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In situ study of high voltage performance of $Li_3Fe_2(PO_4)_3$ cathodes for Li ion batteries

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In order to meet the increasing demands on energy storage capacities in Li ion batteries, new cathode materials with increased energy density must be developed. One way of achieving this is to use cathodes with multivalent transition metals, which can accommodate more than one Li ion per metal ion. Iron based compounds constitute a very attractive class of cathode materials as they are cheap, environmentally benign, and potentially a candidate for multivalent electrodes, as iron can exist in several different oxidation states. Despite a large interest, cathodes involving Fe^{4+} is a great challenge as Fe^{4+} is unstable in most solid state structures. This instability is observed in layered $LiFeO_2$, which irreversibly converts into a spinel-type $LiFe_5O_8$ structure after cycling (1). Recently, Li_2FeSiO_4 is starting to get attention as a possible new Fe^{4+}-based cathode (2), although the reversibility of this process is still to be determined.

In this study, we investigate whether Fe^{4+} can be formed and stabilized in rhombohedral β-$Li_3Fe_2(PO_4)_3$, which is based on the highly stable NASICON framework (3). Intercalation of Li ions into the structure involving the Fe^{2+}/Fe^{3+} transition is well known (4,5), but this work is focused on the possible extraction of Li ions involving the Fe^{3+}/Fe^{4+} transition. The work is based on an *in situ* synchrotron X-ray powder diffraction (XRPD) study of the structural changes, that occur during charging of β-$Li_3Fe_2(PO_4)_3$ up to 5.2 V *vs.* Li/Li^+. A novel capillary-based micro battery cell for *in situ* XRPD has been designed for this (figure 1). The advantage of this cell is that it allows diffractions from the individual electrode layers, and also facilitates time-resolved studies of chemical gradients within the electrode layers.

A small contraction in volume was observed during charge to 5.2V, indicating Li ion extraction (figure 2). The volume change is anisotropic, with a decrease in the *a* parameter and an increase in the *c* parameter during the extraction of 0.2 Li ions per $Li_3Fe_2(PO_4)_3$. The charging is performed at potentials above the stability window of the organic electrolyte and some electrolyte oxidation reaction cannot be avoided. However, the observed volume changes show that Li^+ extraction has occurred probably associated with Fe^{4+} formation. The change of oxidation state of iron was investigated by Mössbauer spectroscopy using an *in situ* setup in order to fully subtract all background absorption, however no evidence of Fe^{4+} formation was observed. Instability of the Fe^{4+} towards the organic electrolyte could possibly explain this. Li^+ extraction occurs at a plateau above 4.5 V but no discharge plateau above 3 V was observed. This is also the case for intercalation into $FeSiO_4$ (2). This indicates that the intercalation of Li ions into these materials is not followed by a simple Fe^{4+}/Fe^{3+} reduction. Future work will be addressed to understand this lack of plateau.

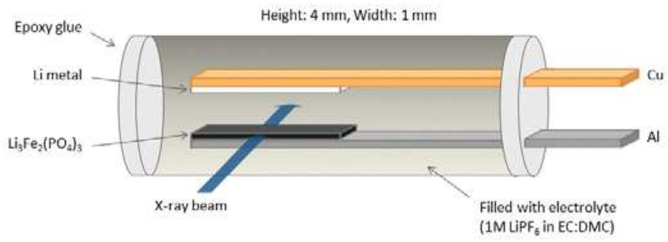

Figure 1: Illustration of a new capillary-based micro battery cell for *in situ* synchrotron XRPD.

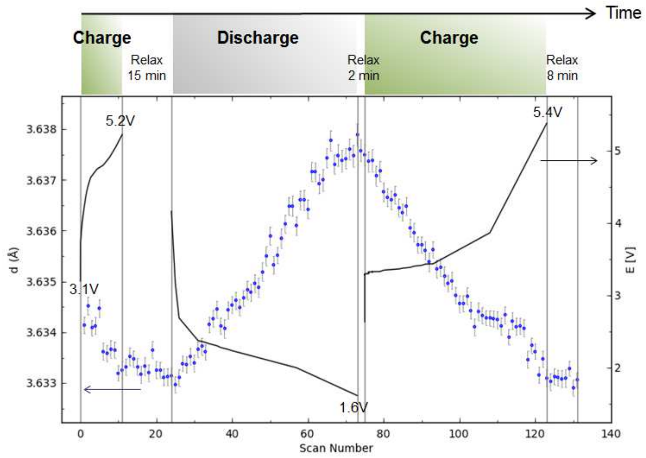

Figure 2: Change in *d*-spacing of the (113) planes in $Li_3Fe_2(PO_4)_3$ measured by *in situ* synchrotron XRPD. Charging the cell results in contraction of the structure while discharge results in expansion, associated with the extraction and intercalation of Li ions.

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