Electronic supplementary material for

Understanding the Lithium Storage Mechanism in Core-Shell Fe_2O_3@C Hollow Nanospheres Derived from Metal-Organic Frameworks: An *In operando* Synchrotron Radiation Diffraction and *in operando* X-ray Absorption Spectroscopy Study

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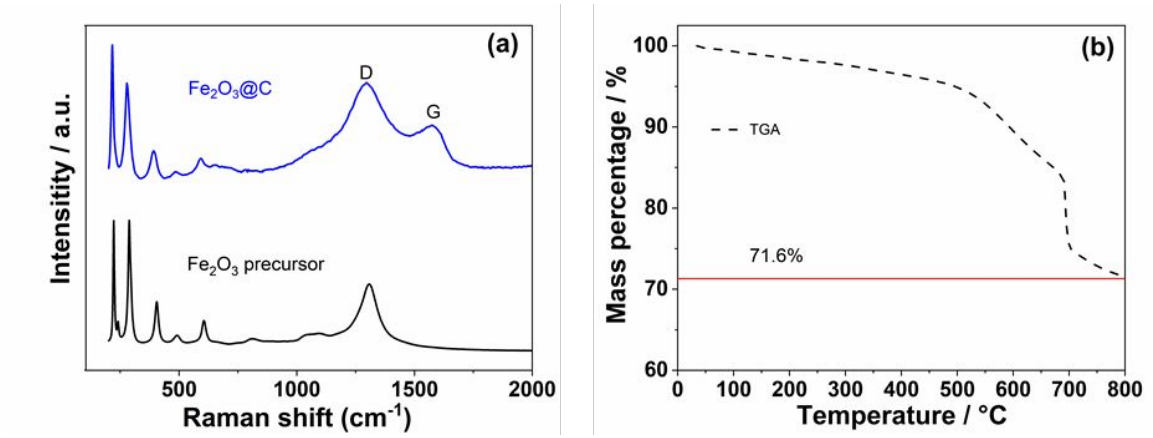

Figure S1. (a) The Raman spectra of the Fe_2O_3 precursor and Fe_2O_3@C and (b) TGA curve of the Fe_2O_3@C composite material.

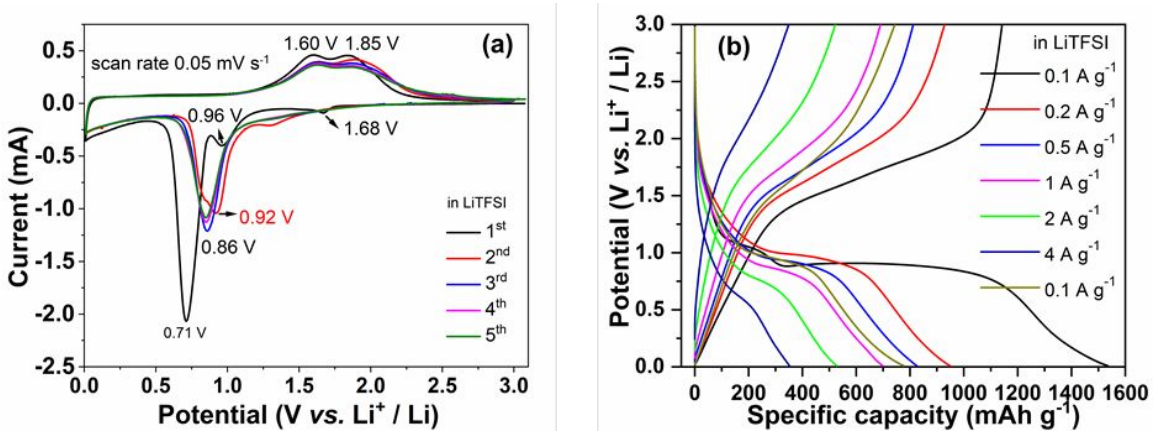

Figure S2. (a) CV profiles of the 1st to 5th for the Fe_2O_3@C at a sweep rate of 0.05 mV s^{-1} in LiTFSI. (b) The galvanostatic profiles at various current densities in LiTFSI.

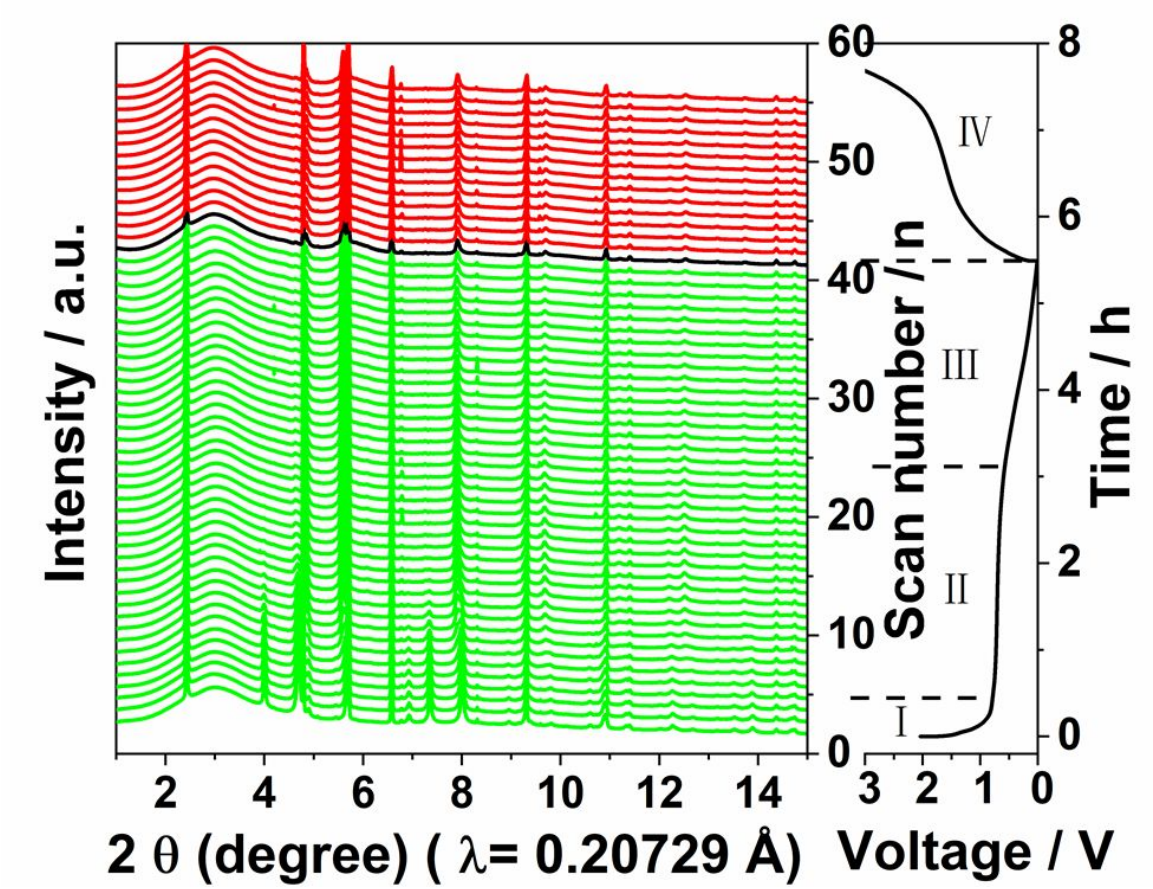

Figure S3. *In operando* XRD investigate of the lithium storage mechanism of the Fe_2O_3@C electrode: The structural evolution during the first lithiation /de-lithiation processes in LiTFSI.

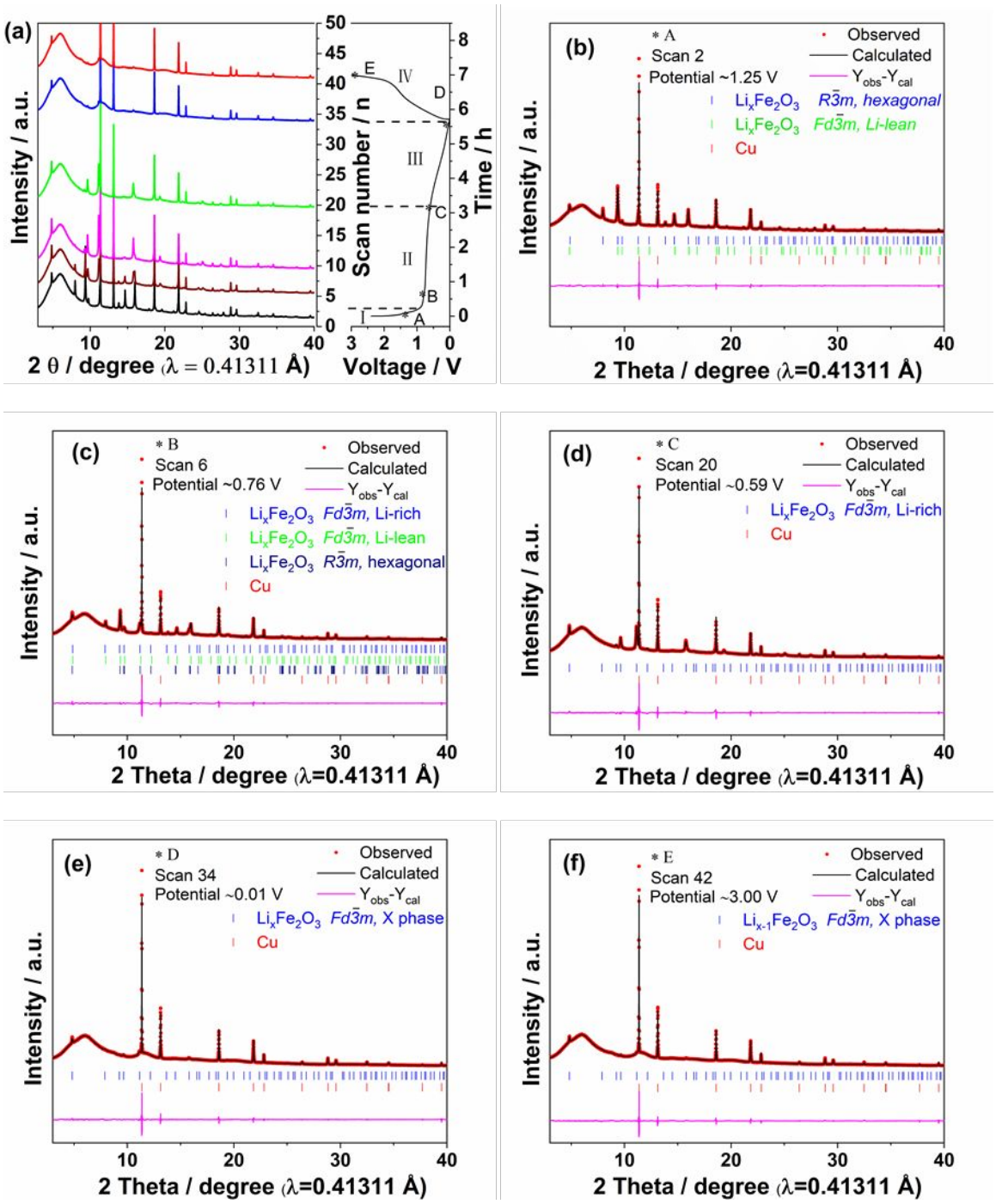

Figure S4. (a) *In operando* SRD patterns of the Fe_2O_3@C electrode was collected at various potential states. The Rietveld refinement results of the electrode at some selected potentials (A-E): the 1st lithiation to 1.25 V (b), 0.76 V (c), 0.59 V (d), 0.01 V (e), and the1st de-lithiation to 3.00 V (f).

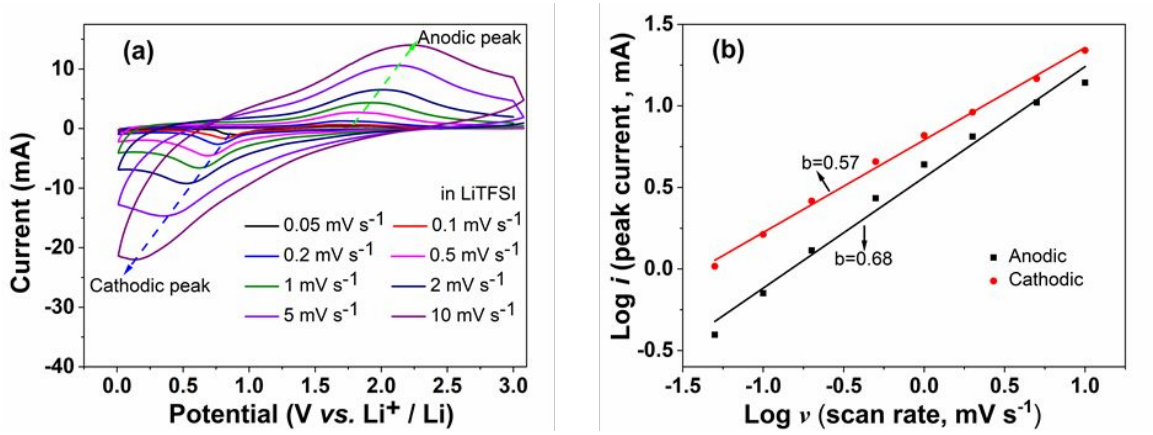

Figure S5. Kinetics characterization of the Fe_2O_3@C electrode in LiTFSI: (a) CV profiles with scan rates between 0.05 to 10 mV s^{-1}. (b) The linear relationship of log *i* (peak current) *vs.* log *v* (scan rate) for anodic and cathodic peaks.

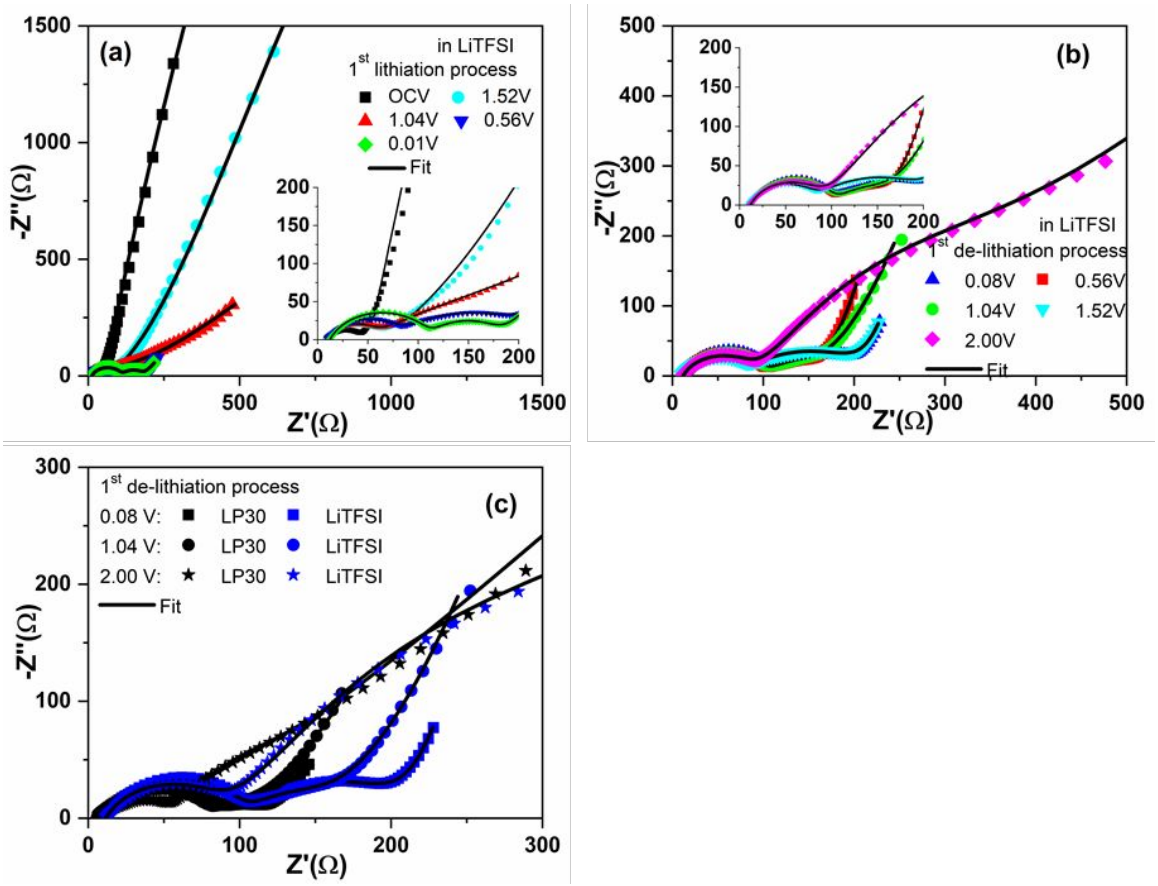

Figure S6. Nyquist plots of the Fe_2O_3@C electrode measured on the freshly assembled cell (OCV) and at selected potentials during the first lithiation (a) and de-lithiation (b) processes in LiTFSI. Comparison of the Nyquist plots of Fe_2O_3@C electrode was evaluated at 2.0, 1.04, and 0.01 V vs. Li^+/Li during the de-lithiation process in LP30 and LiTFSI (c).