Dynamic Charge-Discharge Phase Transitions in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Cathodes

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Abstract

Monoclinic $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ is a promising cathode material for future Li-ion batteries due to its high theoretical capacity, good capacity retention and relatively high ionic conductivity. The material undergoes a series of complex phase transitions which depend on the number of Li-ions extracted during charge. The phase behavior has been extensively studied under (quasi-) equilibrium conditions, however insight into the phase evolution during dynamic conditions is lacking. Through *operando* synchrotron X-ray diffraction we report the complex series of structural phase transitions under dynamic battery charge-discharge conditions in $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ cathodes with extraction of both two and three Li-ions. For extraction of two Li-ions, the phase evolution follows the series of expected two-phase transitions, while for extraction of three Li-ions the dynamic phase behavior differs significantly from that observed by equilibrium studies, e.g. we reveal unexpected solid solution behavior during removal of the last Li-ion and unforeseen structural hysteresis between charge and discharge. Our results are further reinforced by electrochemical analysis. This paper joins a series of recent reports, where extended solid solution behavior in battery electrode materials is observed under *operando* conditions, and reinforces the importance of these types of measurements to provide a more realistic picture of working battery materials.

Keywords: Li-ion batteries; phase transition; $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; *operando* PXD; cathode materials

1. Introduction

Rechargeable Li-ion batteries are today one of the most promising technologies for energy storage, and are expected to play a key role in especially automotive applications. However, in order to meet the demands of future applications, significant improvements to the present technology are required such as enhanced rate capability, longer cycle life and lower production costs [1]. These characteristics are to a large extent governed by the nature of the electrode materials and the processes occurring therein during battery charge and discharge, i.e. the thermodynamics and kinetics of the oxidation/reduction and the accompanying phase transformation [2]. Thus, to truly select and develop novel superior batteries one must understand the details of these underlying processes.

The development of intercalation-type batteries has produced a wide selection of cathode materials, each with distinct advantages and disadvantages. Since the first commercialized cobalt-based oxides, especially phosphate-based intercalation materials have attracted much attention following the work of Goodenough and co-workers [3]. Among these, monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ often denoted $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ shows promise due to its high theoretical capacity (197 mAh g^{-1}), good capacity retention and relatively high ionic conductivity [4–6]. Like other phosphate-based cathode materials, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has a high operating voltage due to the inductive effect of the phosphate groups [7], but on the down side a low intrinsic electronic conductivity. To enhance the latter, the materials are therefore often coated with carbon.

It has been shown, that under equilibrium (or pseudo-equilibrium) conditions $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ undergoes a series of four consecutive phase-transitions during battery charge (see reactions equations 1-4), visible by four plateaus in a galvanostatic potential profile [8,9].

The listed potentials in Equation 1-4 are the measured values [10], which are very close to the equilibrium potential for extraction of the first two Li-ions (Equation 1-3), while the overpotential for extraction of the last Li-ion is significantly higher (Equation 4) [8,11–13]. On subsequent discharge, the potential profile of the material will depend on the number of Li-ions extracted during charging [8]. Following extraction of two Li-ions (Equation 1-3), the pathway of the delithiation is reversible, and lithiation goes through the reverse reactions, exhibiting the same number of plateaus in the galvanostatic potential profile. In contrast, when all three Li-ions are extracted during charge, the subsequent discharge is characterized by sloping potentials until the insertion of two Li-ions is complete. This behavior points towards Li-disorder and solid solution reaction during insertion of two Li-ions according to Equation 5. Insertion of the third Li-ion is again characterized by a flat potential plateau and two-phase behavior (Equation 2 and 1) [10]:

The hysteretic phase evolution is explained by charge-ordering on the vanadium ions [8,14]. The structure of α - $Li_3V_2(PO_4)_3$ (space group $P2_1/n$) includes three crystallographic distinct Li-ions (see Figure 1), where Li1 is 4-fold coordinated, while Li2 and Li3 are 5-fold coordinated [12,13]. When extracting the first Li-ion, Li3 is preferentially removed, since it has the highest energy [15]. This gives rise to an ordering of the charge on vanadium, where columns of either V^{III} or V^{IV} form along the b -axis. The position of the Li2-ion changes slightly, while the Li1-positions remain fixed. Due to repulsion between V^{IV} and Li, Li1 is preferentially extracted secondly. If lithium is now reinserted, it will first enter back into the Li1 position and subsequently into the Li3-position as the

site energy of the Li3-site is higher. This ensures that the lithiation is the reverse of the delithiation. If on the other hand all three Li-ions are extracted, V^{IV} and V^V are formed and are randomly distributed in the structure. Since there is no order left to guide the lithiation, Li-ions will be randomly inserted on both the Li1- and Li2-sites. This disorder results in the solid solution behavior observed during discharge. When the Li1- and Li2-sites are fully occupied, only the Li3-site is vacant, and the two-phase behavior reemerges.

Figure 1. Crystal structure and powder X-ray diffraction data of monoclinic α - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Left: The structure of monoclinic α - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (Space group $P2_1/n$, $a = 8.611(5)\text{\AA}$, $b = 8.598(4)\text{\AA}$, $c = 12.044(7)\text{\AA}$ and $\gamma = 90.605(49)^\circ$ (lattice parameters from refinement of diffractogram to the right)). PO_4 -tetrahedra in purple, VO_6 -octahedra in light blue, Li1 in blue, Li2 in yellow and Li3 in green. Right: Rietveld refinement profile of *ex situ* synchrotron powder X-ray diffraction data of as-prepared α - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (from this work, $\lambda = 0.2071\text{\AA}$, P02.1, PetraIII).

Thus, the phase behavior of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is quite well understood under equilibrium (or pseudo-equilibrium) conditions based on studies of the individual chemically prepared stable phases as well as indirectly from electrochemical observations. However, to this point the described phase transformation mechanisms have not been observed and well analyzed directly from experimental data. Furthermore, very little is known about the structural phase evolution of this material

occurring during battery operation, i.e. under dynamic working conditions. Measurement of the structure under equilibrium conditions might not reveal important features of the structural evolution of a cathode material under realistic conditions, since a battery in operation inherently is not at equilibrium. The importance of performing *operando* measurements in order to properly understand the structural phase transformation mechanism has recently been highlighted by several discoveries of unexpected transition pathways involving widely extended Li-regimes of metastable solid solutions in LiFePO_4 [16] and $\text{LiMn}_{1-y}\text{Fe}_y\text{PO}_4$ [17,18], and formation of a nanocrystalline solid solution in the $\text{NaFePO}_4\text{-FePO}_4$ system [19], which alleviates misfit strain between the two end-members. For $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, investigation have so far mainly relied on non-*operando* diffraction measurements, either *ex situ* following chemical oxidation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [8], or pseudo *in situ*, i.e. an *ex situ* measurement following a current pulse when equilibrium has been obtained [12]. A single *operando* synchrotron radiation powder X-ray diffraction investigation on $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has been published [20]. Unfortunately, this study only presents a single measurement, where all Li-ions are extracted and the discharge data is not analyzed in detail, i.e. changes in unit cell dimensions are not extracted. Furthermore, in the charge state, the cathode in this study contains a mix of $\text{Li}_2\text{V}_2(\text{PO}_4)_3$, $\text{LiV}_2(\text{PO}_4)_3$ and $\text{V}_2(\text{PO}_4)_3$, i.e. single phase $\text{V}_2(\text{PO}_4)_3$ is not reached.

Here, we use *operando* synchrotron powder X-ray diffraction (SR-PXD) and Rietveld analysis combined with standard material- and electrochemical-characterization techniques to investigate the structural phase evolution of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathodes during dynamic battery charge and discharge. We elucidate how the phase transition mechanism dependent on the degree of Li-extraction and surprisingly we discover that contrary to previous equilibrium studies the extraction of the final Li-ion does not proceed via a two-phase reaction mechanism.

2. Experimental

2.1. Synthesis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

For this study, $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ was synthesized using an approach similar to that reported by Li et al. [21]. Herein, 3.000 g V_2O_5 ($\geq 99.6\%$, Sigma-Aldrich), 5.692 g $\text{NH}_4\text{H}_2\text{PO}_4$ ($\geq 98\%$, Sigma-Aldrich) and 1.828 g Li_2CO_3 ($\geq 99\%$, Sigma-Aldrich) were dissolved in 100 mL distilled water. 15.845 g citric acid (99%, Sigma Aldrich) was dissolved in 20 mL distilled water and slowly added to the solution. The solution was stirred at 80 °C for 30 minutes and left at room temperature (without stirring) for two days. At this point it had transformed into a blue gel. The gel was dried in an oven for three days at 80 °C, after which a green xerogel was obtained. The xerogel was ground by hand in a mortar and heated at 300 °C for 4 hours in argon. The product was then reground and heated at 750 °C for 4 hours in argon to form the final product.

2.2 Product characterization

Ex situ SR-PXD data was measured on the as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powder mounted in a kapton tube (ID 1.00mm) at beamline P02.1 at PetraIII, DESY, Hamburg. The selected wavelength was 0.20713 Å. The data was collected using a Perkin Elmer amorphous silicon detector and an X-ray exposure time of 1 second and 30 subframes. The data image was reduced to 2theta-intensity data using Fit2d [22]. Rietveld refinement was performed using the Fullprof software [23]. The background was described by linear interpolation between selected points, while pseudo-Voigt profile functions were used to fit the diffraction peaks [23]. The atomic positions and cell parameters obtained by Yin and co-workers were used as starting points for the structural model [8,9]. The crystallite size was estimated from the data using the Scherrer equation via Fullprof. A highly crystalline CeO_2 NIST standard was used to determine the instrument resolution for correction of the data.

The particle size of the as-prepared material was determined by Brunauer-Emmett-Teller (BET) analysis. Here, the material surface area was measured using a Nova2200e surface area and pore size analyzer from Quantachrome. The material was outgassed overnight at 300 °C under vacuum prior to the measurement. The average particle size was determined from BET-surface area measurements using the spherical approximation relation, i.e. particle diameter = $6000/(\text{BET-surface} \cdot \text{density})$.

The carbon content of the as-prepared material was measured on an Elementar Vario Macro Cube™ CHNS analyzer.

2.3 *Electrode preparation and battery cell construction*

The cathodes for electrochemical characterization were made by casting a slurry of 80 wt% as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, 10 wt% Super P C45 (CENERGY) and 10 wt% PVDF (HSV900 PVDF, MTI Corporation) in N-methyl-2-pyrrolidone (99.5 %, anhydrous, Sigma-Aldrich) onto aluminum foil. After drying at 60 °C under vacuum overnight, 10 mm diameter discs were cut, pressed with 2 ton and dried over night at 60 °C under vacuum. The active material loading was $\sim 4.6 \text{ mg cm}^{-2}$. 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%, Aldrich).

For the *operando* SR-PXD experiments, free standing cathode pellets were made from a composite of 75 wt% as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, 10 wt% Super P C45 (CENERGY) and 15 wt% PVDF (HSV900 PVDF, MTI Corporation) mixed in acetone. After drying, the composite was ground to a fine powder, and pressed to pellets of 7 mm in diameter each weighing around 10 mg. The AMPIX cell [24] 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 construction was carried out in an Argon filled glovebox equipped with a circulation purifier and O₂/H₂O levels kept below 1 ppm.

2.4 Electrochemical characterization

The electrochemical characterization was carried out using a BioLogic MPG2. For galvanostatic charge/discharge two identical cells were cycled at C/10-rate, where C refers to the extraction of three lithium ions. One cell was cycled between 4.4 V and 3.0 V and the other between 5.0 V and 3.0 V to extract two and three Li-ions, respectively. For cyclic voltammetry (CV), two identical cells were also prepared and cycled with a voltage scanning speed of 0.05 mV s⁻¹. One cell was cycled between 4.4 V and 3.0 V and the other between 5.0 V and 3.0 V. Prior to the CV measurements, both cells were galvanostatically cycled between 4.4 V and 3.0 V in order to ensure formation of similar SEI layers in the two cells.

2.5 Synchrotron Radiation Powder X-ray Diffraction (SR-PXD)

The SR-PXD measurements were performed at beamline P02.1 at PetraIII, DESY, Hamburg using a selected wavelength of 0.2071 Å. For the measurements, a slightly modified version of the AMPIX battery test cell [24] was used to collect simultaneous SR-PXD data and electrochemical information about the galvanostatic charge and discharge. Two similar cells were used for the experiments. Prior to the *operando* diffraction measurements, the cells were cycled between 4.4 V and 3.0 V at C/5 to ensure formation of similar solid electrolyte interphase (SEI) layers in the two cells. During collection of *operando* SR-PXD data, one cell was cycled between 4.4 V and 3.0 V and the other between 5.0 V and 3.0 V. To increase the PXD-time resolution near the plateaus corresponding to the redox pairs Li₃V₂(PO₄)₃/Li_{2.5}V₂(PO₄)₃ and Li_{2.5}V₂(PO₄)₃/Li₂V₂(PO₄)₃, a current rate of C/20 was used in the voltage interval 3.5-3.8 V on charging, and 3.7-3.4 V on discharge. C/10 was used elsewhere. The diffractograms were obtained using a Perkin Elmer amorphous silicon detector and an X-ray exposure time of 1 second with 30 subframes. The data

images were reduced to 2theta-intensity data using Fit2d [22]. The SR-PXD data were analyzed using Rietveld refinement performed using the software Fullprof [23]. The backgrounds were described by linear interpolation between selected points, while pseudo-Voigt profile functions were used to fit the diffraction peaks [23]. The scale factor, unit cell parameters, Full-Width-at-Half-Max (FWHM) parameters and zero-point offset were refined for each pattern. Again, the atomic positions, occupancies, thermal factors and cell parameters obtained by Yin and co-workers were used as starting point [8,9]. The atomic positions, occupancies and thermal factors were kept fixed throughout the refinement of the *operando* data.

3. Results and discussion

The main focus of our investigation is to understand the phase evolution in $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ during dynamic charge-discharge by *operando* SR-PXD and detailed analysis by Rietveld refinement. To provide a thorough understanding of the material utilized in the present study, we start this section by describing the results and observations of the general material characterization.

3.1 General material characterization

From Rietveld refinement of *ex situ* SR-PXD data (Figure 1, right), our as-prepared material is identified as phase pure monoclinic $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ with space group and unit cell parameters matching those previously reported from single and powder X-ray diffraction [8,12,13]. Based on the SR-PXD data, the crystallite size was estimated to 59(5) nm in diameter. This entails that the as-prepared material is comprised of agglomerates of a few crystallites as the average spherical particle diameter, determined from BET surface area analysis, is ~130 nm (surface area: $15.12 \text{ m}^2 \text{ g}^{-1}$). The carbon content in the as-prepared material is 21 wt% determined by CHNS elemental analysis. This is accounted for in all calculated capacities.

The CV data (Figure 2) shows a number of peaks corresponding to the number of plateaus in the galvanostatic potential curves (Figure 3), and the observed potentials coincide well with the potentials in Equation 1-5. The voltammogram for the cell cycled between 4.4 V and 3.0 V, i.e. only two Li-ions are extracted (Figure 2, left), shows three narrow peaks during both oxidation and reduction, i.e. Li-extraction and –reinsertion, respectively. The voltammogram for the cell cycled between 5.0 and 3.0 V, i.e. all three Li-ions are extracted (Figure 2, right), is noticeably different, in accordance with previous reports [21,25]. Here, an additional broad oxidation peak is observed near 4.6 V for the transition between $\text{LiV}_2(\text{PO}_4)_3$ to $\text{V}_2(\text{PO}_4)_3$, while during reduction a very broad peak with a center at ~ 3.9 V is observed, which likely corresponds to the transition from $\text{V}_2(\text{PO}_4)_3$ to $\text{Li}_2\text{V}_2(\text{PO}_4)_3$. This is in contrast to the sharp reduction peak just above 4.0 V observed when only two Li-ions are extracted. The two sharp reduction peaks at 3.63 and 3.55 V are observed for this cell, however, on subsequent cycles these peaks are seen to lose significantly intensity. A similar result was obtained by Saïdi and co-workers [26], who noticed that the majority of the capacity loss during lithiation occurs during insertion of the last Li-ion.

Figure 2. Cyclic voltammetry data for Li-extraction and -insertion in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Cyclic voltammograms of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ vs. Li at 0.05 mV/s with cycling between (left) 4.4 and 3.0V, and (right) 5.0 and 3.0 V, corresponding to extraction of two and three Li-ions, respectively. Data are shown for the first six cycles. Each current peak is labelled with the relevant redox pair.

Overall, the cycling is significantly less reversible, when the final Li-ion is extracted. As discussed later, the broad peaks are interpreted to indicate solid solution behavior, while sharp peaks indicate two-phase transitions. Our electrochemical observations support previous findings and are generally in line with the description of the proposed phase transition mechanism. However, CV (Figure 2) hints that extraction of the third Li, i.e. the phase transition between $\text{LiV}_2(\text{PO}_4)_2$ and $\text{V}_2(\text{PO}_4)_3$ may not be accompanied by two phase behavior, but rather a solid solution reaction based on the broad character of the oxidation peak.

3.2 Dynamic charge-discharge phase evolution

To investigate the details of the phase transition mechanism under dynamic conditions, *operando* SR-PXD experiments were performed during charge and discharge for extraction of both two and three Li-ions, which produced a total of 140 and 174 diffractograms, respectively. The diffractograms are shown in Figure 3 along with the simultaneously measured galvanostatic potential profile and the unit cell volumes obtained from Rietveld refinement. From the overview-plots (top Figure 3), a number of two-phase transformations between isostructural phases can be observed (see also the zoom of a selected data region in Figure 4). Upon such transformations, new reflections, slightly displaced in their angular values, appear as new phases with different Li-composition form. In contrast, if the existing phase takes up or releases Li via a solid solution reaction, the angular position of the reflections will change gradually as the composition changes. The overview-plots of the diffractograms of the two samples reveal that, as would commonly be expected, a plateau in the galvanostatic potential profile is generally associated with a two-phase

system, while a more curved potential profile is associated with a single-phase (solid solution) system. It is also clear, that the number of Li-ions extracted has a significant influence on the structural evolution and reversibility, as expected.

When extracting only two Li-ions (Figure 3, left), the material undergoes an almost identical series of three two-phase transformations on charge and discharge, i.e. the galvanostatic potential profile and the diffractogram overview-plot are both roughly symmetrical around the fully charged state. Thus, upon extraction of two Li-ions the phase transitions follow equation 1-3 reversibly as expected. This is further evidenced by the extracted unit cell volumes, which remains relatively constant for the individual phases independently of state of charge or discharge, i.e. the Li-content and thus the V-oxidation state remain constant in the individual phases.

Figure 3. Operando X-ray diffraction data collected during battery charge and discharge. (Top) Overview-plots of the *operando* SR-PXD data as a function of time, and (bottom) galvanostatic potential

profile and unit cell volumes extracted from Rietveld refinement as a function of time. The white stripes in the overview-plots are due to interruptions in the X-ray beam. C/10 and C/20 refer to the used current rates. The left plot shows data for charge to 4.4 V, corresponding to the extraction of two Li-ions and the right plot shows data for charge to 5.0 V, corresponding to the extraction of three Li-ions.

When extracting the last Li-ion from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (i.e. extracting all three Li-ions), the behavior changes significantly (Figure 3, right). As opposed to the first three phase transitions during charge, the last Li is extracted from $\text{LiV}_2(\text{PO}_4)_3$ via a continuous solid solution reaction forming $\text{V}_2(\text{PO}_4)_3$ according to equation 6.

This is in contrast to previous *ex situ* investigations, which report formation of $\text{V}_2(\text{PO}_4)_3$ from $\text{LiV}_2(\text{PO}_4)_3$ during charge via a two-phase reaction (as described by eq. 4) [12,20]. However, we found no sign of a two-phase system between $\text{LiV}_2(\text{PO}_4)_3$ and $\text{V}_2(\text{PO}_4)_3$ and in the entire Li-range $1 < x < 0$ no satisfactory fits were obtained by Rietveld refinement using two phases. Solid solution behavior of $\text{V}_2(\text{PO}_4)_3$ is also implied by the *operando* PXD study by Yoon et al. [20] as the data shows varying unit cell volume for this phase during charge, however the behavior is less clear due to the presence of multiple phases ($\text{Li}_2\text{V}_2(\text{PO}_4)_3$, $\text{LiV}_2(\text{PO}_4)_3$ besides $\text{Li}_x\text{V}_2(\text{PO}_4)_3$). To test if the solid solution is metastable, a battery was charged at C/10 current rate and stopped during the solid solution reaction after removal of $\sim 2.5\text{Li}$, i.e. $\text{Li}\sim 0.5\text{V}_2(\text{PO}_4)_3$ is formed. The battery was disassembled and *ex situ* PXD data was collected from the cathode after 24 hours of rest (Figure S5, supplementary information). No signs of phase separation or other kinds of phase instability were observed during these relaxation conditions.

Figure 4. Overview of phase transition mechanisms during charge and discharge. (Top) Expanded view of the *operando* SR-PXD data for charge and discharge of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Note, that for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ the (020), (200), (112) and (-112) reflections overlap. Upon formation of $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$, $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ and $\text{LiV}_2(\text{PO}_4)_3$ the (020) reflection separates and for $\text{V}_2(\text{PO}_4)_3$ only the (200) and (112) reflections overlap. (Bottom) Sketch of the $\text{Li}_x\text{V}_2(\text{PO}_4)_3$ phases formed during operation, as observed from the SR-PXD and CV data. Left: Extraction of 2 Li-ions. Right: Extraction of 3 Li-ions.

Upon recharge, the solid solution behavior continues for the insertion of the first two Li-ions, i.e. the transition from $\text{V}_2(\text{PO}_4)_3$ to $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ as described by equation 5. Hereafter, two-phase behavior reappears for the formation of $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, which is also indicated in the potential profile with the presence of two plateaus. Our observations for the dynamic charge-discharge phase transition are summarized in the schematic in Figure 4, which also shows an enlargement of the *operando* SR-PXD data for clarity. From this enlargement, a reversible loss of diffracted intensity upon charging can be seen. An estimate of the relative de- and increase in the diffracted intensity can be made from the scale factors extracted from the Rietveld refinement (see

Figure S3, supplementary information). This reveals that when extracting all three Li-ions ~20% of the diffracted intensity is lost, while only ~8% is lost when removing only two Li-ions. This may suggest a reversible reduction of the crystallinity, which on extraction of all Li-ions has been noticed by other authors as well [8]. Similar intermediate loss of crystallinity has also been observed in other systems, e.g. NaFePO₄ [19]. In the case of extraction of two Li-ions, the full crystallinity is regained after a full charge-discharge cycle, while ~2% crystallinity appears to be lost after having extracted and re-inserted three Li-ions. This loss in long-range order during the extraction of three Li-ions may be contributing to the observed capacity fade.

3.3 Analysis of the structural changes

The unit cell volumes (Figure 3) and parameters (Figure S1 and S2, supplementary information) extracted by Rietveld refinement are well in accordance with those previously reported for the Li-extraction by both equilibrium [8,9] and dynamic methods. [12,20]. For the reinsertion of Li, lattice dimensions have only been reported from equilibrium methods and here we observe significant differences.

As expected, the unit cell volume decreases with the extraction of two Li-ions and the accompanying oxidation of V(III) to V(IV). It is also no surprise that upon removal of the last Li-ion and formation of V₂^{IV/V}(PO₄)₃ from LiV₂^{IV}(PO₄)₃, the unit cell volume increases due to the repulsion between the phosphate anions in the absence of the positively charged Li-ions [13]. However, it is rather surprising that upon lithium reinsertion, the unit cell does not re-subtract. Instead the unit cell volume expands directly from that of V₂(PO₄)₃ to that of Li₂V₂(PO₄)₃. This observation indicates that the Li-intercalation mechanism is different from the Li-deintercalation mechanism. In a previous quasi-equilibrium study [8], the unit cell volume of LiV₂(PO₄)₃, prepared by chemical lithiation of V₂(PO₄)₃, was found to be significantly smaller than that of V₂(PO₄)₃. In that study, Li-insertion even caused the unit cell volume of LiV₂(PO₄)₃ (812.1 Å³) to go below that

of $\text{LiV}_2(\text{PO}_4)_3$ formed during chemical Li-extraction ($823.8 \text{ \AA}^3$) from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. This was explained by simultaneous insertion into two Li-sites close to the original Li1 and Li2 sites. In contrast, during delithiation only the Li2 site is occupied in $\text{D-LiV}_2(\text{PO}_4)_3$. The additional contraction was explained by attraction between the oxygen sub-lattice and Li-ions from two sites, instead of just one [8]. In this study, no contraction is observed upon lithiation, and the cell expands continuously from $\text{V}_2(\text{PO}_4)_3$ until $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ is formed during Li-insertion. The observed cell volume is likely simultaneously influenced by the Li^+ -oxygen interaction (contraction) and the increase in vanadium radius on reduction (expansion). The fact that discrepancy is observed between in-situ and ex-situ measurements, indicates that high degree of metastability is present in the system. Another explanation of the herein observed charge-discharge hysteresis in terms of the intercalation pathway may be charge ordering of V^{4+} and V^{5+} in $\text{V}_2(\text{PO}_4)_3$. No charge ordering has however been observed in this phase in equilibrium studies. To further explore the nature of the intercalation sites, *in situ* or *operando* neutron diffraction or nuclear magnetic resonance spectroscopy is needed.

Another very interesting observation is that upon discharge after extraction of all three Li-ions, the unit cell volumes of both $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ increases beyond those of their delithiation (charge) counterparts. This is highlighted in Figure 5, which shows the diffractograms in the vicinity of the phase transformation between $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ for both the delithiation (charge) and lithiation (discharge). It is clearly seen that the peaks from $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ are shifted towards lower angles during lithiation compared to delithiation. The larger unit cell volumes can be explained either by solid solution behavior, i.e. the structures being able to intercalate more than 2 and 2.5 Li-ions for $\text{R-Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ and $\text{R-Li}_2\text{V}_2(\text{PO}_4)_3$, respectively, or by differences in intercalation Li-sites giving rise to larger unit cell volumes during discharge

Figure 5. Operando SR-PXD data for the transition between $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ during discharge and charge. Note how the peaks of $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ are observed at lower angles during charge (lithiation) than during discharge (delithiation). The scan numbers are shown on the right side of the figure; there is approximately six minutes between each scan. The arrows are meant as a guide for the eye.

The evolution in the unit cell parameters (see Figures S1 and S2, supplementary information) extracted from Rietveld refinement of the *operando* SR-PXD data shed further light on the structural evolution during the phase transformations in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. During the extraction of two Li-ions, the major changes to the lattice dimensions occur along the *a*- and *c*-axis, which decrease in steps until the formation of $\text{LiV}_2(\text{PO}_4)_3$ (in total -3.6 and -3.3%, respectively). In contrast, the *b*-axis increases slightly on formation of $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ (~0.3%), but then decreases significantly on formation of $\text{LiV}_2(\text{PO}_4)_3$ (-1.2%). When lithium is reinserted, the unit cell parameters reverse back to their initial values in a symmetrical fashion. When the third Li-ion is extracted, i.e. as $\text{V}_2(\text{PO}_4)_3$ forms from $\text{LiV}_2(\text{PO}_4)_3$, the *c*-axis remains constant and the *b*-axis decreases only slightly (ca. -0.2%), while the *a*-axis increases significantly (1.2%). On lithium reinsertion, the cell axes increase continuously until $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ is reformed, at which point the step-wise behavior reemerges. The structure of $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ can be described as alternating layers

of [VO₆]-octahedra and [PO₄]-tetrahedra interconnected through corner-sharing between all corners of the polyhedra (see Figure S4, supplementary information). The layers are parallel to [101], i.e. they lie along the *ac*-face diagonal parallel to the *b*-axis. The first Li-ion to be extracted, Li3, lies in the [VO₆]-layers, while the second and third Li-ions, Li1 and Li2 lie in the layers of [PO₄]. Thus, as the first Li-ion, Li3, is extracted the repulsion between the [VO₆]-octahedra increases, which outweighs the decrease in radius of the vanadium ion and causes the *b*-axis to only increase slightly. The second Li-ion, Li1, is extracted from the [PO₄]-layer and causes a close to isotropic decrease in unit cell parameters.

Conclusion

The structural evolution of α -Li₃V₂(PO₄)₃ was measured during Li-ion battery charge and discharge using synchrotron radiation powder X-ray diffraction under *operando* conditions. When only two of three lithium ions are extracted, the structural evolution as well as the galvanostatic potential profile and CV are fully reversible, showing a series of three two-phase transitions. However, when all three lithium ions are extracted, a clear hysteresis is observed, with solid solution behavior during the extraction of the last lithium ion, and during subsequent insertion of two lithium ions. The phase transformation mechanism we observed under dynamic charge-discharge conditions coincides for some part with that observed at equilibrium. However, upon extraction of the last Li-ion we observe a solid solution transformation instead of a two-phase transition between LiV₂(PO₄)₃ and V₂(PO₄)₃. Our observation seems to be supported by the cyclic voltammograms (Figure 3), which shows a very broad current peak for the extraction of the last Li-ion, while the peaks for the previous Li-ion extractions are much narrower. Additionally, the current peak for the reinsertion of two Li-ions occurring by solid solution formation is similarly very broad. Furthermore, the unit cell volume is not observed to re-subtract upon Li-insertion and formation of LiV₂(PO₄)₃ from V₂(PO₄)₃. Instead

the volume increases continuously between $V_2(PO_4)_3$ and $Li_2V_2(PO_4)_3$. We ascribe these important differences to metastability only observable under operando conditions.

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