Supplementary Figures

**Supplementary Figure 1 | Construction of chemical phase maps using improved data processing method.**

(a) Absorption-contrast image shown along with the chemical phase maps constructed using different data process approaches (b, c) for the same region in a FeF₃ MW electrode. We took XANES spectra from the areas with and without the FeF₃ MWs respectively and used them as examples to demonstrate the difference of data processing approaches in generating chemical phase maps. The randomly selected single pixel XANES spectrum from the sample-containing area and the background spectrum are shown in (d). The background spectrum contains information on X-ray attenuation by all the other components in the *operando* cell, such as electrolyte, polymeric binder, carbon black, current collector, and separator. (e) shows the spectrum directly normalized using previously reported methods⁴⁻⁷, which is clearly off the normal scale (typically 0–2 in the y-axis) compared with the reference standard spectra in **Supplementary Figure 2**. When all the other spectra at other pixels were treated the same way and fitted, only very few of them could be preserved to generate the unsatisfactory phase map in (b). In contrast, (f) shows the spectrum correctly normalized and scaled using our new approach. The background X-ray attenuation was subtracted first before the normalization. High-quality chemical phase maps, such as that shown in (c), can then be generated by fitting the background subtracted normalized spectra at each pixel.
Supplementary Figure 2 | Reference spectra used for fitting to generate chemical phase maps. XANES spectra were collected from commercial Fe$^{3+}$F$_3$, Fe$^{2+}$F$_2$, and metallic Fe powders using TXM-XANES.
Supplementary Figure 3 | Complete structural characterization of the FeF₃ polyhedra. (a) SEM image of the FeF₃ polyhedra with rhombohedral crystal structure. (b) Representative TEM image of a polyhedron. (c) Selected-area electron diffraction pattern taken from the same polyhedron in (b), showing that the polyhedron is single-crystalline. (d) Powder X-ray diffractograms of the polyhedra before and after thermal treatment in comparison with the reference standard PDF cards. The as-made polyhedra are phase-pure cubic FeF₃ and they are fully converted to rhombohedral FeF₃ after the thermal treatment in argon at 350 °C for 30 min. (e) shows the crystal structures of cubic and rhombohedral FeF₃. The conversion from the cubic phase to the rhombohedral phase involves rotation and distortion of the corner-sharing FeF₆ octahedra. The crystallographic information of cubic FeF₃ was obtained from the Inorganic Crystal Structure Database (ICSD). Note that rhombohedral FeF₃ is the thermodynamically stable phase.
Supplementary Figure 4 | Complete structural characterization of the FeF₃ MWs. (a) SEM image of the FeF₃ MWs. (b) Powder X-ray diffractograms of the MWs before and after thermal conversion in comparison with the reference standard PDF cards. The thermal dehydration of α-FeF₃·3H₂O MWs led to the formation of MWs of rhombohedral FeF₃. FeF₂ was also produced as a minor impurity phase during the dehydration. (c) shows the crystal structures of α-FeF₃·3H₂O, FeF₃, and FeF₂. α-FeF₃·3H₂O is made of separate FeF₃(H₂O)₃ octahedra with F⁻ and H₂O randomly distributed. FeF₃ and FeF₂ are made of FeF₆ octahedra connected by sharing corners or edges. The dehydration and conversion of α-FeF₃·3H₂O involves the loss of H₂O and reorganization of the octahedra. (d) Low-magnification TEM image of a FeF₃ wire, suggesting porosity. (e) High-resolution TEM image of the FeF₃ wire shown in (d) showing that the wire is polycrystalline and contains many grain boundaries. The inset is a selected-area electron diffraction pattern taken from the wire in (d). The diffraction ring pattern can be indexed to rhombohedral FeF₃ and confirms the polycrystallinity of the wire. (f) Nitrogen adsorption/desorption profile of the FeF₃ MWs, revealing that the MWs are mesoporous. The inset shows the pore size distribution. The BET surface area is ~30 m²/g and the mode (most frequent value) of the pore size is ~17 nm.
Supplementary Figure 5 | Electrochemical capacity tests of the FeF$_3$ polyhedra and MWs packed in coin-cell batteries. The FeF$_3$ polyhedra and MWs were mixed with carbon black and polymeric binder in a 7:2:1 weight ratio and packed into two different 2032-type coin cells for testing. The discharge/charge current was set at 50 mA/g (~1/14.2 C, 1C = 712 mA/g).
Supplementary Figure 6 | TXM-XANES visualization of the electrochemical reaction of FeF$_3$ microwire electrode in potentiostatic mode. (a) Absorption-contrast image of the area of analysis. (b) Voltammogram of the operando cell at voltage scan rate of 0.3 mV/s. The black segments on the voltammogram indicate the time periods when the XANES data were collected. (c) Reference standard spectra collected from commercial FeF$_3$, FeF$_2$, and Fe powders. (d) Chemical phase maps at different states of discharge/charge. Conversion from Fe$^{3+}$ to Fe$^{2+}$ and Fe can be clearly seen in (Panel e 1–4). Reconversion from Fe went through Fe$^{2+}$-containing phases and did not go back to Fe$^{3+}$ (Panel e 5–8). (e) Selected-area XANES spectra to show the changes during the electrochemical conversion/reconversion. The white squares in (a) and (c) mark the area used to generate the XANES spectra. (f) The mole percentage of the Fe species in different oxidation states in map c1 to c8.
Supplementary Figure 7. Chemical phase maps generated from other areas of the same operando FeF$_3$ electrode (made of a mixture of MWs and polyhedral) at the end of discharge and charge. (a) and (b) are absorption-contrast image and the resulting chemical phase map, respectively, taken at the end of discharge. It is clear that the MWs reacted more completely than the polyhedra. (c) and (d) are absorption-contrast image and the resulting chemical phase map, respectively, taken at the end of charge. The recharge reaction was not complete. Metallic Fe and Fe$^{2+}$ were found to co-exist at the end of recharge, indicating the reconversion must go through Fe$^{2+}$-containing intermediate(s) during recharge.
Supplementary Figure 8 | Two representative best fits of XAS spectra. The linear combinational fitting was performed in the energy range from 7109.48 to 7159.48 eV. The X-ray absorption data were processed and analyzed using IFEFFIT-ATHENA.
Supplementary Figure 9 | Ex Situ XAS on electrodes cycled to different states of discharge and charge. The electrodes were recovered from coin cells dissembled inside a glovebox and sealed between Kapton tapes.
Supplementary Figure 10 | Representative SEM image of FeF$_3$ microwire electrode with binders and carbon black.
### Supplementary Table 1 Details for the linear combinational fitting results in Figure 4d

| XAS Data No. | R-factor | $\chi^2$ | Fe$^{3+}$F$_3$ | Fe$^{2+}$F$_2$ | Fe | Weight | Error | Weight | Error | Weight | Error |
|--------------|----------|----------|----------------|----------------|-----|--------|-------|--------|-------|--------|-------|
| 1            |          | Did not fit. Pristine FeF$_3$ electrode |                |                |     |        |       |        |       |        |       |
| 2            | 0.0008   | 0.0184   | 0.8939         | 0.0068         |     | 1.061  | 0.0038 |        |       |        |       |
| 3            | 0.0001   | 0.0013   | 0.7688         | 0.0023         |     | 0.1779 | 0.0018 |        |       |        |       |
| 4            | 0.0001   | 0.0024   | 0.6722         | 0.0032         |     | 0.2464 | 0.0024 |        |       |        |       |
| 5            | 0.0005   | 0.0065   | 0.6277         | 0.0052         |     | 0.2964 | 0.0040 |        |       |        |       |
| 6            | 0.0003   | 0.0058   | 0.4634         | 0.0049         |     | 0.3820 | 0.0038 |        |       |        |       |
| 7            | 0.0004   | 0.0086   | 0.4010         | 0.0060         |     | 0.4235 | 0.0046 |        |       |        |       |
| 8            | 0.0008   | 0.0140   | 0.3766         | 0.0076         |     | 0.4691 | 0.0058 |        |       |        |       |
| 9            | 0.0013   | 0.0295   | 0.2772         | 0.0111         |     | 0.5236 | 0.0085 |        |       |        |       |
| 10           | 0.0026   | 0.0614   | 0.2111         | 0.0160         |     | 0.6020 | 0.0122 |        |       |        |       |
| 11           | 0.0006   | 0.0127   | 0.2175         | 0.0073         |     | 0.5056 | 0.0056 |        |       |        |       |
| 12           | 0.0006   | 0.0081   | 0.2007         | 0.0058         |     | 0.4835 | 0.0044 |        |       |        |       |
| 13           | 0.0005   | 0.0108   | 0.1601         | 0.0067         |     | 0.5086 | 0.0051 |        |       |        |       |
| 14           | 0.0009   | 0.0186   | 0.1090         | 0.0088         |     | 0.5284 | 0.0067 |        |       |        |       |
| 15           | 0.0008   | 0.0164   | 0.0731         | 0.0082         |     | 0.5137 | 0.0063 |        |       |        |       |
| 16           | 0.0008   | 0.0156   | 0.0166         | 0.0080         |     | 0.4873 | 0.0062 |        |       |        |       |
| 17           | 0.0030   | 0.0396   | 0.0000         | 0.0128         |     | 0.4035 | 0.0098 |        |       |        |       |
| 18           | 0.0030   | 0.0330   | 0.0000         | 0.0117         |     | 0.2668 | 0.0089 |        |       |        |       |
| 19           | 0.0029   | 0.0276   | 0.0000         | 0.0107         |     | 0.1719 | 0.0082 |        |       |        |       |
| 20           | 0.0044   | 0.0387   | 0.0000         | 0.0127         |     | 0.1260 | 0.0097 |        |       |        |       |
| 21           | 0.0042   | 0.0361   | 0.0000         | 0.0122         |     | 0.1137 | 0.0094 |        |       |        |       |
| 22           | 0.0012   | 0.0113   | 0.0000         | 0.0068         |     | 0.1467 | 0.0052 |        |       |        |       |
| 23           | 0.0017   | 0.0168   | 0.0000         | 0.0084         |     | 0.1636 | 0.0064 |        |       |        |       |
| 24           | 0.0013   | 0.0134   | 0.0059         | 0.0074         |     | 0.1778 | 0.0057 |        |       |        |       |
| 25           | 0.0015   | 0.0201   | 0.0000         | 0.0091         |     | 0.2829 | 0.0070 |        |       |        |       |
| 26           | 0.0011   | 0.0181   | 0.0011         | 0.0086         |     | 0.3581 | 0.0066 |        |       |        |       |
| 27           | 0.0018   | 0.0333   | 0.0000         | 0.0117         |     | 0.4650 | 0.0090 |        |       |        |       |
| 28           | 0.0016   | 0.0316   | 0.0000         | 0.0115         |     | 0.5052 | 0.0088 |        |       |        |       |
| 29           | 0.0014   | 0.0312   | 0.0000         | 0.0114         |     | 0.5431 | 0.0087 |        |       |        |       |
| 30           | 0.0013   | 0.0275   | 0.0292         | 0.0107         |     | 0.5578 | 0.0082 |        |       |        |       |
| 31           | 0.0013   | 0.0291   | 0.0959         | 0.0110         |     | 0.6083 | 0.0084 |        |       |        |       |
| 32           | 0.0013   | 0.0312   | 0.1370         | 0.0114         |     | 0.6297 | 0.0087 |        |       |        |       |
| 33           | 0.0014   | 0.0253   | 0.1976         | 0.0102         |     | 0.5778 | 0.0078 |        |       |        |       |
| 34           | 0.0013   | 0.0249   | 0.2280         | 0.0102         |     | 0.5706 | 0.0078 |        |       |        |       |
| 35           | 0.0013   | 0.0234   | 0.2515         | 0.0098         |     | 0.5508 | 0.0075 |        |       |        |       |
| 36           | 0.0013   | 0.0219   | 0.2890         | 0.0095         |     | 0.5249 | 0.0073 |        |       |        |       |
| 37           | 0.0012   | 0.0227   | 0.3034         | 0.0097         |     | 0.5358 | 0.0074 |        |       |        |       |

- The linear combinational fitting was performed in the energy range from 7109.48 to 7159.48 eV.
- The rutile FeF$_2$ phase was used to represent all the possible rutile related Fe$^{3+}$-containing phases.
Supplementary Methods

Materials:

All chemicals were used as received without further purification. Hydrofluoric acid (aqueous HF solution, 48 wt%, CAS # 7664-39-3. Warning: HF solution is highly corrosive and must be handled with care and proper protection. Please see the MSDS document in Sigma-Aldrich website), iron (III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O, ≥98.0%, CAS # 7782-61-8], commercial iron trifluoride powder (FeF₃, ≥98.0%, CAS # 7783-50-8), iron difluoride powder (FeF₂, ≥98.0%, CAS # 7789-28-8), metallic iron particles (Fe, >99.0%, CAS # 7439-89-6), lithium ribbon (0.75 mm in thickness, >99.9%, CAS #7439-93-2) were purchased from Sigma Aldrich. Ethanol (200 proof, CAS #64-17-5) was purchased from Decon Laboratories Inc. N-methyl-2-pyrrolidone (NMP, ≥99.5%, CAS # 872-50-4), polyethylene separator membranes, polyvinylidene difluoride (PVDF, ≥99.5%, CAS # 24937-79-9) binder, lithium foils (15.6 mm in diameter × 0.45 mm in thickness, >99%, CAS #7439-93-2) and 2032-type coin cell cases were purchased from MTI Corporation. 1 M lithium hexafluorophosphate (LiPF₆) dissolved in 1:1 (v:v) ethyl carbonate (EC)/dimethyl carbonate (DMC) electrolyte was purchased from BASF. Carbon black [Super P® conductive, ≥99% (metal basis), CAS # 1333-86-4] and aluminum foils [0.025 mm in thickness, ≥99.45% (metal basis), CAS # 7429-90-5] were purchased from Alfa Aesar. Carbon Papers (Toray Paper 030 TGP030-1005, 110 μm in thickness) were purchased from Fuel Cell Earth LLC.

Synthesis of FeF₃ Microwires and Polyhedra:

We developed the syntheses of two new FeF₃ (rhombohedral structure, \( \bar{R}3c \)) samples with different morphologies and microstructures by rationally controlling the supersaturation of growth solution\(^1\sim3\). In both syntheses, ethanol was used as the solvent, Fe(NO₃)₃·9H₂O as the Fe\(^{3+}\) source, and HF as the F\(^-\) source. Both F\(^-\) and H₂O act as ligands in complex with Fe\(^{3+}\) to control the supersaturation.
FeF$_3$ microwires (MWs) were prepared by thermal dehydration of $\alpha$-FeF$_3$$\cdot$3H$_2$O MWs in argon atmosphere. The precursor $\alpha$-FeF$_3$$\cdot$3H$_2$O MWs were synthesized via a new synthesis developed based on our previous work$^1$. A diluted HF/ethanol solution (~5 M HF) was first prepared by mixing 1.812 mL HF aqueous solution (48 wt%) with 8.3 mL ethanol in a plastic centrifuge tube. Then, 7.0 mL ethanol, 1.0 mL diluted HF (~5 M), 1.0 mL deionized water were sequentially added into a 15 mL plastic centrifuge tube with caution. The centrifuge tube was sealed and gently shaken by hand with great caution to allow the liquids to mix. An Fe$^{3+}$ solution in ethanol with a concentration of 532 mM was made by dissolving 1.616 g Fe(NO$_3$)$_3$$\cdot$9H$_2$O in 7.5 mL ethanol. 1.000 mL of this Fe$^{3+}$/ethanol solution was then quickly injected into the HF/ethanol mixture using an Eppendorf pipet. The resulting colorless solution with a concentration ratio of $c$(Fe$^{3+}$) : $c$(HF) : $c$(H$_2$O) $\approx$ 53.2 mM: 500 mM: 11575 mM was gently mixed by shaking and kept in an oven at 60 °C for 18 h. No substrate was used during the reaction and aggressive agitation was avoided to suppress the formation of large $\beta$-FeF$_3$$\cdot$3H$_2$O crystals. The white cloudy precipitate that appeared over time was collected by centrifugation at 5000 rpm for 5 min, washed with dry ethanol twice and vacuum-dried at room temperature. Typically, ~15 mg product of $\alpha$-FeF$_3$$\cdot$3H$_2$O MWs could be obtained from a 10 mL scale synthesis, corresponding to a reaction yield of ~17 % based on the limiting reagent of Fe. In order to make the anhydrous FeF$_3$ MWs, the as-synthesized white precipitate of $\alpha$-FeF$_3$$\cdot$3H$_2$O MWs was dehydrated in an inert atmosphere using a quartz tube reactor equipped with pressure and gas flow controls and placed a tube furnace (Lindberg/Blue M). Briefly, a large alumina boat containing ~150 mg $\alpha$-FeF$_3$$\cdot$3H$_2$O MWs were placed at the center of the tube furnace. The tube reactor was first slowly evacuated and flushed three times with argon gas and then the MWs were kept under vacuum (~40 mTorr) at 50 °C to for 20 min to dry completely. Then under a flowing argon gas at a flow rate of 100 sccm and a pressure of 770 Torr, the furnace temperature was slowly ramped from 50 °C to 350 °C in 150 min (~2 °C min$^{-1}$) and held at 350 °C for 30 min before naturally cooling down to produce a pale greenish/brownish product (~100 % reaction yield).

Rhombohedral phase FeF$_3$ polyhedra were prepared by thermal conversion of metastable cubic phase FeF$_3$ polyhedra, which were synthesized in ethanol solution. Briefly, a diluted HF/ethanol solution (~1 M HF) was first prepared by mixing 0.719 mL HF aqueous solution (48 wt%) with 19.3 mL ethanol in a plastic centrifuge tube.
Then, 7.5 mL ethanol, 1.0 mL diluted HF (~1 M), 0.5 mL deionized water were sequentially added into a 15 mL plastic centrifuge tube with caution. The centrifuge tube was sealed and gently shaken by hand with great caution to allow the liquids to mix. An Fe$^{3+}$ solution in ethanol with a concentration of 200 mM was made by dissolving 0.808 g Fe(NO$_3$)$_3$$\cdot$9H$_2$O in 10.0 mL ethanol. 1.000 mL of this Fe$^{3+}$/ethanol solution was then quickly injected into the HF/ethanol mixture using an Eppendorf pipet. The resulting colorless solution with a concentration ratio of $c$(Fe$^{3+}$) : $c$(HF) : $c$(H$_2$O) $\approx$ 20 mM: 100 mM: 4670 mM was gently mixed by shaking and kept in an oven at 60 °C for 24 h. No substrate was used during the reaction and aggressive agitation was avoided to suppress the formation of large β-FeF$_3$$\cdot$3H$_2$O crystals. The light yellow precipitate that appeared over time was collected by centrifugation at 5000 rpm for 5 min, washed with dry ethanol twice and vacuum-dried at room temperature. Typically, 5–6 mg product of the cubic phase FeF$_3$ polyhedra could be obtained from a 10 mL scale synthesis, corresponding to a reaction yield of 22–27 % based on the limiting reagent of Fe. The as-synthesized cubic phase FeF$_3$ polyhedra were thermally annealed in an argon atmosphere at 350 °C for 30 min in the same quartz tube reactor described above to produce the rhombohedral phase FeF$_3$ polyhedra (~100 % reaction yield).

**Material Characterization:**

Scanning electron microscopy (SEM) images were acquired using a LEO 55 VP field emission scanning electron microscope at a working voltage of 5 kV. Transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were acquired using either a Tecnai T-12 transmission electron microscope (120 kV) or a FEI Titan transmission electron microscope (200 kV). The TEM samples were prepared by dropcasting FeF$_3$ samples in ethanol onto lacey-carbon grids (Ted Pella Inc. lacey carbon type-A, 300 Mesh). Air/moisture-exposure was minimized as much as possible. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 diffractometer using Cu K$\alpha$ radiation and corrected for background. The PXRD samples were prepared by drop-casting the ethanol suspensions of the samples onto glass substrates and dried. The Brunauer–Emmet–Teller
(BET) specific surface area and pore size distribution of the FeF$_3$ MWs were obtained from nitrogen adsorption–desorption isotherms measured by a Quantachrome Autosorb-1 gas sorption analyzer.

**Processing of FeF$_3$ Cathode and Electrochemical Measurements:**

Electrochemical measurements were performed on electrodes pasted on aluminum foils (~25 µm thickness), which were prepared from slurries containing 70 wt% active material, 20 wt% conductive carbon black and 10 wt% PVDF binder using NMP as the solvent. The mass loading of the active material (FeF$_3$) is around 2 mg cm$^{-2}$. CR2032-type coin cells were assembled in an argon-filled glovebox, using Li metal as the counter/quasi-reference electrode, 1 M LiPF$_6$ in EC/DMC (1/1 by volume) as the electrolyte, and electrolyte-soaked polyethylene films as the separator. All cells were aged a few hours before any tests. Electrochemical impedance spectroscopy (EIS) was performed using a Biologic SP-200 Potentiostat operated using EC-Lab software. EIS measurements were carried out over a frequency range from 200 kHz to 50 mHz with a perturbation voltage of 10 mV. Constant current discharge/charge tests were carried out using a Biologic VMP-3 potentiostat/galvanostat in a voltage window of 4.5–1.0 V at different current rates. All reported performance was calculated based on the mass of the active material.

**Fabrication of Batteries for Operando Studies:**

The *operando* experiments were performed using perforated 2032-type coin cells with ~4 mm holes on both sides of the cell cases. The holes were sealed using Kapton tapes. The holes need to be small to ensure a small cell impedance. The FeF$_3$ samples (polyhedra and MWs 1:1 by weight) were mixed with carbon black and PVDF binder in a weight ratio of 3:5:2 in NMP. The resulting slurry was pasted onto thin aluminum foils (~8 µm thickness) or carbon papers (~110 µm thickness) and then dried in vacuum to make electrodes. The thin aluminum foils and thin carbon papers are quite transparent to hard X-rays but still robust enough for handling, which is critical to the *operando* experiment. The density of samples on the electrodes was checked using an
optical microscope or a scanning electron microscope before packing into coin cells. The *operando* cells were assembled in an argon-filled glovebox using Li metal as the counter/quasi-reference electrode and polyethylene films soaked with 1 M LiPF₆ EC/DMC (1/1 by volume) electrolyte as the separator. No additional electrolyte was added during the cell packing in order to minimize the X-ray attenuation caused by the electrolyte liquid. The as-made cells were aged for a few hours and checked using electrochemical impedance spectroscopy before being used in the *operando* experiments, during which the cell was held by a custom-modified coin cell holder and discharged and charged at rate of ~1/15 C (1 C = 712 mA/g). The coin cell holder was purchased from MTI Corporation and attached to a stainless steel rod standing on the motorized stage. The positive lead of the cell holder was modified to make contact with the coin cell from the side so that the X-ray was not blocked. We also put a piece of perforated stainless steel foil between the positive lead and the coin cell to apply a gentle pressure to make better electrical contact.

*Operando* Hard X-ray Spectro-Imaging:

The *operando* hard X-ray spectro-imaging experiments were performed using the full-field transmission X-ray microscope (FFTXM) at beamline X8c, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The TXM operates using a bending magnetic source and a Si (111) double-crystal monochromator. It routinely operates in absorption contrast mode over a wide energy range from 5 to 11 keV with spatial and energy resolutions of ~25 nm and ΔE/E = 10⁻⁴, respectively.

In the *operando* experiment, the *operando* coin cell was mounted on an motorized X, Y, Z, θ stage and aligned so that the X-ray beam could transmit through the two holes in the cell. A field of view of 40 × 40 μm² with a 2048 × 2048 CCD camera was used. The cell was continuously cycled in galvanostatic or potentiostatic mode and the X-ray absorption-contrast images (X-ray transmitted through the sample) and reference background images (X-ray passing through air) were collected in sequence under dynamic conditions. To track the phase transformations in the electrode, a full series of TXM images were collected at each states of discharge and charge. Each TXM image series was collected by scanning across the Fe K-edge (7112 eV) from 7091 to 7285 eV, with a
step size of 2 eV, and taking one TXM image at each energy step, which generated 1024 × 1024 XANES spectra with 2 × 2 binned pixels or 512 × 512 XANES spectra with 4 × 4 binned pixels depending on the choice of camera binning. The exposure time for each image was chosen depending on the intensity of the beam and was typically 8–10 seconds for 2 × 2 camera binning and 4–5 seconds for 4 × 4 camera binning during our experiments. Each chemical phase map took ~8 minutes to finish when using 4 × 4 camera binning and the output pixel size is ~80 nm.

Data Processing and Chemical Map Construction:

Each set of TXM images was first aligned using the Xradia Controller Software to correct the positioning errors of the motor stage, X-ray optics, or sample. Then all data were analyzed using a customized program developed in house using Matlab R2011b.

We first carried out background normalization for all TXM images using the unique reference background images (X-ray passing through air) collected at each energy to get the absorption-contrast images. One example is shown in Supplementary Figure 1a, which is a field-of-view taken from an operando cell discharged to ~2.0 V. Then we could extract the XANES spectrum (X-ray attenuation versus energy raw data) at each pixel (1024 × 1024 pixels for binning 2, 512 × 512 pixels for binning 4). Here we used the single pixel spectrum (red open circles in Supplementary Figure 1b) extracted from point S1 in Supplementary Figure 1a to explain the data normalization procedures and compare the effectiveness of our methods with previously reported methods 4–7.

XANES spectra need to be normalized and scaled in order to be directly compared with each other and correctly fitted using standard reference spectra. The normalization is done using the data points in the pre-edge and post-edge regions 4–7, which involves five major steps: 1) Fit the pre-edge spectrum to a linear function and subtract it from the spectrum over the entire range of energy; 2) Identify the threshold energy $E_0$, which is the maximum of the 1st derivative of the spectrum; 3) Fit the post-edge spectrum to a linear function; 4) Determine the edge-jump value, which is the difference between the pre-edge function and post-edge function at the
threshold energy \( E_0 \); 5) Normalize the spectrum using the edge-jump value to make the pre-edge become \( \sim 0 \) and the post-edge become \( \sim 1 \).

The normalized spectrum can then be fitted to standard reference spectra to determine the ratio between different phases. This is because based on Beer’s Law, the total X-ray attenuation at each pixel can be considered as the sum of X-ray attenuation from each constituent phase with attenuation coefficient \( \mu \) and thickness \( t \), which can be written as:

\[
-\ln\left(\frac{I}{I_0}\right) = \mu(\text{FeF}_3) \cdot t(\text{FeF}_3) + \mu(\text{FeF}_2) \cdot t(\text{FeF}_2) + \mu(\text{Fe}) \cdot t(\text{Fe})
\]  

(1)

where \( I_0 \) is the incident X-ray intensity and \( I \) is the X-ray intensity after it passes through the sample. Note that attenuation coefficient \( \mu \) and \( -\ln\left(\frac{I}{I_0}\right) \) are energy dependent [as the \( -\ln\left(\frac{I}{I_0}\right) \) versus energy plot is the XANES spectrum] and the rutile FeF\(_2\) phase was used to represent all the possible rutile related Fe\(^{2+}\)-containing phases. This is a reasonable approximation because it was reported that the Li\(_x\)FeF\(_3\) (when \( x \approx 1.0 \)) phase contains structural features that are found in the rutile FeF\(_2\) structure (23). As other battery components in the pathway of the beam (such as electrolyte, carbon, PVDF binder, and separator) also attenuate the X-ray during the operand experiment, their contribution (denoted by \( A_{\text{bkg}} \)) is non-trivial and should also be taken into consideration. The modified equation can be written as:

\[
-\ln\left(\frac{I}{I_0}\right) = \mu(\text{FeF}_3) \cdot t(\text{FeF}_3) + \mu(\text{FeF}_2) \cdot t(\text{FeF}_2) + \mu(\text{Fe}) \cdot t(\text{Fe}) + A_{\text{bkg}}
\] 

(2)

Previous methods depend heavily upon the strong X-ray absorption of large-sized samples (10−20 \( \mu \)m) and considered the X-ray absorption of the materials under study approximately equal to the total X-ray absorption\(^4\)−\(^7\). This approximation is no longer valid for the smaller and weakly absorbing samples investigated herein. As a result, those methods failed to correctly normalize the XANES spectra for smaller and less X-ray absorbing samples, such as the porous FeF\(_3\) MWs examined herein (Supplementary Figure1a). An example of such improperly normalized spectra is shown in Supplementary Figure1e, which is clearly off the scale compared with the standard reference spectra (Supplementary Figure2). When the fitting was carried out using these improperly normalized spectra at all the pixels, the quality of the resulting chemical phase map is unsatisfactory (see
Supplementary Figure 1b), because very few pixels could be fitted correctly to pass the R-value filter (misfit filter).

We solved this normalization problem by approximating the internal background X-ray absorption ($A_{bg}$, black circles in Supplementary Figure 1d) using the X-ray attenuating information readily available from the area that does not contain the FeF$_3$ sample but all the other components in the operando cell, such as electrolyte, polymeric binder, carbon black, current collector, and separator (the black box in Supplementary Figure 1a). We first subtracted the internal background spectrum (black circles in Supplementary Figure 1d) from the total X-ray attenuation (red circles in Supplementary Figure 1d) and then carried out the data normalization following the aforementioned five-step procedure, which yielded correctly normalized spectrum as shown in Supplementary Figure 1f. Using our custom-developed program, this normalization procedure could be conveniently applied to the spectra at all pixels.

The correctly normalized spectrum at each pixel was then fitted with the linear combination of three $\mu t$ values. The ratio of the weighing factor is an analogue of the thickness fraction and therefore represents the volume fractions of solid state phases containing different Fe oxidation states. The fitting was carried out by minimizing the $R$ value (a measure of misfit) for each spectrum at each pixel, which is defined as:

$$ R = \frac{\sum_{Ei} (dataE - refE)^2}{\sum_{Ei} dataE^2} $$

where $E_i$ is 7091 eV, $Ef$ is 7285 eV, $dataE$ is the normalized spectrum at each pixel for the given energy $E$, and $refE$ is the possible fitting reference value that is a linear combination of X-ray attenuation of FeF$_3$, FeF$_2$, and Fe. The standard reference XANES spectra were collected from commercial FeF$_3$, FeF$_2$, and Fe powders under the same conditions using TXM and verified using a standard spectroscopy beamline X18A at NSLS, BNL. During the fitting, we considered all possible combinations with FeF$_3$, FeF$_2$, and Fe with 2 vol% resolution, which was a total of 1326 possible combinations. $R$ values were minimized at each pixel to find the best-matched phase combination of different Fe oxidation states so that Red-Green-Blue (Red: Fe$^{3+}$, Green: Fe$^{2+}$, Blue: Fe) colors can be assigned accordingly to generate the chemical phase map (Supplementary Figure 1c). We applied an R-value
filter (misfit filter) to the resulting phase map and only pixels with $R < 0.08$ were displayed in order to give the most accurate chemical phase information. The comparison between Supplementary Figure 1c and S1b clearly show that our new data processing procedures could generate a higher quality chemical phase map compared with the previously reported methods. These new data processing procedures were consistently employed to yield the chemical phase maps shown in Figure 2 and 3 in the manuscript text and Supplementary Figure 6 and 7 in the Supplementary Information.

**Operando X-ray Absorption Spectroscopy Experiment on FeF$_3$ Microwires:** The *operando* X-ray absorption experiments were performed at beamline X18A, National Synchrotron Light Source, Brookhaven National Laboratory. The measurements were performed in transmission mode using a Si (111) double-crystal monochromator, which was detuned to ~35% of its original maximum intensity to eliminate the high order harmonics in the beam. A reference X-ray absorption spectrum of Fe ($K$-edge 7112 eV) was simultaneously collected using a standard Fe foil. Energy calibration was done using the first inflection point of the Fe $K$-edge spectrum as the reference point. The X-ray absorption data were processed and analyzed using IFEFFIT-ATHENA. Standard reference spectra from commercial FeF$_3$, FeF$_2$, and Fe powders were also collected in order to carry out linear combination analysis to determine the ratio between different Fe oxidation states. The rutile FeF$_2$ phase was used to represent all the possible rutile related Fe$^{2+}$-containing phases. This is a reasonable approximation because it was reported that the Li$_x$FeF$_3$ (when $x \approx 1.0$) phase contains structural features that are found in the rutile FeF$_2$ structure$^{38}$. The *operando* experiments were performed using perforated 2032-type coin cells with holes on both sides of the cell cases. The holes were sealed using Kapton tapes. The FeF$_3$ MWs were mixed with carbon black and PVDF binder in a weight ratio of 7:2:1 in NMP. The resulting slurry was pasted onto thin aluminum foils (~25 µm thickness) to make electrodes. The *operando* cells were assembled in an argon-filled glovebox using Li metal as the counter/quasi-reference electrode and polyethylene films soaked with 1 M LiPF$_6$ EC/DMC (1/1 by volume) electrolyte as the separator. The as-made cells were aged for a few hours and checked using electrochemical
impedance spectroscopy before being used in the operando experiments, during which the cell was discharged and charged at rate of ~1/12 C (1 C = 712 mA/g).

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