

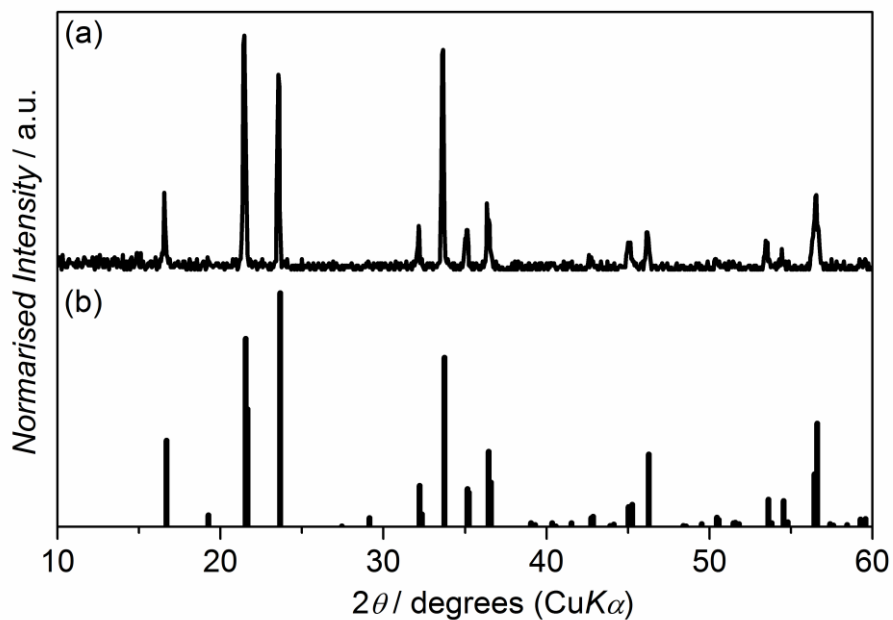
**Electronic Supplementary Information**

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

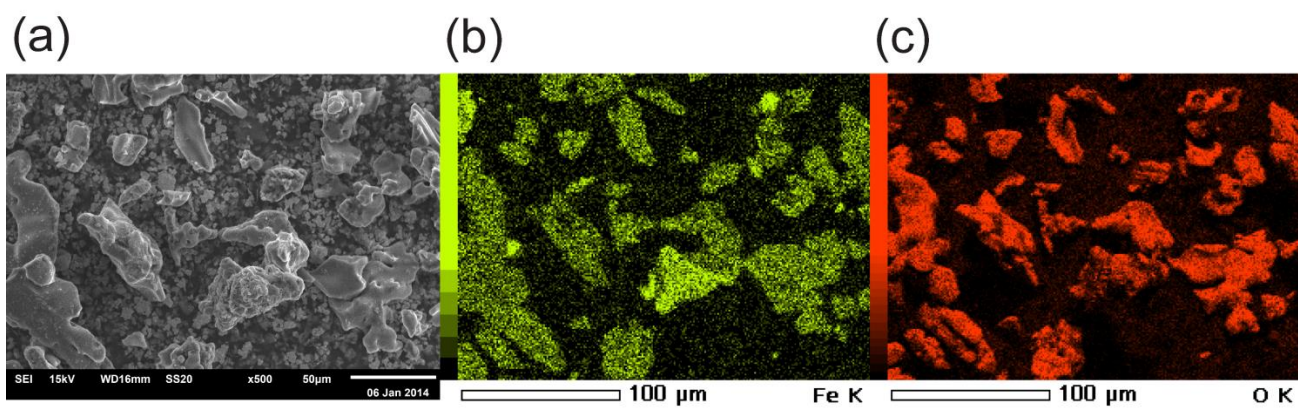
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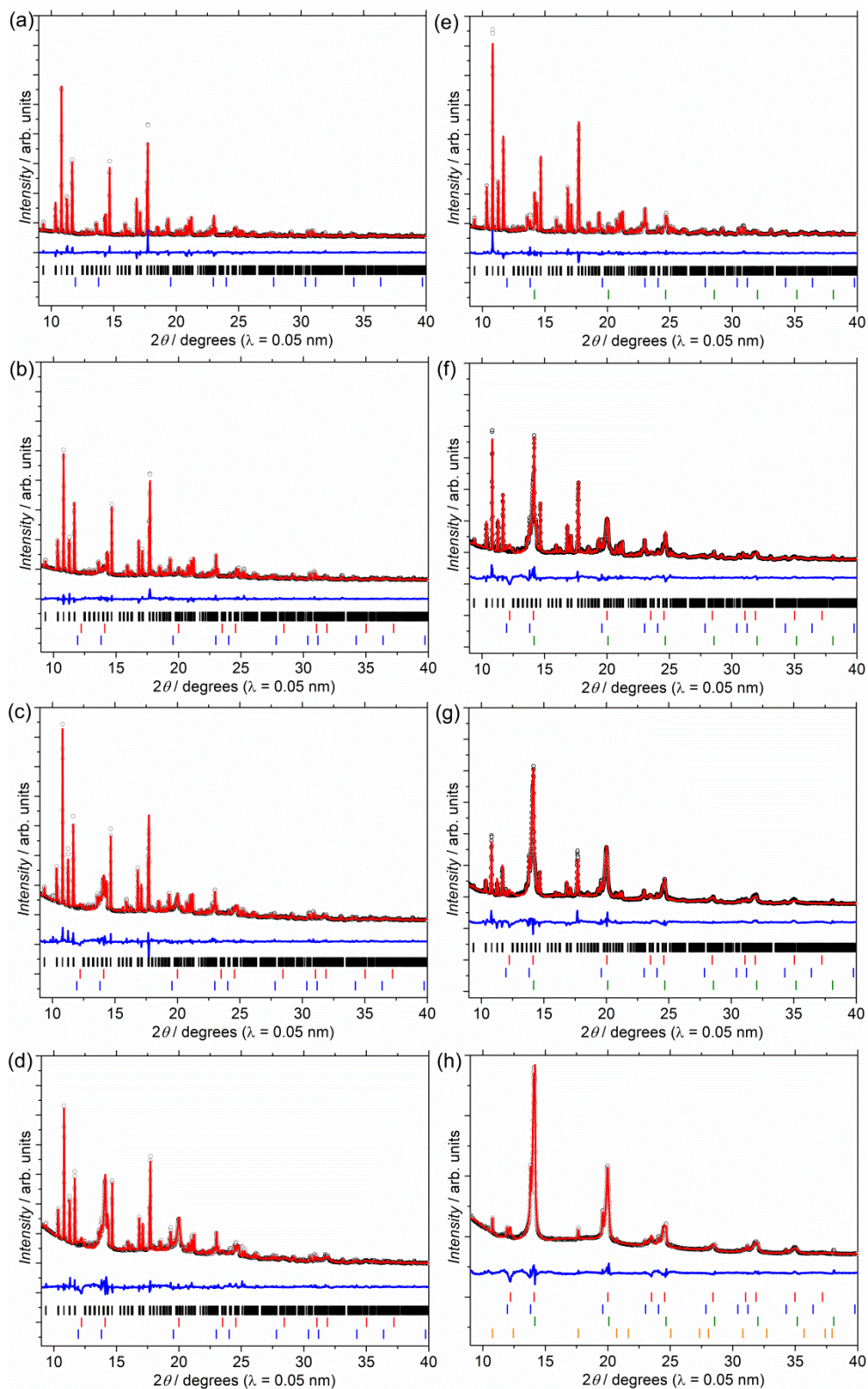
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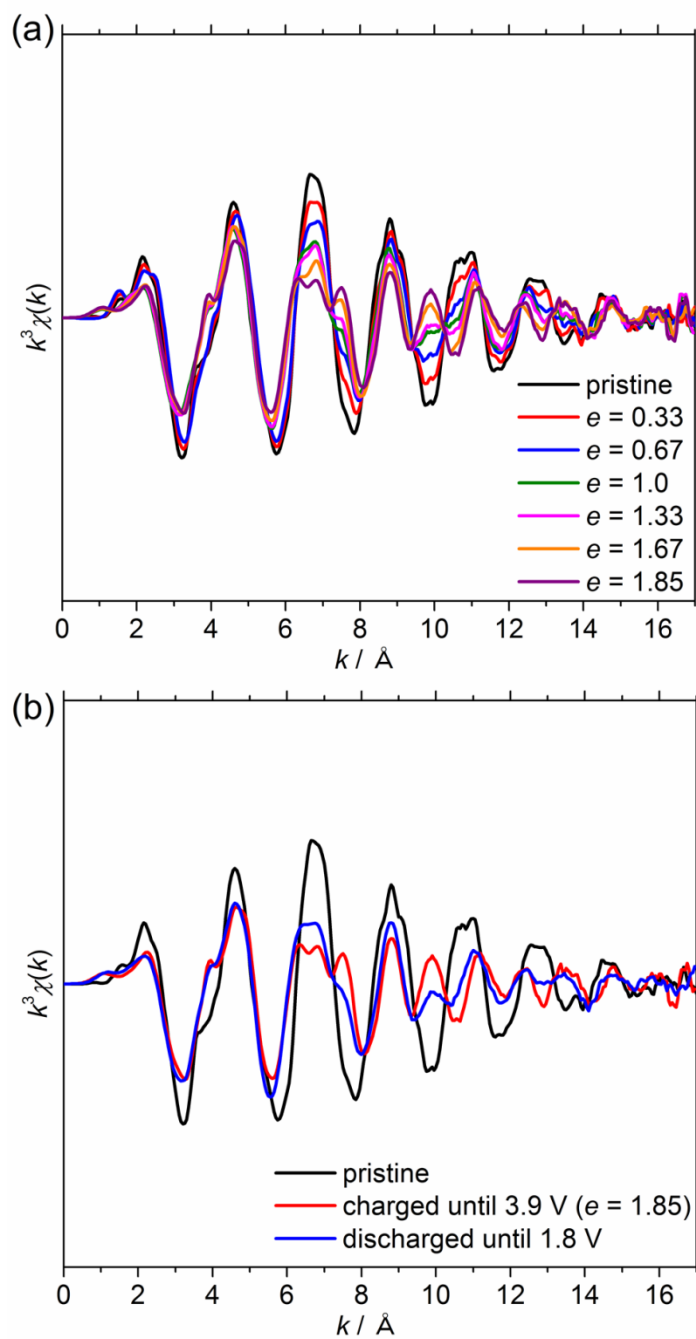
**Fig. S1** (a) X-ray diffraction pattern of a synthesised compound. (b) Reference pattern for a Li<sub>5</sub>FeO<sub>4</sub> low-temperature phase (JCPDS card #01-075-1253).



**Fig. S2** (a) SEM image of synthesised Li<sub>5</sub>FeO<sub>4</sub>. 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  $58 \text{ mAh g}^{-1}$ , #1), (c) 0.66 (charged until  $116 \text{ mAh g}^{-1}$ , #1), (d) 1 (charged until  $173 \text{ mAh g}^{-1}$ , #1), (e)  $e = 0$  (pristine, #2), (f) 1 (charged until  $173 \text{ mAh g}^{-1}$ , #2), (g) 1.5 (charged until  $260 \text{ mAh g}^{-1}$ , #2) and (h) 1.85 (fully charged until  $320 \text{ mAh g}^{-1}$ , #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 ( $\text{Li}_5\text{FeO}_4$ ), red (generated PC-LFO;  $\text{Li}_\alpha\text{FeO}_2$ ), blue ( $\text{LiFeO}_2$  impurity), green (Fe impurity), and orange ( $\text{Li}_2\text{O}$ ).



**Fig. S4** Pseudo-radial structure functions of *ex situ* Fe *K*-edge EXAFS oscillations for (a) electrochemical samples halted during the first charging process, (b) electrochemically charged/discharged samples.