Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Sodium uptake in cell construction and subsequent *in operando* electrode behaviour of Prussian Blue Analogues, $Fe[Fe(CN)_6]_{1-x}\cdot yH_2O$ and $FeCo(CN)_6$

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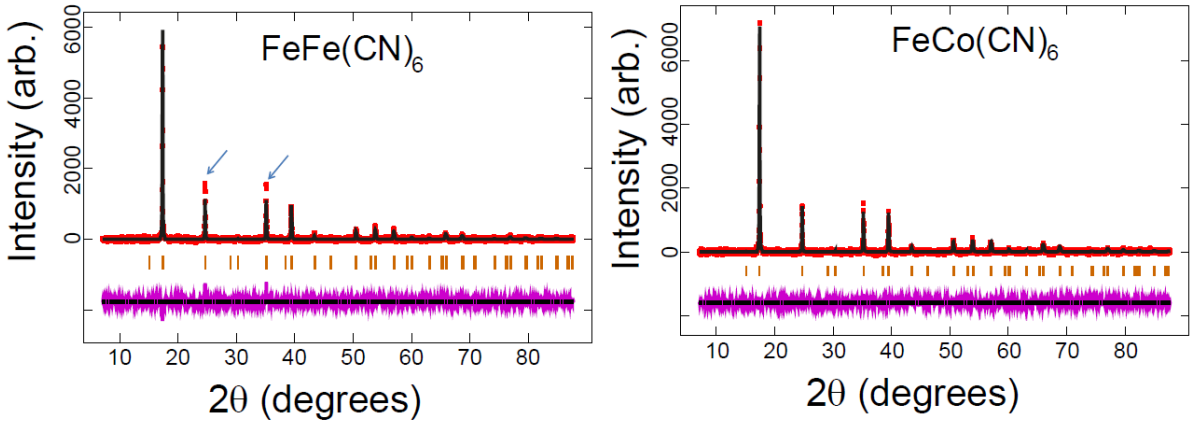
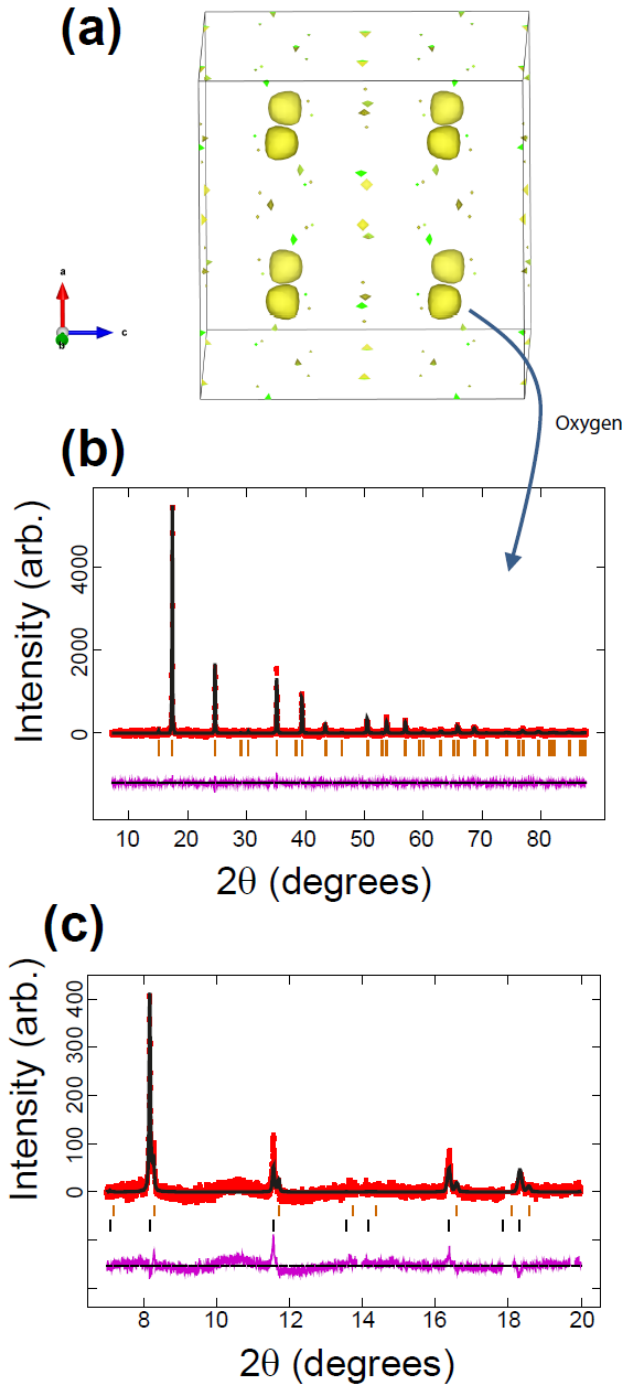


Supplementary Information Figure 1. Rietveld refined fit of the simple vacancy-free $FeFe(CN)_6$ (left) and $FeCo(CN)_6$ (right) models to laboratory XRD data. Data are shown as crosses, the calculated Rietveld model as a line through the data, and the difference between the data and the model as the line below the data. The refined lattice parameters are noted in the manuscript text. Note the blue arrows in the $FeFe(CN)_6$ illustrate a mismatch of the calculated intensities with the observed data.



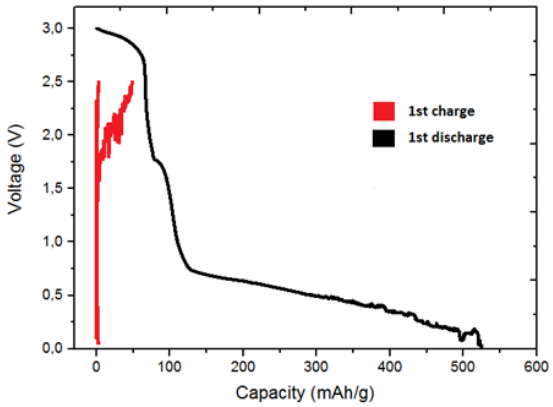
Supplementary Information Figure 2. Fourier electron density (yellow) difference map using the $FeFe(CN)_6$ model (atoms omitted for clarity) with XRD data. **(b)** Rietveld refined fit of the $FeFe(CN)_6 \cdot 0.473(24)H_2O$ model to XRD data in the $8 \leq 2\theta \leq 90^{\,0}$ region. Data are shown as crosses, the calculated Rietveld model as a line through the data, and the difference between the data and the model as the line below the data. **(c)** Rietveld refined fit of the $FeFe(CN)_6 \cdot 0.473(24)H_2O$ model to *in situ* synchrotron XRD data in the $6 \leq 2\theta \leq 20^{\,0}$ region. Note there are excluded regions for the sodium metal and aluminium reflections, in addition the features in the background arise in part due to carbon-containing components in the electrode, e.g. PVDF and carbon black.

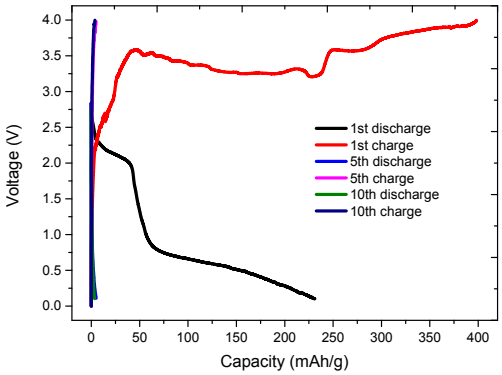
Supplementary Information Table 1. The refined structure of '$FeFe(CN)_6$' – the vacancy-containing model.

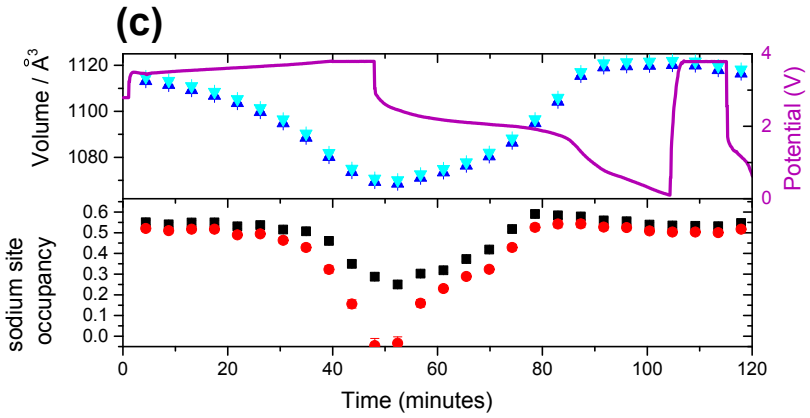
Atom	*X*	*Y*	*Z*	SOF	Isotropic ADP* (× 100)/Å²
Fe(1)	0	0	0	0.85(7)	2.91
Fe(2)	0.5	0	0	1	2.89
C	0.19	0	0	0.88(4)	3.89
N	0.31	0	0	0.88(4)	0.92
O	0.25	0.25	0.25	0.473(24)	6.54

*Refined and subsequently fixed

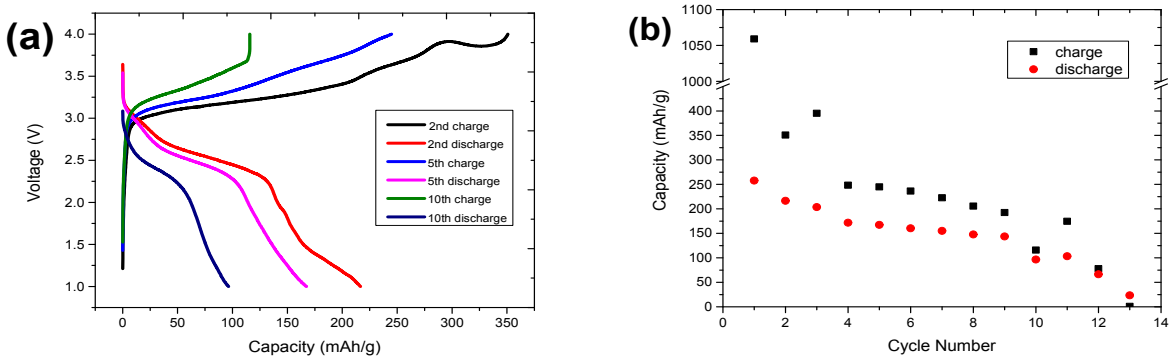
Spacegroup = *Fm*-3*m*, a = 10.2260(5) Å, 24 refinement parameters of which 20 are background parameters, χ^2= 1.05, R_p = 3.03 %, wR_p = 3.84 %, atomic displacement parameter (ADP), site occupancy factor (SOF).



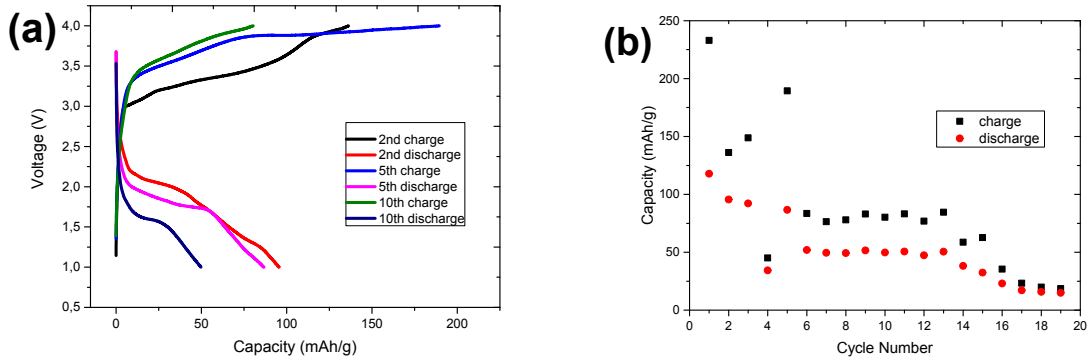




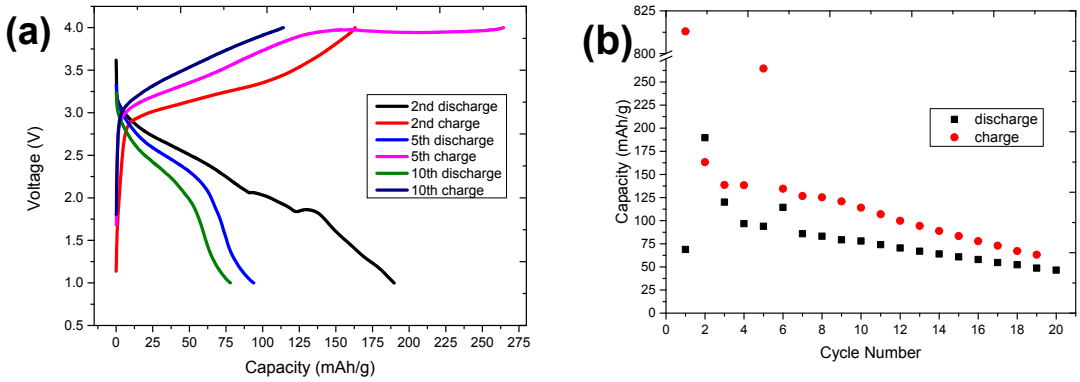
Supplementary Information Figure 3. (a) $Fe[Fe(CN)_6]_{1-x}\cdot yH_2O$ and **(b)** $FeCo(CN)_6$ discharged to 0.1 V at 0.1 mA and charged to 2.5 or 4 V at 0.1 mA. At the end of discharge the electrode appears to degrade. Consequently the charge curve shows significant capacity loss and overall poor charging. **(c)** The evolution of the sodium site occupancy for the vacancy-free (black) and vacancy-containing models (red), and unit cell volume (blue and cyan for the vacancy-free and vacancy-containing models respectively) of the major ~$Na_{0.5}FeFe(CN)_6$ phase as a function of time, with the potential profile included.



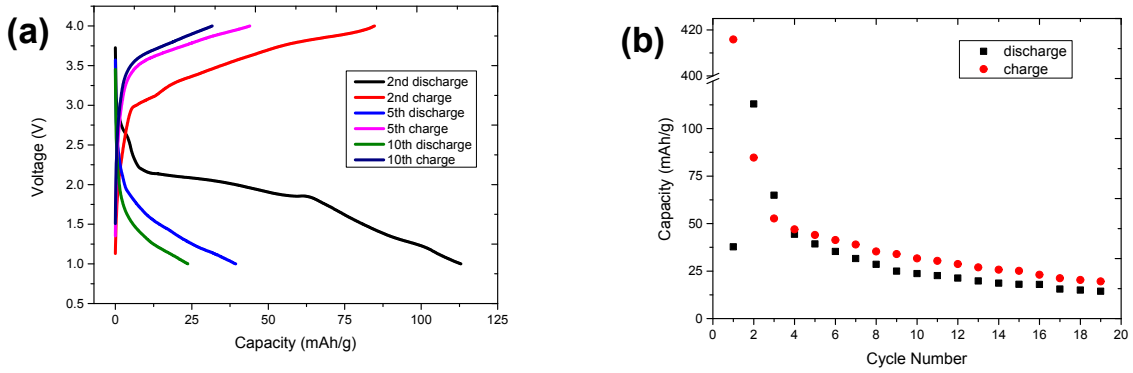
Supplementary Information Figure 4. (a) Voltage vs. capacity of the $Fe[Fe(CN)_6]_{1-x}\cdot yH_2O$-containing battery charged first to 4 V at 0.1 mA and discharged to 1 V at the same rate. **(b)** Capacity vs. cycle number showing that capacity stabilises around 180 mAh/g but is effectively zero at the 14th cycle, indicating a short lifetime. Note the charging process in these electrodes corresponds to the removal of sodium from the structure.



Supplementary Information Figure 5. (a) Voltage vs. capacity of the $FeCo(CN)_6$-containing battery charged first to 4 V at 0.1 mA and discharged to 1 V at the same rate. **(b)** Capacity vs. cycle number showing that capacity is slightly higher on charge relative to discharge but the overall capacity is lower than the $Fe[Fe(CN)_6]_{1-x}\cdot yH_2O$ electrode. Note the capacity is effectively zero at the 19th cycle, indicating a short lifetime.



Supplementary Information Figure 6. (a) Voltage vs. capacity of the $Fe[Fe(CN)_6]_{1-x}\cdot yH_2O$-containing battery discharged to 1 V at 0.1 mA and charged to 4 V at the same rate. **(b)** Capacity vs. cycle number showing that capacity is lower than the charge-first process. However, the electrode shows better stability and longer lifetimes. The reversible capacity stabilises around 85 mAh/g. Note, the discharging process in these electrodes corresponds to the insertion of sodium into the structure.



Supplementary Information Figure 7. (a) Voltage vs. capacity of the $FeCo(CN)_6$-containing battery discharged to 1 V at 0.1 mA and charged to 4 V at the same rate. (b) Capacity vs. cycle number showing that capacity is lower than the charge-first process. However, the electrode shows better stability and longer lifetimes similar to the $Fe[Fe(CN)_6]_{1-x}\cdot yH_2O$ electrodes. The reversible capacity stabilises around 85 mAh/g. Note, the discharging process in these electrodes corresponds to the insertion of sodium into the structure.