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The Effect of Oxygen Defects on the Structural Evolution
of LiVPO$_4$F$_{1-y}$O$_y$ Cathode Materials

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Abstract
Lithium vanadium fluorophosphate, LiVPO$_4$F, is a promising cathode material for Li-ion batteries due to its high intercalation potential (4.24 V vs Li/Li$^+$) and high stability. However, recent studies show that as-synthesized LiVPO$_4$F very often contains oxygen-defects on the fluoride site giving rise to a general composition of LiVPO$_4$F$_{1-y}$O$_y$ with vanadium in a mixed +III/+IV valence state. The inclusion of oxygen naturally influences the electrochemical properties greatly, and a thorough material characterization is necessary to understand the performance. In this study, we synthesize lithium vanadium fluorophosphate by two common strategies: solid-state and hydrothermal synthesis. We show that solid-state synthesis provides LiVPO$_4$F, while the hydrothermal method, in contrast to previous reports, leads to inclusion of ca. 35% oxygen on the fluoride site and significant disorder in the material. The different electrochemical properties were probed by operando synchrotron X-ray powder diffraction to investigate the effects of oxygen inclusion on the structural evolution during electrochemical lithiation and delithiation. This reveals that while LiVPO$_4$F exhibits a typical biphasic phase evolution, the sample with oxygen inclusion on the fluoride site displays extended solid-solution behavior. This explains previous observations of improved capacity retention due to defects.

Keywords: Li-ion batteries; phase transition; LiVPO$_4$F$_{1-y}$O$_y$; operando synchrotron XPD; disordered materials
1. Introduction

Following the success of phosphate-based olivines, especially LiFePO$_4$, new phosphate-based cathode materials based on the triclinic Tavorite (LiFePO$_4$OH) structure have shown great promise. The compounds are generally based on the formula LiMPO$_4$X, where M is a transition metal, typically Fe or V, and X is an anion, typically F$^-$, O$_2^-$ and/or OH$^-$. Depending on the stable oxidation states of the transition metal, more than one Li-ion may be inserted into and extracted from the structure. LiMPO$_4$F compounds are of special interest as fluoride provides an increase in the potential for a given transition metal redox couple compared with oxide and hydroxide. Both LiFePO$_4$F and LiVPO$_4$F have been considered for Li-ion battery cathode materials. LiVPO$_4$F is especially interesting, as its redox potential against Li is at 4.24 V, which fits well with the stability window of the electrolyte and is significantly higher than for LiFePO$_4$F (2.75 V vs Li/Li$^+$). The high redox potential observed for the $+{\text{IV}}$/$+{\text{III}}$ redox couple can be explained by the highly ionic V-F bond, which stabilizes the anti-bonding molecular orbital and increases the redox potential, an inductive effect, as well as results in higher thermal stability than LiFePO$_4$. Furthermore, the $+{\text{III}}$ oxidation state of vanadium in LiVPO$_4$F means that vanadium can be both oxidized and reduced. Hence, Li-ions can be both extracted from and inserted into the structure of LiVPO$_4$F, producing VPO$_4$F and Li$_2$VPO$_4$F, respectively:

$$\text{LiV}^{\text{III}}\text{PO}_4\text{F} \rightarrow \text{V}^{\text{IV}}\text{PO}_4\text{F} + \text{Li}^+ + e^- \quad \text{E}^0: 4.24 \text{V vs Li/Li}^+ \quad (1)$$

$$\text{LiV}^{\text{III}}\text{PO}_4\text{F} + \text{Li}^+ + e^- \rightarrow \text{Li}_2\text{V}^{\text{II}}\text{PO}_4 \quad \text{E}^0: 1.80 \text{V vs Li/Li}^+ \quad (2)$$

The triclinic structure of LiVPO$_4$F consists of chains of VO$_4$F$_2$-octahedra connected through the F-vertices in the [001] direction (Figure 1a). The chains are connected by phosphate groups at each of the oxide ions in the octahedra to form a 3D-lattice. This structure creates channels in the [100] direction where the Li-ions can move. Li$_2$VPO$_4$F and VPO$_4$F have the same polyhedra-framework as LiVPO$_4$F but can be described by the monoclinic C2/c space group.
Figure 1: a) Triclinic crystal structure of LiVPO$_4$F. The chains of VO$_4$F$_2$-octahedra run in the [001] direction via the F-vertices. The two crystallographically inequivalent vanadium octahedra are shown in blue and orange, respectively. b) Comparison of the octahedra chains in LiVPO$_4$F and LiVPO$_4$O. Notice that the octahedra chain runs in the [010] direction in LiVPO$_4$O. c) The three vanadium octahedron moieties in LiVPO$_4$F$_{1-y}$O$_y$. Vanadium ions are shown in black, phosphorous in light purple, oxygen in red, fluorine in grey and lithium in green. Reproduced from Chem. Mater. 2018, 30, 5682–5693. Copyright 2020 American Chemical Society.

The synthesis of phase-pure LiVPO$_4$F is challenging, and many publications report small impurities of especially Li$_3$V$_2$(PO$_4$)$_3$, which is also redox-active.$^8,11,14$ Most importantly, recent studies show that as-synthesized LiVPO$_4$F very often contains defects such as hydroxide and oxide inclusion on the fluoride anion site. The latter results in a general composition of Li(V$^{III}$)$_{1-y}$V$_y$(PO$_4$)$_{1-y}$O$_y$.$^{10,15–17}$ The endmember for this composition (y = 1) is LiVPO$_4$O, which has a Tavorite structure similar to that of LiVPO$_4$F, but with a twice as large unit cell due to the non-centrosymmetric VO$_4$O$_2$-octahedra caused by the short vanadyl double bond and long V--O single bond (Figure 1b). The oxygen substitute for the fluoride ions and are thus located along the octahedra chain. This results in a complex arrangement of short V=O vanadyl bonds and longer V-X (X = F, O) bonds in the LiVPO$_4$F$_1$. 
$yO_y$ solid solution structure (see Figure 1c). The oxygen substitution in LiVPO$_4$F$_{1-y}$O$_y$ naturally also affects the electrochemistry. This is mainly ascribed to the covalent nature of the vanadyl V=O bond, which, in contrast to the highly ionic M-F bond in LiVPO$_4$F, lowers the redox potential,\textsuperscript{15} a so-called anti-inductive effect.\textsuperscript{1} Thus, for VPO$_4$O, insertion of Li-ions (battery discharge) gives rise to voltage plateaus at 3.95 V vs. Li for the +V/+IV redox couple and at 2.48, 2.21 and 2.03 V vs. Li-metal for the +IV/+III redox couple.\textsuperscript{8} The effect of the vanadyl group on the redox potential is so great that in LiVPO$_4$F$_{1-y}$O$_y$, the V$^{IV}$=O/V$^{V}$=O redox couple in octahedra containing a vanadyl bond is activated before the V$^{III}$/V$^{IV}$ redox couple in vanadyl-free, fluoride-rich octahedra on charging.\textsuperscript{18} Studies of LiVPO$_4$F$_{1-y}$O$_y$ have so far focused mainly on the effect of oxygen defects on the electrochemistry. In this study, we investigated the effect on the structural evolution during lithiation and delithiation and found that it also is greatly affected by the oxygen defects.

The most widely used synthesis method for LiVPO$_4$F was initially developed by J. Barker et al.\textsuperscript{3,19} In this synthesis, LiVPO$_4$F is prepared in a two-step synthesis. Firstly, orthorhombic VPO$_4$ is prepared by a carbothermal reaction between V$_2$O$_5$ and NH$_4$H$_2$PO$_4$ (eq. 3):

$$0.5V_2O_5(s) + NH_4H_2PO_4(s) + C(s)\rightarrow VPO_4(s) + NH_3(g) + 1.5H_2O(g) + CO(g)$$  

Secondly, LiVPO$_4$F is prepared through an addition reaction between LiF and VPO$_4$ (eq. 4)

$$VPO_4(s) + LiF\rightarrow LiVPO_4F(s)$$

The addition reaction can be done in multiple ways, for example by high-temperature solid-state synthesis above 700 °C.\textsuperscript{8,11,20} Alternatively, the addition reaction has also been reported to proceed during hydrothermal synthesis carried out in a Teflon\textsuperscript{TM}-lined autoclave at temperatures below 250 °C.\textsuperscript{19} In this work, we explore both of these approaches. We show that the choice of synthesis method has significant influence on the chemical composition of the product – more specifically on the amount of oxygen inclusions in LiVPO$_4$F$_{1-y}$O$_y$, which contrasts with previous reports.\textsuperscript{19} Our initial
aim was to prepare oxygen-free LiVPO$_4$F using both methods, but electrochemical analysis showed very different behavior for the two synthesis products. This prompted us to conduct a thorough investigation of composition and structure of the products using X-ray powder diffraction (XPD), neutron powder diffraction (NPD), solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. Subsequently, we went on to study the difference in structural evolution between the samples during battery charge and discharge, i.e. delithiation and lithiation. For this, we employed operando synchrotron XPD, which showed a remarkable difference in structural features between the two samples.

2. Experimental

2.1. Synthesis of VPO$_4$

LiVPO$_4$F$_{1-y}$O$_y$ was synthesized using two methods. For both, VPO$_4$ was first prepared through a carbothermal synthesis. Subsequently, LiVPO$_4$F$_{1-y}$O$_y$ was prepared through a reaction between LiF and VPO$_4$ using either a solid-state approach inspired by Mba et al.$^8$ or a hydrothermal approach inspired by Barker et al.$^{19}$

For the synthesis of VPO$_4$, 4.000 g V$_2$O$_5$ (≥99.6 %, Sigma-Aldrich), 5.0594 g NH$_4$H$_2$PO$_4$ (≥99.999 %, Sigma-Aldrich) and 0.6868 g carbon (Super P C45 (CNERGY), 30 wt% excess relative to Equation 1) was transferred to an 80 mL tungsten carbide ball mill vial containing 12 ø1 cm tungsten carbide balls, acetone was added to the edge of the powder layer, and the mixture was ball-milled in a planetary ball-mill for 30 minutes at 400 rpm. The powder was subsequently uniaxially pressed to a ø2 cm pellet using 20 kN. The pellet was heated in a tube furnace at 300 °C for 8 hours under argon flow, using a heating rate of 100 °C/hour and a cooling rate of 300 °C/hour. The pellet was ground, and the obtained powder was ball-milled using the same procedure as described above. The obtained powder was repressed to a pellet with 20 kN and heated in a tube furnace at 800 °C for 10 hours under
an argon flow, using a heating and cooling rate of 300 °C/hour. Finally, the pellet was ground to obtain the VPO₄ powder (see Figure S1 for the X-ray diffractogram of VPO₄). This contains a residual amount of unreacted carbon, which was quantified using an Elementar Vario Macro Cube™ CHNS analyzer to 8.7 wt%. VPO₄ was then reacted with LiF using two different approaches: a solid-state reaction (SSR) and a hydrothermal reaction (HTR).

2.2 Solid-state synthesis of LiVPO₄F₁₋ₓOₓ (SSR)

For preparation of LiVPO₄F₁₋ₓOₓ through the solid-state reaction (SSR), 1.1766 g of as-prepared VPO₄ (containing 8.7 wt% carbon) and 0.1910 g LiF (≥99 %, Sigma-Aldrich) was ball-milled in an 80 mL tungsten carbide vial with 20 φ1 cm tungsten carbide balls at 450 rpm for 30 minutes. Acetone was added to the edge of the powder layer. The dried powder was pressed to a φ1 cm pellet using 20 kN. The pellet was placed in an alumina crucible and placed in a custom-made, air-tight steel container in an argon-filled glovebox, with oxygen and water concentrations below 1 ppm, along with strands of copper wool to absorb any traces of oxygen. The steel container was placed in a pottery furnace and kept at 750 °C for 30 minutes with a heating rate of 750 °C/hour. The container was then extracted from the furnace and placed on an alumina plate for fast cooling in order to avoid possible release of VF₃ from the sample. After cooling to room temperature, the pellet was ground to a fine powder. The residual carbon content in the as-prepared material as determined by CHNS elemental analysis was 7.89 wt%.

2.3 Hydrothermal synthesis of LiVPO₄F₁₋ₓOₓ (HTR)

For the hydrothermal reaction (HTR) between VPO₄ and LiF, 1.0282 g of as-prepared VPO₄ and 0.1669 g LiF (≥99 %, Sigma-Aldrich) were placed in a 100 mL Teflon™ container with 50 mL distilled water. The suspension was stirred for 30 minutes. Afterwards, the container was closed with
a Teflon™ lid and sealed in a steel autoclave. The autoclave was heated in an oven at 210 °C for three
days using a heating and cooling rate of 100 °C/hour. The obtained powder was washed three times
with 25 mL distilled water and once with 25 mL ethanol before drying at 60 °C overnight under
vacuum. The residual carbon content in the as-prepared material as determined by CHNS elemental
analysis was 8.39 wt%.

2.4 Product characterization

The PXD diffractograms of all synthesis products were measured on a Rigaku Miniflex600 using Cu
Kα-radiation, 2θ = 10-70°; step size: 0.02°, 2°/min.

Scanning Transmission Electron Microscopy (STEM) images and elemental mapping using Energy
Dispersive X-ray Spectroscopy (EDX) were performed on a JEOL 2010FEG equipped with an
Oxford INCA EDX detector, operated with an acceleration voltage of 200 kV. The samples were
prepared by dispersing a spatula tip of the dried cathode powder in 5 mL ethanol and sonicating the
dispersion for five minutes. The dispersion was then drop-casted onto lacy carbon cupper TEM
girds.

Infrared transmission spectra were measured using a Perkin Elmer Spectrum 65 FT-IR spectrometer
in the range 400-4000 cm⁻¹. For each sample, 1 mg powder was ground together with 300 mg dried
KBr and placed in an oven for further drying before pellets were pressed. Baseline correction was
applied to all spectra.

NPD measurements were conducted in a Debye–Scherrer geometry at the high-resolution powder
diffractometer SPODI, MLZ, Garching under ambient conditions.21 Monochromatic neutrons with a
wavelength of λ=1.5482 Å shaped to a rectangular cross section of 40 mm × 20 mm (height x width)
were incident on the sample. The monochromator take-off angle was 155°. A neutron detector array
consisting of 80 vertical position sensitive detectors collected data with Δ2θ=0.1°. The sample
powders were filled into thin-walled vanadium canisters. The measured canisters were continuously rotated during the entire measurement to reduce texture and orientation effects over the whole volume. Five diffraction patterns were measured for each sample with an acquisition time of $\approx$48 min each so that the integration time for the averaged data sets was $\approx$4 h for each sample. Instrumental resolution function was determined with a NAC ($\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$) reference material to calculate full width half maximum (FWHM) of Bragg reflections from the samples. The ex-situ X-ray and neutron diffractograms were analyzed using Rietveld refinement both by single pattern refinement and by combined pattern refinement. The approach used was similar to the one used for the operando X-ray synchrotron diffractograms, see below.

2.5 Electrode preparation and battery cell construction

The cathodes for electrochemical characterization were made by casting a slurry of 81 wt% as-prepared LiVPO$_4$F$_{1-y}$O$_y$ (SSR or HTR), 10 wt% Super P C45 (CNERGY) and 9 wt% PVDF (HSV900 PVDF, MTI Corporation) in a 3 wt% N-methyl-2-pyrrolidone (99.5 %, anhydrous, Sigma-Aldrich) solution onto graphite-coated aluminum foil (MTI Corporation). After drying at 60 $^\circ$C overnight, 10 mm diameter discs were cut, pressed with 1 ton and dried over night at 60 $^\circ$C under vacuum. The active material loading was $\sim$4.5-5.5 mg cm$^{-2}$. A spring-loaded Swagelok-type cell was assembled in a glovebox using a cathode disc as the working electrode, a glass fiber separator (Wattman GF/B) soaked with 1 M LiPF$_6$ in 1:1 v/v diethylene carbonate and dimethyl carbonate (Solvionic, 99.9 %) and a lithium foil anode (99.9 %, Sigma-Aldrich).

For the operando synchrotron radiation X-ray powder diffraction (SR-XPD) experiments, free standing cathode pellets were made from a composite of 80 wt% as-prepared LiVPO$_4$F, 10 wt% Super P C45 (CNERGY) and 10 wt% PVDF (HSV900 PVDF, MTI Corporation) mixed in acetone. After drying, the composite was ground to a fine powder and uniaxially pressed to pellets of 7 mm in
diameter, each weighing around 10 mg. The AMPIX cell for operando SR-XPD was assembled with the cathode pellet, a glass fiber (Wattman GF/B) separator soaked with 1 M LiPF$_6$ in 1:1 v/v diethylene carbonate and dimethyl carbonate (Solvionic, 99.9 %) and a lithium foil anode (99.9 %, Aldrich).

All handling of the prepared electrodes and cell assembly was carried out in an argon-filled glovebox equipped with a circulation purifier and O$_2$/H$_2$O levels kept below 1 ppm.

2.6 Electrochemical characterization

The electrochemical characterization was carried out using a BioLogic MPG2. For cyclic voltammetry (CV), a voltage sweep rate of 0.02 mV s$^{-1}$ between 4.7 and 1 V was used. For Galvanostatic Intermittent Titration Technique (GITT) on two fresh cells, 30 minutes charge/discharge pulses were used at C/10, followed by rest periods of two hours. 20 pulses were used for charging, and 40 pulses for discharging. Prior to the GITT measurements, Potentio Electrochemical Impedance Spectroscopy (PEIS) was performed on each of the cells using a voltage amplitude of 10 mV, and a voltage range of 20 kHz - 0.5 Hz with 10 points per decade. This was done to ensure similar resistive contributions for the two cells as dissimilar resistance can lead to erroneous conclusions about the observed overpotentials. The two samples have similar initial charge-transfer resistances (see Figure S7) of 32.3 and 31.4 $\Omega$ cm$^2$ for LiVPO$_4$F$_{1-y}$O$_y$ SSR and LiVPO$_4$F$_{1-y}$O$_y$ HTR, respectively, in a Swagelok cell.

2.7 Synchrotron Radiation X-ray Powder Diffraction (SR-XPD)

The SR-XPD measurements were performed at the Swiss-Norwegian beamline BM01 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, using a selected wavelength of 0.70508 Å. For the measurements, a slightly modified version of the AMPIX battery test cell was
used to collect simultaneous SR-XPD data and electrochemical information about the galvanostatic charge and discharge. During collection of operando SR-XPD data, both cells were cycled between 4.5 V and 0.5 V at a current rate of C/10. The diffractograms were obtained using a Pilatus 2M area detector and an X-ray exposure time of 1 second per subframe and 30 subframes. The sample frame-detector distance was calibrated using a LaB$_6$ standard and was found to be 395 mm. For each sample, a diffractogram was obtained every 5 minutes and 52 seconds. The data images were reduced to 20-intensity data using Fit2d,$^{23}$ and diffraction spots from the Li-metal anode were masked. The SR-XPD data was analyzed using Rietveld refinement performed using the software Fullprof.$^{24}$ In this study, we use the structural model for LiVPO$_4$F adopted by Mba et al.$^8$ (ICSD-184601) for LiVPO$_4$F, and the models developed by Ellis et al.$^7$ for VPO$_4$F and Li$_2$VPO$_4$F (ICSD-183878 and ICSD-183877). In the Rietveld refinements, backgrounds were described by linear interpolation between selected points, while pseudo-Voigt profile functions were used to fit the diffraction peaks.$^{24}$ A clear anisotropic broadening was observed for LiVPO$_4$F$_{1-y}$O$_y$ HTR, but not for LiVPO$_4$F$_{1-y}$O$_y$ SSR. Thus, an anisotropic size model was used due to the difference in sample morphology, as described below. The scale factor, unit cell parameters, size and strain parameters, zero-point offset, background and atomic positions were refined for the first pattern. The zero-point off-set and background were then fixed. Serial refinement was used on the 192 patterns for LiVPO$_4$F$_{1-y}$O$_y$ SSR and 229 patterns for LiVPO$_4$F$_{1-y}$O$_y$ HTR. For two phase regions, the atomic positions were fixed to the values obtained for the single phase diffractograms immediately before and after the two-phase region. One two-phase region between triclinic Li$_x$VPO$_4$F$_{1-y}$O$_y$ and monoclinic VPO$_4$F$_{1-y}$O$_y$ for LiVPO$_4$F$_{1-y}$O$_y$ HTR proved too difficult to refine by Rietveld refinement, and the unit cell parameters were instead extracted by full pattern Le Bail fitting.
2.8 Solid-state MAS NMR spectroscopy

Solid-state $^7$Li, $^{19}$F, and $^{31}$P Magic Angle Spinning (MAS) NMR spectra were recorded at 14.1 T ($^1$H at 599.98 MHz) on an Agilent INOVA 600 MHz NMR spectrometer using a 1.6 mm triple resonance MAS NMR probe and spinning speeds in the range 30-35 kHz. $^7$Li, $^{19}$F, and $^{31}$P NMR spectra are referenced relative to an aqueous 1 M LiCl solution, 1 M KF solution, and 85 % phosphoric acid, respectively. Single pulse $^7$Li MAS NMR spectra were recorded with a short (10°) pulse, 833 kHz spectral window, and the carrier at 100 ppm (233.0 MHz). $^{19}$F and $^{31}$P MAS NMR spectra were recorded with a rotor-synchronized Hahn-echo ($90^\circ$-$\tau$-$180^\circ$-$\tau$-acquisition; $\tau$ = one rotor period), 2.5 MHz spectral window and with the rf-carrier located at different positions (0-1400 for $^{19}$F) and (0, 1000, 2000, 3000, and 4000 ppm for $^{31}$P). Typically, 10000 ($^7$Li and $^{19}$F) and 30000 ($^{31}$P) scans were recorded with a relaxation delay of 0.2-0.5 s.

3. Results and discussion

3.1 Structural and chemical characterization of the synthesis products

The XPD diffractograms of the product from two synthesis methods, i.e. solid-state reaction (denoted SSR) and hydrothermal reaction (HTR) both matched triclinic LiVPO$_4$F (Figure 2) and no crystalline impurities were observed. However, as the electrochemical analysis revealed significantly different behavior for the two compounds (discussed in section 3.2.) more thorough structural analysis was undertaken.

Rietveld refinement of the XPD data using the structural model for triclinic LiVPO$_4$F revealed that the unit cell obtained by HTR is 0.64 vol% smaller than the unit cell obtained by SSR, see Table 1. The difference in unit cell volume can be linked to a difference in the degree of oxygen substitution in LiVPO$_4$F$_{1+y}$O$_y$, i.e. $y$. Using a Vegard plot from the cell volumes of LiVPO$_4$F and LiVPO$_4$O presented in Reference 8 and 15, we estimated the value of $y$ in LiVPO$_4$F$_{1+y}$O$_y$. As the hydrothermal
conditions are evidently able to supply oxygen, the product of the HTR reveals that \( \approx 35 \% \) of the fluoride was substituted by oxygen, i.e. the HTR yields LiVPO\(_4\)F\(_{0.65}\)O\(_{0.35}\). In other studies, oxygen has been introduced by heating samples of LiVPO\(_4\)F in air.\(^{10,25}\) In contrast, based on the Vegard relation, the product of the solid-state reaction has a composition of LiVPO\(_4\)F\(_{0.99}\)O\(_{0.01}\). A 1 \% oxygen inclusion is not significant, and it easily arises from differences in unit cell volume between our and reported values, e.g. due to small differences in temperature during data collection. Hence, this analysis indicates that the SSR yields oxygen-free LiVPO\(_4\)F in line with the inert (oxygen-free) synthesis conditions which is in agreement with reported literature.\(^{3,8}\)

The X-ray scattering power of Li is low, so we included NPD in our structural analysis to gain information about the Li-sublattice. The estimated compositions from the Vegard analysis were then used to perform a combined Rietveld refinement on the XPD and NPD data for both synthesis products as depicted in Figure 2. The scattering power of O and F are almost similar for both X-rays and neutrons, so their occupancies were not refined. The results of the Rietveld refinements are summarized in Table 1, and tables S1 and S2 in the Supporting Information. The combined refinement did not change the value of the unit cell volumes. Since the oxygen content in LiVPO\(_4\)F\(_{1-y}\)O\(_{y}\) SSR is not significant, the sample will hereafter be referred to as LiVPO\(_4\)F SSR. The HTR sample will be referred to as LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR. From the Rietveld refinement, the crystallite sizes were also extracted (see Table 1) using Scherrer analysis.
Figure 2: Ex-situ X-ray and neutron powder diffractograms (Cu Kα-radiation) of LiVPO$_4$F$_{1-y}$O$_y$ SSR (a) and LiVPO$_4$F$_{2/3}$O$_{1/3}$ HTR (b). The diffractograms were analyzed in a combined refinement for each sample. The scattered intensity is shown as a function of the momentum transfer, $Q$, to allow for comparison of the two radiation types. The values of $y$ are determined from the unit cell volume as explained in the text.

Table 1: Structural and chemical information for LiVPO$_4$F$_{1-y}$O$_y$ SSR and HTR samples. More details can be found in Tables S1 and S2 in the Supporting Information.
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</tbody>
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ᵃ Obtained from a Vegard plot of unit cell volumes from ref ¹⁵ and ⁸. The number in the parenthesis is the standard deviation of the estimated crystallite sizes for the individual reflections and thus reflects the size anisotropy.

Figure 3: Representative STEM images of LiVPO₄F₁₋ₓOₓ SSR (a) and LiVPO₄F₁₋ₓOₓ HTR (b). The vanadium elemental maps based on the Kα₁ transition are shown as insets. See Figure S2 and S3 for additional elemental maps.

STEM reveals a large difference in particle morphology between the two samples, see Figure 3. The LiVPO₄F SSR particles are spherical, while the LiVPO₄F₂/₃O₁/₃ HTR particles are needle-like. The EDX elemental maps confirm the presence of vanadium, phosphorous and fluoride (Figure S2 and S3). The isotropic crystallite size obtained from XPD were similar for the two samples, which indicates that the particles shown in Figure 3 are conglomerates of smaller crystallites for both samples. The anisotropy of the crystallite size is five times larger for LiVPO₄F₂/₃O₁/₃ HTR than for LiVPO₄F SSR, which fits well with the STEM result.
In order to obtain more chemical information and probe the local structural environment in the synthesis products, IR and solid-state MAS NMR spectroscopy were performed. IR spectroscopy offers a simple qualitative tool to confirm the presence of oxygen defects, as the vanadyl bond shows a strong stretching mode at 900 cm\(^{-1}\), which is confirmed in LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR with a signal at exactly 900 cm\(^{-1}\). This is not observed for LiVPO\(_4\)F SSR, see Figure S4. This confirms that oxygen substitution takes place during hydrothermal synthesis but not during the solid-state process. We note that, O-H stretch and H-O-H bend vibrations are also present, and as other authors,\(^{15}\) we interpret this as contributions from surface water.

**Figure 4:** \(^7\)Li MAS NMR spectra of as-prepared LiVPO\(_4\)F SSR (a) and LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR (b). Asterisks indicate the isotropic chemical shift.

For LiVPO\(_4\)F SSR, the \(^7\)Li MAS NMR spectra (Figure 4) shows a sharp isotropic resonance at \(\delta_{iso}(^7\text{Li}) = 115 \text{ ppm}\), while a broad isotropic resonance is observed at \(\delta_{iso}(^7\text{Li}) = 80 \text{ ppm}\) for LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR. Our observations are in agreement with earlier studies, which have assigned the site at \(\delta_{iso}(^7\text{Li}) = 115 \text{ ppm}\) to the single Li-site in LiVPO\(_4\)F, while the \(\delta_{iso}(^7\text{Li}) = 80 \text{ ppm}\) has been assigned to the two overlapping Li-sites in LiVPO\(_4\)O.\(^{10,16,26}\) The signal for LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR is
much broader than for LiVPO$_4$F SSR, which indicates that there is a distribution of different Li environments and/or stronger paramagnetic interactions. A small resonance at 115 ppm, indicating a LiVPO$_4$F environment can also be seen. LiVPO$_4$F$_{2/3}$O$_{1/3}$ HTR can thus be perceived as a solid solution between LiVPO$_4$F and LiVPO$_4$O with lithium environments resembling these environments. Hence, $^7$Li MAS NMR confirms the conclusions based on XPD, NPD and IR. However, we note that weak NMR resonances from other phases can be observed for both samples, e.g. a small signal at around 0 ppm is due to small amounts of unreacted LiF. Bamine et al. used DFT and NMR in a very recent publication to show that the F-rich and O-rich environments likely segregate into domains and are therefore not completely randomly distributed. Their samples had different compositions synthesized by high-temperature synthesis and therefore slightly different spectra than ours. It is possible that the synthesis method has an influence on the defect segregation. We hope to explore this further in a future publication focused on the local octahedra environment.

The $^{31}$P MAS NMR spectrum of LiVPO$_4$F SSR (Figure S5) shows a resonance at $\delta^{(31)P} \approx 4000$ ppm, which is partially split into a number of broad, overlapping spinning sidebands. The resonance reflects the single P-site in LiVPO$_4$F. The signals are somewhat broader as the spectra were recorded at a higher magnetic field (14.1 T) when comparing to earlier studies (2.35 T, 30 kHz spinning speed). The $^{31}$P MAS NMR spectrum of LiVPO$_4$F$_{2/3}$O$_{1/3}$ HTR is much more complex and spans nearly 4500 ppm with maximum intensity around 3000 ppm. Thus, four $^{31}$P MAS NMR spectra were recorded with the radio frequency carrier located between 0 and 4000 ppm in steps of 1000 ppm to acquire the entire spectrum (Figure S5). We note that the spectra are not quantitative as the echo sequence has a finite, non-uniform excitation band width. No spinning sideband features can be identified reflecting large variation in the local environment and/or strong residual paramagnetic line broadening. Thus, $^{31}$P MAS NMR spectrum of LiVPO$_4$F$_{2/3}$O$_{1/3}$ HTR contains a range of different local P environments. Earlier reported $^{31}$P MAS NMR spectra of LiVPO$_4$O contain two sites at
\[ \delta_{\text{iso}}(^{31}\text{P}) = 1593 \text{ and } 1418 \text{ ppm, respectively.}^{10,28} \] For LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR, the maximum intensity (\(\approx 3000 \text{ ppm}\)) is in between LiVPO\(_4\)O (1593 and 1418 ppm)\(^{10}\) and LiVPO\(_4\)F (3998 ppm)\(^{10}\), which implies presence of substantial amounts of oxygen species in line with the suggested LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) stoichiometry. The broad range of chemical shifts, i.e. different local P environments indicates significantly structural disorder in the LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR sample. Similarly, \(^{19}\text{F} \text{ MAS NMR spectra (Figure S6) show that the LiVPO}_4\text{F}_{2/3}\text{O}_{1/3} \text{ HTR sample is more disordered than LiVPO}_4\text{F SSR, but the poor resolution of the } ^{19}\text{F} \text{ MAS NMR spectra prevents further analyses. We note that DFT calculations predicts } \delta(^{19}\text{F}) = -1500 \text{ ppm for LiVPO}_4\text{F}.^{28} \]

### 3.2 Electrochemical characterization

Cyclic voltammetry (Figure 5) for LiVPO\(_4\)F SSR shows two narrow oxidation peaks at 4.27 and 4.33 V (a and b, black), with the integral of the left peak being roughly one third of that of the right peak. This corresponds nicely with the formation of a new phase with the composition Li\(_{0.67}\)VPO\(_4\)F followed by the formation of VPO\(_4\)F, in two biphasic reactions, as also observed by Mba et al.\(^{13}\) On subsequent reduction, only a single peak is observed at 4.16 V (c, black), which indicates that Li\(_{0.67}\)VPO\(_4\)F is not reformed during Li-insertion, but instead LiVPO\(_4\)F is directly formed. Reaching 1.74 V (d, black), another peak is observed for the formation of Li\(_2\)VPO\(_4\)F; the peak is rather asymmetric with a tail towards lower potentials, which indicates that the reaction is kinetically limited. Similarly, on subsequent oxidation, a redox peak is observed at 1.85 V (e, black) with a tail towards higher potentials. For LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR, a double peak is also observed in CV, but at noticeably lower potentials (4.2 V, a and b, red) in line with the potential decreasing for increasing concentrations of oxygen due to the anti-inductive effect described in the introduction. The effect has also been observed by other authors.\(^{10,15}\) The two peaks are also overlapping much more than for LiVPO\(_4\)F SSR, despite a similar scan speed of 0.02 mV/s. A double peak could indicate a two-phase
reaction with a formation of an intermediate lithiated composition, possibly \( \text{Li}_{0.5}\text{VPO}_4\text{F}_{2/3}\text{O}_{1/3} \) based on the equal intensities of the two peaks. As for \( \text{LiVPO}_4\text{F} \) SSR, only a single reduction peak is observed for the reinsertion of one Li-ion (c, red). The redox peaks at low potentials corresponding to insertion and extraction of the second Li-ion at around 2.5 to 2.0 V (d and e, red) are very broad, in line with the variation in local environment around vanadium expected for this compound based on the NMR results.

Curiously, for \( \text{LiVPO}_4\text{F}_{2/3}\text{O}_{1/3} \) HTR, another redox couple is observed at \( \approx1.4 \) V (f and g, red). The origin of these peaks is not obvious, but they have been observed previously.\(^{15}\) It is possibly from the reduction of \( \text{V}^{3+} \) only coordinating to oxygen (i.e. as in fluoride-free \( \text{LiVPO}_4\text{O} \)), but no reports of the further reduction of \( \text{Li}_2\text{VPO}_4\text{O} \) exist to confirm this. It is also possible that it is simply from the reduction of \( \text{V}^{3+} \) in a mixed fluoride/oxygen environment, as the reduction of \( \text{V}^{3+} \) in oxygen-free \( \text{LiVPO}_4\text{F} \) is 1.8 V, and this potential might be lowered slightly due to the presence of oxygen defects.\(^{15}\)

![Figure 5](image)

**Figure 5:** a) Cyclic voltammograms for \( \text{LiVPO}_4\text{F} \) SSR and \( \text{LiVPO}_4\text{F}_{2/3}\text{O}_{1/3} \) HTR. The scan speed was 0.02 mV/s, and the voltage interval was 4.7 to 1.0 V. b) GITT results for \( \text{LiVPO}_4\text{F} \) SSR and \( \text{LiVPO}_4\text{F}_{2/3}\text{O}_{1/3} \) HTR. C/10 pulses of 30-minute durations, followed by a two-hour rest period, were used. 20 pulses were used for oxidation, and 40 for reduction, leading to extraction of one Li-ion per formula unit, followed by the insertion of two Li-ions.
The GITT data for both samples (Figure 5, right) shows a voltage plateau for the extraction of Li-ions near 4.2 V with a small overpotential (ca. 15 mV). The voltage plateau is ≈110 mV higher for LiVPO₄F SSR than for LiVPO₄F₂/₃O₁/₃ HTR, which matches the CV-result. For LiVPO₄F SSR, a change in the equilibrium potential of ca. 15 mV is seen after the extraction of roughly a third of a Li-ion per VPO₄F unit, showing again the formation of Li₀.₆₇VPO₄F via a two-phase transformation. The overpotential for extraction of Li-ions from Li₀.₆₇VPO₄F is apparently slightly higher (≈37 mV) than for LiVPO₄F, as indicated by the larger voltage relaxation. LiVPO₄F₂/₃O₁/₃ HTR also shows a change in the equilibrium potential (≈70 mV) around x = 0.5, again matching the CV result, although this is not nearly as well resolved as for LiVPO₄F SSR. For insertion of the second Li-ion, a voltage plateau is observed for LiVPO₄F SSR around 1.8 V, which initially has a low overpotential (≈40 mV). However, after insertion of roughly 1.2 Li-ions per formula unit, the dynamic voltage decreases (i.e. the voltage during the current pulses decreases) but relaxes back to the plateau value during the relaxation. Hence, in this region the overpotential is large (540 to 700 mV) indicating a large kinetic limitation in the Li-ion diffusion. After insertion of 1.4 Li-ions per formula unit, it is doubtful that as many Li-ions are inserted into the cathode as indicated from Coulomb counting, as the voltage no longer relaxes back to 1.8 V. It has previously been argued that even small amounts of oxygen defects can have a detrimental impact on the low-voltage performance.¹⁰

For insertion of the second Li-ion into LiVPO₄F₂/₃O₁/₃ HTR, a plateau is never observed, but instead a sloping voltage is seen, indicating solid solution behavior, with a large associated overpotential (250 to 650 mV). The slope starts around 2.5 V, in agreement with the presence of a LiVPO₄O-like environment, but without discreet plateaus as observed in fluoride-free LiVPO₄O.

Overall, various literature reports indicate that the introduction of oxygen defects is detrimental for the electrochemical performance in the low-voltage regime.¹⁰,¹⁵ However, despite the slight decrease
in redox potential, small amounts of oxygen might be beneficial in the high-voltage regime, e.g. Boivin et al. showed that while large concentrations of oxygen defects were detrimental for the capacity retention, for samples with small amounts of oxygen defects, the capacity retention was significantly better than for pure LiVPO$_4$F.\textsuperscript{15} The polarization was also lower, which might be due to better electronic conductivity from the mixed valence states.

### 3.2 Dynamic charge-discharge phase evolution

The diffractograms obtained under operando conditions using synchrotron X-ray radiation are displayed in Figure 6 in an overview-plot as a function of Li-content (determined by coulombic counting). It is immediately clear that there is a large difference in the structural evolution between the two studied compositions. LiVPO$_4$F SSR exhibits a series of constant angle reflections, which change discretely during a series of two-phase reactions as expected (see reactions 1 and 2). LiVPO$_4$F$_{2/3}$O$_{1/3}$ HTR also exhibits regions of coexisting phases, but their respective reflections change in angular position continuously. This phenomenon has been observed before for well-known olivine compounds such as LiFePO$_4$.\textsuperscript{29,30} In single-phase regions, LiVPO$_4$F$_{2/3}$O$_{1/3}$ HTR exhibits simple solid solution behavior. For both samples, the two-phase regions coincide with plateaus in the potential profile for the extraction and insertion of one Li-ion at 4.2 V as expected. However, for the extraction/insertion of the second Li-ion, around 1.8 V, two phases are still observed, despite the potential profile being sloped.
Figure 6: Results for operando SR-XPD on LiVPO$_4$F SSR (a, c) and LiVPO$_4$F$_{2/3}$O$_{1/3}$ (b, d). a) and b): Overview-plots of the obtained diffractograms as a function of Li-content. The intensity of the peaks is shown in a gray scale, with more intense peaks shown in darker colors. c) and d): Potential profile and relative unit cell volume per formula unit, extracted by Rietveld refinement, as a function of Li-content. For the two-phase system between LiVPO$_4$F$_{2/3}$O$_{1/3}$ and Li$_2$VPO$_4$F$_{2/3}$O$_{1/3}$ in HTR (d), the color-fading of data points represents a visual estimation of the fraction of the two phases. For all other data points, the color-fading directly represents the weight percentages as extracted by Rietveld refinement.

To further investigate the structural evolution, Rietveld refinement was performed. By close inspection of the individual patterns and the overview plots, it was decided whether to fit with a single or two phases. In the two-phase region between LiVPO$_4$F$_{2/3}$O$_{1/3}$ and Li$_2$VPO$_4$F$_{2/3}$O$_{1/3}$ for the HTR sample, numerous refinement attempts failed to produce sensible results, even for fixed atomic...
positions and profile parameters, due to overlap between the reflections of the two phases. Instead, full pattern Le Bail fitting was performed to extract the cell parameters in this region.

The unit cell volume per formula unit relative to the first pattern in the series is shown in Figure 6 (bottom) for the various phases as a function of the Li-content. The cell parameters for triclinic LiVPO$_4$F are difficult to compare with monoclinic VPO$_4$F and Li$_2$VPO$_4$F, as the unit cells for the latter are twice as large and the axes are differently defined. In LiVPO$_4$F, all three cell lengths are defined as certain V-V vectors, so the corresponding vectors were located in VPO$_4$F and Li$_2$VPO$_4$F as well as the angles between them.$^{31}$ Thus, all cell parameters are converted to a LiVPO$_4$F-like system. The cell parameters extracted in this way are shown in Figure S8 and S9 in the Supporting Information.

For LiVPO$_4$F SSR, firstly a two-phase reaction between two isostructural triclinic phases (space group $P\overline{1}$) takes place upon charging. This phase transition is complete at $x = 0.62$, which corresponds well with the LiVPO$_4$F/Li$_{0.67}$VPO$_4$F couple also observed in the CV and GITT experiments. During the phase transformation, the b-axis contracts, while the a- and c-axes remain constant (Figure S8), and the volume change is less than 2% (Figure 6). Shortly after the complete formation of Li$_{0.67}$VPO$_4$F, a new two-phase transition initiates between the triclinic Li$_{0.67}$VPO$_4$F and the monoclinic VPO$_4$F phase (space group $C2/c$), which naturally concludes at $x = 0$. During this transition, the a- and b-axes contract, while the c-axis actually expands.$^{31}$ This is likely due to the repulsion of the phosphate groups in the absence of the positive lithium ions, which results in a slight stretching of the octahedra chain. The volume change is 8 % relative to the starting LiVPO$_4$F phase.

As also noted by Mba et al.,$^{32}$ the Li$_{0.67}$VPO$_4$F phase is not observed upon subsequent lithiation, but instead VPO$_4$F transforms directly to LiVPO$_4$F. Near the voltage plateau at 1.8 V, reflections appear for the monoclinic Li$_2$VPO$_4$F phase. The refinement was able to explain all observed peaks for Li$_2$VPO$_4$F, except for a single small reflection at 13.05°. This peak was not observed by Masquelier
et al. or Ellis et al.,\textsuperscript{7,32} but is identified by Fullprof as the \((2; 02)\) reflection. The emergence of the peak with increasing values of \(x\) is shown in Figure 7. The peak differs from the rest of the emerging peaks for the \(\text{Li}_2\text{VPO}_4\text{F}\) phase as it appears to reach a saturation intensity, after which the peak does not increase in intensity with increasing values of \(x\), while the rest of the \(\text{Li}_2\text{VPO}_4\text{F}\) peaks do. The \((2; 02)\) lattice plane is shown in Figure S10 in the Supporting Information. This plane intersects the single vanadium site (V1), an oxygen site (O2) and a lithium site (Li1). We attempted to explain the peak by anti-site defects by inserting vanadium ions on the Li-ion positions and vice versa; however, all attempts gave fits that were very significantly poorer than the ordered structure.

\textbf{Figure 7:} Diffractograms of \(\text{LiVPO}_4\text{F}\) SSR during insertion of the second Li-ion per formula unit. The \((2; 02)\) reflection is indicated in the figure. \(x\) is \(\text{Li}_x\text{VPO}_4\text{F}\). The background signal centered around \(11^\circ\) is due to the carbon windows in the AMPIX cell.

The phase transformation between \(\text{LiVPO}_4\text{F}\) and \(\text{Li}_2\text{VPO}_4\text{F}\) is anisotropic with the a-axis expanding significantly more (\(\approx0.18\ \text{Å}\)) than the b- and c-axes (\(\approx0.06\) and \(\approx0.05\ \text{Å}\), respectively. The c-axis evolves in a continuous fashion). The overall volume change is however again 8\% relative to the starting \(\text{LiVPO}_4\text{F}\) phase. As the sample does not reach \(x = 2\) before hitting the voltage limit of 0.5 V
(where \( x = 1.9 \)), the sample still contains the LiVPO\(_4\)F phase upon recharging. The structural evolution analysis confirms the study of Mba et al.,\textsuperscript{32} which also shows that LiVPO\(_4\)F, with low amounts of oxygen defects, is delithiated/lithiated via biphasic reactions with relative volume changes of 8%.

For LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR, the reflections for LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) vary in their angular positions, indicating solid solution behavior. The Li\(_{0.67}\)VPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) phase is not observed for this sample on charging, but on close inspection of the individual patterns in this region, the reflections evolve in a fashion that could be interpreted as a two-phase transformation with simultaneous solid solution behavior, see Figure 8. This phenomenon was also described recently by Boivin et al.\textsuperscript{18} But they argued that a phase transition was expected when the lithium content \( x \) reaches the oxygen concentration \( y \), so when \( x = y \). For LiVPO\(_4\)F SSR, the phase transformation to Li\(_{0.67}\)VPO\(_4\)F is evident primarily by the emergence of a reflection near 10.4°. A similar reflection also appears to emerge for LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) HTR, but with a smaller shift in angular position, and with a slight continuous change in angle upon continued Li-extraction. A new reflection can also be gleaned at 13.25°, but this is in fact just a splitting of the (110) reflection from the (1;−1;−2) reflection in LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\), which in LiVPO\(_4\)F SSR do not split during the formation of Li\(_{0.67}\)VPO\(_4\)F. Attempts to refine this region with two triclinic phases did not produce sensible results, and thus only the LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\) phase is shown in Figure 6. If another phase exists with a Li-content less than 1, for example \( x \approx 0.5 \) as indicated by CV and GITT, the structure and unit cell size are very close to those of LiVPO\(_4\)F\(_{2/3}\)O\(_{1/3}\). Extracted diffractograms are also shown in Figure S11 for both samples to further highlight the difference in behavior.
Figure 8: Diffractograms of LiVPO$_4$F SSR and LiVPO$_4$F$_{2/3}$O$_{1/3}$ HTR during extraction of the first Li-ion per formula unit.

Li-extraction will eventually lead to the formation of the monoclinic VPO$_4$F$_{2/3}$O$_{1/3}$ phase. The two-phase regime between LiVPO$_4$F$_{2/3}$O$_{1/3}$ and VPO$_4$F$_{2/3}$O$_{1/3}$ is, however, significantly shorter than for LiVPO$_4$F SSR, both during Li-extraction and the subsequent Li-insertion (Figure 6). Instead, an extended single-phase solid solution regime is observed from $x \approx 0.3$ (Li-extraction) to $x \approx 0.16$ (Li-insertion). Furthermore, the volume change is only 3.2 to 5.8 % relative to the starting LiVPO$_4$F$_{2/3}$O$_{1/3}$ phase, compared to the 8 % for LiVPO$_4$F SSR. The change of 5.8 % matches the result of Boivin et al. very well. Between the starting LiVPO$_4$F$_{2/3}$O$_{1/3}$ phase and the VPO$_4$F$_{2/3}$O$_{1/3}$ phase at $x = 0$, the a-axis decreases slightly, while the b-axis decreases significantly ($\approx 0.08$ and $\approx 0.22 \text{Å}$, respectively). The c-axis also increases significantly ($\approx 0.19 \text{Å}$), even more than for LiVPO$_4$F SSR, which is the reason for the lower volume decrease. However, these changes occur gradually, and in the two-phase regions, the difference in unit cell axes is significantly lower ($\approx 0.009$, $\approx 0.09$ and $\approx 0.15 \text{Å}$, respectively; the effect is especially large for the b-axis). This likely helps to alleviate the strain during phase transformation. The same trend is observed upon formation of the monoclinic Li$_2$VPO$_4$F$_{2/3}$O$_{1/3}$ phase,
though the volume change is 8% as for LiVPO₄F SSR at the end of discharge. The change in the a-, b- and c-axes is ≈0.19, ≈0.06 and ≈0.13 Å, respectively. Again, the difference is significantly lower in two-phase regions, where the b-axis is initially virtually identical for the LiVPO₄F₂/₃O₁/₃ and Li₂VPO₄F₂/₃O₁/₃ phases. Noticeably, the c-axis appears to decrease only to increase again during discharge. The reason for this behavior is not clear.

The observation that the phase evolution for the more disordered LiVPO₄F₂/₃O₁/₃ sample is exhibiting significantly more solid solution behavior than for the ordered sample is very important, as it can help to explain a very recent study, where it was found that LiVPO₄F₀.₆₅O₀.₃₅ cathodes had a significantly better capacity retention than LiVPO₄F cathodes.¹⁵ Due to the much less abrupt changes in unit cell volume of the cathode material, the strain is lower, which could hinder the capacity fade. As mentioned previously, the oxygen defects must be under a certain concentration, as the capacity will otherwise suffer.¹⁰,¹⁵ This study therefore adds to the conclusion that an optimal defect concentration can be found, where the voltage, capacity and capacity retention is in balance.

4. Conclusion

The structural evolution of LiVPO₄F₁₋ₓOₓ, prepared both by a classic solid-state reaction method (SSR) and by a hydrothermal reaction method (HTR), was investigated using operando synchrotron X-ray powder diffraction and STEM. The latter revealed that LiVPO₄F₁₋ₓOₓ SSR had spherical particles, while LiVPO₄F₁₋ₓOₓ HTR had needle-formed particles. LiVPO₄F₁₋ₓOₓ HTR was shown to contain a large concentration of oxygen defects (LiVPO₄F₂/₃O₁/₃), while LiVPO₄F₁₋ₓOₓ SSR was mostly ordered (fluoride-rich, x ≈ 0). Large structural differences were observed for the two samples during operation. LiVPO₄F SSR exhibited classic two-phase behavior between the phases LiVPO₄F, VPO₄F and Li₂VPO₄F, as well as an off-stoichiometric triclinic Li₀.₆₇VPO₄F phase. LiVPO₄F₂/₃O₁/₃ HTR, on the other hand, showed much narrower two-phase regions and instead showed extended
solid-solution regimes as well as an overall lower volume change for lithium extraction. This leads
to lower strain upon phase transformation, which can help reduce capacity fade. However, the
discharge potential was slightly lower than for LiVPO$_4$F SSR, leading to a slightly lower energy
density. This study shows that oxygen defects have a large impact on the structural behavior and adds
to previous studies in the conclusion that an optimal concentration of oxygen defects in the structure
exists, where the electrochemical properties are balanced between LiVPO$_4$O and LiVPO$_4$F.

Associated Content
Supplementary Information
VPO$_4$ diffractogram, Rietveld refinement data, STEM images, FT-IR spectra, $^{31}$P and $^{19}$F MAS NMR
spectra, impedance spectra, unit cell parameters, (2;02) lattice plane

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Notes
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