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High-Pressure Synthesis of Cation-Disordered Rock-Salt Oxyfluorides with High Crystallinity

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ABSTRACT

Lithium-excess transition metal (*M*) oxyfluorides, $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$, have received considerable attention as positive electrode materials for lithium-ion batteries. Little is known about the relationship between the crystallinity and electrochemical reactivities although this offers further understanding and improvement of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$, because conventionally ball-milled $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ exhibits limited crystallinity, i.e., amorphous-like nanoparticles. We herein adapted a high-pressure/high-temperature method at 12 GPa and 1000 °C to synthesize high-crystallinity $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ (*M* = Fe, Mn, V, Nb, Mo, and W) and investigated the electrochemical properties of this series. Rietveld analyses based on X-ray diffraction (XRD) and cross-sectional elemental mapping clarified that $\text{Li}_3\text{VO}_3\text{F}$ and $\text{Li}_4\text{WO}_4\text{F}$ crystallized as an almost-single-phase rock-salt structure with homogenous cation/anion distributions and formed well-faceted particles with sizes of 1–20 μm. Their rechargeable capacities over 1.8–5.0 V vs. Li^+/Li were ~40 mAh g⁻¹ and ~10 mAh g⁻¹, respectively. According to *ex situ* XRD measurements of the cycled $\text{Li}_3\text{VO}_3\text{F}$ electrodes, these partial rechargeable capacities were caused by a decomposition reaction during the initial charge, which differed from the topotactic reaction proposed for the low-crystallinity phases. This information is helpful for designing the microstructure of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ to improve its performance now that both crystal and amorphous $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ phases are attainable.

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1. Introduction

Lithium-excess transition metal (*M*) oxyfluorides, $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$, where *x* and *y* ($x \geq y > 0$) represent the amounts of Li and F, with a rock-salt structure (*Fm* $\bar{3}$ *m* space group) have recently drawn significant attention as high-energy-density positive electrode materials for lithium-ion batteries (LIBs) to realize a sustainable and decarbonized society.^{1,2} Assuming the transfer of *n* electrons, the electrochemical reaction of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ is reported to proceed in a topotactic manner as follows:^{1,2}

where the theoretical capacity (Q_{theo}), is expressed as a function of *x*, *y*, *n*, and *M*, when ignoring an O^{2-} removal reaction. In Fig. 1, the Q_{theo} of some $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ exceeds that of a currently commercialized positive electrode material, LiCoO_2 (= 274 mAh g⁻¹),³ e.g., 436 mAh g⁻¹ for Li_2MnOF_2 (*y* = 2), 431 mAh g⁻¹ for Li_3NbOF_3 (*y* = 3), and 497 mAh g⁻¹ for Li_4MoOF_4 (*y* = 4), when *n* = *y*.

Over the past half decade, V-,^{4–6} Mo-,^{7,8} and Mn-based^{9,10} $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ with *y* > ~1 have been reported. $\text{Li}_2\text{VO}_2\text{F}$ exhibits a discharge capacity (Q_{dis}) of ~420 mAh g⁻¹ in the range of 1.3–4.1 V vs. Li^+/Li ; however the charge capacity (Q_{cha}) is ~90 mAh g⁻¹ lower than the Q_{dis} in the initial cycle because of the lithium deficiency,⁴ as also observed in $\text{Li}_2\text{MoO}_2\text{F}$.⁷ When these compounds are operated in full cells with non-lithium-containing negative electrode materials such as graphite and silicon, this difference between Q_{cha} and Q_{dis} decreases the rechargeable capacity (Q_{recha}). On the other hand, $\text{Li}_{1.9}\text{Mn}_{0.95}\text{O}_{2.05}\text{F}_{0.95}$ displays Q_{recha} of 280 mAh g⁻¹ over 2–4.8 V, which corresponds to 150 mAh g⁻¹ from the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox and 130 mAh g⁻¹ from the O redox.⁹ The

Figure 1. Changes in Q_{theo} of a series of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ (*M* = Fe, Mn, V, Nb, Mo, and W), assuming the charge transfer number of *y*, along with Q_{theo} of LiCoO_2 .

latter reaction, which is caused by the overlapping energy levels of the Mn-3*d* and O-2*p* orbitals,^{2,10} triggers capacity fading during long-term cycling, as previously reported for $\text{Li}[\text{Li}_{0.15}\text{Mn}_{1.85}]\text{O}_4$.¹¹

Table 1. Synthesis conditions of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$: nominal compositions, starting materials, Q_{theo} , notations, and obtained phases.

nominal composition	starting materials	$Q_{\text{theo}}/\text{mAh g}^{-1}$	notation	phases*
LiFeOF	$\text{FeO} + \text{LiF}$	274	HP(Fe, 1)	$\text{FeO}^\dagger$, LiF
$\text{Li}_2\text{MnO}_2\text{F}$	$0.5\text{Mn}_2\text{O}_3 + \text{LiF} + 0.5\text{Li}_2\text{O}$	224	HP(Mn, 1)	$\text{MnO}^\dagger$, MnF_3 , LiF
Li_2MnOF_2	$\text{Li}_2\text{O} + \text{MnF}_2$	436	HP(Mn, 2)	$\text{MnO}^\dagger$, LiF
$\text{Li}_3\text{VO}_3\text{F}$	$0.25\text{V}_2\text{O}_3 + 0.25\text{V}_2\text{O}_5 + \text{LiF} + \text{Li}_2\text{O}$	193	HP(V, 1)	$\text{Li}_3\text{VO}_3\text{F}^\dagger$, LiV_2O_4 , LiF
$\text{Li}_3\text{VO}_2\text{F}_2$	$0.5\text{V}_2\text{O}_3 + 2\text{LiF} + 0.5\text{Li}_2\text{O}$	378	HP(V, 2)	$\text{VO}^\dagger$, LiF
$\text{Li}_3\text{NbO}_3\text{F}$	$\text{NbO}_2 + \text{LiF} + \text{Li}_2\text{O}$	148	HP(Nb, 1)	$\text{Li}_4\text{NbO}_4\text{F}$, $\text{Nb}_3\text{O}_7\text{F}$, $\text{LiNbO}_2^\dagger$, LiNbO_3 , Li_2O , LiF
$\text{Li}_3\text{NbO}_2\text{F}_2$	$0.5\text{NbO}_2 + 0.5\text{NbO} + 2\text{LiF} + 0.5\text{Li}_2\text{O}$	292	HP(Nb, 2)	$\text{LiNbO}_2^\dagger$, LiNbO_3 , NbO, LiF
Li_3NbOF_3	$\text{NbO} + 3\text{LiF}$	431	HP(Nb, 3)	$\text{NbO}^\dagger$, LiF
$\text{Li}_4\text{MoO}_4\text{F}$	$0.5\text{MoO}_2 + 0.5\text{MoO}_3 + \text{LiF} + 1.5\text{Li}_2\text{O}$	130	HP(Mo, 1)	$\text{Li}_{4+\delta_1}\text{Mo}_{1-\delta_1}\text{O}_{5-\delta_2}\text{F}_{\delta_2}$, Li_2MoO_4 , $\text{Li}_2\text{MoO}_3^\dagger$
$\text{Li}_4\text{MoO}_3\text{F}_2$	$\text{MoO}_2 + 2\text{LiF} + \text{Li}_2\text{O}$	256	HP(Mo, 2)	$\text{Li}_{4+\delta_1}\text{Mo}_{1-\delta_1}\text{O}_{5-\delta_2}\text{F}_{\delta_2}$, $\text{Li}_2\text{MoO}_3^\dagger$, LiMoO_2 , LiF
$\text{Li}_4\text{WO}_4\text{F}$	$0.5\text{WO}_2 + 0.5\text{WO}_3 + \text{LiF} + 1.5\text{Li}_2\text{O}$	91	HP(W, 1)	$\text{Li}_4\text{WO}_4\text{F}^\dagger$, $\text{Li}_2\text{W}_2\text{O}_7$
$\text{Li}_4\text{WO}_3\text{F}_2$	$\text{WO}_2 + 2\text{LiF} + \text{Li}_2\text{O}$	180	HP(W, 2)	$\text{Li}_4\text{WO}_{4-\delta_3}\text{F}_{\delta_3}^\dagger$, $\text{Li}_2\text{W}_2\text{O}_7$, $\text{Li}_2\text{WO}_4\text{F}$, LiF

*The primary phase of each sample is denoted by $\dagger$.

Regardless of several efforts to substitute the original M ($= \text{V}$,^{5,6} Mo,⁸ Mn¹⁰) with another, these two intrinsic drawbacks, i.e., the decrease and fading in Q_{recha} , remain unresolved.

Syntheses of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ exclusively have been entrusted to ball-milling methods,² which form only amorphous-like nanoparticles. Note that a solid-state method forms partially-fluorinated particles.¹² The limited structural and morphological state hinders further understanding and improvement of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$, including the remaining decrease and fading in Q_{recha} . Generally, an annealing treatment is utilized to control the microstructures of electrode materials and optimize their performance for LIBs, as two types of carbon negative electrode materials exist: crystalline graphite and amorphous hard carbon.¹³ Annealing, however, is inapplicable to the metastable $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ rock-salt phase. In this contribution, we employed a high-pressure/high-temperature (HP/HT) method to attain high-crystallinity $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ and thus to clarify the relationship between its crystallinity and electrochemical properties. The reason to select the HP/HT method was that the high concentration of F^- ions and the stabilization of the rock-salt structure are achievable under HP/HT conditions (12 GPa and $\sim 1000^\circ\text{C}$) as reported in $\text{CrO}_{2-p}\text{F}_p$ ($p \leq 0.3$)¹⁴ and Li–Co–Mn oxides,¹⁵ respectively, and the high crystallinity of the compounds is maintained. We successfully synthesized high-crystallinity $\text{Li}_3\text{VO}_3\text{F}$ and $\text{Li}_4\text{WO}_4\text{F}$ and revealed that their electrochemical reactions involving a decomposition reaction. They exhibited Q_{recha} of ~ 40 and $\sim 10 \text{ mAh g}^{-1}$ over 1.8–5.0 V, respectively, in contrast with the conventional topotactic reaction for the low-crystallinity phases.

2. Experimental

2.1 Sample preparation and phase identification

$\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ ($M = \text{Fe}$, Mn, V, Nb, Mo, and W) was synthesized using the HP/HT method with a Walker-type apparatus installed at Osaka Prefecture University.^{14,15} Table 1 lists the synthetic conditions such as the nominal compositions, starting materials, and Q_{theo} values. The nominal compositions were designed based on $\text{Li}_x\text{MO}_{1+x}$ oxides with a large Li (x) content to maximize Q_{theo} . Stoichiometric combinations of M oxide(s), LiF (Wako Pure Chemical Industries) (or MF_2), and Li_2O (Wako Pure Chemical Industries) were employed as starting materials. M oxides and MF_2

included FeO , MnF_2 , Mn_2O_3 , V_2O_3 , V_2O_5 , NbO, NbO₂, MoO₂, MoO₃, WO₂, and WO₃, all of which were purchased from Kojundo Chemical Industries, except MoO₂, which was obtained from Sigma-Aldrich. Approximately 100 mg of each stoichiometric mixture, which was sealed in a Pt capsule, was treated at 12 GPa and at 1000°C for 30 min. The procedure has been described in further detail elsewhere.^{14,15} Hereafter, the retrieved powdery samples are denoted by HP(M , y), as listed in Table 1.

Phases in the HP(M , y) samples were identified from X-ray diffraction (XRD) patterns (D8 ADVANCE, Bruker AXS), which were captured using Fe-K α radiation.

2.2 Characterization and electrochemical properties of HP(V, 1) and HP(W, 1) samples

Among the HP(M , y) samples, HP(V, 1) and HP(W, 1) samples crystallized as an almost-single-phase lithium-excess M oxyfluoride. Thus, the crystal structures were determined by Rietveld analyses using RIETAN-FP software¹⁶ and drawn using VESTA software.¹⁷ The particle morphologies and cross-sectional elemental distribution were examined by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX; SU3500, Hitachi High-Technologies) with an accelerating voltage of 15 kV. For the distributions of O, F, and V or W, the particles were embedded in epoxy resin and then cut into specimens with a polished flat side using a cross-section polisher with an Ar⁺ ion beam (SM-09010, JEOL). The surfaces were coated with Os, which was thin enough (2–3 nm) to detect the characteristic X-rays of O and F, by glow discharging (HPC-1S, Vacuum Device).

Electrochemical reactivities of HP(V, 1) and HP(W, 1) were examined using nonaqueous lithium cells. The working electrode was prepared in a dry process because the sample weight was less than 100 mg. Each sample was mixed with acetylene black (Denka), and polytetrafluoroethylene (Daikin Industries) at 70 : 20 : 10 wt%, and then, the black viscoelastic mixture was placed onto an Al mesh current collector with a diameter of 16 mm. Lithium pressed onto a stainless-steel plate with a diameter of 19 mm was used as the counter electrode, two sheets of a porous polyethylene membrane (Tonen-General Sekiyu) were utilized as the separator, and 1 M LiPF₆ dissolved in ethylene carbonate and dimethyl carbonate (3/7 by volume) (Kishida Chemical) was employed as the electrolyte.

Figure 2. XRD patterns of HP(*M*, *y*) samples with *y* = 1, 2, or 3: (a) *M* = Fe, (b) Mn, (c) V, (d) Nb, (e) Mo, and (f) W. Diffraction lines from the target lithium-excess *M* oxyfluorides are filled with orange and lime green in (c) and (f), respectively. Diffraction lines from unidentified phase(s) are marked by stars in (d).

The lithium cells were fabricated in an Ar-filled glove box. The cells were operated at a current density of 0.05 mA cm⁻² and at 25 °C, and the voltage range was set to 3–4.8 V for the first five cycles to examine the general properties of the positive electrode material and 1.8–5 V for the subsequent five cycles to reveal the entire reaction.

To clarify structural changes during the electrochemical reaction, the HP(V, 1) and HP(W, 1) electrodes were examined after cycling via *ex situ* XRD. The cycled sample was removed from the current collector and thoroughly rinsed with a diethyl carbonate solution (Kishida Chemical) in the Ar-filled glove box. The sample was sealed with polyimide tape to avoid any reactions with moist air during the measurements. Only the cycled HP(V, 1) sample was also inserted in a glass capillary tube with a diameter of 0.5 mm (WJM-Glas Müller), and then sealed with epoxy resin to obtain the XRD pattern with the improved signal-to-noise ratio, which was captured using Cu-Kα radiation.

3. Results and Discussion

3.1 Attempts to synthesize Li_xMO_{1+x-y}F_y by the HP/HT method

We first systematically conducted HP/HT syntheses of Li_xMO_{1+x-y}F_y to reveal the possible combinations of *M* and *y*. Figures 2a–2f show the XRD patterns of all the HP(*M*, *y*) samples with *y* = 1, 2, or 3 in the order *M* = Fe, Mn, V, Nb, Mo, and W. Table 1 summarizes the obtained products, and the primary phase in each sample is marked by †. Note that no compounds containing Pt was detected, indicating that the Pt capsule was unreacted with the

samples. The target lithium-excess *M* oxyfluoride with the rock-salt structure was observed in a limited combination of *M* and *y*, namely, HP(V, 1) and HP(W, 1) samples, as indicated by diffraction lines filled in orange and lime green, respectively (see Figs. 2c and 2f). The former consisted of Li₃VO₃F except for a small amount of LiV₂O₄ and LiF, whereas the latter comprised Li₄WO₄F and a trace amount of Li₂W₂O₇, as will be described later.

However, the other samples contained mainly separate (lithium) *M* oxides and LiF (or *M* fluorides) phases, not oxyfluorides. The *M* ions of some (lithium) *M* oxides were oxidized or reduced during the HP/HT treatments. The reason for this oxidation or reduction is currently unknown, although there is a possibility of a slight nonstoichiometry in the starting materials, an oxygen release, or a charge disproportionation reaction during the HP/HT treatments. HP(Fe, 1) consisted of unreacted FeO and LiF. Similarly, the products of HP(Mn, 1) and HP(Mn, 2) both contained MnO and LiF, and the former also contained MnF₃; when *M* = V, the HP(V, 2) sample separated into VO and LiF.

In the case of *M* = Nb, the XRD pattern of HP(Nb, 1) showed several phases such as LiNbO₂, LiNbO₃, Li₄NbO₄F, Nb₃O₇F, LiF, and Li₂O. Although two oxyfluorides (Li₄NbO₄F and Nb₃O₇F) existed, O²⁻ and F⁻ ions became increasingly likely to separate as *y* increased; that is, LiNbO₂, LiNbO₃, NbO, and LiF for HP(Nb, 2) and NbO and LiF for HP(Nb, 3). Note that unidentified phase(s) were detected for *y* = 1 at 32.9° and *y* = 2 at 55.6°, as marked by stars.

Likewise, with *M* = Mo, the HP(Mo, 1) sample consisted of Li_{4+δ1}Mo_{1-δ1}O_{5-δ2}F_{δ2}, Li₂MoO₄, Li₂MoO₃, but the HP(Mo, 2) sample contained only Li_{4+δ1}Mo_{1-δ1}O_{5-δ2}F_{δ2} as the oxyfluoride, besides Li₂MoO₃, LiMoO₂, and LiF. Here, the Li_{4+δ1}Mo_{1-δ1}O_{5-δ2}F_{δ2} phase crystallized as the rock-salt structure with *a*_c = 4.1292(5) Å, which was smaller than that of Li₄MoO₅ (= 4.14 Å),¹⁸ indicating the nonstoichiometry of cations and anions as represented using δ₁ and δ₂ parameters, respectively. For *M* = W, the rock-salt Li₄WO₄F phase disappeared at *y* = 2; that is, the HP(W, 2) sample was composed of Li₂W₂O₇, Li₂WO₄F, and LiF, besides the Li₄WO_{4-δ3}F_{δ3} phase, in which δ₃ is above zero because *a*_c of Li₄WO_{4-δ3}F_{δ3} [= 4.140(3) Å] was smaller than that of Li₄WO₅ (= 4.15 Å),¹⁸ but δ₃ value has not been elucidated yet.

The difference in compatibility between O²⁻ and F⁻ ions in solids arises from the changes in ionic radius of *M* ions (*r*_{*M*}). As *y* increases, the *r* of *M* ions increases with the decreasing valence; for example, *r*_{Mn³⁺} = 0.65 Å in Li₂MnO₂F (*y* = 1) with Mn³⁺ and *r*_{Mn²⁺} = 0.83 Å in Li₂MnOF₂ (*y* = 2) with Mn²⁺ with the coordination number of six and the high-spin state.¹⁹ Among Li_xMO_{1+x-y}F_y compounds, *r*_{V⁴⁺} (= 0.58 Å), *r*_{Mo⁵⁺} (= 0.61 Å), and *r*_{W⁵⁺} (= 0.62 Å) are prominently small,¹⁹ which stabilizes their ions in octahedral environments to form the rock-salt structure under HP conditions. Consequently, the HP/HT methods provided Li₃VO₃F and Li₄WO₄F, in addition to partially substituted Li_{4+δ1}Mo_{1-δ1}O_{5-δ2}F_{δ2}, whereas the ball-milling method yielded the Mn phases,^{9,10} in addition to V⁴⁻⁶ and Mo^{7,8} phases instead of W phases.

3.2 Structural, morphological, and compositional analyses of HP(V, 1) and HP(W, 1)

3.2.1 HP(V, 1)

We next examine the crystal structures, particle morphology, and elemental distributions of the successfully synthesized Li_xMO_{1+x-y}F_y. Figure 3a shows the Rietveld result of HP(V, 1), and Table S1 lists the determined structural parameters. For the Li_xMO_{1+x-y}F_y primary phase with the *Fm* $\bar{3}$ *m* space group, we fixed that Li/V ions occupy 4*a* site by the ratio of 3 : 1 and O/F ions occupy 4*b* site by the ratio of 3 : 1, because the signal-to-noise ratio of the XRD pattern was insufficient to determine Li/V/O/F ratios. In this rock-salt structure, *M*–O bond length can be calculated as 0.5 × *a*_c. The calculated *a*_c of Li₃VO₃F was 4.08506(7) Å. Note that the total

Figure 3. Results of the Rietveld analysis, particle morphology observations, and SEM-EDX spectrometry of HP(V, 1). (a) Rietveld refinement results, images of the particle morphology at (b) 50- μm and (c) 10- μm scales, and (d) cross-sectional BSE image and corresponding (e) O, (f) F, and (g) V mappings. The inset in (a) illustrates the determined crystal structure of $\text{Li}_3\text{VO}_3\text{F}$. Li, V, O, and F atoms appear as yellow, orange, gray, and blue spheres, respectively. Magenta, cyan, and orange vertical lines indicate the Bragg positions of $\text{Li}_3\text{VO}_3\text{F}$, LiF, and LiV_2O_4 , respectively.

Li/V/O/F ratio was determined to be 3.0/1.0/3.0/1.1 based on calculated weight (molar) fraction of $\text{Li}_3\text{VO}_3\text{F}$: LiF : LiV_2O_4 = 95.4 (87.4) : 2.2 (10.8) : 2.4 (1.8) wt% (mol%).

Figures 3b and 3c show conventional SEM images at a 50- and 10- μm scales, respectively. Figs. 3d–3g present cross-sectional backscattered electron (BSE) images with the corresponding O, F, and V mapping results, respectively. Some primary particles exhibited well-faceted but irregular shapes with sizes of 2–20 μm . All O, F, and V were uniformly distributed inside the particles. Note that the O mapping was somewhat unclear owing to overlapping from the characteristic X-rays of V-L α , resulting in the deviated V/O/F ratio of 1.0/2.1/2.1 (Fig. S1). This bulky $\text{Li}_3\text{VO}_3\text{F}$ is newly categorized as a lithium-excess vanadium oxyfluoride with the

Figure 4. Results of the Rietveld analysis, particle morphology observations, and SEM-EDX spectrometry of HP(W, 1). (a) Rietveld refinement results, images of the particle morphology at (b) 50- μm and (c) 10- μm scales, and (d) cross-sectional BSE image and corresponding (e) O, (f) F, and (g) W mappings. The inset in (a) illustrates the determined crystal structure of $\text{Li}_4\text{WO}_4\text{F}$ is illustrated. Li, W, O, and F atoms appear as yellow, lime green, gray, and blue spheres, respectively. Magenta and cyan vertical lines indicate the Bragg positions of $\text{Li}_4\text{WO}_4\text{F}$ and $\text{Li}_2\text{W}_2\text{O}_7$, respectively.

highest lithium concentration because only $\text{Li}_2\text{VO}_2\text{F}$ ⁴ and its derivatives^{5,6} have been reported so far.

3.2.2 HP(W, 1)

Figure 4a shows the Rietveld analysis results of HP(W, 1), which revealed the stoichiometric $\text{Li}_4\text{WO}_4\text{F}$ primary phase with the rock-salt structure. The calculated a_c and weight (molar) fraction of $\text{Li}_4\text{WO}_4\text{F}$ were determined to be 4.13747(5) Å and 99.3 (99.6) % (Table S1), respectively, which were consistent with the larger a_c of Li_4WO_5 (= 4.15 Å).¹⁸

As shown in Figs. 4b and 4c, most primary particles were also irregular but well faceted with an average size of 15 μm , and some small 1–3 μm particles aggregated on their facets. According to the cross-sectional BSE image (Fig. 4d) accompanied by O, F, and W

mappings (Figs. 4e–4g), the large and small particles had the same composition with uniform distributions of O, F, and W. The W/O/F ratio determined by the EDX spectrum (Fig. S2) was 1.0/4.3/1.9, which was almost comparable to the XRD result. To our best knowledge, lithium-excess tungsten oxyfluorides have never been reported; therefore, $\text{Li}_4\text{WO}_4\text{F}$ is considered the first compound in this class.

3.3 Electrochemical properties and reaction mechanism of high-crystallinity $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$

The electrochemical properties of the high-crystallinity $\text{Li}_3\text{VO}_3\text{F}$ and $\text{Li}_4\text{WO}_4\text{F}$ yielded by the HP/HT method were investigated using nonaqueous lithium cells. For HP(V, 1), if we ignore the contributions of LiF and LiV_2O_4 impurities, the electrochemical reaction is represented as

where the valence of V changes between +4 and +5, resulting in Q_{theo} of 193 mAh g^{-1} . As shown in Fig. 5a, as the initial charge reaction proceeded, the voltage (E) monotonically increased from the open-circuit voltage of $\sim 2.6 \text{ V}$, then flattened briefly ($\sim 3.8 \text{ V}$) at $\sim 60 \text{ mAh g}^{-1}$, and finally gradually increased to the upper limit of 4.8 V . The discontinuous change in E at $\sim 3.8 \text{ V}$ was probably due to a structural change of $\text{Li}_3\text{VO}_3\text{F}$ because stoichiometric LiCoO_2 undergoes a transition between rhombohedral and monoclinic symmetry with a cusp at $\sim 4.1 \text{ V}$.²⁰ The initial Q_{cha} was 99 mAh g^{-1} , corresponding to 0.5 mol of Li^+ removed from $\text{Li}_3\text{VO}_3\text{F}$ if no other side reactions occurred, such as electrolyte decomposition. The subsequent Q_{cha} and Q_{dis} were ~ 20 and $\sim 15 \text{ mAh g}^{-1}$, respectively, over $3.0\text{--}4.8 \text{ V}$; over $1.8\text{--}5 \text{ V}$, however, Q_{cha} and Q_{dis} were both $\sim 40 \text{ mAh g}^{-1}$, which were below the Q_{recha} of low-crystallinity $\text{Li}_2\text{VO}_2\text{F}$ ($\sim 420 \text{ mAh g}^{-1}$).⁴

For HP(W, 1), the reaction can be represented as follows:

where Q_{theo} is calculated to be 91 mAh g^{-1} . As shown in Fig. S3, the initial Q_{cha} was 12 mAh g^{-1} , which was equivalent to 0.13 mol of Li^+ removed from $\text{Li}_4\text{WO}_4\text{F}$. In the subsequent curves, Q_{recha} over $3\text{--}4.8 \text{ V}$ was almost 0 mAh g^{-1} , whereas that over $1.8\text{--}5 \text{ V}$ was $< 10 \text{ mAh g}^{-1}$. The delithiation reaction of the high-crystallinity phases in Eqs. (2) and (3) is more difficult to occur than that of low-crystallinity phases.

Ex situ XRD was conducted on the cycled $\text{Li}_3\text{VO}_3\text{F}$ and $\text{Li}_4\text{WO}_4\text{F}$ electrodes to clarify the structural changes during cycling. The patterns, which were measured using polyimide tape, revealed that HP(V, 1) and HP(W, 1) consisted of rock-salt phases with $a_c = 4.100(1) \text{ \AA}$ (Fig. S4) and $4.140(1) \text{ \AA}$ (Fig. S5), respectively. These a_c values were only slightly larger than the pristine a_c , indicating that these diffraction lines originated from unreacted phases. As shown in Fig. 5b, the XRD pattern, which was captured using the glass capillary, also demonstrated that HP(V, 1) decomposed into nonstoichiometric LiVO_2 , i.e., Li_zVO_2 with $a_h = 2.908(8) \text{ \AA}$ and $c_h = 14.72(2) \text{ \AA}$.

Based on the *ex situ* XRD results, the reaction of high-crystallinity $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ proceeded with the decomposition, which differed from the topotactic reactions reported for ball-milled low-crystallinity V-,^{4–6} Mo-,^{7,8} or Mn-based^{9,10} $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$. Figure 5c shows a possible reaction scheme for $\text{Li}_3\text{VO}_3\text{F}$. During the initial charge, Li^+ was removed from some domains of the lattice to form $\text{Li}_2\text{VO}_3\text{F}$ as shown in Eq. (2), and then the delithiated phase decomposed into LiVO_2 , LiF, and O_2 as follow:

The LiVO_2 phase appeared on the particle surface. In the subsequent charge (discharge), only the layered LiVO_2 domain was electrochemical active as below:

Figure 5. Electrochemical properties and reaction mechanism of HP(V, 1): (a) charge and discharge curves; (b) *ex situ* XRD pattern using a glass capillary after cycling [as denoted by the red circle in (a)]; (c) possible reaction scheme during operation. In (a), blue and red solid lines indicate the first five cycles (3.0–4.8 V) and subsequent five cycles (1.8–5.0 V), respectively. The first cycles in each voltage range are shown as darker colors. In (b), diffraction lines derived from an unidentified phase and the glass capillary are marked by stars and daggers, respectively. In (c), the initial charge reaction proceeds with delithiation from $\text{Li}_3\text{VO}_3\text{F}$ to form $\text{Li}_2\text{VO}_3\text{F}$ [Eq. (2)], and then the decomposition reaction into LiVO_2 , LiF, and O_2 occurs [Eq. (4)], finally the reversible electrochemical reaction proceeds between LiVO_2 and Li_zVO_2 [Eq. (5)].

causing a sudden decrease in Q_{recha} . Notably, the reason $\text{Li}_3\text{VO}_3\text{F}$ had a higher initial Q_{cha} than $\text{Li}_4\text{WO}_4\text{F}$ is because during charging, V ions in octahedral (4a) sites migrate to tetrahedral (8c) sites when they oxidize ($\text{V}^{4+} \rightarrow \text{V}^{5+}$), as seen in $\text{LiMg}_q\text{Zn}_{1-q}\text{VO}_4$ with $0 \leq q \leq 1$,²¹ thus creating lithium diffusion pathways ($4a \rightarrow 8c \rightarrow 4a$).

In this study, we revealed that the high-crystallinity $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ exhibited unique possible selections of M and electrochemical properties, including Q_{recha} and the electrochemical reaction mechanism, which differed from those of low-crystallinity phases. These findings will enable designing the degree of crystallinity of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ specifically with $M = \text{V}$, and intermediate crystallinity will be the next target to further understand $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ positive electrodes and to design their microstructures towards practical LIBs with well-balanced performance metrics such as

energy density, power density, cycling life, safety, and cost. Future work contains single-phase synthesis and improvement of signal-to-noise ratio in XRD patterns for detailed structural and compositional determination of HP/HT-synthesized $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$, in addition to the adjustment of the degree of crystallinity.

4. Conclusions

We synthesized several high-crystallinity $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ using the HP/HT method at 12 GPa and 1000 °C, and examined their electrochemical properties to elucidate the relationship between crystallinity and electrochemical reactivities. The systematic HP/HT syntheses of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ as a function of M ($= \text{Fe}, \text{Mn}, \text{V}, \text{Nb}, \text{Mo}, \text{and W}$) and y ($= 1, 2, \text{or } 3$) demonstrated that almost-single-phase $\text{Li}_3\text{VO}_3\text{F}$ (95.4 wt% purity) and $\text{Li}_4\text{WO}_4\text{F}$ (99.3 wt% purity) crystallized in the rock-salt structure. Moreover, XRD-based Rietveld and cross-sectional SEM-EDX analyses revealed that both exhibited well-faceted primary particles with sizes of 1–20 μm , in addition to homogenous cation/anion distributions at the macro- and microscopic-scales. The Q_{recha} values over 1.8–5.0 V were ~ 40 and $\sim 10 \text{ mAh g}^{-1}$ for $\text{Li}_3\text{VO}_3\text{F}$ and $\text{Li}_4\text{WO}_4\text{F}$, respectively, and these partial Q_{recha} s were attributed to a decomposition reaction during the initial charging, unlike the topotactic reaction with low-crystallinity phases. This information will be useful for further understanding and improving the electrochemical behavior of $\text{Li}_x\text{MO}_{1+x-y}\text{F}_y$ positive electrode materials by controlling their microstructures although future work is required to improve phase purity, to determine detailed structure and compositions, and to study the adjustment of the degree of crystallinity under several HP/HT conditions.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-65130>.

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