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Mapping Trends in Electronic Structure Variation With Aging in $LiFePO_4$ Cathodes: A Lorentz Oscillator Model Approach

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Electron energy loss spectroscopy (EELS) is a powerful tool for the simultaneous determination of local structure, chemistry and bonding in a material. Previously [1], we utilized EELS in the low energy loss regime (-10 → 90eV) for the qualitative determination of phase composition in a series of artificially aged commercial $LiFePO_4$ battery cathodes. An attempt was made to quantify these phases using Multiple Linear Least Square fitting. The failure of the above approach for quantification set the stage for further analysis of the complex electronic structure of these aged cathodes. In this paper, we propose the use of Lorentz Oscillator modelling as a tool for tracking changes in electronic structure occurring in the cathode as the battery is aged.

A123® 20Ah prismatic $LiFePO_4$ cells were artificially aged using a charge-depletion profile defined by the United States Advanced Battery Consortium [2]. Within this profile, charge-discharge rate, temperature and capacity retention were varied. The resulting set of cells was unwrapped and cathode material was extracted from each cell. An optimized Dual Beam FIB procedure [1] was utilized to prepare thin foils from the cathode materials of the various cells while minimizing ion-beam induced damage. Low loss EELS was performed in the energy range (-10 → 90eV) on an FEI®-Tecnai, with an energy dispersion of 0.1eV/channel and energy resolution of 1eV (FWHM of zero loss peak (ZLP)). The energy loss function was derived from these spectra after ZLP subtraction and Fourier log deconvolution. The energy loss function was fit to a combination of six Lorentz oscillators, each defined by oscillator energy, width and intensity (fig. 1a). Lorentz oscillator modelling is a proven classical and quantum mechanical approach to modelling the dielectric response of a material to an incident electromagnetic or electron wave. According to this model, a combination of Lorentz oscillators oscillating at different frequencies in response to an incident wave comprises the dielectric response of the material. The position of each oscillator on the energy axis provides information about interband transitions occurring in the material and the combined area under the oscillators gives the effective valence electron density in the region being probed.

Fig. 1(a) shows the process of modelling the energy loss function as a combination of oscillators. Fig.1 (b) shows a comparison between the electronic structure of an unaged and heavily aged cathode. Oscillator energies and areas are plotted as a function of the region of the sample being probed. Studying the oscillator energy (representative of interband transitions in the material), it appears that they are similar in different regions of a given sample (unaged/aged), but vary across samples. From the oscillator area charts, it appears that aging the oscillator area values are more homogenous in the aged sample compared to the unaged sample. These trends in electronic structure as a function of aging have important implications to the nature of phases formed in the cathode as the batteries are cycled thousands of times and help propose an aging mechanism at the nanometer length scale.

References:

[1] S.A. Channagiri *et al*, Microscopy and Microanalysis 20 S3 (2014), p. 432.
[2] Battery Test Manual for Plug-In Hybrid Vehicles, U.S. Department of Energy, Vehicle Technologies Program, March 2008
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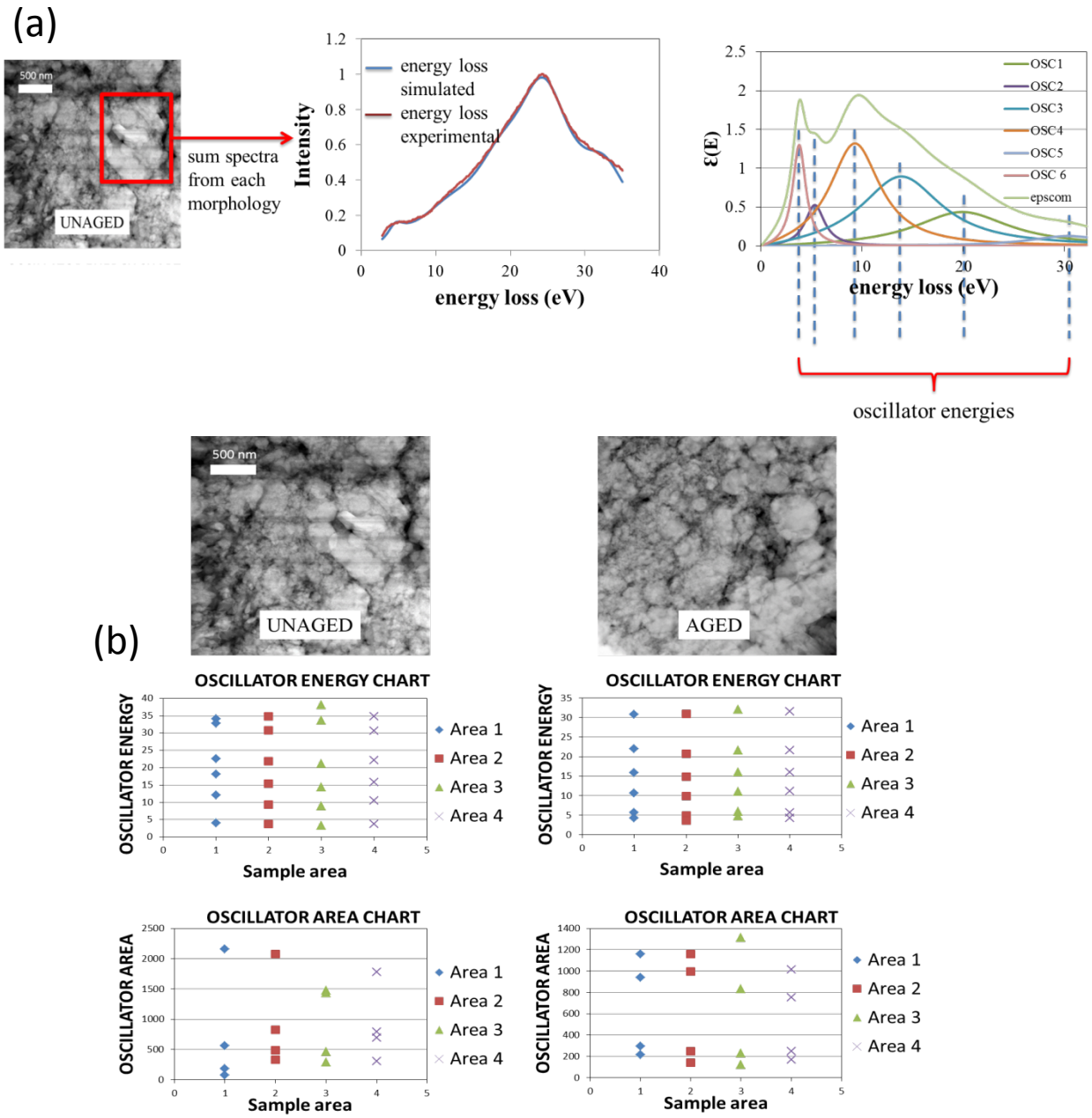

Figure 1. (a) Flowchart showing the obtaining of a spectrum from a focus box and the fitting of the energy loss function to six Lorentzian oscillators. (b) Comparison of oscillator areas and energies between an unaged and aged sample in different areas within the microstructure.

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