In situ studies of Fe$^{4+}$ stability in $\beta$-Li$_3$Fe$_2$(PO$_4$)$_3$ cathodes for Li ion batteries

In commercial Fe-based batteries, the Fe$^{2+}$/Fe$^{3+}$ redox states are utilized, however by also utilizing the Fe$^{4+}$ oxidation state, intercalation of up to two Li ions per Fe ion could be possible. In this study, we investigate whether Fe$^{4+}$ can be formed and stabilized in $\beta$-Li$_3$Fe$_2$(PO$_4$)$_3$. The work includes in situ synchrotron X-ray powder diffraction studies (XRPD) during charging of $\beta$-Li$_3$Fe$_2$(PO$_4$)$_3$ up to 5.0 V vs. Li/Li$^+$. A novel capillary-based micro battery cell for in situ XRPD has been designed for this. During charge, a plateau at 4.5 V was found and a small contraction in volume was observed, indicating some Li ion extraction. The volume change of the rhombohedral unit cell is anisotropic, with a decrease in the a parameter and an increase in the c parameter during the Li ion extraction. Unfortunately, no increased discharge capacity was observed and Mössbauer spectroscopy showed no evidence of Fe$^{4+}$ formation. Oxidation of the organic electrolyte is inevitable at 4.5 V but this alone cannot explain the volume change. Instead, a reversible oxygen redox process ($\text{O}_2^-$ → $\text{O}^-$) could possibly explain and charge compensate for the reversible extraction of lithium ions from $\beta$-Li$_3$Fe$_2$(PO$_4$)$_3$.