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Structural evolution of disordered Li$_x$V$_2$O$_5$ bronzes in V$_2$O$_5$ cathodes for Li-ion batteries

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ABSTRACT: Vanadium pentaoxide, V$_2$O$_5$, is an attractive cathode material for Li-ion batteries, which can store up to three Li-ion per formula unit. At deep discharge an irreversible reconstructive phase transition occurs with formation the disordered ω-Li$_x$V$_2$O$_5$ bronze, which despite the lack of long range order exhibits a high reversible capacity (~310 mAh/g) without regaining the crystallinity upon recharge. Here, we utilize operando powder X-ray diffraction and total scattering (i.e. pair distribution function analysis) to investigate the atomic-scale structures of the deep-discharge phase ω-Li$_x$V$_2$O$_5$ (x ~ 3) and, for the first time, the highly disordered phase β-Li$_x$V$_2$O$_5$ (x ~ 0.3) formed during subsequent Li-extraction. Our studies reveal, that the deep discharge ω-Li$_x$V$_2$O$_5$ phase consists of ~60 Å domains rock salt structure with a local cation ordering on ~15 Å length scale. The charged β-Li$_x$V$_2$O$_5$ phase only exhibits very short range ordering (~10 Å). The phase transition between these phases is structurally reversible and appears unexpectedly to occur via a two-phase transition mechanism.

1. INTRODUCTION

Layered oxide materials, capable of reversible Li-ion intercalation, is of wide interest for electrode applications in rechargeable batteries as these tend to provide high specific capacities and facile ion storage.1-3 One of the main objectives has been to find a replacement for LiCoO$_2$, which has been utilized commercially since the Li-ion battery was brought to market. This effort entails both direct substitution of cobalt with other transition metals and investigation of other layered transition metal oxide structure. Vanadium pentaoxide, V$_2$O$_5$, is one of the widely studied layered oxides for cathode applications. The material has been in commercial back-up Li-ion batteries produced by Panasonic since the early 2000s, and it still attracts lot of both academic and industrial interest.4-7 The main advantages of V$_2$O$_5$ are that the lower oxidation states of vanadium (+2 and +3) are easily accessible and that upon intercalation of electron donating ions, V$_2$O$_5$, becomes both an electronic and ionic conductor.8 The most commonly utilized form, orthorhombic α-V$_2$O$_5$, is built from [VO$_4$] square pyramids connected via the base edges and corners. The layers are held together by weak van der Waals interactions, allowing for efficient ion intercalation between the layers yielding a number of crystalline Li$_x$V$_2$O$_5$ bronzes.4,9,10 It is well-known that deep-discharge with intercalation of more than two Li-ions, results in an irreversible loss of crystallinity with the structural transformation to ω-Li$_x$V$_2$O$_5$, as it was shown in 1991 for the first time by Delmas et al.13 Some efforts have been made to investigate the structural nature of this phase and a tetragonal as well as a cubic unit cell has been proposed.13,14 Based on the latter, a Li$_x$V$_2$O$_5$ rock salt (or Halite) structure with statistically disordered cations was suggested. On subsequent charge, i.e. extraction of Li, none of the crystalline phases observed during the 1st discharge reforms. Instead the material becomes increasingly disordered. It has been determined in several studies that ω-Li$_x$V$_2$O$_5$ can provide ~310 mAh/g stable reversible capacity when cycled between 1.5 and 3.8 V, which exceed the capacities of e.g. LiCoO$_2$ and “Li-rich LiNiCoMn$_{1-x}$O$_2$ (NMC)” (240 and 280 mAh/g, respectively). Based hereon, ω-Li$_x$V$_2$O$_5$ has been deemed one of the most promising vanadium oxide materials for Li-ion battery cathodes.13,14 It is quite remarkable that the crystalline-to-crystalline phase transitions in α-V$_2$O$_5$ cathodes and the nature of the crystalline Li$_x$V$_2$O$_5$ bronzes have been studied so intensively for more than 50 years and still receives a lot of attention, when very limited knowledge exists about neither the structures nor the ion-storage mechanism in the disordered phases Li$_x$V$_2$O$_5$ phases. The material structure on the atomic scale and the structural transition between the Li$_x$V$_2$O$_5$ phases govern the electrochemical properties of ω-Li$_x$V$_2$O$_5$ and is determining for its prospects as cathode material. Furthermore, such disordering phenomena and ion-storage in disordered or amorphous materials is
relevant for other systems undergoing order-disorder transitions, e.g. NMC\textsuperscript{15,16} rutile TiO\textsubscript{2}\textsuperscript{17-19} and olivine NaFePO\textsubscript{4}\textsuperscript{20}

Herein, we utilize a combination of ex situ and operando powder X-ray diffraction (PXRD) and total scattering (TS) to investigate the structures of the disordered Li\textsubscript{x}V\textsubscript{2}O\textsubscript{5} bronze phases, which forms at deep discharge and subsequent charge-discharge cycling of an α-V\textsubscript{2}O\textsubscript{5} cathode. From the operando pair distribution functions (PDF) obtained from TS measurements we monitor changes in the local structures of and thereby reveal the phase transition mechanism under dynamic conditions within the disordered Li\textsubscript{x}V\textsubscript{2}O\textsubscript{5} phases.

2. EXPERIMENTALS

2.1. Electrode fabrication. α-V\textsubscript{2}O\textsubscript{5} was purchased from Sigma Aldrich (>99.6%) and used as-received as active material in the electrode composite. For this, α-V\textsubscript{2}O\textsubscript{5} was mixed with conductive carbon (SuperP C45, CNERGY) and polyvinylidene fluoride binder (HSV900 PVDF, MTI Corporation) in weight ratio 6:2:2 in ~2 mL of acetone. The slurry was shaken for ~10 minutes using a vortex mixer, poured onto a glass plate for the acetone to evaporate and subsequently scraped off the plate to obtain a powdered electrode composite. The composite powder was uniaxial pressed into Ø 7 mm free standing cathode pellets of approximately 12 mg each yielding pellets of a thickness of ~130 μm.

2.2. Chemical lithiation. The as-received α-V\textsubscript{2}O\textsubscript{5} powder was dried for two days at 60°C under vacuum after which ~500 mg (2.77 mmol) of the powder was suspended in anhydrous heptane and 3 mole equivalent of n-butyllithium (1.6 M in hexane) was added to the suspension under magnetic stirring in argon atmosphere. The mixture was left to react for two days. The remaining liquid was removed, and the resultant black powder was washed once with heptane and twice with acetone and finally dried under vacuum.

2.3. X-ray diffraction and total scattering. In-house ex situ powder X-ray diffraction (PXRD) data was collected on a Rigaku-MiniFlex 600 diffractometer in reflection geometry using Cu Kα radiation. The diffractograms were collected in a 2θ-range of 5° to 90° with 0.02° step size and scanning speed of 5 °/min. For ex situ synchrotron radiation PXRD and X-ray total scattering (TS), powdered samples were mounted in polyimide tubes (1.0 mm inner diameter, Cole-Parmer). Ex situ PXRD and TS data of pristine and chemically lithiated samples were collected with a wavelength of 0.2113Å at beamline 11-ID-B at APS, Argonne, USA. Operando SR-PXRD and TS measurements were performed at beamline P02.1 at the synchrotron PETRA III at DESY, Hamburg, Germany. For the experiments cathode pellets (prepared as described above) were mounted in AMPIX-type battery cells\textsuperscript{21} specially designed for X-ray scattering measurements. The cathode pellets were mounted together with Ø 14 mm discs of Whatman GL/B separators whetted in 1m LiPF\textsubscript{6} in ethylene carbonate:dimethyl carbonate 1:1 v/v (99.9%, Solvionic) and Ø 12 mm diameter discs of Li-metal anodes. Galvanostatic cycling was performed using a potential window of 1.5 to 4.2 V with a current density of 44.2 mAh/g corresponding to a C/10 current-rate with respect to 3Li per V\textsubscript{2}O\textsubscript{5}. During discharge and charge operando scattering patterns were collected with an X-ray wavelength of 0.2073Å using a Perkin Elmer (XR621) area detector. A patterns were collected every ~6 and ~30 min with total X-ray exposure times of 30 and 240 seconds for PXRD and TS measurements, respectively. Both the ex situ and operando data were calibrated using a CeO\textsubscript{2} standard (NIST 674b) placed at the sample position either in a polyimide tube or at the cathode pellet position in the AMPIX cell. Using Fit2D software,\textsuperscript{22} the diffraction spots originating from the anode metal were masked before azimuthal integration of the raw scattering data. All patterns (PXRD and TS separately) were scaled to compensate for beam intensity fluctuations using the intensity of the primary beam shoulder average over a 2θ- or Q-range at small angles. TS data was treated using the PDFgetX3 software\textsuperscript{23} to obtain PDFs. The Q\textsubscript{poly} value was set to 0.9 Å and upper Q-range cutoffs (Q\textsubscript{max} - instrument) of 21Å\textsuperscript{-1} and 24Å\textsuperscript{-1} were used for the operando and ex situ data, respectively. The structural models were fitted in real space to the PDF data using the PDFgui software\textsuperscript{24}. Instrumental broadening parameter, Q\textsubscript{broad}, was determined by fitting the PDF of the standard, CeO\textsubscript{2} for each setup, yielding a value of about 0.03 Å\textsuperscript{-1}

2.4. Scanning Electron Microscopy. Scanning electron micrographs were collected on a 435VP SEM from LEO operated at 5.0 kV with a beam current of 200 pA.

3. RESULTS AND DISCUSSION

3.1 Evolution of long-range structure during battery operation

The evolution of the long-range structure of the vanadium oxide bronzes, Li\textsubscript{x}V\textsubscript{2}O\textsubscript{5} during discharge and charge of a Li-ion battery was monitored in an operando PXRD experiment. An α-V\textsubscript{2}O\textsubscript{5} cathode was cycled vs. Li between 1.5 and 4.2 V at a C/10 current rate, i.e. Li was intercalated and extracted from Li\textsubscript{x}V\textsubscript{2}O\textsubscript{5} (Figure 1). Prior to the experiment it was confirmed by ex situ PXRD and PDF that the active material is phase pure α-V\textsubscript{2}O\textsubscript{5}. PXRD shows no sign of peak broadening due to nano-crystallites and SEM reveals that the powder consists of particles with a typical size of 200-400 nm in diameter assembled in well-defined box-like agglomerates of 2-10 μm in diameter (see supporting information Figure S1). The particle size has previously been shown to significantly affect the electrochemical capacity with
Instead, we will turn our attention towards the supporting information. As the known crystalline transitions are summarized in Figures S2 in the operando PXRD patterns at end of 1st and 2nd discharge, and end of 1st charge and end of 2nd discharge. The (200), (220) and (222) peak positions of the rock salt \( \omega-\text{Li}_x\text{V}_2\text{O}_5 \) cell are marked by dotted lines along with the peak intensities which clearly decreases significantly during charge. These data highlight the need for studying this system by a technique that probes the non-crystalline part of the sample.

Figure 1. (A) Overview plot of the operando PXRD data collected during discharge-charge cycling of an \( \alpha-\text{V}_2\text{O}_5 \) cathode vs. Li and (B) the simultaneously measured galvanostatic potential profile. The data shows the expected series of crystalline-to-crystalline phase transitions during the first discharge and formation of the highly disordered \( \omega-\text{Li}_x\text{V}_2\text{O}_5 \) at deep discharge (note the broad reflections at \( \approx 20^\circ \omega \)). (C) Selected operando PXRD patterns at end of 1st and 2nd discharge, and end of 1st charge and of 2nd discharge. The (200), (220) and (222) peak positions of the rock salt \( \omega-\text{Li}_x\text{V}_2\text{O}_5 \) cell are marked by dotted lines along with the peak intensities which clearly decreases significantly during charge. These data highlight the need for studying this system by a technique that probes the non-crystalline part of the sample.

exhibits the expected behavior both regarding electrochemistry and diffraction. The potential-composition profile (Figure 1B) displays four distinct potential plateaus during discharge (at \( \approx 3.3, 3.1, 2.3 \) and 1.9 V) and a plateau-less continuously increasing potential during recharge, which is reversible upon the second discharge. The overview plot of the operando PXRD data (Figure 1A), confirms the expected series during insertion Li-ions in the first discharge. Intercalation of the first two Li-ions, results in a series of crystalline-to-crystalline transitions generally accepted to follow the sequence \( \alpha \rightarrow \epsilon \rightarrow \delta \rightarrow \gamma \rightarrow \omega-\text{Li}_x\text{V}_2\text{O}_5 \). The transformation from \( \alpha-\text{Li}_x\text{V}_2\text{O}_5 \) to \( \epsilon-\text{Li}_x\text{V}_2\text{O}_5 \) only brings a minor structural change by increasing the buckering of the \( \text{V}_2\text{O}_5 \) layers, while \( \delta \) and \( \gamma-\text{Li}_x\text{V}_2\text{O}_5 \) (\( 1.0 < x < 2.0 \)) are significantly different structures with every other \( \text{V}_2\text{O}_5 \)-layer shifted and severe buckering of the layers.\(^{49-12} \) These crystalline-to-crystalline phase transitions are summarized in Figures S2 in the supporting information. As the known crystalline \( \text{Li}_x\text{V}_2\text{O}_5 \) polymorphs are not the focus of this study, these will not be discussed in further detail herein. Instead, we will turn our attention towards the \( \omega-\text{Li}_x\text{V}_2\text{O}_5 \) polymorph formed at deep-discharge, i.e. by insertion of \( >2 \) Li-ions. For this phase, only a few rather broad Bragg reflections are visible by PXRD, pointing to a high degree of disorder or a significant reduction in the crystallite size. No significant broadening is observed for \( \gamma-\text{Li}_x\text{V}_2\text{O}_5 \) as compared to \( \alpha-\text{V}_2\text{O}_5 \), thus no significant crystallite size reduction has occurred during the \( \alpha \rightarrow \epsilon \rightarrow \delta \rightarrow \gamma \) transformations. Upon charge, the \( \omega \rightarrow \gamma-\text{Li}_x\text{V}_2\text{O}_5 \) phase transformation is clearly not reversible, and \( \gamma-\text{Li}_x\text{V}_2\text{O}_5 \) does not reform. Note that a small amount of \( \gamma-\text{Li}_x\text{V}_2\text{O}_5 \) is left at the end-of-discharge (as \( <3 \) Li are intercalated), which gives rises to reformation of a small amount of the \( \delta \rightarrow \epsilon \rightarrow \alpha \) phases). Incomplete transformation from \( \gamma \)- to \( \omega-\text{Li}_x\text{V}_2\text{O}_5 \) has also been reported in several previous studies.\(^{13,14} \) During charge, only very subtle changes are observed in the diffraction data (Figure 1A and C). The diffraction from \( \omega-\text{Li}_x\text{V}_2\text{O}_5 \) becomes even weaker, while the angular peak positions do not change significantly. No new Bragg peaks appear in this process. During the second discharge, the peaks from \( \omega-\text{Li}_x\text{V}_2\text{O}_5 \) again increase in intensity, while their angular position still remains unchanged. This behavior indicates that the amount of \( \omega-\text{Li}_x\text{V}_2\text{O}_5 \) changes while the Li-
Figure 2. (A) Overview plot of the operando PDF data (obtained from X-ray TS measurements) collected during discharge-charge cycling of a $\alpha$-V$_2$O$_5$ cathode vs. Li and (B) the simultaneously measured galvanostatic potential profile (the noise in the data for the first hour of discharge was due to a poor initial wire-to-cell contact). (C) Comparison of selected operando PDFs collected at end of discharge and charge. Note the significant and reversible decrease in PDF intensity and correlation length between discharge and charge. (D) Illustrations of the $\omega$-Li$_x$V$_2$O$_5$ rock salt structure and $\beta$-Li$_{0.3}$V$_2$O$_5$ structures, which represent the discharged and charge states, respectively.

smaller particles (~2 µm) performing almost 50% better than larger particles (2-50 µm). The operando PXRD shows that Li-intercalation and extraction in Li$_x$V$_2$O$_5$ composition (i.e. the V oxidation state) in this phase remains constant. Capacity is definitely stored and drawn from the battery cell witnessed by the potential-composition profile. Hence, lithium extraction and insertion in the cathode might take place as a two-phase transition between $\omega$-Li$_x$V$_2$O$_5$ and an amorphous phase as there is no sign of changes accounting for the vanishing diffraction intensity of $\omega$-Li$_x$V$_2$O$_5$ in the crystalline part of the sample.

3.2. Evolution of short-range structure during battery operation

To study the structural nature of the disordered phases and to understand the transformation pathway between these during repeated charge-discharge cycling of Li$_x$V$_2$O$_5$, another similar operando experiment was conducted. However, instead of only focusing on the diffraction signal the X-ray TS data were collected and the PDFs were subsequently obtained (Figure 2). The PDF shows the inter-atomic correlations (bond lengths) in a material in real space and contains information not only about the crystalline (ordered) but also the amorphous (disordered) part of the material. Thus, from the operando PDF data, the local structure of the cathode can be monitored, and in the overview plot (Figure 2A), correlations are clearly observed in the lower $r$-region through-out the discharge-charge process and in subsequent cycles as well. During the first discharge, the $\alpha \rightarrow \epsilon \rightarrow \delta \rightarrow \gamma \rightarrow \omega$ phase transitions can once again be monitored. In short, the close resemblance of the $\alpha$- and $\epsilon$-Li$_x$V$_2$O$_5$ structures results in minor continued changes in the atomic correlations (e.g. at 20 Å), while the layer shearing taking place in the $\epsilon \rightarrow \delta$ transformation, results in an abrupt change in the PDF (at ~2.5 hours). Formation of $\gamma$-Li$_x$V$_2$O$_5$ is again observed as continuous changes in the correlations mainly due to the $\delta \rightarrow \gamma$-Li$_x$V$_2$O$_5$ two-phase transition taking place over a wide Li-composition range. Finally, $\omega$-Li$_x$V$_2$O$_5$ forms at deep discharge. The $\gamma \rightarrow \omega$ transition is clearly a two-phase phase transition, and judging from PDF, $\omega$-Li$_x$V$_2$O$_5$ appears to be quite different from $\gamma$-Li$_x$V$_2$O$_5$ as new correlations are
3.3. Structure of fully lithiated ω-Li$_x$V$_2$O$_5$

To understand the transitions observed in the operando PDF experiment, it is necessary to gain a more precise description of the ω-Li$_x$V$_2$O$_5$ structure. In an effort to avoid unwanted correlations in the PDF from the electrode additives and the AMPIX cell (for more details see supporting information Figure S3), pure α-V$_2$O$_5$ was chemically lithiated using n-butyl lithium to reach a composition of Li$_3$V$_2$O$_5$. The ex situ PXRD data of the lithiated sample is similar to that of the discharged sample in the operando PXRD experiment, which confirms that ω-Li$_x$V$_2$O$_5$ was successfully obtained. The PXRD data can be described by a cation-disordered rock salt Li$_x$V$_2$O$_5$ structure (or Li$_{0.6}$V$_{1.4}$O, Fm-3m, $a = 4.0986(2)$ Å) (See Supporting information, Figure S4) as suggested by Hélène Cognac-Auradou in her Ph.D. thesis of 1993. Scherrer analysis provides an estimated spherical crystallite size of ~80 Å. The structure can be described as a cubic close packed oxygen lattice with Li and V randomly distributed in octahedral holes (Figure 2D). It is interesting to note that layered metal oxides of the α-NaFeO$_2$ structure type, such as LiCoO$_2$ and its derivatives e.g. NMC also transform to a disordered rock salt structure upon repeated cycling. A recent study have shown that low cycling rates (≤1C) promotes formation of the rock salt structure due to higher quantity of Li-vacancies, which increases ion-diffusion.

The PDF of the chemically produced ω-Li$_x$V$_2$O$_5$ can also be reasonably well fitted ($R_w = 0.23$) with the cation-disordered rock salt structure (Figure 3A). However, from the PDF fit it is evident, that the intermediate $r$-range of the PDF ($5.5 - 20$ Å) is not completely described by the fully cation-disordered rock salt model. Thus, the structure holds some additional order on this length scale. To explain this, a residual was produced by firstly fitting the rock salt structure to the high $r$-range of the data ($20 - 50$ Å), and secondly fixing all parameters while expanding the $r$-window to include the intermediate range ($5.5$ to $50$ Å). Naturally, the presence of local domains resembling other Li$_x$V$_2$O$_5$ polymorphs (e.g. the α-, β-, γ-, δ- and ε-polymorph) were initially tested by including these as a second phase. However, none of these provided a good (or even fair) description of the residual (e.g. $R_w = 1.02$ for α-V$_2$O$_5$). This may to some extent be obvious from the PDF fit of the cation-disordered rock salt (Figure 3A, top). Here it seems...
that the intensity differences between the observed and calculated PDF mainly appears at the positions of maxima in the $G(r)$ curve. This suggests that the structural framework, i.e. the rock salt structure, is correct and that the error is related either to the coordination numbers or the nature of the atomic-neighbor pairs. Thus, the residual is assumed to arise from local cation ordering in the $[OM_6]-$octahedra. This is reasonable considering the $3:2:5$ (or $0.6:0.4:1$) composition of the rock salt $\omega$-Li$_3$V$_2$O$_5$, which means that the total number of cations per formula unit is not a factor of six (each oxygen atom coordinates to an integer number of V and Li atoms, which sums to six for octahedral coordination). The cation-ordering possibilities in ordered rock salt superstructure oxides are described in detail in a review by Mather et al.\textsuperscript{30} In the case of Li$_3$V$_2$O$_5$, the cation ordering must locally follow LiVO$_2$ (i.e. $[OLiV_2]_6$-octahedra) and Li$_2$VO$_3$ (i.e. $[OLiV_2]_6$-octahedra) stoichiometries in a 1:1 molar mixture to comply with the overall stoichiometry and the oxidation states, i.e. Li(I), V(III) and V(IV). The residual from the fit of the rock salt structure was fitted with models describing two types of cation ordering (Figure 2B): Clustered and dispersed cation ordering. The clustered tendency arises when cations of the same element sit closest together, and it can be modelled by an $\alpha$-NaFeO$_2$ structure for the

**Table 1. Structural parameters from fit of the ex situ PDF (Figure 3) for $\omega$-Li$_3$V$_2$O$_5$ obtained by chemical lithiation (corresponding to the fully discharged state).** Information for the disordered $\omega$-Li$_3$V$_2$O$_5$ rock salt and the two structures used for modeling the local dispersed cation ordering is listed. For the latter two only V-V correlations were computed.

<table>
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<th>Structure type</th>
<th>a (Å)</th>
<th>b (Å</th>
<th>c (Å)</th>
<th>$\beta$ (°)</th>
<th>Domain size (Å)</th>
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<tr>
<td>Rock salt ($Fm\overline{3}m$)</td>
<td>4.098(2)</td>
<td>9.61(17)</td>
<td>5.44(12)</td>
<td>116.3(1.7)</td>
<td>59(3)</td>
</tr>
</tbody>
</table>

**Dispersed cation ion order model 1:**

<table>
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<tr>
<th>Structure type</th>
<th>Li$_2$ZrO$_3$ ($C2/c$)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\beta$ (°)</th>
<th>Domain size (Å)</th>
</tr>
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<tbody>
<tr>
<td>LiVO$_3$</td>
<td>Li$_2$ZrO$_3$ ($C2/c$)</td>
<td>5.89(13)</td>
<td>9.61(17)</td>
<td>5.44(12)</td>
<td>116.3(1.7)</td>
<td>59(3)</td>
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**Dispersed cation ion order model 2:**

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<th>Structure type</th>
<th>$\gamma$-LiFeO$_2$ ($I4_1/amd$)</th>
<th>a = b (Å)</th>
<th>c (Å)</th>
<th>Domain size (Å)</th>
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<tbody>
<tr>
<td>LiVO$_3$</td>
<td>$\gamma$-LiFeO$_2$ ($I4_1/amd$)</td>
<td>4.07(1)</td>
<td>8.34(6)</td>
<td>14(8)</td>
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**Overall ADPs**

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<th>$U_{iso}$ V</th>
<th>0.027(3)</th>
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</thead>
<tbody>
<tr>
<td>$U_{iso}$ O</td>
<td>0.029(3)</td>
</tr>
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</table>

Figure 4. PDF data for the Li$_3$V$_2$O$_5$ cathode in the charged state (low Li-content) obtained during the *operando* PDF experiment (Figure 2) with fits of various relevant candidate structures. Observed data is shown in blue, the fitted models in red and the difference ($G(r)_{\text{diff}} = G(r)_{\text{obs}} - G(r)_{\text{calc}}$) in black. The $\beta$-Li$_3$V$_2$O$_5$ structure (bottom) is the only phase providing a satisfactory description of the data.

LiVO$_3$ stoichiometry and a $\beta$-Li$_2$SnO$_3$ structure for the Li$_3$V$_2$O$_5$ stoichiometry. The dispersed tendency arises when cations of the same element sit furthest apart. This can be modelled by the $\gamma$-LiFeO$_2$ structure for the LiVO$_3$ stoichiometry. For the Li$_3$V$_2$O$_5$ stoichiometry, there are no known structures which fully achieve the dispersed arrangement; however it is partly achieved in the Li$_3$ZrO$_3$ structure, wherein half the oxygen atoms see a dispersed arrangement and the other half a clustered arrangement. While the clustered arrangement does not provide a good description of the residual signal ($R_w = 0.82$), the dispersed cation arrangement yields a relatively good fit ($R_w = 0.57$). Note that it is a fit to the residual of another fit. Hence, the signal to noise ratio is lower than in the original data and a low $R_w$ value cannot be expected, but when including the dispersed cation arrangements as local structures in the fit of the ex situ PDF signal of the $\omega$-Li$_3$V$_2$O$_5$ phase, the fit becomes significantly better, i.e. $R_w$ decreases from 0.23 to 0.16 (Figure 3C and Table 1).
domains wherein the Li and V cations are locally ordered in a dispersed manner in ~15 Å subdomains. Interestingly, a structural analysis of the γ-Li$_x$V$_2$O$_5$ structure (see Fig. S5 in supporting information) reveals that a topotactic transformation from the γ- to the ω-polymer is not possible while maintaining the correct V:O ratio and obtaining the ccp oxygen lattice of the rock salt structure, as this requires breaking a corner sharing connecting between two [VO$_6$] octahedra and replacing this with an edge sharing connecting. This will natural change the stoichiometry. Hence, the γ → ω transition requires a reconstructive phase transformation. This explains also the relatively small ordered domains.

3.4. Structure of lithium poor Li$_x$V$_2$O$_5$

Now we turn our attention towards the lithium-poor Li$_x$V$_2$O$_5$ phase during the charge, i.e. upon extraction of Li from ω-Li$_x$V$_2$O$_5$. As mentioned, at end of charge the overall intensity in the PDF decreases (Figure 2C) and at $r > 11$ Å the signal becomes comparable to the noise level. Thus, in the charged Li$_x$V$_2$O$_5$ the domain size and the local order in the domains appear to be significantly smaller than in ω-Li$_x$V$_2$O$_5$. Unfortunately, a chemically produced sample displaying the same degree of disorder was not obtained, and the analysis is thus carried out using the operando PDF obtained for the charged state. To account for the contributions in the operando PDF from the carbon additive, a graphite model with artificially increased atomic displacement parameters (ADPs) in the c-direction (to suppress interlayer correlations and thereby account for the turbostratic disorder) was added as a second phase in all fits of the data.

Based on the sloping potential curve observed beyond the first discharge, a solid solution reaction between ω-Li$_x$V$_2$O$_5$ and the charged state would be expected and has also been suggested in several studies.

However, the rock salt structure or modifications hereof (e.g. changing the unit cell parameters and removing 2.7Li) did not provide a good fit for the PDF (Figure 4) and a solid solution reaction between two isostructural framework structures are discarded. Structurally this makes sense as vanadium in oxidation states IV and V are more likely found in distorted octahedral, (distorted) square pyramidal or even tetrahedral coordination. Hence, a rock salt structure with perfect octahedral coordination is unlikely. A number of other known and hypothetical Li$_x$V$_2$O$_5$ structures were tested. α-V$_2$O$_5$ or ε-Li$_x$V$_2$O$_5$ (which are structurally very similar to each other) could from a valence state perspective be good candidates since α-V$_2$O$_5$ is the equilibrium structure of the oxidized form, i.e. charged state. However, neither of these phases describes the PDF well. Nor does the other phases observed at higher state-of-charge, i.e. δ- and γ-Li$_x$V$_2$O$_5$. Glassy or amorphous V$_2$O$_5$ is also well known. It has a tetrahedral [VO$_4$] coordination. A hypothetical quartz derived V$_2$O$_5$ structure was therefore used to mimic the glassy V$_2$O$_5$ structure. ADPs were enlarged to account for the disorder, however this was also discarded. Finally, the monoclinic polymorph, β-Li$_x$V$_2$O$_5$ was found to provide a convincing description of the data (Figure 4, bottom and Table 2). The composition is determined from the electrochemistry (Figure 2B). The β-Li$_x$V$_2$O$_5$ (0.22 < x < 0.37) structure (Figure 2D and Table 2) was first described by Galy et al. It consists of chains of 2 x 2 distorted [VO$_6$] octahedra running in parallel to the b-axis. Within the chains the octahedra are connected by edge sharing. Along the a-axis, the chains are interconnected by corner sharing between octahedra from two different chains while along the c-axis the chains are interconnected by two [VO$_6$] square pyramids sharing an edge. The spherical domain size of the β-Li$_x$V$_2$O$_5$ phase is estimated from the PDF fit to be ~10 Å, which corresponds to only approx. 0.67 x 3 x 2 unit cells. Thus, assuming that the domains are indeed spherical, the chains of [VO$_6$] octahedra are ~6 octahedra long, while no more than two chains are interconnected in either of the two directions. Hence, this phase should indeed be regarded as highly disordered and should be termed β-Li$_x$V$_2$O$_5$-like.

### Table 2. Structural parameters for the disordered β-Li$_x$V$_2$O$_5$ phase extracted by fitting the operando PDF (Figure 4, bottom) obtained after the first charge.

<table>
<thead>
<tr>
<th>Atom positions</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(1)</td>
<td>0.37654(13)</td>
<td>0</td>
<td>0.08491(16)</td>
</tr>
<tr>
<td>V(2)</td>
<td>0.15528(8)</td>
<td>0</td>
<td>0.1139(2)</td>
</tr>
<tr>
<td>V(3)</td>
<td>0.28605(11)</td>
<td>0</td>
<td>0.4000(13)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.8012(3)</td>
<td>0</td>
<td>0.0899(6)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.6408(8)</td>
<td>0</td>
<td>0.105(9)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.4217(5)</td>
<td>0</td>
<td>0.2130(8)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.2629(5)</td>
<td>0</td>
<td>0.2299(6)</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.0989(4)</td>
<td>0</td>
<td>0.2859(6)</td>
</tr>
<tr>
<td>O(7)</td>
<td>0.2893(8)</td>
<td>0</td>
<td>0.5791(8)</td>
</tr>
<tr>
<td>O(8)</td>
<td>0.3392(4)</td>
<td>0</td>
<td>0.4732(12)</td>
</tr>
<tr>
<td>Li</td>
<td>0.535</td>
<td>0</td>
<td>0.33</td>
</tr>
<tr>
<td>$U_{iso}(V)$</td>
<td>0.12(14)·10$^{-5}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U_{iso}(O)$</td>
<td>0.52(8)·10$^{-5}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Figure 5. Schematic showing the phase transformation pathway of an α-V₂O₅ cathode. During the first discharge a series of crystalline-to-crystalline phase transformations takes place (α → ε → δ → γ-LiₓV₂O₅) and with intercalation of >2Li the irreversible transformation to ~60 Å domains of ω-LiₓV₂O₅ rock salt with local ~15 Å domains with dispersed cation ordering represented by γ-LiFeO₂ and Li₂ZrO₃ model structures. Subsequent charge-discharge cycling occurs via a reversible phase transition between ω-LiₓV₂O₅ and β-LiₓV₂O₅ present at ~10 Å large domains. Parts of the β-LiₓV₂O₅ structure provides the local dispersed cation ordering as marked by purple (γ-LiFeO₂) and cyan (Li₂ZrO₃) in the illustration of the crystal structures. The black line patterns represent the oxygen sublattice frameworks, i.e. layered complex for α-, ε-, δ-, and γ-LiₓV₂O₅ and cubic grid for ccp in ω-LiₓV₂O₅. The β-Liₓ₀.₃V₂O₅ contains small bits of distorted ccp.

3.5. Nature of the ω- to β-LiₓV₂O₅ transformation

From our analysis it is now clear that the ~60 Å domains of ω-LiₓV₂O₅ in the discharged state transforms into the highly disordered β-LiₓV₂O₅ with a domain size of only ~10 Å during charge (Figure 5). Fitting the two phases to the operando PDFs result in significant changes only in the scale factors, i.e. that of ω-LiₓV₂O₅ decreases while that of β-Liₓ₀.₃V₂O₅ increases during charge and vice versa during the 2nd discharge. This points to a two-phase transition between the two phases. The sloping potential observed both under dynamic galvanostatic charge-discharge cycling and by use of galvanostatic intermittent titration technique (GITT) may be caused by the Li-site energies being non-constant in the highly disordered LiₓV₂O₅ structures.

By comparing the ω- and β-LiₓV₂O₅ structures one can to understand the process of this transformation. The chains of [VO₆] octahedra in β-Liₓ₀.₃V₂O₅ resemble a distorted rock salt structure with a ccp oxygen lattice and the [VO₆] octahedra sharing edges. Thus,
this part of the β-Li$_{0.3}$V$_2$O$_5$ phase likely stems from fractions of the rock salt ω-Li$_{1.5}$V$_2$O$_5$ structure. This is further supported by the local octahedral connectivity having motifs similar to the γ-LiFeO$_2$ and the Li$_2$ZrO$_3$ structure representing the dispersed cation arrangement found in ω-Li$_{1.5}$V$_2$O$_5$ at end-of-discharge. The square pyramidal part of β-Li$_{0.3}$V$_2$O$_5$, which connects the [VO$_5$] octahedra along the c-axis, resembles ε- and δ-Li$_x$V$_2$O$_5$ with the pyramids sharing edges and their direction alternating within the layers. Hence, this part of the structure adopts an energetically favorable structure for V(V) and V(IV) and in the β-Li$_{0.3}$V$_2$O$_5$ structure, the Li-ions are positioned in between the layers of [VO$_5$] pyramids like in ε- and δ-Li$_x$V$_2$O$_5$.

Remarkably upon the 2nd discharge, the rock salt ω-Li$_{1.5}$V$_2$O$_5$ domain size recovers to ~60 Å with local domains of cation ordering. Thus, the phase transformation process is reversible. This is clearly observed from both the increased correlation length in operando PDF (Figure 2C) and the full reappearance of the intensity of the rock salt (200), (220) and (222) diffraction peaks in operando PXRD data (Figure 1C). The formation of the rock salt structure is likely facilitated by growth from the charged β-Li$_{0.3}$V$_2$O$_5$ state remains somewhat coherent and that the small domain size herein is not caused by cracking at the nanoscale. Interestingly, a study of the capacity retention by Leger et al. showed that a stable capacity of ~310 mAh/g is achieved when ω-Li$_{1.5}$V$_2$O$_5$ is cycled between 1.5 and 3.8 V, while the capacity decreases to ~230 mAh/g when cycled between 2.1 and 3.8 V. This suggest that the complete transformation from β-Li$_{0.3}$V$_2$O$_5$ to ω-Li$_{1.5}$V$_2$O$_5$ is more favorable than only a partly conversion. In general, the reversibility of the transformation from the highly disordered β-Li$_{0.3}$V$_2$O$_5$ phase to the significantly more ordered phase ω-Li$_{1.5}$V$_2$O$_5$ evidences the high stability of the rock salt structure.

CONCLUSIONS

In this work, the structures of the disordered Li$_x$V$_2$O$_5$ bronzes formed during deep discharge and upon recharge of a V$_2$O$_5$ Li-ion battery cathode have been studied by means of ex situ and operando PXRD and PDF analysis. In the discharged state, ω-Li$_{1.5}$V$_2$O$_5$ is characterized as a rock salt structure with domain size of ~60 Å containing ~15 Å large subdomains with local dispersed cation ordering within the ccp oxygen lattice. The Li$_x$V$_2$O$_5$ bronze of the discharged state was found to have a short-range order of just ~10 Å. The structure is best described as β-Li$_{0.3}$V$_2$O$_5$ built from edge and corner sharing [VO$_5$] octahedra linked by corner sharing [VO$_5$] square pyramids. The ω-Li$_{1.5}$V$_2$O$_5$ to β-Li$_{0.3}$V$_2$O$_5$ transition appears to occur via a reversible two-phase reaction. Remarkably, the larger extent of order in ω-Li$_{1.5}$V$_2$O$_5$ reappears during discharge even though the phase forms from the highly disordered β-Li$_{0.3}$V$_2$O$_5$. The stability of the disordered structures confirms the potential for applying ω-Li$_{1.5}$V$_2$O$_5$ as a cathode material in Li-ion batteries.

ASSOCIATED CONTENT

Supporting Information. PXRD, PDF and TEM analysis of α-V$_2$O$_5$, operando PXRD overview plots, ex situ and operando PDFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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ABBREVIATIONS

APD, atomic displacement parameter; ccp, cubic close packed; DOE, Department of Energy; PDF, Pair Distribution Function; PVDF, polyvinylidene-fluoride; PXRD, Powder X-ray Diffraction; SEM, Scanning Electron Microscope; TS, total scattering

REFERENCES


