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Abstract

Lithium-excess transition metal (M) oxyfluorides, Li$_x$M$\text{O}_{1+x-y}$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 Li$_x$M$\text{O}_{1+x-y}$F$_y$, because conventionally ball-milled Li$_x$M$\text{O}_{1+x-y}$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 Li$_x$M$\text{O}_{1+x-y}$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 Li$_3$VO$_3$F and Li$_4$WO$_4$F crystalized 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 Li$_3$VO$_3$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 Li$_x$M$\text{O}_{1+x-y}$F$_y$ to improve its performance now that both crystal and amorphous Li$_x$M$\text{O}_{1+x-y}$F$_y$ phases are attainable.

Keywords: Lithium-Ion Battery, Positive Electrode Material, Lithium-Excess Metal Oxyfluoride, Cross-Sectional Observation
1. Introduction

Lithium-excess transition metal (M) oxyfluorides, \( \text{Li}_x\text{MO}_{1+\gamma}\text{F}_\gamma \), where \( x \) and \( y \) (\( x \geq y > 0 \)) represent the amounts of Li and F, with a rock-salt structure (\( Fm\overline{3}m \) 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 \( \text{Li}_x\text{MO}_{1+\gamma}\text{F}_\gamma \) is reported to proceed in a topotactic manner as follows:\(^1,2\)

\[
\text{Li}_x\text{MO}_{1+\gamma}\text{F}_\gamma \leftrightarrow \text{Li}_{x-n}\text{MO}_{1+\gamma}\text{F}_\gamma + n\text{Li}^+ + ne^-, \tag{1}
\]

where the theoretical capacity (\( Q_{\text{theo}} \)), is expressed as a function of \( x \), \( y \), \( n \), and \( M \), when ignoring an \( \text{O}^{2-} \) removal reaction. In Fig. 1, the \( Q_{\text{theo}} \) of some \( \text{Li}_x\text{MO}_{1+\gamma}\text{F}_\gamma \) exceeds that of a currently commercialized positive electrode material, \( \text{LiCoO}_2 \) (\( = 274 \text{ mAh g}^{-1} \)),\(^3\) e.g., 436 mAh g\(^{-1}\) for \( \text{Li}_2\text{MnOF}_2 \) (\( y = 2 \)), 431 mAh g\(^{-1}\) for \( \text{Li}_3\text{NbOF}_3 \) (\( y = 3 \)), and 497 mAh g\(^{-1}\) for \( \text{Li}_4\text{MoOF}_4 \) (\( y = 4 \)), when \( n = y \).

Over the past half decade, V-,\(^4,5,6\) Mo-,\(^7,8\) and Mn-based\(^9,10\) \( \text{Li}_x\text{MO}_{1+\gamma}\text{F}_\gamma \) with \( y > \sim 1 \) have been reported. \( \text{Li}_2\text{VO}_2\text{F} \) exhibits a discharge capacity (\( Q_{\text{dis}} \)) of \( \sim 420 \text{ mAh g}^{-1} \) in the range of 1.3–4.1 V vs. Li\(^+\)/Li; however the charge capacity (\( Q_{\text{cha}} \)) is \( \sim 90 \text{ mAh g}^{-1} \) lower than the \( Q_{\text{dis}} \) 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 \( Q_{\text{cha}} \) and \( Q_{\text{dis}} \) decreases the rechargeable capacity (\( Q_{\text{recha}} \)). On the other hand, \( \text{Li}_{1.9}\text{Mn}_{0.95}\text{O}_{2.05}\text{F}_{0.95} \) displays \( Q_{\text{recha}} \) of 280 mAh g\(^{-1}\) over 2–4.8 V, which corresponds to 150 mAh g\(^{-1}\) from the Mn\(^{3+}/\text{Mn}^{4+} \) redox and 130 mAh g\(^{-1}\) from the O redox.\(^9\) The 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 \( \text{Li}[\text{Li}_{0.15}\text{Mn}_{1.85}]\text{O}_4 \).\(^{11}\) Regardless of several efforts to
substitute the original $M$ (= V$^{5.6}$, Mo$^8$, Mn$^{10}$) with another, these two intrinsic drawbacks, i.e., the decrease and fading in $Q_{\text{recha}}$, remain unresolved.

Syntheses of Li$_x$M$^{1+x-y}$O$_{1-x}$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 Li$_x$M$^{1+x-y}$O$_{1-x}$F$^y$, including the remaining decrease and fading in $Q_{\text{recha}}$. 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 Li$_x$M$^{1+x-y}$O$_{1-x}$F$^y$ rock-salt phase. In this contribution, we employed a high-pressure/high-temperature (HP/HT) method to attain high-crystallinity Li$_x$M$^{1+x-y}$O$_{1-x}$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 ~1000 °C) as reported in CrO$_{2-p}$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 Li$_3$VO$_3$F and Li$_4$WO$_4$F and revealed that their electrochemical reactions involving a decomposition reaction. They exhibited $Q_{\text{recha}}$ of ~40 and ~10 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
Li$_x$M$^{1+x-y}$O$_{1-x}$F$^y$ ($M =$ 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 $Q_{\text{theo}}$ values. The nominal compositions were designed based on Li$_x$MO$_{1+x}$ oxides with a large Li ($x$) content to maximize $Q_{\text{theo}}$. Stoichiometric combinations of $M$ oxide(s), LiF (Wako Pure Chemical Industries) (or $M$F$_2$), and Li$_2$O (Wako Pure Chemical Industries) were employed as starting materials. $M$ oxides and $M$F$_2$ included FeO, MnF$_2$, Mn$_2$O$_3$, V$_2$O$_3$, V$_2$O$_5$, NbO, NbO$_2$, MoO$_2$, MoO$_3$, WO$_2$, and WO$_3$, all of which were purchased from Kojundo Chemical Industries, except MoO$_2$, 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. 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$_\alpha$ 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 crystalized as an almost-single-phase lithium-excess $M$ oxyfluoride. Thus, the crystal structures were determined by Rietveld analyses using RIETAN-FP software and drawn using VESTA software. 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. 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 LiₓMO₁₊ₓ₋ₓFₓ by the HP/HT method

We first systematically conducted HP/HT syntheses of LiₓMO₁₊ₓ₋ₓFₓ to reveal the possible combinations of M and y. Figs. 2a–f 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 f). The former consisted of Li$_3$VO$_3$F except for a small amount of LiV$_2$O$_4$ and LiF, whereas the latter comprised Li$_4$WO$_4$F and a trace amount of Li$_2$W$_2$O$_7$, 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 MnF$_3$; 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 LiNbO$_2$, LiNbO$_3$, Li$_4$Nb$_2$O$_7$F, Nb$_2$O$_7$F, LiF, and Li$_2$O. Although two oxyfluorides (Li$_4$Nb$_2$O$_7$F and Nb$_2$O$_7$F) existed, O$^{2-}$ and F$^-$ ions became increasingly likely to separate as $y$ increased; that is, LiNbO$_2$, LiNbO$_3$, 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$_{4+\delta_1}$Mo$_{1-\delta_1}$O$_{5-\delta_2}$F$_{\delta_2}$, Li$_2$MoO$_4$, Li$_2$MoO$_3$, but the HP(Mo, 2) sample contained only Li$_{4+\delta_1}$Mo$_{1-\delta_1}$O$_{5-\delta_2}$F$_{\delta_2}$ as the oxyfluoride, besides Li$_2$MoO$_3$, LiMoO$_2$, and LiF. Here, the Li$_{4+\delta_1}$Mo$_{1-\delta_1}$O$_{5-\delta_2}$F$_{\delta_2}$ phase crystalized as the rock-salt structure with $a_c = 4.1292(5)$ Å, which was smaller than that of Li$_4$MoO$_5$ (= 4.14
Å), indicating the nonstoichiometry of cations and anions as represented using $\delta_1$ and $\delta_2$ parameters, respectively. For $M = W$, the rock-salt Li$_4$WO$_4$F phase disappeared at $y = 2$; that is, the HP(W, 2) sample was composed of L$_2$W$_2$O$_7$, WF$_6$, and LiF, besides the Li$_4$WO$_{4-\delta}$F$_{\delta}$ phase, in which $\delta_3$ is above zero because $a_c$ of Li$_4$WO$_{4-\delta}$F$_{\delta}$ $[= 4.140(3)$ Å] was smaller than that of Li$_4$WO$_5$ ($= 4.15$ Å), but $\delta_3$ value has not been elucidated yet.

The difference in compatibility between O$^{2-}$ 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, $r_{Mn}^{3+} = 0.65$ Å in Li$_2$MnO$_2$F ($y = 1$) with Mn$^{3+}$ and $r_{Mn}^{2+} = 0.83$ Å in Li$_2$MnOF$_2$ ($y = 2$) with Mn$^{2+}$ with the coordination number of six and the high-spin state.$^{19}$ Among Li$_x$MO$_{1+x-\gamma}$F$_y$ compounds, $r_{V^{4+}}$ ($= 0.58$ Å), $r_{Mo^{5+}}$ ($= 0.61$ Å), and $r_{W^{6+}}$ ($= 0.62$ 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 Li$_3$VO$_4$F and Li$_4$WO$_4$F, in addition to partially substituted Li$_{4-\delta_1}$Mo$_{1-\delta_1}$O$_{5-\delta_2}$F$_{\delta_2}$, whereas the ball-milling method yielded the Mn phases,$^{9,10}$ in addition to V$_{4-6}$ 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$_x$MO$_{1+x-\gamma}$F$_y$. Figure 3a shows the Rietveld result of HP(V, 1), and Table S1 lists the determined structural parameters. For the Li$_x$MO$_{1+x-\gamma}$F$_y$ primary phase with the $Fm\overline{3}m$ 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 $0.5 \times a_c$. The calculated $a_c$ of Li$_3$VO$_3$F was 4.08506(7) Å. Note
that the total Li/V/O/F ratio was determined to be 3.0/1.0/3.0/1.1 based on calculated weight (molar) fraction of Li$_3$VO$_3$F:LiF:LiV$_2$O$_4$ = 95.4 (87.4):2.2 (10.8):2.4 (1.8) wt% (mol%).

Figs. 3b and 3c show conventional SEM images at a 50- and 10-μm scales, respectively, Figs. 3d–g 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-Lα, resulting in the deviated V/O/F ratio of 1.0/2.1/2.1 (Fig. S1). This bulky Li$_3$VO$_3$F is newly categorized as a lithium-excess vanadium oxyfluoride with the highest known lithium concentration because only Li$_2$VO$_2$F$_4$ and its derivatives 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 Li$_4$WO$_4$F primary phase with the rock-salt structure. The calculated $a_c$ and weight (molar) fraction of Li$_4$WO$_4$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$_4$WO$_5$ (= 4.15 Å). 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–g), 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, Li$_4$WO$_4$F is considered the first compound in this class.

3.3. Electrochemical properties and reaction mechanism of high-crystallinity Li$_{x}$MO$_{1+x-y}$F$_{y}$
The electrochemical properties of the high-crystallinity Li$_3$VO$_3$F and Li$_4$WO$_4$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$_2$O$_4$ impurities, the electrochemical reaction is represented as

$$\text{Li}_3\text{VO}_3\text{F} \leftrightarrow \text{Li}_2\text{VO}_3\text{F} + \text{Li}^+ + e^-,$$

(2)

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

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

$$\text{Li}_4\text{WO}_4\text{F} \leftrightarrow \text{Li}_3\text{WO}_4\text{F} + \text{Li}^+ + e^-,$$

(3)

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

*Ex situ* XRD was conducted on the cycled Li$_3$VO$_3$F and Li$_4$WO$_4$F electrodes to clarify the structural changes during cycling. The patterns, which was measured using polyimide tape,
revealed that HP(V, 1) and HP(W, 1) consisted of rock-salt phases with $a_c = 4.100(1)$ Å (Fig. S4) and 4.140(1) Å (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$_x$VO$_2$ with $a_h = 2.908(8)$ Å and $c_h = 14.72(2)$ Å.

Based on the ex situ XRD results, the reaction of high-crystallinity Li$_x$M$^{1+}$x$^{-y}$F$_y$ proceeded with the decomposition, which differed from the topotactic reactions reported for ball-milled low-crystallinity V-, Mo-, or Mn-based Li$_x$M$^{1+}$x$^{-y}$F$_y$. Figure 5c shows a possible reaction scheme for Li$_3$VO$_3$F. During the initial charge, Li$^+$ was removed from some domains of the lattice to form Li$_2$VO$_3$F as shown in eq 2, and then the delithiated phase decomposed into LiVO$_2$, LiF, and O$_2$ as follow:

$$\text{Li}_2\text{VO}_3\text{F} \rightarrow \text{LiVO}_2 + \text{LiF} + 0.5\text{O}_2. \quad (4)$$

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:

$$\text{LiVO}_2 + (z - 1)\text{Li}^+ + (z - 1)e^- \leftrightarrow \text{Li}_z\text{VO}_2, \quad (5)$$

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

In this study, we revealed that the high-crystallinity Li$_x$M$^{1+}$x$^{-y}$F$_y$ exhibited unique possible selections of $M$ and electrochemical properties, including $Q_{\text{recha}}$ and the electrochemical reaction mechanism, which differed from those of low-crystallinity phases. These findings will enable designing the degree of crystallinity of Li$_x$M$^{1+}$x$^{-y}$F$_y$ specifically with $M = V$, and intermediate crystallinity will be the next target to further understand Li$_x$M$^{1+}$x$^{-y}$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 Li$_x$MO$_{1+y}$F$_y$, in addition to the adjustment of the degree of crystallinity.

4. Conclusions

We synthesized several high-crystallinity Li$_x$MO$_{1+y}$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 Li$_x$MO$_{1+y}$F$_y$ as a function of $M$ (= Fe, Mn, V, Nb, Mo, and V) and $y$ (= 1, 2, or 3) demonstrated that almost-single-phase Li$_3$VO$_3$F (95.4 wt% purity) and Li$_4$WO$_4$F (99.3 wt% purity) crystalized 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 $Q_{\text{recha}}$ values over 1.8–5.0 V were ~40 and ~10 mAh g$^{-1}$ for Li$_3$VO$_3$F and Li$_4$WO$_4$F, respectively, and these partial $Q_{\text{recha}}$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 Li$_x$MO$_{1+y}$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: xxxxxxxxxxxxx.

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

| nominal composition | starting materials | $Q_{\text{theo}} / \text{mAh g}^{-1}$ | notation | phases* |
|---------------------|--------------------|--------------------------------------|----------|---------|
| LiFeOF              | FeO + LiF          | 274                                  | HP(Fe, 1) | FeO$^{\dagger}$, LiF |
| Li$_2$MnO$_2$F      | 0.5Mn$_2$O$_3$ + LiF + 0.5Li$_2$O | 224                                  | HP(Mn, 1) | MnO$^{\dagger}$, MnF$_3$, LiF |
| Li$_2$MnOF$_2$      | Li$_2$O + MnF$_2$  | 436                                  | HP(Mn, 2) | MnO$^{\dagger}$, LiF |
| Li$_3$VO$_2$F       | 0.25V$_2$O$_3$ + 0.25V$_2$O$_5$ + LiF + Li$_2$O | 193                                  | HP(V, 1)  | Li$_3$VO$_3$F$^{\dagger}$, LiF, LiF |
| Li$_3$VO$_3$F$_2$   | 0.5V$_2$O$_3$ + 2LiF + 0.5Li$_2$O | 378                                  | HP(V, 2)  | VO$^{\dagger}$, LiF |
| Li$_3$NbO$_3$F      | NbO$_2$ + LiF + Li$_2$O | 148                                  | HP(Nb, 1) | Li$_3$NbO$_3$F, NbO$_2$-F, LiNbO$_2$$^{\dagger}$, LiNbO$_3$, LiF, LiF |
| Li$_3$NbO$_2$F$_2$  | 0.5NbO$_2$ + 0.5NbO + 2LiF + 0.5Li$_2$O | 292                                  | HP(Nb, 2) | LiNbO$_2$$^{\dagger}$, LiNbO$_3$, NbO, LiF |
| Li$_3$NbOF$_3$      | NbO + 3LiF         | 431                                  | HP(Nb, 3) | NbO$^{\dagger}$, LiF |
| Li$_3$MoO$_3$F      | 0.5Mo$_2$O$_3$ + LiF + 1.5Li$_2$O | 130                                  | HP(Mo, 1) | Li$_4$$^{\dagger}$Mo$_{1-d}$$^{d-0.5}$O$_{5-d}$$^{d-1}$F$_{d-0.5}$, Li$_2$MoO$_4$, Li$_3$MoO$_3$ |
| Li$_3$MoOF$_2$      | Mo$_2$O$_2$ + 2LiF + Li$_2$O | 256                                  | HP(Mo, 2) | Li$_4$$^{\dagger}$Mo$_{1-d}$$^{d-0.5}$O$_{5-d}$$^{d-1}$F$_{d-0.5}$, Li$_3$MoO$_3$$^{\dagger}$, LiMoO$_2$, LiF |
| Li$_3$WO$_4$F       | 0.5WO$_2$ + 0.5WO$_3$ + LiF + 1.5Li$_2$O | 91                                   | HP(W, 1)  | Li$_4$WO$_{2+d}$$^{d}$F$_{d-0.5}$, Li$_2$WO$_7$$^{\dagger}$, Li$_4$WO$_5$, WF$_6$, LiF |
| Li$_3$WO$_3$F$_2$   | WO$_2$ + 2LiF + Li$_2$O | 180                                  | HP(W, 2)  | Li$_4$WO$_{2+d}$$^{d-0.5}$F$_{d-0.5}$, Li$_2$WO$_7$$^{\dagger}$, Li$_4$WO$_5$, WF$_6$, LiF |

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


Figure captions

**Figure 1.** (Color online) Changes in $Q_{\text{theo}}$ of a series of Li$_x$MO$_{1+y-x}$F$_y$ ($M$ = Fe, Mn, V, Nb, Mo, and W), assuming the charge transfer number of $y$, along with $Q_{\text{theo}}$ of LiCoO$_2$.

**Figure 2.** (Color online) 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).

**Figure 3.** (Color online) 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 Li$_3$VO$_3$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 Li$_3$VO$_3$F, LiF, and LiV$_2$O$_4$, respectively.

**Figure 4.** (Color online) 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 Li$_4$WO$_4$F is illustrated. Li, V, O, and W atoms appear as yellow, lime green, gray, and blue spheres, respectively. Magenta and cyan vertical lines indicate the Bragg positions of Li$_4$WO$_4$F and Li$_2$W$_2$O$_7$, respectively.
Figure 5. (Color online) 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 Li$_3$VO$_3$F to form Li$_2$VO$_3$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$_z$VO$_2$ (eq5).
Figure 1. T. Uyama, K. Mukai, and I. Yamada
Figure 2. T. Uyama, K. Mukai, and I. Yamada
Figure 3, T. Uyama, K. Mukai, and I. Yamada
Figure 4. T. Uyama, K. Mukai, and I. Yamada
Figure 5. T. Uyama, K. Mukai, and I. Yamada