

Supporting Information

Direct Evidence of Concurrent Solid-Solution and Two-Phase Reactions and the Non- Equilibrium Structural Evolution of LiFePO_4 .

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Figure S1. Scanning electron microscopy image of the as-purchased LiFePO_4 powder.

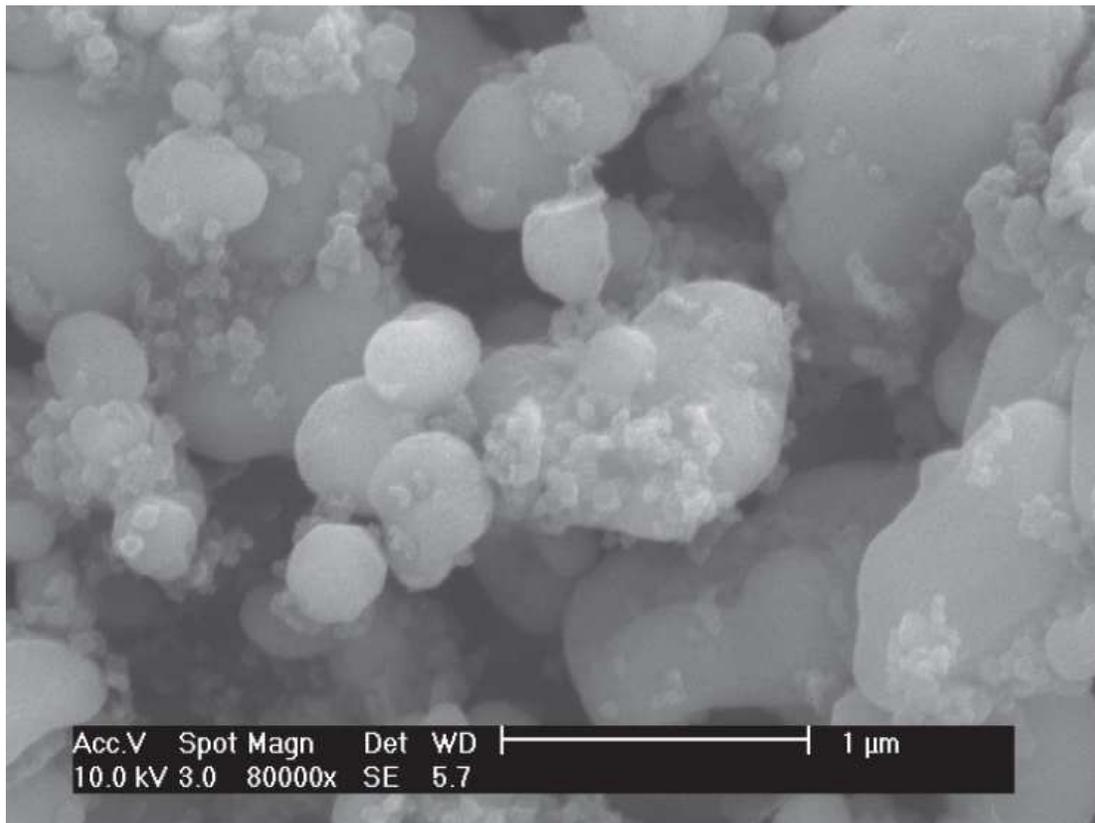
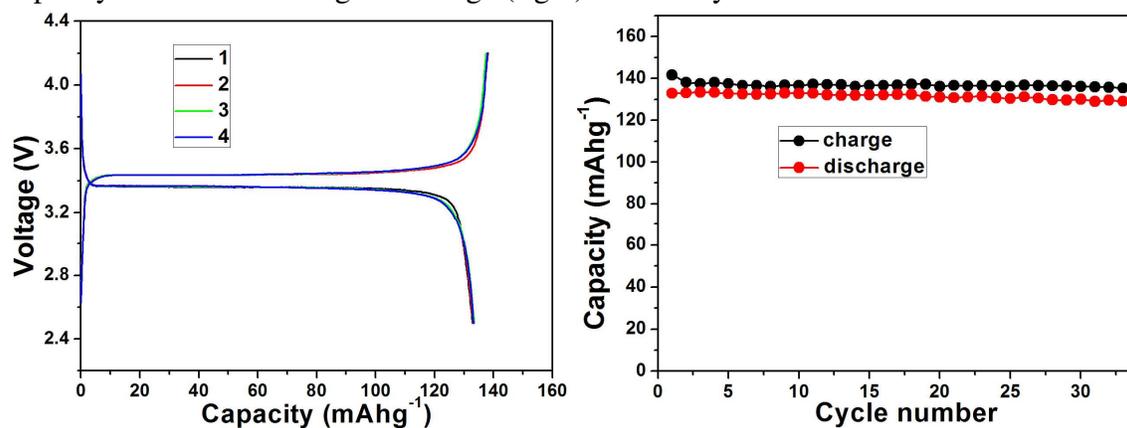


Figure S2. The electrochemical performance of the LiFePO_4 materials used in this study under conventional conditions; between 2.5 and 4.2 V, and with a current density of 0.1 mA cm^{-2} . The charge/discharge curves (left) from the first to the fourth cycle and capacity retention on charge/discharge (right) over 35 cycles.



S3. Neutron powder diffraction

In situ NPD data were collected on WOMBAT, the high-intensity powder diffractometer, at the Open Pool Australian Light-water (OPAL) reactor facility at the Australian Nuclear Science and Technology Organisation (ANSTO)¹. NPD data were collected every 5 minutes for 67 hours between $16 \leq 2\theta \leq 136^\circ$ at $\lambda = 2.4053(1) \text{ \AA}$. The wavelength was determined using an Al_2O_3 SRM 676 standard. Data correction, reduction, and visualisation were undertaken using the program LAMP². During NPD data collection the LiFePO_4 battery was electrochemically cycled in galvanostatic (constant-current) mode with applied currents ranging from ± 1 to 12 mA using an Autolab potentiostat/galvanostat (PG302N).

Rietveld refinements were carried out using the GSAS³ suite of programs with the EXPGUI⁴ interface. Single-peak fits using a Gaussian peakshape were undertaken using LAMP². The figures of merit for the sequential multi-phase Rietveld analyses were profile factors (R_p) ranging between $2.40 \leq R_p \leq 3.02\%$, weighted profile factors (wR_p) between $3.08 \leq wR_p \leq 3.82\%$, and the goodness of fit term (χ^2) between $1.76 \leq \chi^2 \leq 2.71$. The time dependence of the lattice parameters and phase fractions were determined, and atomic parameters such as the lithium site-occupancy factors and atomic displacement parameters were refined only for the first dataset and fixed during subsequent refinements in a similar manner to our earlier work^{5,6}. The relatively low angular resolution of the powder diffraction data meant that simultaneous unconstrained modelling of the LiFePO_4 and FePO_4 lattice parameters and phase fractions using Rietveld analysis was not possible where these phases co-exist. In this region, quantitative phase analysis for the LiFePO_4

and FePO₄ phases was performed using Rietveld analysis with lattice parameter constraints, and the results overlaid in Figure 4, where the lattice parameters of only the dominant phase were refined.

References:

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