

Solid Electrolyte Interphase Formation in Iron (II) Fluoride Conversion Electrodes

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Iron Fluoride-based materials show great promise as energy storage media, due to the availability of iron's oxidation states during its reduction to metallic iron nanoparticles. As with all lithium-based secondary batteries, a solid-electrolyte interphase (SEI) is formed in these iron fluoride conversion materials during first cycle. Despite substantial advances in secondary battery performance over the decades, very little is understood about the degradation of in-situ solvent which provides the basis for the formation of the SEI.

In this investigation, we examine the SEI at several levels of charge/discharge of FeF₂ in order to better understand the chemical reaction pathways underlying the resultant products. We used Magic-angle Spinning Nuclear Magnetic Resonance (MAS NMR) to characterize the resultant SEI formation. The electrolyte consisted of a typical binary mixture of cyclic and linear carbonates, in this case ethylene carbonate (EC) and dimethyl carbonate (DMC) in 1:1 volume ratios, with 1M LiPF₆. In order to track the decomposition pathways, ¹³C isotopic enrichment was used, where only one the carbonates in the binary mixture (either EC or DMC) was 33% enriched at a time.

Three levels of charge/discharge coin cells were produced. In the First set, the cells were permitted to discharge to 1.5V, then held at 1.5V for 24h; In the Second set, the cells were permitted to discharge to 1.5V, then recharged to 4.5V and held at 4.5V for 24h; the Third set the cells were immediately charged to 4.5V (no discharge permitted) and held at 4.5V for 24 hours.

Figure 1 depicts a Hahn Echo MAS NMR spectrum of the directly observed ¹³C, for the third charge protocol (immediate charge to 4.5V; no discharge permitted). Well-defined peaks are present at 157 and 61ppm, indicative of carbonyl and ethylene carbons, respectively. The much larger carbonyl intensity reflects the isotopic enrichment of the EC at only the carbonyl position. The breadth of the spinning sideband manifold (1500ppm total) is attributed to interactions with paramagnetic host.

To support this, Figure 2 displays a ¹H-¹³C cross polarization (CP) MAS NMR spectrum with a short (500μs) contact time. The promotion of the new isotropic peaks seen at 182ppm, 163ppm, 132ppm and 111ppm imply proximity (~1.3-1.8Å) to available protons.

To conclude, these new peaks demonstrate that some decomposition of the EC has occurred and that these products reside in the SEI. Differences in SEI composition will be correlated with the different charge/discharge protocols and whether enrichment was done for EC or DMC

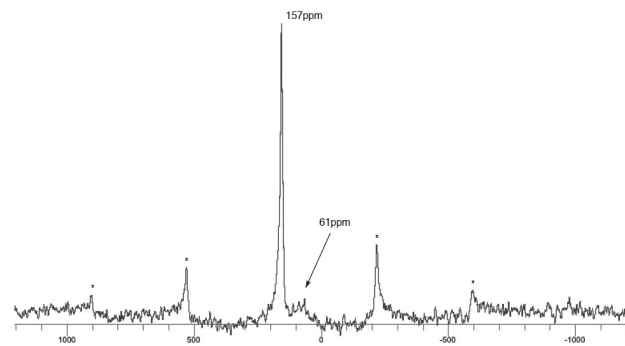


Figure 1: Directly polarized Hahn-Echo . Asterisks indicate spinning sidebands; 27.8kHz spinning speed.

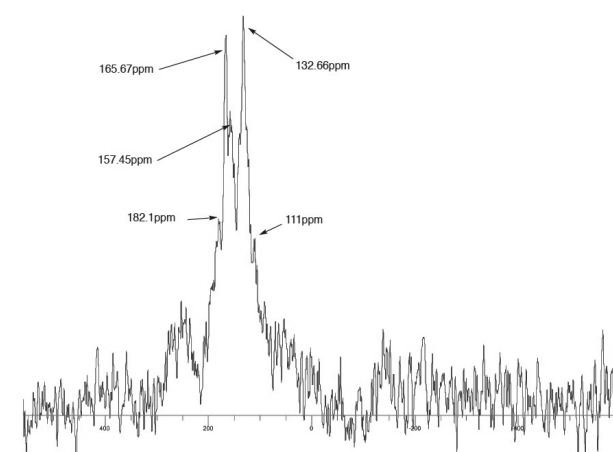


Figure 2: ¹H-¹³C cross polarization spectrum of sample following Protocol 3 (charged to 4.5V, no discharge permitted) depicting additional peaks. 8.5kHz spinning speed.

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