In Situ Study of High Voltage Performance of Li$_3$Fe$_2$(PO$_4$)$_3$ Cathodes for Li Ion batteries

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In this study, we investigate whether Fe\textsuperscript{4+} can be formed and stabilized in thomboedral \(\beta\)-Li\textsubscript{2}Fe\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, which is based on the highly stable NASICON framework \(^{(1)}\). Intercalation of Li ions into the structure involving the Fe\textsuperscript{3+/4+} transition is well known \(^{(2), (3)}\), but this work is focused on the possible extraction of Li ions involving the Fe\textsuperscript{3+/4+} transition. The work is based on an \textit{in situ} synchrotron X-ray powder diffraction (XRPD) study of the structural changes, that occur during charging of \(\beta\)-Li\textsubscript{2}Fe\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} up to 5.2 V vs. Li/Li\textsuperscript{+}. A novel capillary-based micro battery cell for \textit{in situ} synchrotron 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 5.2 V, 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\textsubscript{2}Fe\textsubscript{2}(PO\textsubscript{4})\textsubscript{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\textsuperscript{+} extraction has occurred probably associated with Fe\textsuperscript{3+} formation. The change of oxidation state of iron was investigated by Mössbauer spectroscopy using an \textit{in situ} setup in order to fully subtract all background absorption, however no evidence of Fe\textsuperscript{3+} formation was observed. Instability of the Fe\textsuperscript{4+} towards the organic electrolyte could possibly explain this. Li\textsuperscript{+} 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\textsubscript{4} \(^{(2)}\). This indicates that the intercalation of Li ions into these materials is not followed by a simple Fe\textsuperscript{3+/4+} reduction. Future work will be addressed to understand this lack of plateau.

### References