Structural Changes in a High-Energy Density VO₂F Cathode upon Heating and Li Cycling

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S Supporting Information

ABSTRACT: Structural changes in VO₂F, which allow twoelectron transfer during electrochemical Li cycling, were investigated. This compound adopts a rhombohedral structure, space group R3c, with O and F sharing one site, and was synthesized by high-energy ball-milling. The thermal stability of VO₂F, which is related to the battery safety, is studied by in situ XRD upon heating and by thermal gravimetric analysis. VO₂F is found to be stable up to 160 °C under inert atmosphere; above this temperature, it converts into vanadium oxide with fluorine loss. The structure evolution upon



lithium cycling was studied by ex situ X-ray diffraction and absorption techniques. The results show that lithiation of VO₂F goes through a solid-solution reaction, and the rhombohedral structure is preserved if no more than one lithium ion is intercalated. Upon a second Li insertion, an irreversible transition to a rock-salt structure occurs. We show using first-principles calculations that this irreversible transformation can be explained by an asymmetric energetic preference between the rhombohedral and rock-salt forms of $Li_{v}VO_{2}F$, which result in large thermodynamic driving forces to convert to the rock-salt structure at x > 1 and relatively small thermodynamic driving forces to convert back to the rhombohedral structure when delithiating to x < 1.

KEYWORDS: lithium ion battery, cathode, vanadium oxyfluoride, thermal stability, structure evolution

INTRODUCTION

Lithium ion batteries (LIBs) have been successfully launched in the market for portable electronic devices. However, to meet the demands of electrical vehicles, lithium ion batteries with higher energy density are required.¹⁻⁸ Tremendous efforts are devoted to the development of the advanced cathodes for lithium ion batteries, since the working voltage and cost of LIBs are usually constrained by the cathode part.9-18 The voltage of a cathode is related to the electronic and crystal structure of the active compound, which reflects its chemical bonding. Fluoride-based materials, which have strong M-F bonds, could offer a higher average working potential than oxide compounds. However, pure metal fluorides are usually insulating and exhibit sluggish kinetics and low Coulombic efficiency.¹⁹⁻²² Partial substitution of oxygen with fluorine could offer a higher average working potential than pure oxide compounds and better conductivity than pure fluoride-based compounds.^{14,23–28}

Li₂VO₂F with a disordered cubic rock-salt structure (c- Li_2VO_2F , space group $Fm\overline{3}m$) reported by Chen et al. in 2015 has a theoretical capacity of 462 mAh/g, which significantly exceeds that of the conventional LiCoO₂ and LiFePO₄ cathode materials.²³ This high theoretical capacity and initially lithiated state make Li₂VO₂F a competitive cathode candidate. We have previously investigated the thermal stability and structure evolution of Li₂VO₂F and demonstrated that the disordered rock-salt structure is stable up to 250 °C under argon atmosphere and is preserved upon Li cycling.¹¹ However, we could not completely extract the two Li ions to form VO₂F.

The VO_2F phase with a rhombohedral R3c structure (r-VO₂F) was synthesized by Perez-Flores et al. using a hightemperature high-pressure solid-state reaction.²⁷ This structure is different from the disordered rock-salt structure of c-Li₂VO₂F. r-VO₂F was shown to initially intercalate more than 1.5 Li with a sloping voltage profile from 3.9 to 2.2 V followed by a plateau at 2.15 V. In subsequent cycles, the plateau was not observed.²⁷ Later, VO₂F was also prepared by high-energy ball-milling.^{25,28} After ball-milling, the material was found to

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Figure 1. (a) X-ray diffraction pattern of r-VO₂F with Rietveld refinement. Inset shows structure model. (b) TEM image and (c) selected area electron diffraction of r-VO₂F. (d-g) TEM-EDX images of V, O, and F element distribution in r-VO₂F.

deliver higher capacity with a sloping voltage profile upon one Li cycling. This material was found to cycle about one Li in the voltage range of 2.1 to 4.3 V, in a continuous solid-solution $\text{Li}_x \text{VO}_2 \text{F}$, delivering about 208 mAh/g over 20 cycles at C/ 20.²⁵ A structural transition to the c-Li_xVO₂F phase was observed upon deeper discharge to 1.3 V.²⁸ However, the exact composition of $\text{Li}_x \text{VO}_2 \text{F}$ when the transformation from rhombohedral to cubic phase occurs remains not clear, and the relative stability of the cubic and rhombohedral phases of $\text{Li}_x \text{VO}_2 \text{F}$ as a function of Li content deserve further investigation.

In this paper, we investigate the stability of r-VO₂F upon heating and Li cycling. The thermal stability of electrode compounds plays a key role in the safety of lithium ion batteries, especially in large-scale automotive applications. Both Li_2VO_2F and VO_2F should ideally be stable over the battery working temperature range to ensure their safe use in lithium ion batteries. We also investigate the structural transition of rhombohedral VO_2F to rock-salt Li_xVO_2F upon cycling more than one lithium ion, both experimentally and using firstprinciple calculations.

EXPERIMENTAL METHODS

 VO_2F was prepared by mixing V_2O_5 and VOF_3 in a 1:1 molar ratio. The precursors, 0.5947 g of V_2O_5 and 0.4053 g of VO_2F , with 10 tungsten carbide balls (diameter = 10 mm) were sealed inside 50 mL tungsten carbide ball-milling jars and ball milled in a Retsch PM 100 machine for 20 h. After planetary ball-milling, the powder was collected in a helium-filled glovebox. The VO_2F powder was found to be air and moisture sensitive; therefore, all further sample preparation, including electrode making, was done in a helium-filled glovebox.

Room-temperature X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance diffractometer with Bragg–Brentano geometry and a Cu K α source. The samples were mounted on a Bruker domed sample holder in a helium-filled glovebox to avoid air exposure during the measurements. Phase identification was performed using Bruker DIFFRAC.EVA software coupled with the PDF-2016 database, while Bruker TOPAS (version 5.0) was used for the Rietveld refinement.

Thermogravimetric analysis (TGA) coupled with mass spectrometry (MS) was performed on TG 209 FI IRIS, Netzsch, by heating the sample loaded in an aluminum crucible at 5 °C/min under N_2 flow. In situ heating XRD under helium flow from room temperature to 700 °C was tested at beamline 17 BM Advanced Photon Source, Argonne National Laboratory. During testing, the sample was placed inside a capillary with the two ends connecting the tube for gas flow through. The resistive heater wire around the capillary provides the heating, with a thermocouple placed inside the capillary controlling the temperature. More details about this in situ heating setup can be found elsewhere.²⁹ The heating protocol was as follows. First, the sample was heated at 20 °C/min from room temperature to 250 °C, then 5 °C/min heating was used from 250 to 350 °C, followed by holding at 350 °C for 10 min. Further heating from 350 to 700 °C was done at 5 °C/min. After finishing the heating sequence, the sample was cooled down to 20 °C in 15 min. XRD patterns were collected continuously in this process.

XAS data were collected at beamline 9-BM, Advanced Photon Source, Argonne National Laboratory. Data processing was carried out using the software ATHENA of the package IFEFFIT.^{30,31} Transmission electron microscopy (TEM) work and electrochemical characterization were done in a similar way to that described in our previous work.¹¹ The details of these experimental methods can be found in the Supporting Information.

COMPUTATIONAL METHODS

We investigated the relative energies of the rhombohedral $(R\overline{3}c,$ denoted using an "r"-prefix) and cubic disordered rock-salt $(Fm\overline{3}m,$ denoted using a "c"-prefix) structures of Li_xVO₂F (x = 0, 0.5, 1, 1.5, and 2) using density functional theory (DFT) calculations.

The r-VO₂F crystal exhibits disorder on the O and F sites. We first enumerated and computed the energies of all symmetrically distinct O-F orderings in the $1 \times 1 \times 3$ supercell of r-VO₂F. The lowestenergy ordering of VO₂F (see below for details) was then used to generate the r-Li_xVO₂F structures. Specifically, the set of possible Li interstitial sites in VO₂F were first identified using a Voronoi tessellation-based algorithm, followed by structural enumeration for all distinct Li orderings at each given x of 0.5, 1, 1.5, and 2.

The c-Li₂VO₂F crystal exhibits both Li–V as well as O–F disorder. To obtain candidate structures for c-Li_xVO₂F (x = 0, 0.5, 1, 1.5, and 2), the Li–V ratio was modified from the disordered c-Li₂VO₂F to achieve the necessary Li concentration, followed by an enumeration of all symmetrically distinct orderings based on the modified structure. The energies of all orderings were then computed.

The DFT total energy calculations were performed using the Vienna Ab Initio Simulation Package (VASP) package within the projector augmented wave approach.³² The electron–electron exchange correlation was described using the Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA)³³ functional with the application of an effective Hubbard U^{34-36} of 3.25 eV for vanadium (GGA + U), similar to that used in the Materials Project.³⁷ A plane wave energy cutoff of 520 eV and *k*-point density of at least 1000/(number of atoms in unit cell) was used for all calculations. With these parameters, the energies are converged to be



Figure 2. (a) In situ XRD patterns of r-VO₂F upon heating under helium atmosphere from room temperature to 700 °C; (b) schematic diagram of vanadium-based phase structures formed upon heating; (c) image of reaction set up from 17BM, APS in Argonne National Lab; (d) Rietveld refinement result of VO₂F heated at 250 °C; (e) phase evolution upon heating of VO₂F; (f) TGA–MS curves of VO₂F from room temperature to 700 °C.

within 5 × 10⁻⁵ eV/atom. We also performed calculations using the screened hybrid Heyd–Scuseria–Ernzerhof (HSE) functional for the lowest-energy Li_xVO₂F configurations (*x* = 0, 1, and 1.5) as a basis of comparison with the GGA + U and experimental voltages.³⁸

RESULTS AND DISCUSSION

The structure of as-synthesized VO₂F was determined by powder X-ray diffraction. The Rietveld refinement (Figure 1a) shows that VO₂F has a rhombohedral structure with space group $R\overline{3}c$ (space group number: 167). The lattice parameters, a = b = 5.1371(3) Å, c = 13.0129(8) Å, and volume V =297.4(4) Å³, are in good agreement with literature report.²⁸ The structure model is shown in the inset of Figure 1a. r-VO₂F has an anion disordered structure where O and F share one site. The V–O/F octahedra are linked by corner sharing and form a three-dimensional rhombohedral structure. The morphology, element distribution, and selected area electron diffraction (SAED) were studied using TEM. The related images (Figure 1b,d) reveal 400–700 nm secondary particles made of smaller nanoparticles for the as-synthesized r-VO₂F. The SAED patterns can be indexed to the same $R\overline{3}c$ space group as the XRD patterns. In addition, EDX was carried out to detect the element distribution in the as-synthesized r-VO₂F. EDX results show that the O, F, and V are uniformly distributed within the particles.



Figure 3. (a) Charge and discharge curves of $r-VO_2F$ in the 1st, 2nd, and 10th cycles tested at C/20 from 2.0 to 4.1 V and (b) corresponding cycling data for $r-VO_2F$ involving one lithium cycling; (c) cycling data of $r-VO_2F$ from 2.0 to 4.1 V at different C rates involving one lithium ion; (C rates from C/60 to C, followed by jump back to low rates of C/60 and C/20); (d) charge and discharge curves of $r-VO_2F$ in 1st, 2nd, and 10th cycles tested at C/20 from 1.3 to 4.1 V and (e) corresponding cycling data for $r-VO_2F$ involving more than one lithium in the electrochemical cycle; (f) cycling data of $r-VO_2F$ at different C rates for more than one lithium ion involved. (1C = 526 mAh/g).

The r-VO₂F has only been synthesized by either highpressure solid-state or ball-milling methods so far.^{25,27,28} This raises the question of its thermal stability, which is a crucial factor related to the reliability and safety of its use in lithium ion batteries. In situ XRD studies combined with TG-MS (Figure 2) were conducted to investigate the thermal stability of r-VO₂F under helium atmosphere from room temperature to 700 °C. The related XRD patterns are shown in Figure 2a, and a schematic diagram of vanadium-based structures formed upon heating of VO₂F is shown in Figure 2b. Rietveld refinement was used to index the XRD patterns and determine phase contents. One example of the Rietveld refinements, VO₂F heated at 250 °C, is shown in Figure 2d, and the related results are summarized in Figure 2e. TG-MS results used to monitor the weight change and gas release during heating of VO₂F up to 700 °C under N₂ are presented in Figure 2f.

Both XRD and TGA-MS show that VO₂F is stable up to 160 °C in helium. Upon a temperature increase to 170 °C, VO₂F starts to decompose, and V₂O₅ is observed along with VO₂F in XRD patterns. These two phases coexist from 170 to 350 °C. The ratio of V2O5 to VO2F increases over this temperature range, indicating VO₂F decomposition. At 350 °C, still about 10% of VO₂F exists according to the Rietveld refinement result. However, upon holding at this temperature for 10 min, VO_2F completely decomposes into V_2O_5 , and some V₄O₉ forms. This result is in a good agreement with the TGA test (Figure 2f), which indicates an onset of weight loss at about 170 °C, and a sharp two-step weight loss from 200 to 400 °C. The MS data shows F (19) peak and 85 peaks assigned to VOF at each of the two weight-loss steps. No oxygen or water MS signals were observed. Combining the in situ XRD and MS data, we propose the chemical reaction upon thermal decomposition of VO₂F from room temperature to 400 °C:

$$\begin{split} 8 VO_2 F &\rightarrow V_2 O_5(solid) + V_4 O_9(solid) + 2 VOF(gas) \\ &+ 3 F_2(gas) \end{split}$$

The weight loss calculated according to this equation is about 35%, which is in a good agreement with the TGA test showing similar weight loss from room temperature to 400 °C. Upon a further temperature increase to 500 $^{\circ}$ C, a V₆O₁₃ phase starts to form. However, at 600 °C, around 47% of silica is observed in the XRD pattern, which is attributed to the quartz tube damage by the fluorine released during the heating of VO₂F. At 700 °C, only silica is found in the XRD pattern. When the experimental setup was disassembled after cooling, the quartz capillary was in fact found broken. Taking into account that TGA-MS does not show weight change above 500 °C, we believe that we have captured the key phase transformations upon heating, before the capillary was broken. To summarize, the VO₂F phase converts to V₂O₅, V₄O₉, and V_6O_{13} with fluorine loss upon heating. V_2O_5 is a layered structure, where VO₅ pyramids are linked by corner and edge sharing to form two-dimensional layers. The long sixth V-O bond points toward the interlayer space. Compared to the layered structure of V2O5, the V4O9 structure is denser and linked in all three dimensions. It is formed by corner and edge sharing of VO₅ pyramids and VO₆ octahedra. The V_6O_{13} is even denser with double layers of VO₆ octahedra alternating with single layers; the layers being connected by corner sharing. This densification upon temperature increase may be attributed to higher stability of more dense and close packed structures at high temperatures. From the practical point of view, VO₂F thermal stability is high enough to satisfy the requirements of automotive applications and is at par with that of layered oxides.³⁹



Figure 4. (a) XRD patterns of VO_2F tested between 2.0 and 4.1 V at different states of charge in the first and second cycles; related lattice parameters, *a* and *c*, at different states of charge, are shown in (b) and (c), respectively.



Figure 5. (a) XRD patterns of VO₂F tested between 1.3 and 4.1 V at different states of charge in the first and second cycles. Unmarked peaks at 31.5, 35.6, and 48.3° belong to WC impurity introduced by ball-milling; (b) evolution of lattice parameter *a* of the rock-salt phase at different states of charge.

The electrochemical performance of $r-VO_2F$ was determined by galvanostatic cycling (Figure 3). Two different electrochemical voltage windows (2.0–4.1 and 1.3–4.1 V) were selected and compared to study the influence of the amount of lithium ions involved in the reaction on the cycling performance. In the 2.0–4.1 V voltage window, a capacity of 276 mAh/g (1.04 Li) was delivered in the first cycle at C/20, which dropped to 206 mAh/g (0.8 Li) in the second cycle (Figure 3a). However, very good cyclability was obtained after the second cycle: around 97.5% capacity of the second cycle was kept after 100 cycles (Figure 3b). Within the extended cycling voltage window (1.3–4.1 V), more than one lithium ion would take part in the reaction, resulting in a much higher capacity: 406 mAh/g (1.54 Li) and 328 mAh/g (1.25 Li) in the first and second cycles, respectively (Figure 3d). However, the cyclability is much poorer than that within the narrower voltage window (2.0-4.1 V); only around 60% capacity of the second cycle is kept after 50 cycles (Figure 3e). Besides the cycling performance, the rate behavior in these two different voltage windows was compared (Figures 3c,f and S1). Similarly to the cycling performance: 58% capacity of C/60 at 1C vs 41% capacity of C/60 at 1C for the larger voltage window. Worse electrochemical performance over the larger voltage range may

be attributed to more significant structural changes involved with increased amount of Li cycled, as confirmed by the extra reduction peak observed at around 1.5 V for the larger voltage window (Figure S2).

To carefully study and compare the structural evolution during the lithiation and delithiation over these two different voltage windows, ex situ XRD was performed, and the results are shown in Figures 4 and 5. Figure 4 gives ex situ XRD patterns of VO₂F cycled between 2.0 and 4.1 V over the first and second cycles, where the samples were tested at C/60, and the cathode materials were collected at different charge and discharge states for the XRD test. It can be seen that the rhombohedral structure of VO₂F is preserved in the first and second cycles, as no extra peaks are found in the XRD patterns. Lattice parameters at each state were obtained by LeBail fitting; the results are shown in Figure 4b,c. The lattice parameter *a* only changes slightly during charge and discharge. On the contrary, the lattice parameter c clearly shows reversible increase and decrease with lithiation and delithitaion.

For the extended voltage window (1.3-4.1 V) (Figure 5), the XRD patterns do not reveal any major structural changes upon discharging to 2.0 V and are the same as that in Figure 4, indicating the same structural evolution during the reaction. However, upon lowering the discharge voltage to below 2.0 V, the peaks of the rock-salt structure like Li₂VO₂F are observed. The rhombohedral structure and rock-salt structure coexist in the discharge process at 1.7 and 1.5 V. Upon further lithiation to 1.3 V, the rhombohedral structure disappears, and only the peaks of rock-salt structure are observed. A similar structural change at the end point of r-VO₂F lithiation was previously observed.²⁸ Interestingly, upon charge back to 4.1 V, the compound does not revert to the rhombohedral structure, and the rock-salt structure is preserved upon the following electrochemical cycling. A reversible decrease and increase of the lattice parameter a of the rock-salt structure are observed during the charge and discharge steps due to the lithium intercalation and deintercalation from the structure (Figure 5b). This irreversible structural change is similar to the one observed upon Li cycling in V_2O_5 , which irreversibly converts from layered to the disordered rock-salt structure of ω - Li_3V_2OS upon discharge to 1.9 V, and this structure is preserved upon further Li cycling.⁴⁰ A similar transition is also observed upon lithiation of LiVO3, which irreversibly transforms to disordered rock-salt phase Li₂VO₃.⁴¹ It is interesting to note that the Li₂VO₃ structure obtained by chemical lithiation of LiVO3 has different cation ordering than that of Li₂VO₃ obtained by mechanochemical synthesis,¹⁹ while in the case of Li₂VO₂F, the electrochemically and mechanochemically obtained materials appear to have similar structures.

To further confirm the transition to the rock-salt phase, we used X-ray absorption to characterize the local structure of the Li_2VO_2F obtained by electrochemical lithiation of rhombohedral VO_2F . The evolution of the vanadium valence during electrochemical cycling of VO_2F using XANES was studied by Chen et al.²⁸ Their results indicate vanadium valence decrease with lithium insertion into VO_2F and increase with lithium ion extraction. Here, to further verify the local structural changes upon insertion of more than one Li in Li_xVO_2F , EXAFS data of the sample discharged to 1.3 V and equilibrated at this voltage for 10 h were fitted using the rock-salt Li_2VO_2F phase.²³ Since Li_2VO_2F contains oxygen and fluorine anions in the ratio 2:1, an overall theoretical model explaining the experimental

EXAFS data involved the sum of two FEFF calculations, one based on all anions being O and the other based on all anions being F in the Li₂VO₂F structure. The amplitude of all oxygen backscattering paths in the FEFF calculations was set to 0.67, while that of all fluorine paths FEFF calculations was set to 0.33 (i.e., to account for O and F in a ratio of 2:1). The amplitude of all vanadium backscattering paths from both calculations was set to 0.5. A good agreement between the data and theory was achieved up to ~4 Å as shown in Figure 6, evidencing the formation of the Li₂VO₂F-type rock-salt phase. EXAFS fitting parameters for the sample discharged to 1.3 V are shown on Table S1.



Figure 6. EXAFS fit to the data of the VO_2F sample discharged to 1.3 V. The dotted lines indicate the fitting range.

The obtained data indicates that rhombohedral VO₂F can cycle up to one Li ion by a solid-solution reaction mechanism. However, when more than one lithium ion is inserted into the VO₂F, the rhombohedral structure irreversibly converts into the rock-salt structure. Further Li cycling in the rock-salt structure also occurs by the solid-solution mechanism. Cycling one Li within the rhombohedral phase ensures better cycling stability, while more than one Li cycling in the rock-salt phase leads to more significant capacity loss. It is also interesting to notice that the capacity fades faster at smaller current density, which suggests that reasons other than Li diffusion kinetics affect the electrochemical performance. Thus, to enable two Li cycling in VO₂F, two research directions can be taken. First, improve the structural stability of r-Li_xVO₂F over a wider range of Li content x, possibly through the transition metal substitution. Second, optimize the electrode and electrolyte composition to facilitate electronic and ionic transport and to minimize side reactions. For example, in this work, we used an electrolyte with FEC, as it helps to improve the capacity and cycling stability as compared to the standard EC-DMC-based electrolyte.

To gain more insights into the phase evolution during cycling, we performed first-principles DFT calculations to evaluate the energetic preference between the rhombohedral (r-) and rock-salt (c-) $\text{Li}_x \text{VO}_2\text{F}$ at x = 0, 0.5, 1, 1.5, and 2. From Figure 7, we may observe that while r-VO₂F is 18 meV/ atom lower in energy than c-VO₂F, c-Li_xVO₂F becomes increasingly energetically favored over r-Li_xVO₂F with lithiation. In particular, lithiation beyond x = 1 results in a strong energetic preference for the cubic disordered rock-salt phase; the energies of the c-Li₁SVO₂F and c-Li₂VO₂F are ~48





and 135 meV/atom lower than those of r-Li₁₅VO₂F and r-Li₂VO₂F, respectively. On the other hand, delithiation of c-Li₂VO₂F only results in a small thermodynamic driving force to convert back to the rhombohedral phase for x < 1. This asymmetric energetic preference between r-Li, VO2F and c- $Li_x VO_2 F$ supports our experimental observations of an irreversible transition to the cubic disordered rock-salt phase upon the insertion of more than one Li into r-VO₂F. We speculate that structural flexibility of the cubic rock-salt leads to larger average intercation (Li-V) distances (3.02, 2.93, and 3.00 Å for x = 1, 1.5, and 2, respectively) compared to the rhombohedral phase (2.94, 2.82, and 2.87 Å for x = 1, 1.5, and 2, respectively), leading to smaller coulombic repulsion and a clear energetic preference for the rock-salt phase at higher levels of lithiation. Similar instabilities with lithiation due to electrostatics have been observed in the rutile-like FeOF cathode,⁴² though LiFeOF undergoes a conversion to LiF, Fe, and other Li-Fe-O phases instead of a cubic rock-salt. We note that the voltages from both GGA + U and HSE calculations (3.52–3.72 V for r-VO₂F \leftrightarrow r-LiVO₂F and 3.19– 3.32 V for r-VO₂F \leftrightarrow c-Li_{1.5}VO₂F) are somewhat overestimated relative to the experimentally measured voltages (Figure 3a,d), though the relative energetic preference between the rhombohedral and cubic phases with state of lithiation are consistent between the two functionals.

CONCLUSION

In conclusion, we have investigated the structural stability of disordered rhombohedral r-VO₂F (space group $R\overline{3}c_{1}$, lattice parameter is a = b = 5.1371(3) Å, c = 13.0129(8) Å) upon heating and Li cycling. Upon heating in an inert atmosphere, the structure is stable up to 160 °C, decomposing at higher temperatures to a series of vanadium oxides with fluorine release. Electrochemical lithiation of rhombohedral VO₂F proceeds through a solid-solution reaction and is structurally reversible, if limited to one lithium cycling. Under these conditions, VO₂F delivers 276 mAh/g (1.04 Li) and 206 mAh/ g (0.8 Li) at C/20 in its first and second cycles, respectively. After significant capacity loss in the first cycle, a good cycling stability is observed with around 97.5% of capacity maintained after 100 cycles. However, if more than one lithium ion is involved in the electrochemical cycling, the rhombohedral structure irreversibly converts into a disordered rock-salt structure. Under these conditions, around 406 mAh/g (1.54 Li) capacity was achieved with a testing rate of C/60. Cycling of more than one Li results in significant capacity decay with only around 60% of the initial capacity maintained after 50 cycles. DFT calculations reveal that the rock-salt $\text{Li}_x \text{VO}_2 \text{F}$ structure is energetically favorable for x > 1, and there is only a small driving force for conversion of this phase back to the

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ASSOCIATED CONTENT

rhombohedral structure upon delithiation.

Supporting Information

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Experimental details for TEM, XAS, and electrochemical characterization, charge–discharge curves of VO₂F at different current densities, cyclic voltammetry curves of VO₂F, and EXAFS fitting parameters of VO₂F discharged to 1.3 V (PDF)

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The authors declare no competing financial interest.

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REFERENCES

(1) Whittingham, M. S. Lithium Batteries and Cathode Materials. *Chem. Rev.* 2004, 104, 4271-4301.

(2) Whittingham, M. S. History, Evolution, and Future Status of Energy Storage. *Proc. IEEE* 2012, 100, 1518–1534.

(3) Whittingham, M. S. Ultimate Limits to Intercalation Reactions for Lithium Batteries. *Chem. Rev.* **2014**, *114*, 11414–11443.

(4) Chernova, N. A.; Roppolo, M.; Dillon, A. C.; Whittingham, M. S. Layered Vanadium and Molybdenum Oxides: Batteries and Electrochromics. J. Mater. Chem. 2009, 19, 2526–2552.

(5) Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, *22*, 587–603.

(6) Goodenough, J. B.; Park, K. S. The Li-Ion Rechargeable Battery: A Perspective. J. Am. Chem. Soc. 2013, 135, 1167–1176.

(7) Palacin, M. R. Recent Advances in Rechargeable Battery Materials: A Chemist's Perspective. *Chem. Soc. Rev.* **2009**, *38*, 2565–2575.

G

(8) Radin, M. D.; Hy, S.; Sina, M.; Fang, C.; Liu, H.; Vinckeviciute, J.; Zhang, M.; Whittingham, M. S.; Meng, Y. S.; Van der Ven, A. Narrowing the Gap between Theoretical and Practical Capacities in Li-Ion Layered Oxide Cathode Materials. *Adv. Energy Mater.* **2017**, *7*, 1602888.

(9) Wang, F.; Robert, R.; Chernova, N. A.; Pereira, N.; Omenya, F.; Badway, F.; Hua, X.; Ruotolo, M.; Zhang, R.G.; Wu, L. J.; Volkov, V.; Su, D.; Key, B.; Whittingham, M. S.; Grey, C. P.; Amatucci, G. G.; Zhu, Y.; Graetz, J. Conversion Reaction Mechanisms in Lithium Ion Batteries: Study of the Binary Metal Fluoride Electrodes. *J. Am. Chem. Soc.* **2011**, *133*, 18828–18836.

(10) Omenya, F.; Chernova, N. A.; Upreti, S.; Zavalij, P. Y.; Nam, K. W.; Yang, X. Q.; Whittingham, M. S. Can Vanadium Be Substituted into LiFePO₄? *Chem. Mater.* **2011**, *23*, 4733–4740.

(11) Wang, X. Y.; Huang, Y. Q.; Ji, D. S.; Omenya, F.; Karki, K.; Sallis, S.; Piper, L. F. J.; Wiaderek, K. M.; Chapman, K. W.; Chernova, N. A.; Whittingham, M. S. Structure Evolution and Thermal Stability of High-Energy-Density Li-Ion Battery Cathode Li₂VO₂F. *J. Electrochem. Soc.* **2017**, *164*, A1552–A1558.

(12) Kang, K. S.; Meng, Y. S.; Breger, J.; Grey, C. P.; Ceder, G. Electrodes with High Power and High Capacity for Rechargeable Lithium Batteries. *Science* **2006**, *311*, 977–980.

(13) Urban, A.; Lee, J.; Ceder, G. The Configurational Space of Rocksalt-Type Oxides for High-Capacity Lithium Battery Electrodes. *Adv. Energy Mater.* **2014**, *4*, 1400478.

(14) Kim, S. W.; Pereira, N.; Chernova, N. A.; Omenya, F.; Gao, P.; Whittingham, M. S.; Amatucci, G. G.; Su, D.; Wang, F. Structure Stabilization by Mixed Anions in Oxyfluoride Cathodes for High-Energy Lithium Batteries. *ACS Nano* **2015**, *9*, 10076–10084.

(15) Devaux, D.; Wang, X. Y.; Thelen, J. L.; Parkinson, D. Y.; Cabana, J.; Wang, F.; Balsara, N. P. Lithium Metal-Copper Vanadium Oxide Battery with a Block Copolymer Electrolyte. *J. Electrochem. Soc.* **2016**, *163*, A2447–A2455.

(16) Meng, Y. S.; Ceder, G.; Grey, C. P.; Yoon, W. S.; Jiang, M.; Breger, J.; Shao-Horn, Y. Cation Ordering in Layered O3 $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3\cdot x/3}]O_2 \ (0 \le x \le 1/2)$ Compounds. *Chem. Mater.* **2005**, 17, 2386–2394.

(17) Wang, X. Y.; Hao, H.; Liu, J. L.; Huang, T.; Yu, A. S. A Novel Method for Preparation of Macroposous Lithium Nickel Manganese Oxygen as Cathode Material for Lithium Ion Batteries. *Electrochim. Acta* **2011**, *56*, 4065–4069.

(18) Lin, Y. C.; Hidalgo, M. F. V.; Chu, I.-H.; Chernova, N. A.; Whittingham, M. S.; Ong, S. P. Comparison of the Polymorphs of VOPO₄ as Multi-Electron Cathodes for Rechargeable Alkali-Ion Batteries. *J. Mater. Chem. A* **2017**, *5*, 17421–17431.

(19) Chen, R.; Ren, S.; Yavuz, M.; Guda, A. A.; Shapovalov, V.; Witter, R.; Fichtner, M.; Hahn, H. Li⁺ Intercalation in Isostructural Li_2VO_3 and Li_2VO_2F with O^{2-} and Mixed O^{2-}/F^- Anions. *Phys. Chem. Chem. Phys.* **2015**, *17*, 17288–17295.

(20) Amatucci, G. G.; Pereira, N. Fluoride Based Electrode Materials for Advanced Energy Storage Devices. *J. Fluorine Chem.* **2007**, *128*, 243–262.

(21) Gu, W. T.; Sevilla, M.; Magasinski, A.; Zdyrko, B.; Yushin, G. Metal Fluorides Nanoconfined in Carbon Nanopores as Reversible High Capacity Cathodes for Li and Li-Ion Rechargeable Batteries: FeF₂ as an Example. *Adv. Energy Mater.* **2015**, *5*, 1401148.

(22) Hua, X.; Robert, R.; Du, L. S.; Wiaderek, K. M.; Leskes, M.; Chapman, K. W.; Chupas, P. J.; Grey, C. P. Comprehensive Study of the CuF_2 Conversion Reaction Mechanism in a Lithium Ion Battery. *J. Phys. Chem. C* 2014, *118*, 15169–15184.

(23) Chen, R.; Ren, S.; Knapp, M.; Wang, D.; Witter, R.; Fichtner, M.; Hahn, H. Disordered Lithium-Rich Oxyfluoride as a Stable Host for Enhanced Li⁺ Intercalation Storage. *Adv. Energy Mater.* **2015**, *5*, 1401814.

(24) Ren, S.; Chen, R.; Maawad, E.; Dolotko, O.; Guda, A. A.; Shapovalov, V.; Wang, D.; Hahn, H.; Fichtner, M. Improved Voltage and Cycling for Li⁺ Intercalation in High-Capacity Disordered Oxyfluoride Cathodes. *Adv. Science* **2015**, *2*, 1500128. (25) Cambaz, M. A.; Vinayan, B. P.; Clemens, O.; Munnangi, A. R.; Chakravadhanula, V. S. K.; Kubel, C.; Fichtner, M. Vanadium Oxyfluoride/Few-Layer Graphene Composite as a High-Performance Cathode Material for Lithium Batteries. *Inorg. Chem.* **2016**, *55*, 3789– 3796.

(26) Barker, J.; Gover, R. K. B.; Burns, P.; Bryan, A.; Saidi, M. Y.; Swoyer, J. L. Structural and Electrochemical Properties of Lithium Vanadium Fluorophosphate, $LiVPO_4F$. J. Power Sources 2005, 146, 516–520.

(27) Perez-Flores, J. C.; Villamor, R.; Avila-Brande, D.; Gallardo Amores, J. M.; Moran, E.; Kuhn, A.; Garcia-Alvarado, F. VO_2F : a New Transition Metal Oxyfluoride with High Specific Capacity for Li ion Batteries. *J. Mater. Chem. A* **2015**, *3*, 20508–20515.

(28) Chen, R. Y.; Maawad, E.; Knapp, M.; Ren, S. H.; Beran, R.; Witter, R.; Hempelmann, R. Lithiation-Driven Structural Transition of VO₂F into Disordered Rock-Salt Li_xVO₂F. *RSC Adv.* **2016**, *6*, 65112–65118.

(29) Chupas, P. J.; Chapman, K. W.; Kurtz, C.; Hanson, J. C.; Lee, P. L.; Grey, C. P. A Versatile Sample-Environment Cell for Non-Ambient X-ray Scattering Experiments. *J. Appl. Crystallogr.* **2008**, *41*, 822–824.

(30) Newville, M. IFEFFIT: Interactive XAFS Analysis and FEFF Fitting. J. Synchrotron Radiat. 2001, 8, 322–324.

(31) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12, 537–541.

(32) Blochl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953–17979.

(33) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(34) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57*, 1505–1509.

(35) Liechtenstein, A. I.; Anisimov, V. I.; Zaanen, J. Density-Functional Theory and Strong-Interactions: Orbital Ordering in Mott-Hubbard Insulators. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1995**, *52*, R5467–R5470.

(36) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. Phospho-Olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. *J. Electrochem. Soc.* **1997**, *144*, 1188–1194.

(37) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* **2013**, *1*, 011002.

(38) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* **2003**, *118*, 8207–8215.

(39) Lu, L.; Han, X.; Li, J.; Hua, J.; Ouyang, M. A Review on the Key Issues for Lithium-Ion Battery Management in Electric Vehicles. *J. Power Sources* **2013**, *226*, 272–288.

(40) Delmas, C.; Cognac-Auradou, H.; Cocciantelli, J. M.; Menetrier, M.; Doumerc, J. P. The $Li_xV_2O_5$ system: An Overview of the Structure Modifications Induced by the Lithium Intercalation. *Solid State Ionics* **1994**, *69*, 257–264.

(41) Pralong, V.; Gopal, V.; Caignaert, V.; Duffort, V.; Raveau, V. Lithium-Rich Rock-Salt-Type Vanadate as Energy Storage Cathode: $Li_{2-x}VO_3$. *Chem. Mater.* **2012**, *24*, 12–14.

(42) Chevrier, V. L.; Hautier, G.; Ong, S. P.; Doe, R. E.; Ceder, G. First-Principles Study of Iron Oxyfluorides and Lithiation of FeOF. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 094118.