Supplementary Material

Title: Analysis of Chemical and Electrochemical Lithiation/Delithiation of a Lithium-Ion Cathode Material

Author names and affiliations:

Devanshi Gupta [a], Gary M. Koenig Jr.*[a]

[a] Department of Chemical Engineering
University of Virginia
102 Engineers Way, Charlottesville, VA, 22904-4741 (USA)

*corresponding author: Email: gary.koenig@virginia.edu
**Table S1.** ICP-OES data for purchased LFP and FP prepared by oxidation with hydrogen peroxide. Fe and Li concentrations are those from the solution of the dissolved solid that was analyzed in the instrument.

| Compound      | Fe (mg/ml) | Li (mg/ml) | Molar Ratio (Li:Fe) |
|---------------|------------|------------|---------------------|
| LiFePO₄ (LFP) | 3.308      | 0.425      | 1.034               |
| FePO₄ (FP)    | 3.27       | 0.015      | 0.039               |

**Figure S1.** X-ray diffraction patterns for as-received LFP (red) and after chemical oxidation and delithiation to FP (black) via exposure to hydrogen peroxide and acetic acid.
Figure S2. a) Photograph of custom glass cell for electrochemical oxidation of FcBr$_2$ and cyclic voltammetry of redox shuttles. Cell had a platinum wire working electrode and Li foil as both reference and counter electrode. b) Cyclic voltammetry curves for 8 mM Fc (blue) and 2 mM FcBr$_2$ (orange) using the cell in a).
Figure S3. Rate capability testing of coin cells with LFP cathodes at room temperature: a) Voltage versus time and, b) capacity at different rates of charge/discharge. The cathode contained a ratio by weight of 80:10:10 LFP: carbon black: PVDF binder and was 70 µm thick. The anode was lithium metal foil. All charge and discharge cycles were conducted at the same rate and as indicated in b). 1C was assumed to correspond to 160 mA g⁻¹ LFP.
**Figure S4.** UV-Vis extinction at 705 nm for different concentration of FcBr$_2^+$ in the carbonate solvent electrolyte used in this study. The extinction values at these FcBr$_2^+$ concentrations were exclusive of solid LFP particles.

**Figure S5.** UV-Vis extinction at 615 nm for different concentration of Fc$^+$ in the carbonate solvent electrolyte used in this study. The extinction values at these Fc$^+$ concentrations were exclusive of solid FP particles.
**Figure S6.** Stability of 2 mM FcBr₂⁺ solution in electrolyte at 45⁰C. The UV-Visible extinction at the peak wavelength of 705 nm (orange circles) associated with FcBr₂⁺ was monitored over a period of 90 minutes. The decrease in absorbance at 705 nm when adjusted for the extinction at a reference wavelength of 900 nm (black squares) was determined to be 2% reduction of FcBr₂⁺ in the electrolyte.

**Figure S7:** Stability of 8 mM Fc solution in electrolyte at 45⁰C. The UV-Visible extinction at the peak wavelength of 615 nm (black squares) associated with Fc⁺ was monitored over a period of 90 minutes. The change in absorbance at 615 nm when adjusted for the extinction at a reference wavelength of 418 nm (orange circles) was determined to be 0.3% oxidation of Fc in the electrolyte.
Figure S8: \( \log (\log (-1-f)) \) vs \( \log t \) curves where \( f \) is conversion and \( t \) is time for a) chemical oxidation of LFP and b) chemical reduction of FP, at 25 °C (black circles), 35 °C (black triangles), and 45 °C (black squares). Dashed lines represent linear fits of the data.
Figure S9. Rate capability testing of coin cells at room temperature with cathodes containing active material which was FP produced by oxidation of LFP with H₂O₂: a) Voltage versus time and, b) Capacity at different rates of charge/ discharge. The cathode contained a ratio by weight of 80:10:10 FP: carbon black: PVDF binder and was 70 µm thick. The anode was lithium metal foil. All charge and discharge cycles were conducted at the same rate and as indicated in b). 1C was assumed to correspond to 160 mA g⁻¹ LFP.
Figure S10. Chronoamperometry of Li/LFP coin cells under conditions of a) oxidation of LFP at 3.6 V (vs. Li/Li\(^+\)) and b) reduction of FP at 3.3 V (vs. Li/Li\(^+\)). Experiments were conducted at 25 °C (green solid line), 35 °C (red dashed line), and 45 °C (black dashed line).
**Figure S11.** Plots of the ln of the first order rate constant as a function of the inverse temperature (in °K) for a) chemical oxidation of LFP, b) chemical reduction of FP, c) electrochemical oxidation of LFP and, d) electrochemical reduction of FP. Error bars represent the sample standard deviation of 3 measurements. In cases where error bars are not evident, the error bars are smaller than the size of the data points. Dashed lines represent linear regression lines of best fit.