4-7</sup> Nuclear Magnetic Resonance (NMR) makes possible identification of and distinction between lithium environments intercalated into the host material and lithium incorporated into the SEI layer<sup>8</sup>. NMR spectra are also quantitative, that is, the measured signal intensity is directly proportional to the number of nuclei present in different chemical environments within the sample.

<sup>7</sup>Li, <sup>19</sup>F, and <sup>31</sup>P Magic Angle Spinning (MAS) NMR spectroscopy has been used to identify and quantify the different chemical species formed on both LiCoO<sub>2</sub> cathodes and MCMB anode cycled in LiPF<sub>6</sub> based electrolytes. Studies track the SEI formation both as a function of cycle number, state of charge (SOC) during storage, and temperature. The cells were charged and discharged from 2.5 V to 4.2 V (our samples were all cycled 3.0 V to 4.1 V) for a variable number of cycles ranging from 3000 to 9000. In addition, cells were stored at 50% and 100% state of charge at room temperature, 45°C, and 60°C.

Significant differences are seen in the signature of the SEI among the spectra of cells cycled at room temperature versus those stored and/or cycled at elevated temperatures. One of the prominent components of the SEI observed by <sup>19</sup>F NMR is LiF. We have found a correlation between LiF content on both electrode surfaces and cycling/aging conditions. This methodology can provide important information for modeling the SEI and thus facilitate future attempts in tailoring the electrolyte and host electrode materials to control SEI formation.

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**References**

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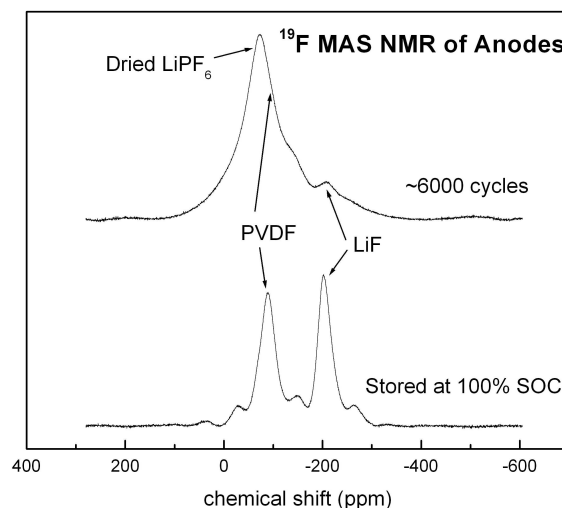


Figure 1. <sup>19</sup>F MAS NMR of MCMB anodes shows that more LiF is formed following storage at 100% state of charge (SOC), than seen following extended cycling of a Li rechargeable cell. The PVDF signal comes from the binder and acts as an internal calibrant for the fluorine content.

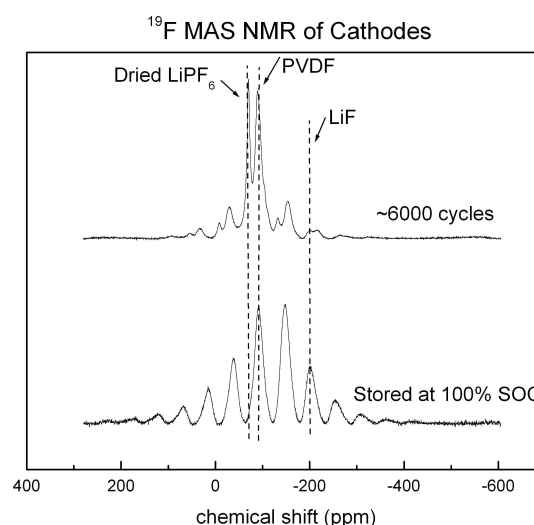


Figure 2. <sup>19</sup>F MAS NMR of LiCoO<sub>2</sub> cathodes cycled in Li ion rechargeable cells.