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Revealing Reaction Pathways of Collective ² Substituted Iron Fluoride Electrode for Lithium Ion Batteries

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16 intercalation-extrusion-cation disordering process during phase 17 transformations from the rutile phase to rocksalt phase, which microscopically corresponds to topotactic rearrangement of Fe/ 18 Co-O/F octahedra. During this process, the diffusion channels of lithium transformed from 3D to 2D while the corner-19 sharing octahedron changed to edge-sharing octahedron. DFT calculations indicate that the Co and O cosubstitution of the $_{20}$ Fe_{0.9}Co_{0.1}OF cathode can improve its structural stability by stabilizing the thermodynamic semistable phases and reducing the 21 thermodynamic potentials. We anticipate that our study will inspire further explorations on untraditional intercalation systems 22 for secondary battery applications.

23 KEYWORDS: in situ/ex situ multimodal analysis, lithium ion batteries, iron fluoride, cathode, reaction mechanism

onversion-type materials have been considered as 24 attractive alternatives to intercalation-type electrode 25 in secondary ion batteries as they can deliver a much 26 27 higher capacity. Various types of conversion compounds have 28 been explored, including metal oxides, sulfides, and fluorides.^{1–5} 29 Among them, only metal fluorides have high working potentials 30 to serve as a cathode.⁶⁻⁸ Despite their high energy densities, 31 drawbacks including poor cycling stability, large voltage 32 hysteresis and low energy efficiency of metal fluorides have 33 impeded their practical applications. Incorporating different 34 elements into fluorides has been implemented to improve 35 electrochemical performance.⁹⁻¹¹ It was shown that partial $_{36}$ substitution of fluorine with oxygen in iron fluorides (e.g., FeF₂ 37 or FeF₃) can prompt the formation of an intermediate Li-Fe-38 O-F cubic phase, which helps achieving better cycle 39 stability.^{11,12} In addition, cation doping in iron fluoride may 40 enhance the electronic conductivity and reduce the resistance 41 for ionic diffusion.^{13,14} By taking advantage of both cation and 42 anion substitutions, Co and O substituted Fe_{0.9}Co_{0.1}OF 43 (FeCoOF) shows a high capacity of 420 mAhg⁻¹ over 1000

15 synchrotron X-ray techniques. Our work revealed a prolonged

cycles, which are even close to the performances of the currently 44 dominating intercalation compounds.¹⁵

Conversion

Higher energy efficiency and better reversibility of FeCoOF 46 are supposed to be originated from the reformed chemistry 47 beyond conversion reaction. Since FeCoOF serves as a cathode, 48 it is important to understand the reaction mechanisms 49 particularly at high voltage. It has been reported that a phase 50 transformation from a rutile (FeOF) to a rocksalt (Li-Fe-O- 51 F) occurs at the initial stage of lithiation (over \sim 2.0 V), while a 52 conversion reaction initiates at lower potentials.⁹ A crucial but 53 not well understood issue is the reaction pathway linking the 54 rutile phase and defected rocksalt phase, which determines the 55 discharge potential and kinetics. This Li⁺ insertion process in 56

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Figure 1. (a) Discharge-charge profiles of FeCoOF between 1 and 4 V at a current density of 50 mA g^{-1} . (b) PDF patterns acquired at each potential. (c) Atomic models of proposed phases with a degree of lithiation. (d) Portion of each phase during lithiation acquired from the PDF data fitting.

57 FeCoOF is less known than the famous intercalation reactions in 58 layered (e.g., $LiCoO_2$, graphite) or spinel (e.g., $LiMn_2O_4$) 59 compounds. The understanding of this lithiation reaction may 60 provide fundamental insights into the efforts of searching 61 innovative intercalation-type electrodes for batteries.

In this work, we examined the structural evolutions of FeCoOF *via* a combination of synchrotron X-ray techniques and *in situ* transmission electron microscopy (TEM). Utilizing the *ex* situ pair distribution function (PDF) method and *in situ* synchrotron X-ray diffraction, we found the reaction pathway from the rutile to a layered structure and then to the rocksalt phase. *In situ* TEM was used to identify the local structural and chemical evolutions at nanoscale. The effects of Co and O cosubstitutions were considered with the help of density functional theory (DFT) calculations. Our result shows the reaction pathway of a topotactic structural deformation process with minimum structural deformation, which sheds light on the design of rutile cathode systems.

75 RESULTS AND DISCUSSION

76 As synthesized $Fe_{0.9}Co_{0.1}OF$ (FeCoOF) samples were examined 77 as shown in Figure S1. Nanorod-like FeCoOF was well-78 crystallized with rutile structure and homogeneous distributions 79 of all the elements (Fe, Co, O, and F) are identified with STEM-80 energy dispersive X-ray spectroscopy (EDX) elemental 81 mapping. Figure 1a presents a discharge–charge profile of 82 FeCoOF electrode for the first cycle at a constant current 83 density of 50 mA g⁻¹. The discharge profile shows two plateaus 84 (~ 2.58 and 1.60 V) while heading to 1.0 V, indicating that 85 various intermediate phases might be evolved during the insertion of lithium ions. To retrieve the reaction pathway, we ⁸⁶ acquired PDF patterns from FeCoOF samples at different states ⁸⁷ of charge, as shown in Figure 1b. Each PDF pattern was fitted ⁸⁸ using PDFgui.¹⁶ When lithium ions are introduced to iron ⁸⁹ fluoride-based compound, the existence of a rocksalt structure ⁹⁰ has been identified at higher potential than at which conversion ⁹¹ reaction starts.^{10–12,17} In addition, inspired from the lithiation ⁹² pathway of rutile TiO₂, which also undergoes structural ⁹³ evolution from rutile structure to cubic phases,^{18,19} we ⁹⁴ considered the monoclinic structures as the intermediate phases ⁹⁵ for data fitting. Fitting result and information of these phases are ⁹⁶ shown at Table 1 and Figure S2 in the Supporting Information. ⁹⁷ ti

Table 1. Lattice Parameters and Unit Cell Volume of Rutile, M1, M2, and Rocksalt Phases

	rutile	
a (Å)	4.67013 (0.013)	
b (Å)	3.07467 (0.014)	
$V(Å^3)$	67.059	
	M1	M2
a (Å)	5.11167 (0.14)	5.56664 (0.1)
b (Å)	2.96751 (0.048)	3.04757 (0.055)
c (Å)	5.01873 (0.12)	4.72063 (0.092)
β (deg)	92.6405(1.6)	71.2518(1.3)
$V(Å^3)$	76.048	75.835
rocksalt		
a (Å)	4. 21296 (0.024)	
$V(Å^3)$	74.776	



Figure 2. In situ X-ray diffraction patterns of FeCoOF during discharge and charge at a rate of 70 mA g^{-1} . R, M1, M2, and RS stand for rutile, monoclinic 1, monoclinic 2, and rocksalt structures. Diffraction peaks marked with * were originated from Al current collector.

98 We identified other two monoclinic phases before the formation of rocksalt phase (Figure 1c). The first monoclinic phase (M1) is 99 slightly distorted from rutile by inserting lithium ions and the 100 second monoclinic phase (M2) has modified arrangement of 101 cation-anion octahedra. Then, rocksalt phase has evolved 102 103 before metallic Fe appears as a result of conversion reaction with introducing further lithium ions. Figure 1d shows the portion of 104 each phase during lithiation. It is clear that there are multiple 105 intermediate phases associating during lithiation of FeCoOF 106 and structural changes induced by lithium insertion are fairly 107 eversible during lithium extraction, but original rutile phase was 108 not obtained, which is in consistent with the previous PDF 109 results of FeOF.^{15,17} To our surprise, the M2 phase exists even 110

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111 after the formation of Fe nanoparticles, which indicates a severe 112 inhomogeneity in the degree of lithiation. As the PDF measurements were performed ex situ, quantified 113 values may not correctly represent the materials' status at each potential. We thereby further studied the structural evolutions of 116 FeCoOF by in situ synchrotron XRD under galvanostatic 117 condition at a current density of 70 mAg⁻¹. Figure 2 shows discrete 2-theta ranges to highlight the changes of samples while 118 diffraction data over the whole 2-theta range is presented at 119 Figure S3. Here, the wavelength of X-ray was 0.1885 Å. As 120 121 electrochemical reaction proceeds, changes in diffraction peaks were observed and they were summarized with the changes in *d*-122 spacings shown at Figure S4a. Figure S4b presents calculated 123 diffraction intensity of intermediate phases from PDF analysis 124 and reference diffraction patterns of FeOF, Fe, Li₂O, LiF. After 125 starting discharge (lithium insertion), (110), (101), (111), 126 127 (211), (002), and (310) diffraction peaks at 3.28°, 4.23°, 4.82°, 128 6.28°, 7.09°, and 7.35°, respectively from rutile structure disappeared, indicating other phase was developed at the 129 expense of rutile. During lithiation, diffraction peaks around 130 3.1° , 4.75° and 7.4° were emerged, gradually shifted negatively, 131 and then disappeared, suggesting evolution and extinction of M1 132 phase. Other peaks around 4.19° and 6.1° were also appeared 133 and shifted in a negative way but kept with decreased intensity 134 until being discharged to 1 V, implying development of M1 then 135 136 M2 phase. In addition, the diffraction peak at 7.2° was well-137 maintained until 1 V, indicating the evolution of rocksalt phase. 138 In other words, changes in diffraction peaks presented at in situ 139 XRD is well matched with sequential development of M1, M2,

and rocksalt phases while a composite of metallic Fe and $Li_2O/140$ LiF matrix is not clearly resolved at XRD. Products from 141 conversion reaction (Fe, Li_2O , LiF) are generally known to be as 142 big as couples of nanometers, which can make them invisible in 143 XRD due to the peak-broadening. When the lithium ions were 144 extracted, the crystal structure was not reverted to the original 145 rutile. However, the diffraction peaks shifted to higher angle 146 during charge, or *d*-spacings became smaller, indicating that 147 lithium extraction did not induce dramatic structural changes 148 like lithium insertion and the structural development during 149 discharge is mainly reversible during charge. 150

Local structural evolutions were studied with an in situ TEM 151 dry cell approach.^{6,20-22} Li/Li₂O on a tungsten tip as anode 152 directly touched a FeCoOF nanowire (top of the sample at 153 Figure 3a, W tip is not shown here) and a negative bias was 154 f3 applied to the sample to promote the lithium diffusion over 155 interfacial resistance. Time-sequence bright-field (BF) TEM 156 images and a video of this experiment are presented in Figure 3 157 and supporting movie S1, respectively. When lithium ions were 158 introduced, the movement of the reaction front was clearly 159 observed (indicated with yellow dotted lines in Figure 3a) 160 accompanying an expansion of nanowire (Figure 3d). Parts b 161 and c of Figure 3 present the selected area electron diffraction 162 (SAED) patterns before and after fully lithiation, respectively. It 163 is found that the pristine rutile structure was transformed to Fe, 164 LiF, and Li₂O phases after 198.7 s, indicating the FeCoOF 165 sample underwent a conversion stage, which occurs at much 166 lower potential.¹⁵ Figure 3d presents the changes in the width of 167 the nanorod at two spots (A and B) as well as the movement of 168 reaction front as a function of reaction time. Changes at "A" 169 position interestingly show a stepwise increase in the width of 170 nanowire, suggesting a series of structural changes may occur 171 with lithium insertion. After full lithiation, Fe, Co, O, and F 172 elemental maps, acquired by scanning TEM (STEM)-electron 173 energy-loss spectroscopy (EELS), are presented in Figure 3e. 174 Homogeneous distributions of Fe and Co are found in the 175 nanorod with an oxygen-rich surface and a fluorine-rich core, 176 which is consistent with previous reports of iron (cobalt) 177 oxyfluorides.^{11,15} We note that the F/O core-shell distribution 178 was formed even without the existence of organic electrolyte 179 which should be originated from the intrinsic bonding natures of 180 iron oxyfluorides. Further in situ selected area electron 181



Figure 3. (a) Time-series of bright-field TEM images from *in situ* lithiation of a single nanorod of FeCoOF. Electron diffraction patterns acquired (b) before and (c) after *in situ* lithiation. (d) Projected width and reaction front movement in function of lithiation time. Widths of nanowire are tracked at two different positions of A and B shown in (a). (e) STEM-EELS elemental maps after lithiation. Scale bar: (a) 50 nm, (e) 10 nm, respectively.

182 diffraction (SAED) during lithiation (Figure S5 and movie S2)
183 confirms intermediate phases emerged and then disappeared
184 during reaction though the diffraction peaks from these phases
185 are too broad to be attributed to certain phases.

Comparing in situ XRD and in situ TEM, detailed 186 187 experimental details may differ: (i) Testing parameters (ending ootential, C-rates, etc.) are controllable for in situ XRD while 188 limited control is possible for in situ TEM. (ii) In situ XRD was 189 performed with conventional liquid electrolyte (1 M LiPF₆ in 190 191 EC and DMC) but naturally oxidized Li₂O on Li metal was used 192 as an electrolyte for *in situ* TEM experiments. (iii) While liquid electrolyte was impregnated into the FeCoOF electrode during 193 the in situ XRD experiment, we only had point contact between 194 FeCoOF and Li₂O in the open-cell configuration for in situ 195 196 TEM. Despite these experimental discrepancies, we believe that 197 lithiation induced phase transformations take place in the same 198 fashion since the phase transformations are the processes to 199 achieve thermodynamically favorable phases upon lithiation.

To track intermediate phases, we performed in situ high- 200 resolution TEM (HRTEM) imaging during lithiation to record 201 lattice rearrangement of FeCoOF (Figure 4a,b and movie S3). 202 f4 Figure S1a presents a HRTEM image along the [001] zone axis 203 acquired from the sample at Figure 4a before lithiation. After the 204 W tip touched the TEM specimen, the nanorod was a little off 205 from the [001] zone axis; however, the corresponding fast 206 Fourier transformation (FFT) patterns (Figure 4b) can still be 207 indexed and show the phase evolution, based on both lattice 208 orientation and lattice constants of Figure S1a. After Li ions 209 inserted into rutile structure, they initially occupied the empty 210 spaces between Fe/Co-O/F octahedra to form the M1 211 structure (Figure 4c), which resulted in a slight distortion in 212 the crystalline unit cell (tetragonal to monoclinic). Further 213 lithiation triggers the rearrangement of Fe/Co-O/F octahedra 214 possibly due to the electrostatic repulsion between Li⁺ and Fe ₂₁₅ (Co) ions.²³ Figures S6 and 4c-ii present the phase transition 216 from M1 to M2: a displacement of a cation at the body-centered 217



Figure 4. (a) HR-TEM images at high magnification during lithiation processes of FeCoOF. Scale bar: 5 nm. (b) Corresponding fast Fourier transformation patterns acquired from (a). R, M1, M2, and RS denote rutile, monoclinic1, monoclinic2, and rocksalt structures, respectively. (c) Atomic structural changes with inserting Li into FeCoOF. (d) Changes in the cation—anion arrangement of Fe/Co–O/F octahedra. A, B, C, and B' indicate the Fe (Co) cation at the center of octahedra. (e) Voltage profiles of different reaction pathways upon lithiation obtained by first-principles calculation.

218 position to in the middle of two octahedrons, which shared a 219 corner with a body-centered octahedron (in other words, to the 220 midpoints of the (001) face of M1 phase (colored in red at 221 Figure S6b-iii) and the rearrangement of anions. This transition changes anion arrangement close to cubic packing. Interestingly, 222 the M2 structure is similar to the layered structure of $LiCoO_{24}$ 223 suggesting that this transition makes the diffusion channels of 224 225 lithium ions change from 3D to 2D. In addition, we can find the 226 LiF phase with evolution of the M2 phase (Figure 4a, 197.2 s), indicating that the second phase transition accompanies with an 2.2.7 228 extrusion of LiF. This extrusion reaction was also suggested in previous reports.^{15,17} Figure 4d shows the schematic of 229 relocation of Fe (Co) cations from rutile to rocksalt. During 230 this process, the arrangement of octahedra is distorted but 231 octahedral bonding character is intact, which may largely reduce 232 the formation energy for phase transformations. Rutile and M1 233 structures are nearly same. The angle among the cations at the 234 235 center of adjacent octahedra ($\angle ABC$ at Figure 4d) is 49.8° in rutile structure and becomes 45.9° in M1. Bonding distance of 236 $_{237}$ AB and BC is 3.62 and 3.8 Å in rutile and M1, respectively, indicating intercalation of Li ions introduces a slight structural 238 deformation but no significant changes occur. On the other 239 240 hand, during M1-M2 transition, bonding character was 241 modified from corner-sharing octahedra to edge-sharing 242 octahedra, which brings about a contraction of unit cell in c 243 direction (Table 1). In the M2 structure, the bonding distance

between cation ions becomes much shorter (3.17 Å) while the 244 angle among the cations ($\angle AB'C$) increases to 61.3°. This 245 rearrangement makes oxygen framework close to cubic-close- 246 packed, inhibiting volume expansion. Bonding length and angles 247 were obtained from the atomic model based on the lattice 248 parameters in Table 1. In addition, cation doping could be 249 advantageous to retain a long-range order before conversion 250 reaction, as bonds of Co-O and Co-F are stronger than those 251 of Fe–O and Fe–F in pristine structure (Table S1). Further 252 lithium insertion induces cation disordering among Li and Fe/ 253 Co, resulting in a formation of rocksalt phase observed in 217.4 254 s. Comparing the unit cell volume of each phase (Table 1), it is 255 found that a series of phase transformations from rutile to 256 rocksalt does not bring a significant volume expansion (at most 257 13.4%), which may partially be attributed to extrusion of LiF 258 while the overall structural framework is being changed from M1 259 to M2 and from M2 to rocksalt. Limited volume expansion may 260 be beneficial to keep structural integrity during operation. 261

DFT calculations were performed to examine how the 262 suggested reaction pathway revealed from *in situ* works affects 263 the discharging processes. Figure 4e presents the calculated 264 voltage profiles with three different pathways: conversion 265 (blue), intercalation to LiFeOF (green), and the proposed 266 pathway (red). To draw the voltage profile, the most 267 energetically favorable Li composition/position were first 268 identified for each phase (Figure S7a). In particular, the most 269

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270 stable Li and F stoichiometry were found in $Li_{(0.625-x)}FeOF_{(1-x)}$ 271 having an M2 structure (Figure S7b). The DFT calculations 272 show the conversion route is the thermodynamically favorable 273 lithiation pathway with the highest equilibrium potential, as 274 shown in Figure 4e. However, the conversion route is known as a kinetically limited pathway due to the sluggish ionic diffusion 275 276 during the conversion reaction, and the much lower potentials shown in Figure 1a denied this route. The proposed route has 277 similar potential with the intercalation route. The calculated 278 phase change potentials for rutile-M1, M1-M2, and M2-2.79 280 rocksalt are 2.43, 2.25, and 1.69 V, respectively, corresponding to the experimental discharge-charge profile shown in Figure 2.81 282 1a. Obviously, the electrochemical mechanism of FeCoOF is 283 fundamentally modified with cosubstitution. In other words, 284 cosubstitution of Co and O stabilizes the thermodynamic 285 semistable phases and reduces the thermodynamic potential for 286 conversion reaction by reducing the critical size of Fe,¹⁵ which 287 favors the reaction pathways going from sluggish direct conversion to a series of kinetic favorable local topotactic 288 phase transformations at long-range order. As evidence, Table 289 290 S2 summarizes the cycling performance electrochemical proper-291 ties of iron fluorides and their derivatives, displaying the positive 292 effect of Co or/and O substitution and addition of water crystals 293 in iron fluorides. Oxygen substitution can induce the evolution of intermediate Li-Fe-O-F cubic phase during lithiation and 294 295 evolution of more durable O-rich surface.^{11,17} Cation doping in 296 iron fluoride can improve the electronic conductivity and reduce 297 the resistance for ionic diffusion^{13,14} or provide another redox $_{298}$ couple (e.g., Cu substituted FeF₂).²⁴ Considering the previous 299 endeavor of anion or cation substitution in iron fluorides, our 300 results demonstrate that the positive impact of each substituent can be combined and FeCoOF can be an effective presentation 301 302 of smart employment of other elements in iron fluorides. 303 Interestingly, a similar rutile to cubic phase transformation was $_{304}$ also observed in lithiation of MnO₂²³ suggesting the modified 305 reaction pathway in FeCoOF can be a general process governing 306 other rutile systems which needs further explorations.

307 CONCLUSION

308 In this work, we investigated the reaction pathway of FeCoOF 309 using multimodal in situ synchrotron X-ray and in situ electron 310 microscopy techniques. The intercalation-extrusion-cation 311 disordering mechanism was found for lithiation, which 312 substantiates the lithiation over an extended range of potentials 313 without a conversion reaction. The reaction pathway revealed in 314 this work involves a local topotactic rearrangement of Fe/Co-315 O/F octahedrons, from corner-sharing octahedra to edge-316 sharing octahedra. The diffusion channels of Li⁺ were 317 accordingly modified from 3D diffusion in rutile structure to 318 2D diffusion in M2 structure. Further lithiation led to the 319 formation of a rocksalt structure where the diffusion channels were blocked and the conversion reaction occurred afterward. 320 Our DFT calculations indicate that this reaction pathway was 321 322 stabilized by the cosubstitution, which thus makes the cycling of 323 FeCoOF more reversible. This work shows that the cosubstitution of anion and cation to conversion-type material is an 324 325 intriguing strategy to tune the reaction chemistry, which 326 provides a greater degree of freedom to adjust the electro-327 chemical properties of electrode materials in designing 328 alternative battery systems.

METHODS

Material Synthesis. Details in synthesizing $Fe_{0.9}Co_{0.1}OF$ were 330 described in the Methods section of a previously published paper.¹⁵ 331

Transmission Electron Microscopy (TÉM). In situ TEM 332 observation were conducted with a JEOL 2100F transmission electron 333 microscope at an accelerating voltage of 200 kV. A nanofactory 334 scanning tunneling microscopy (STM)-TEM holder was exploited for a 335 construction of open-cell where Li/Li₂O on piezo-driven W tip served 336 as anode/solid electrolyte, and Fe_{0.9}Co_{0.1}OF samples were working 337 electrodes. During the *in situ* lithiation, a constant negative bias was 338 applied to the samples to promote the movement of Li. Analytical TEM 339 analysis before/after *in situ* lithiation or before/after electrochemical 340 tests were performed with JEOL 2100F, Thermo-Fisher Talos F200X, 341 and Hitachi HD2700C with a probe corrector, all of which were 342 operated at 200 kV.

Electrochemical Tests. The electrode was prepared as a mixed 344 slurry of 70 wt % of active electrode material ($Fe_{0.9}Co_{0.1}OF$), 15 wt % of 345 conducting carbon, and 15 wt % of polyvinylidene fluoride (PvDF) 346 binder in an N-methylpyrrolidone (NMP) solvent. The mixed slurry 347 was coated onto an Al foil, which was a current collector. The 2032-type 348 of coin cells were assembled with Li metal for an anode, a Celgard 349 separator, and an electrolyte of 1 M lithium hexafluorophosphate 350 (LiPF₆) dissolved in ethylene carbonate (EC)/dimethyl carbonate 351 (DMC) (1:1 in weight). Battery tests were performed on either an 352 Arbin BT2000 battery test station or Biologic SP-200 potentiostat. 353

Synchrotron X-ray Diffraction. In situ X-ray diffraction and PDF 354 experiments were performed at the beamline 28-ID-1 at the National 355 Synchrotron Light Source-II (NSLS-II), Brookhaven National 356 Laboratory, with a wavelength of 0.1885 Å. For in situ measurements, 357 a 2032 type of coin cell was modified with 3 mm diameter coaxial holes 358 on both sides. The holes were sealed with polyimide (Kapton) tapes. 359 For PDF analysis, electrochemical tests were performed ex situ in coin 360 cells. After reaching certain voltages during electrochemical tests, coin 361 cells were disassembled, and electrodes were cleaned with DMC 362 solutions to reduce any residues. Active materials were obtained by 363 abrading Al foils and filled in capillary tubes for PDF analysis. Different 364 image plate detectors were used for diffraction and PDF measurement, 365 respectively. 2-Dimensional (2D) data were integrated into 1- 366 dimensional (1D) pattern using the Fit2D software²⁵ for both 367 diffraction and PDF. xPDFsuite²⁶ software was utilized to process the 368 1D diffraction pattern to acquire G(r), PDF via a sine Fourier transform 369 of the normalized scattering intensity S(Q)370

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) \, dQ$$

where $\rho(r)$ is the microscopic pair density, ρ_0 is the average number 371 density, and Q is the magnitude of the scattering vector. For elastic 372 scattering, $Q = 4\pi \sin(\theta)/\lambda$ where 2θ is the scattering angle and λ is the 373 wavelength of the radiation used.²⁷ Structure models were fitted to the 374 PDF data within PDFgui.¹⁶ 375

First-Principles Calculation. The voltage profiles for the 376 conversion and intercalation path are redrawn according to our 377 previous work.¹⁵ To study the equilibrium potential profile for the 378 proposed path, the ordered structures were enumerated from the 379 disordered structures for M1, M2, and rocksalt phases extracted from 380 the PDF analysis using pymatgen.²⁸ Ten structures obtained by sorting 381 the Ewald summation energy for each phase were calculated to get 382 accurate energies by density functional theory (DFT).²⁹ The most 383 energy favorable structure for each phase was used to calculate the 384 potential profile. All DFT calculations were performed using the Vienna 385 Ab initio Simulation Package (VASP)³⁰ within the projector 386 augmented-wave approach,³¹ and the Perdew-Burke-Ernzerhof 387 (PBE) generalized gradient approximation (GGA) functional was 388 used.^{31,32} In structures containing Fe (Co) and O or F, a value of U = 3894.0 eV (3.32 eV) was used for Fe (Co), as in our previous work. 15 Spin- $_{\rm 390}$ polarized total energy calculations and structure relaxations were 391 performed. The structural matching results were visualized using 392 VESTA.³ 393

394 ASSOCIATED CONTENT

395 **Supporting Information**

396 The Supporting Information is available free of charge at 397 https://pubs.acs.org/doi/10.1021/acsnano.0c03714.

398 Electron microscopy images of pristine FeCoOF, details

about PDF fitting and *in situ* XRD, *in situ* SAED during
 lithiation, atomic models presenting phase transforma-

tions, and details about DFT calculations; tables for
 comparing bonding lengths in pristine material and a

403 summary of cycling performances of iron fluorides and404 their derivatives (PDF)

- 405 In situ TEM video 1 (AVI)
- 406 In situ TEM video 1 (AVI) 406 In situ TEM video 2 (AVI)
- 406 In situ TEM video 2 (AVI) 407 In situ TEM video 3 (AVI)

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443 Notes

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