Supporting information: *In situ* Phase Behaviour of a High Capacity $LiCoPO_4$ Electrode During Constant or Pulsed Charge of a Lithium Cell

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$LiCoPO_4$ was synthesised by mixing 0.03 mol of LiOH (Sigma Aldrich), 0.01 mol of $CoSO_4.7H_2O$ (Sigma Aldrich), 0.01 mol of H_3PO_4 (10%) and a total of 60 ml of H_2O:DEG (1:6). The resulting purple solution was stirred and transferred to an autoclave where it was heated to 180 °C for 10 hours. The blue powder was then washed through with ethanol and water before being heated at 600 °C under air for 3 hours to obtain the product. Phase purity was confirmed using powder X-ray diffraction using a Bruker D2 Phaser with a Cu K_α source and Rietveld refinement of the data used the GSAS package. The Lorentzian L_x component of the peak shape was used to calculate crystallite size. Scanning electron microscopy (SEM) images were collected using a Jeol JSM-6500 FEGSEM with 15 keV accelerating voltage and secondary electron imaging.

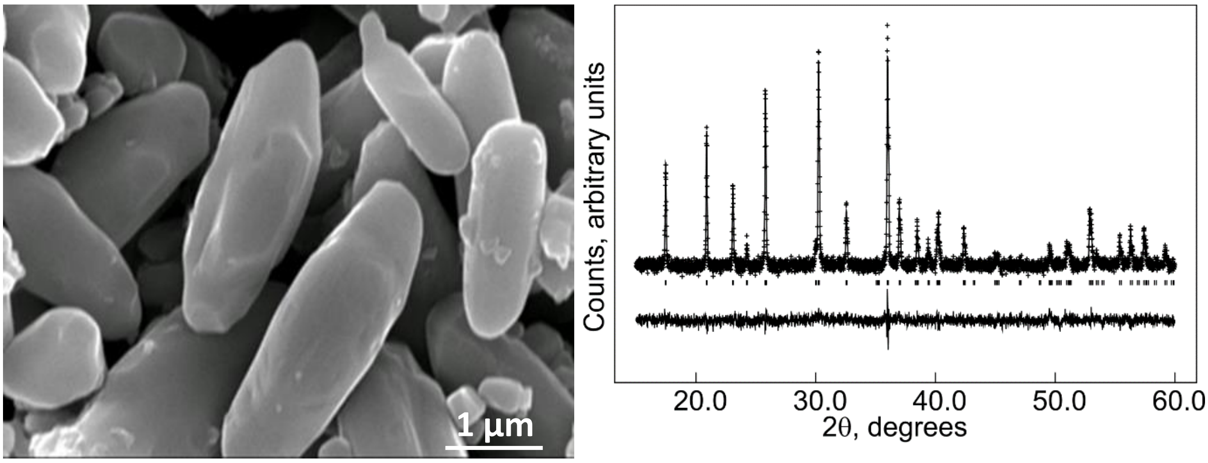

Fig. S1 SEM image (left) and Rietveld fit to the diffraction data (right) for the $LiCoPO_4$ used in this study. In the Rietveld fit crosses mark the data points, the upper continuous line the fit and the lower continuous line the difference. Tick marks show the allowed reflections for $LiCoPO_4$.

Swagelok cells were constructed from fittings made of PFA (Perfluoroalkoxy alkanes) polymer. Pistons and current collectors were machined from aluminium (positive side) and copper (negative side) in-house. Electrode pellets were made by manually mixing 0.2g of $LiCoPO_4$ (75 % by weight) with acetylene black (Shawinigan Black, 20 % by weight) followed by PTFE (6C-N, DuPont, 5 % by weight) in a pestle and mortar. The resulting solid lump was then hand rolled (Durston Rolling Mill) into a film of ~90 µm thickness and cut into disks 12 mm in diameter. The pellets were dried at 120 °C under vacuum overnight to remove any moisture. Cells were assembled with a $LiCoPO_4$ electrode pellet, two electrolyte-soaked 12.7 mm diameter separators (Whatman GF/F grade glass fibre with eight drops of BASF LP57, which contains 1.0 mol dm^{-3} $LiPF_6$ in 1:3 ethylene carbonate/ethyl methyl carbonate mixture) and a lithium metal negative electrode (Rockwood Lithium). Galvanostatic cycling used a Biologic VMP-2 potentiostat.

In situ experiments used 60 µm thick electrodes with a diameter of 8 mm produced from 50 % $LiCoPO_4$, 45 % acetylene black and 5 % PTFE. This atypically dilute composition was to ensure, based on the experience from our previous study on $LiFePO_4$,[1] that the beam could fully penetrate the electrode in the reflection geometry and give patterns representative of the entire electrode thickness. This previous experience also suggested that at moderate charging rates the electrode would be homogeneous through its thickness. Our *in situ* cell design compresses the separator and positive electrode between a hemispherical lithium negative electrode and a 12 µm thick aluminium foil, where the latter provides both the current collector and the X-ray window.[1] The window is glued onto the stainless steel support with black silicone rubber (Loctite type 5910). This geometry allows an even pressure to be applied across the stack countering the deformation of the aluminium window under pressure. The cell was assembled under Ar with a $LiCoPO_4$ pellet positive electrode and separator as described for the Swagelok cells.

In situ XRD data were collected at beamline I07 of the Diamond Light Source (Oxford, UK) with 20 kV beam energy (λ = 0.6199 Å). The sample was mounted on the hexapod stage and visually centred in the XY plane such that the highest point on the curved surface of the aluminium foil was aligned with the centre of the diffractometer circles. The sample position was then adjusted in the vertical direction to allow the sample to cut half of the beam intensity. The electrochemical cycling treatments used a BioLogic SP-150 potentiostat. Galvanostatic cycling was carried out at 0.2 C with an XRD exposure time of one pattern every 8 minutes. Galvanostatic intermittent titration technique (GITT) experiments used 10 minute pulses of current equivalent to a 0.5 C charging rate with 30 minute relaxation times and an XRD exposure time of one pattern every 80 seconds.

Synchrotron XRD data were analysed by Rietveld fitting using the GSAS package, with structure models taken from Ehrenberg *et al*.[2] The narrow aluminium peaks due to the X-ray window were excluded from the refined patterns.

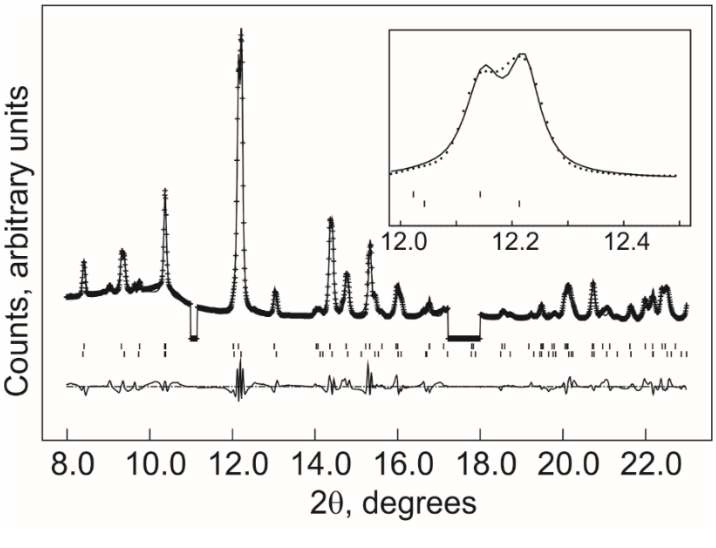

Fig. S2 Example Rietveld fit to the *in situ* diffraction data (λ = 0.619 Å) for the mixture of phase A (≈$LiCoPO_4$) and phase B (≈$Li_{2/3}CoPO_4$) collected at 144 minutes (c.f. Fig. 6), or in the 22nd out of 37 patterns collected during the the 4th GITT pulse/relaxation. Crosses mark the data points, the upper continuous line the fit and the lower continuous line the difference. Tick marks show the allowed reflections for phase A (top) and phase B (bottom). The inset magnifies the position of the 020 reflection.

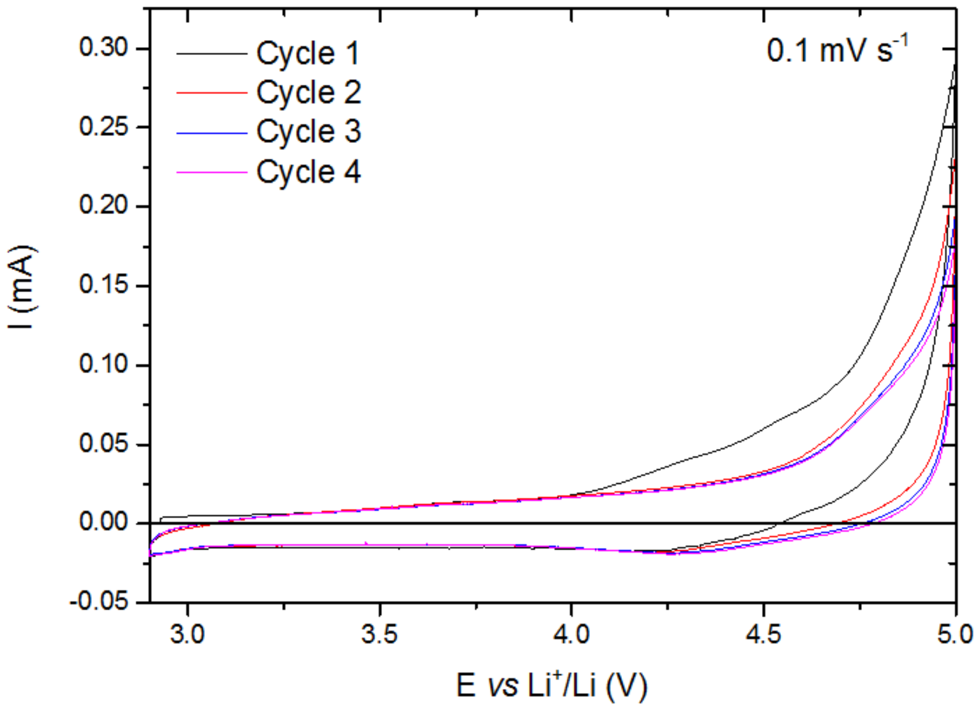

Fig. S3 Cyclic voltammetry of a 0.015 g 80% carbon/20% PTFE pellet *vs* Li at a scan rate of 0.1 V s^{-1} and with the same BASF LP57 electrolyte used in the $LiCoPO_4$ cells. Average current at 4.75 V in the 4th cycle was 0.03 mA, which corresponds to a specific current of 2 mA g^{-1}.

References

1 M. R. Roberts, A. Madsen, C. Nicklin, J. Rawle, M. G. Palmer, J. R. Owen and A. L. Hector, *J. Phys. Chem. C*, 2014, **118**, 6548–6557.

2 H. Ehrenberg, N. N. Bramnik, A. Senyshyn and H. Fuess, *Solid State Sci.*, 2009, **11**, 18–23.