Electronic Supplementary Information

Effect of Bulk and Surface Structural Changes in Li$_5$FeO$_4$ Positive Electrodes during First Charging on Subsequent Lithium-Ion Battery Performance

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**Fig. S1** (a) X-ray diffraction pattern of a synthesised compound. (b) Reference pattern for a Li$_5$FeO$_4$ low-temperature phase (JCPDS card #01-075-1253).

**Fig. S2** (a) SEM image of synthesised Li$_5$FeO$_4$. EDX maps of (b) Fe K-edge and (c) O K-edge.
Fig. S3 Rietveld refinements of ex situ synchrotron X-ray diffraction patterns of electrochemically charged/discharged samples. The differences between the two batches of #1 and #2 are also shown. The number of charged electrons per positive electrode is (a) e = 0 (pristine, #1), (b) 0.33 (charged until 58 mAh g\(^{-1}\), #1), (c) 0.66 (charged until 116 mAh g\(^{-1}\), #1), (d) 1 (charged until 173 mAh g\(^{-1}\), #1), (e) e = 0 (pristine, #2), (f) 1 (charged until 173 mAh g\(^{-1}\), #2), (g) 1.5 (charged until 260 mAh g\(^{-1}\), #2) and (h) 1.85 (fully charged until 320 mAh g\(^{-1}\), #2). Observed, calculated and difference plots are shown by black open circles, red solid lines and blue solid lines, respectively. Diffraction positions are also shown by several colour bars; black (Li\(_2\)FeO\(_4\)), red (generated PC-LFO; Li\(_n\)FeO\(_2\)), blue (LiFeO\(_2\); impurity), green (Fe impurity), and orange (LiO).
Fig. S4 Pseudo-radial structure functions of \textit{ex situ} Fe K-edge EXAFS oscillations for (a) electrochemical samples halted during the first charging process, (b) electrochemically charged/discharged samples.