Supplementary material

Operando XAS and XRD of a Prussian Blue Analogue cathode material: Iron Hexacyanocobaltate

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XRD data analysis

Table S1. Correspondence between Miller planes and 2θ angles.

H	K	L	2θ
2	0	0	11.226
2	2	0	15.902
4	0	0	22.562
4	2	0	25.267
4	2	2	27.724
4	4	0	32.121
4	4	2	34.127
6	0	0	34.127
6	2	0	36.034
4	4	4	39.611
6	4	0	41.3
6	4	2	42.935
8	0	0	46.063
6	4	4	47.567
8	2	0	47.567
6	6	0	49.035
6	6	2	50.472
8	4	0	51.879
6	6	4	54.616

Table S2. Correspondence between collected pattern number and extracted/inserted ion equivalents.

x / equivalents	Pattern number
0.00	1 (pristine)
-0.15	10
-0.30	20
-0.45	30
-0.50	33 (fully charged)
+0.10	40
+0.25	50
+0.40	60
+0.55	70
+0.58	72 (fully discharged)

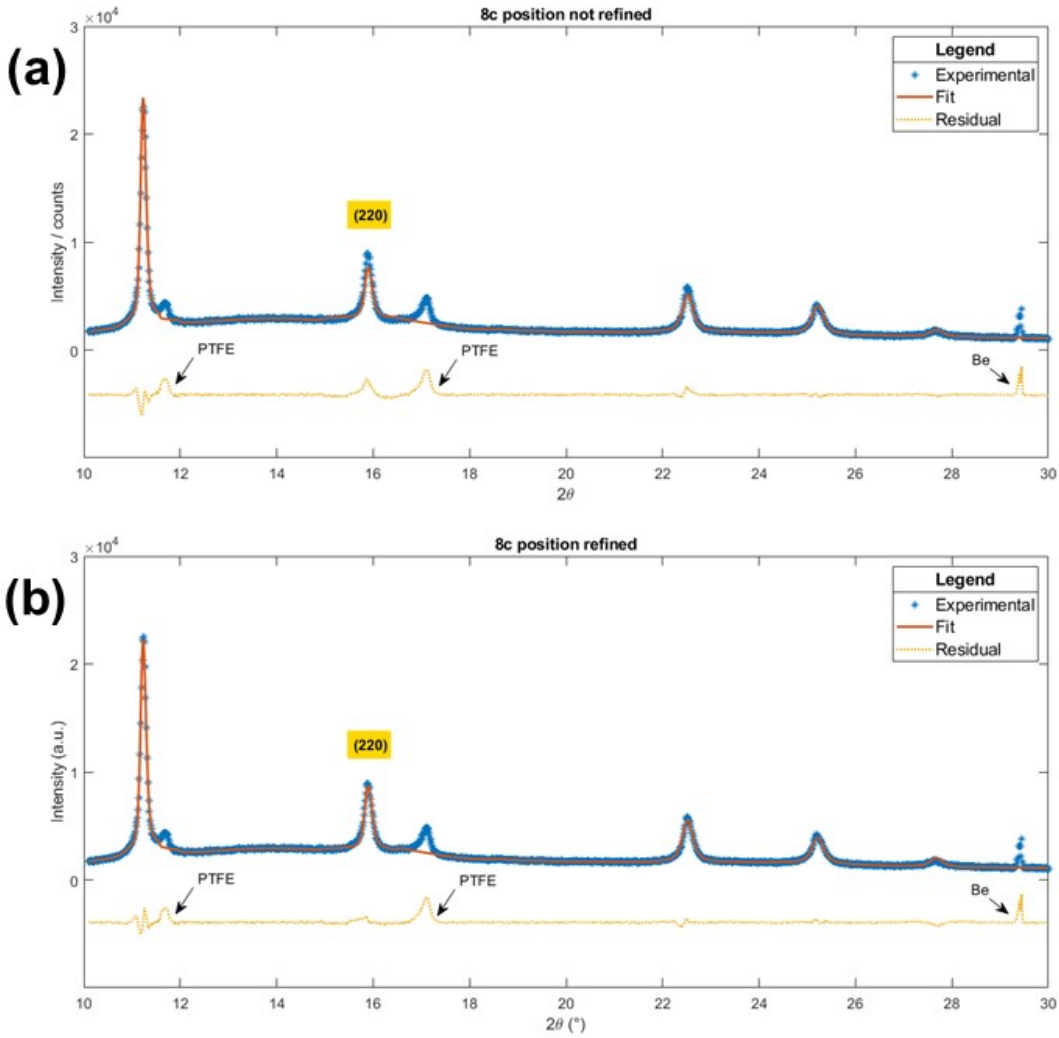


Figure S1. Rietveld refinement on the 60th XRD pattern: (a) 8c position not refined and (b) refined. Note the fit improvement at (220) plane.

XANES data analysis

Table S3. Correspondence between collected spectrum number and extracted/inserted ion equivalents.

x / equivalents	XAFS spectrum
0	0 (pristine)
-0.22	10
-0.44	20
-0.66	30 (partially charged)
-0.88	40
-0.91	42 (fully charged)
+0.18	50
+0.40	60 (partially discharged)
+0.62	70 (fully discharged)

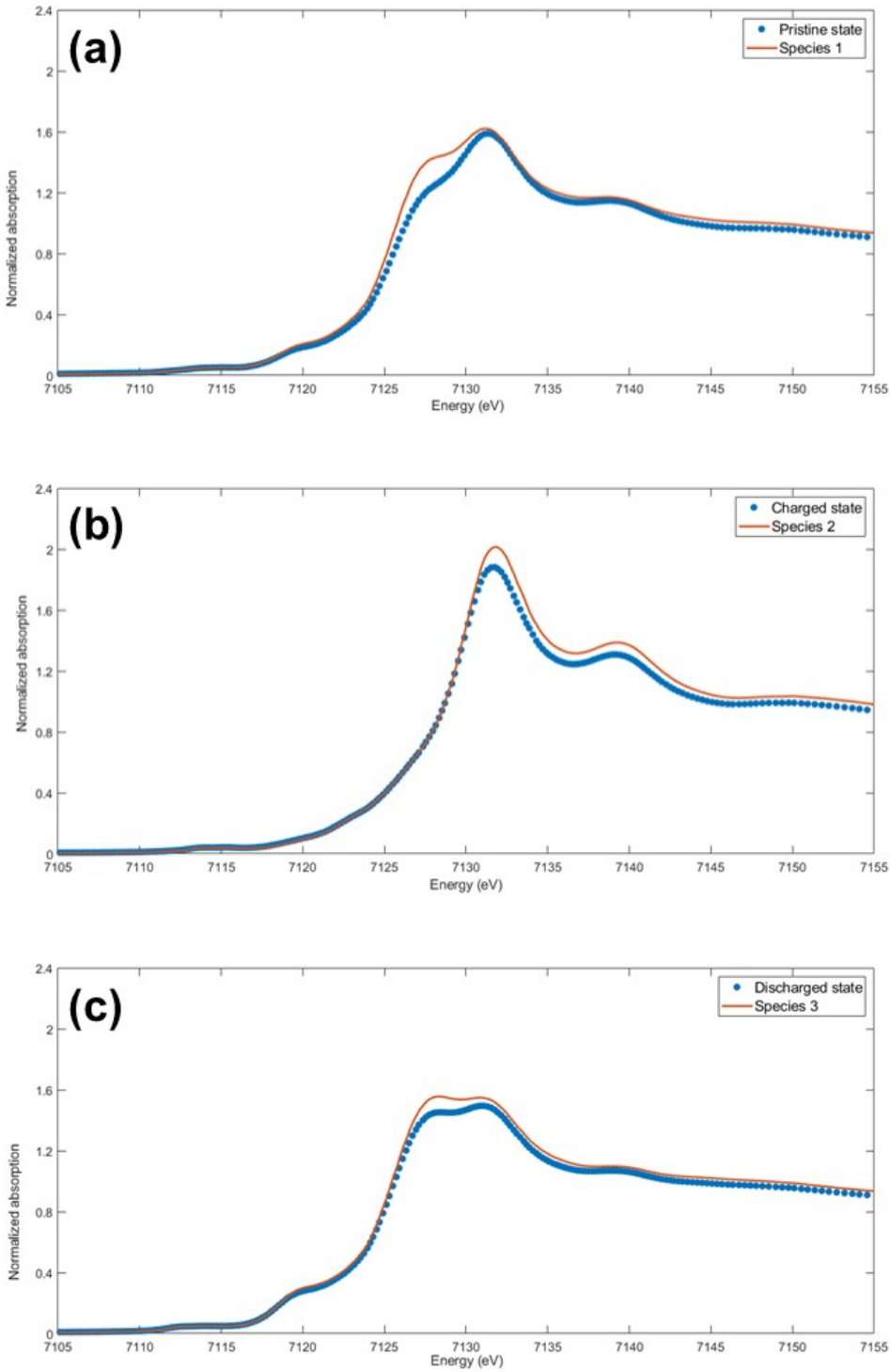
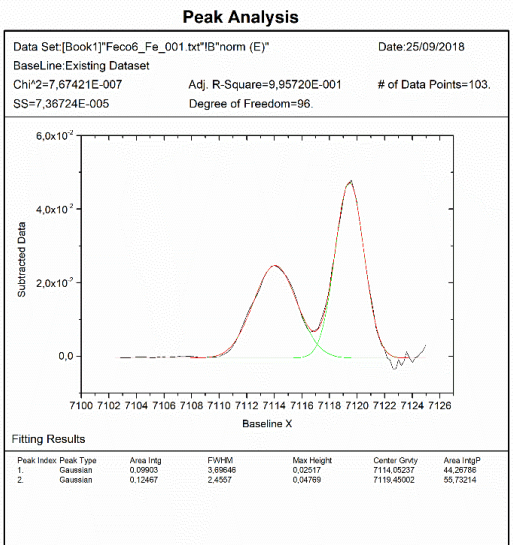
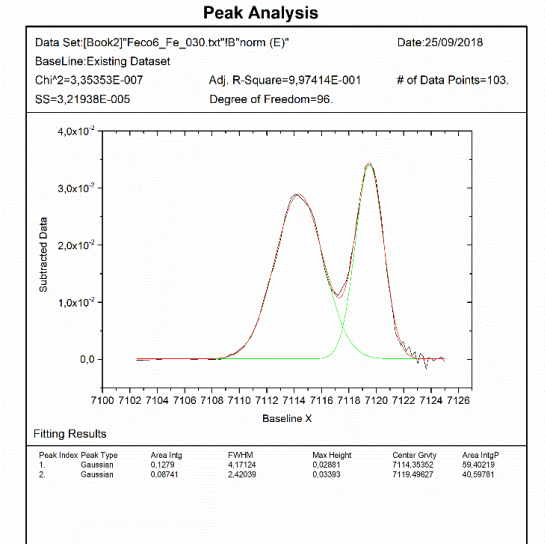


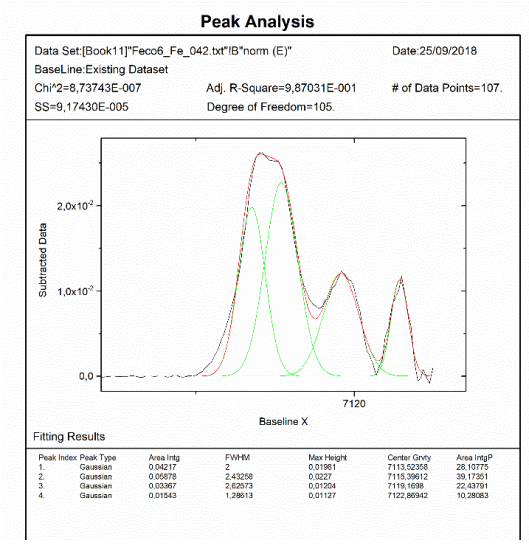
Figure S2. Comparison between: (a) pristine state and first spectral component; (b) charged state and second spectral component; (c) discharged state and third spectral component.



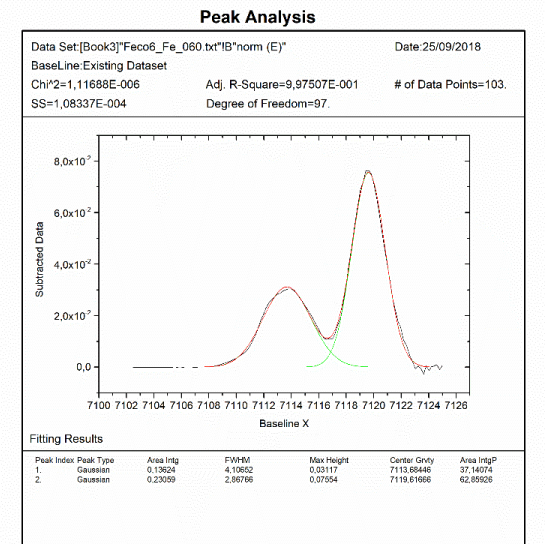
(**a**)



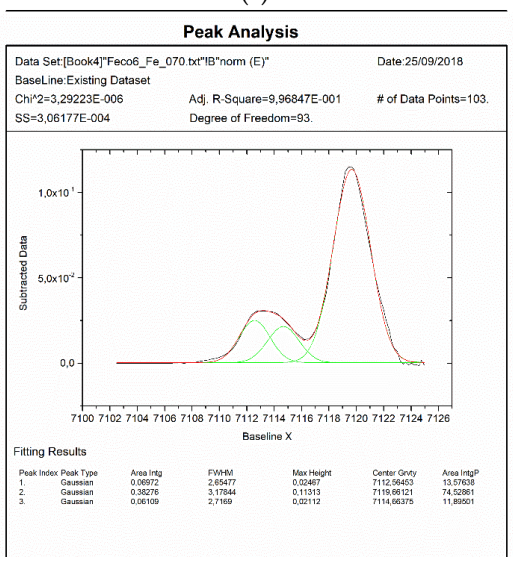
(**b**)



(**c**)



(**d**)



(**e**)

Figure S3. Pre-edge fitting analysis for the (a) 1st; (b) 30th; (c) 42nd; (d) 60th; (e) 70th spectra.

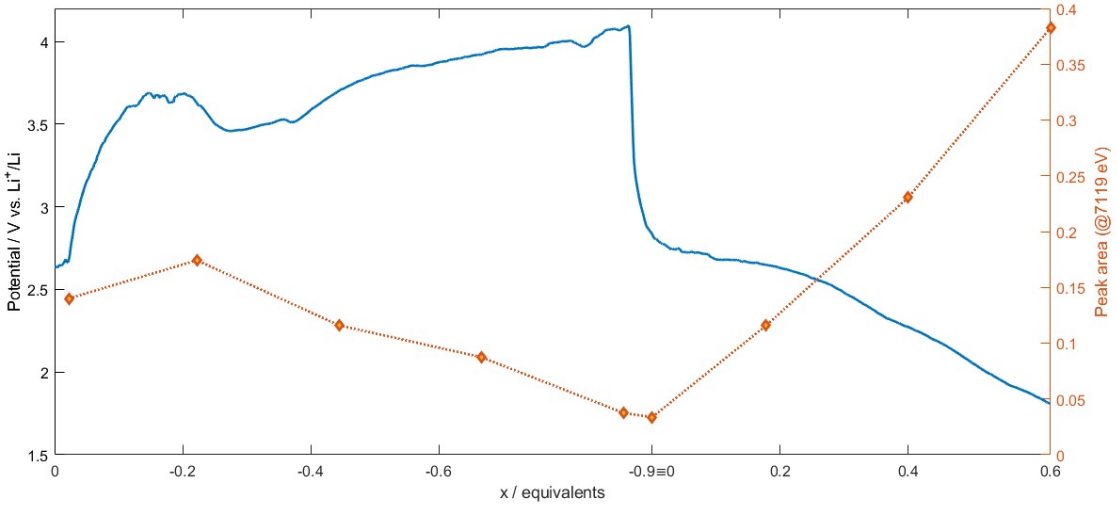


Figure S4. *Operando* XAFS electrochemical profile (blue line) and concomitant 7119 eV peak area evolution (red scatter) are shown.