

Electronic Structure Analysis Of Aged Commercial LiFePO₄ Battery Cathodes Using Low Loss Electron Energy Loss Spectroscopy

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Electron Energy Loss Spectroscopy (EELS) is a powerful tool for the simultaneous probing of structure, chemistry and bonding of a material at very high spatial resolutions [1]. When performed in the low-loss regime, it has the advantage of providing an increased signal to noise ratio while carrying rich information about the local electronic structure of the material. In this paper, low loss EELS spectra were obtained from commercial LiFePO₄ battery cathodes that have been aged using standardized procedures for artificial aging while varying metrics such as temperature, charge-discharge rate and capacity retention (Table 1). An attempt was made to quantify the phases present in these cathodes by assuming a simple linear combination of standard LiFePO₄ / FePO₄ phases by the use of Multiple Linear Least Square fitting (MLLS) technique. The systematic failure of the MLLS approach with this assumption when applied to several aged samples proves that the electronic structure of the composite cathode is more complex than a simple linear combination of standard phases and sets up the challenge for a better understanding of the complex local electronic structure using other tools [2].

LiFePO₄ standard was purchased from Sigma-Aldrich and FePO₄ standard was prepared by an oxidation process described by James et al. [3]. Both powders were heated at 70°C till they dried and crushed into a fine powder in a pestle and mortar and laid on a TEM grid with lacey support for EELS analysis. Standard low loss spectra for LiFePO₄ & FePO₄ standards were obtained in the energy range -10→90eV and energy resolution 1eV with a dispersion of 0.1eV/channel on a FEI Tecnai TF 20 (Fig.1). All EELS spectra were obtained in a STEM mode over 20nm×20nm scan boxes. Commercial A123 20Ah prismatic cells were aged using a United States Advanced Battery Consortium (USABC) charge depletion profile [4], while varying charge-discharge rate, capacity retention and cycling temperature. The resulting matrix of cells is shown in Table 1. Thin foils (~100nm) were extracted from these commercial cathodes utilizing an optimized dual beam FIB procedure [5] to minimize ion-beam induced damage to the specimens. Low loss spectra were obtained from these samples with the same specifications as the standards described earlier. Multiple Linear Least Square fitting is typically used to determine quantitative phase composition when two or more phases are present in a sample. The model assumes a linear combination of the phases to be present in their respective weight percent fractions and iterates these weight fractions using least square fitting till a satisfactory fit to the experimental spectrum is obtained as determined by the residual χ^2 value. Fig.1 shows an example of the application of this procedure to a cathode sample aged at 80% capacity retention, 55°C and charge discharge rate of 2x (entire battery discharged in 30 mins). The fit is clearly a failure, as demonstrated by the poor quality, visible in the 5eV range as well as a poor residual χ^2 value. The above procedure was repeated for all the cells in Table 1 and the results of fitting were equally poor for most samples.

The failure of MLLS fitting assuming a linear combination of standard phases proves that the local electronic structure in these commercial cathodes is more complex and needs further probing. Lorentz oscillator modelling provides such a tool and has been applied on the same samples and results will be

discussed in another manuscript currently in preparation [2]. In that paper, we analyze trends in the dynamic variation of electronic structure in these commercial cathodes and provide a way to map them.

References:

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Table 1. Matrix of cycled A123[®] 20Ah prismatic cells

Sample	Temperature	Capacity retention	Charge / Discharge rate*
1	55 °C	90%	1C
2	55 °C	90%	2C
3	55 °C	80%	1C
4	55 °C	80%	2C
5	35 °C	90%	1C

*Charge / Discharge rate of 1C is equivalent to discharging the entire capacity of the battery in one hour

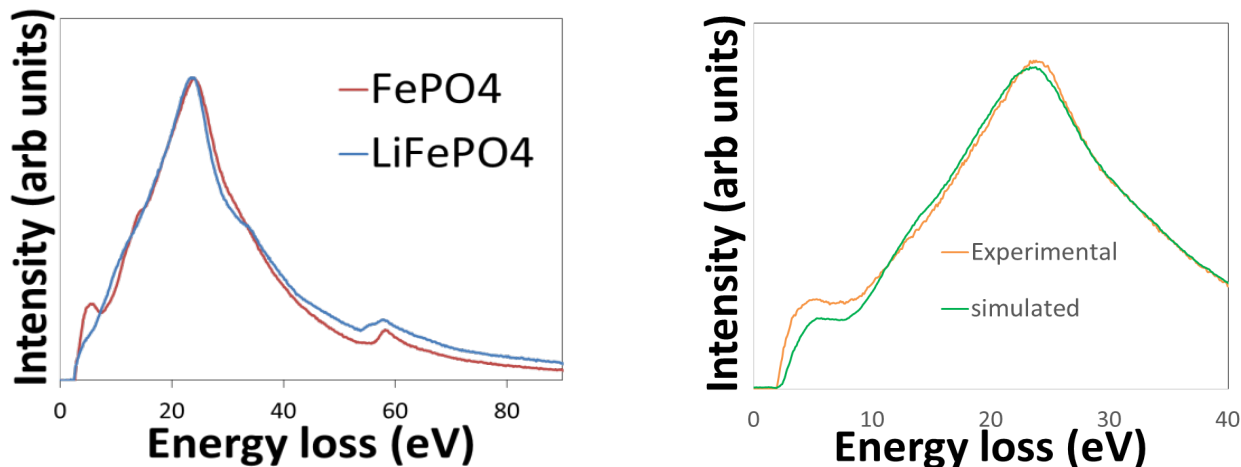


Figure 1. FePO₄ and LiFePO₄ standard low loss spectra (left) and the experimental spectrum (orange) and corresponding MLLS fit (green) in the plot on right.