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EELS Investigations of Aging Mechanisms in $LiFePO_4$ Cathodes Resulting From Prolonged Electrochemical Cycling

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Lithium iron phosphate ($LiFePO_4$) has considerable potential as a cathode in batteries for automotive applications due to its high rate capability, reasonable energy density and environmentally benign nature [1]. However, performance degradation seen after thousands of cycles at high charging-rates (C-Rates) has been a point of major concern [2]. Studies of the aging mechanism suggest that phases ($LiFePO_4/FePO_4$) formed in the cathode during discharge influence the aging profile [3]. Previously, we used electron energy loss spectroscopy (EELS) to demonstrate the use of Li-K edge for identifying lithium in the sample with a potential for quantification [4]. This required a modified procedure for focused ion beam (FIB) milling to minimize ion beam damage during sample preparation [5]. We reduced beam dosage in the electron microscope to prevent knock-on damage to the lithium in the sample. Lithium content, combined with information of the oxidation state of iron, can be used to identify the phases formed upon intercalation. The study was able to identify fine variations in the Li-K edge structure, and hence, phase composition in nanoparticles inside the $LiFePO_4$ composite electrode.

We have produced a series of aged cells and performed the above mentioned EELS analysis on cathode samples extracted from unaged and aged cells. Aged cells were produced for this analysis utilizing capacity retention, cycling temperature and battery size factor (B.S.F) as metrics. For a given B.S.F and temperature, the battery was cycled until it retained 80% or 90% of its capacity. The charging profile used for this purpose was the charge depletion profile prescribed by the USABC for Plug-In Hybrid Electric Vehicles (PHEV's) [6]. A total of eight samples were aged (Table 1). The cells were unwrapped and cathode material extracted at specific sites for further analysis. Electron transparent thin foils were prepared from these materials by FIB milling [5]. We then performed EELS in the low energy-loss regime ($\Delta E<90eV$) at an energy resolution of 1eV and dispersion of 0.1eV /channel in an FEI Tecnai TF20 on both unaged and aged (aged at B.S.F = 1, T = 35°C upto 90% capacity retention) samples. The EELS results obtained at a nanoparticle level are shown in fig.1, with corresponding lower magnification STEM–HAADF images of the microstructures of the respective samples.

Both unaged and aged cells have similar microstructures with a large particle size distribution making it challenging to identify directly structural variations introduced by aging. However, EELS performed in the low loss region exhibit subtle variation in the Li K-edge (fig.1) energy-loss near-edge structure (ELNES). In particular, the intensity and separation of the peaks in ELNES varies within a given sample and between samples. The Fe $M_{2,3}$-edge peak (fig.1) retains its position on the energy axis in all cases, with subtle variations in the shape of its pre-peak in both samples. The correlation between EELS and microstructure is providing new insights into the complex aging mechanism in these electrodes that is in part responsible for the capacity loss with extended cycling.

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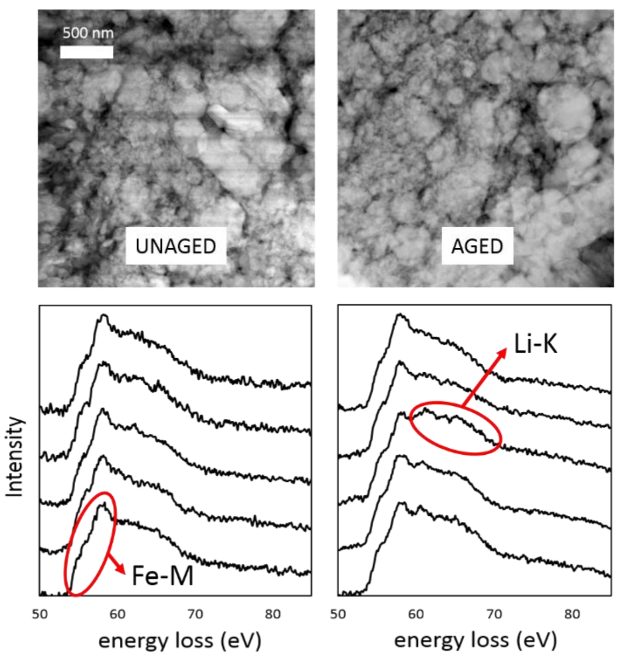

Sample	Temperature (°C)	Capacity retention	Battery size factor (B.S.F)
1	55˚C	90%	1
2	55˚C	90%	2
3	55˚C	80%	1
4	55˚C	80%	2
5	35˚C	90%	1
6	35˚C	90%	2
7	35˚C	80%	1
8	35˚C	80%	2

Table 1: Table of aged cells produced for microstructure analysis. Cell highlighted in yellow is used as ‘aged’ cell in the current EELS analysis.

Fig.1: STEM-HAADF microstructure images (top) and EELS spectra (bottom) of unaged cell (left) and aged cells (right).

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