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Interfacial Effects in $\varepsilon$-$\text{Li}_x\text{VOPO}_4$ and Evolution of the Electronic Structure


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ABSTRACT: The epsilon polymorph of vanadyl phosphate $\varepsilon$-VOPO$_4$ is a promising cathode material for high-capacity Li ion batteries, owing to its demonstrated ability to reversibly incorporate two lithium ions per redox center. As lithium is inserted into the nanosized particles within the cathode, the electrochemical reaction can be largely affected by the interfacial chemistry at the nanoparticle surface. We performed X-ray photoelectron spectroscopy using both soft (XPS) and hard (HAXPES) X-rays to chemically distinguish and depth-resolve the interfacial phase transitions in $\varepsilon$-VOPO$_4$ electrodes as a function of electrochemical discharge. Our analysis shows that the second lithium reaction begins before the full incorporation of the first lithium. This results in a pronounced lithium gradient within the nanoparticles, with the $\varepsilon$-$\text{Li}_2\text{VOPO}_4$ phase only forming near the surface. These results indicate that a disruption of the kinetics are limiting the realized capacity in our hydrothermally synthesized $\varepsilon$-VOPO$_4$. Moreover, from inspection of the valence band region, we were able to monitor the evolution of $\varepsilon$-VOPO$_4$ to $\varepsilon$-$\text{Li}_2\text{VOPO}_4$ at the surface of our nanoparticles. These assignments are confirmed by hybrid density functional theory of the three end phases.

INTRODUCTION

Chemical energy storage in the form of rechargeable Li ion batteries will play an essential role in the future of our energy landscape. The development of high energy Li ion batteries depends largely on the advancement of cathode materials. $\varepsilon$-VOPO$_4$ has a 3D tunnel structure consisting of 1D chains of corner sharing distorted VO$_6$ octahedra connected by PO$_4$ tetrahedra, also by corner sharing. The crystal structures of $\varepsilon$-VOPO$_4$ and the corresponding lithiated LiVOPO$_4$ and...
Li₂VOPO₄ end phases are shown in Figure 1 (see also Table 1) rendered using the VESTA software. The structural framework is essentially retained upon reaction with each lithium, differing only in the distortion of the metal phosphate framework. ε-VOPO₄ has the most distorted VO₆ octahedra with the shortest vanadyl bond and the longest opposite V–O bond (1.572 and 2.556 Å, respectively) running along the chains. In LiVOPO₄, the vanadyl bond lengths (1.626 Å), while the opposite V–O shortens significantly (2.240 Å) leading to more symmetrical VO₆ octahedra and considerably shorter V–V distance. Li ions in this compound occupy two distinct highly distorted five-coordinated sites. The structure of Li₂VOPO₄ was only recently reported featuring the least distorted VO₆ octahedra (V–O bond lengths ranging from 1.98 to 2.04 Å). Li ions occupy five independent crystallographic sites in the channels of the structure, all different from that of LiVOPO₄. Thus, Li ions of Li₂VOPO₄ have to move to different sites upon second Li intercalation. Also, the evidence of intermediate phases with 1.5 and 1.75 Li exists, but their structures are currently unknown.

As in the case of the olivine phosphates, the problem of the inherently low electronic conductivity of ε-VOPO₄ is overcome by the use of nanosized particles within the cathode. As the lithium is inserted at this scale, the electrochemical reaction can be largely affected by the interfacial chemistry at the nanoparticle surface. For example, particle size and shape are both known to influence the electrochemical behavior of LiFePO₄. However, given the importance of the cathode surface, there are remarkably few detailed experimental studies of the surface reactions. While increased particle size of ε-VOPO₄ is generally found to lower the capacity, as in LiFePO₄, even some micron-size particles can achieve similar capacities at the same C/20 rate. Therefore, it is clear that the low capacities are not exclusively due to particle size, suggesting that the surfaces play a more complicated role.

Surfaces of ε-VOPO₄ remain unexplored experimentally. As a bulk material, the VOPO₄ system undergoes significant changes in crystal symmetry upon lithiation. Due to the reduced symmetry and wider range of possible chemical interactions at the surface, this region is expected to display even more complexity than the bulk. Recently, Li et al. predicted some particular LiVOPO₄ surfaces to have lower redox potentials than others, as well as differences from the bulk material.

In this study, by performing X-ray photoelectron spectroscopy using both soft (XPS) and hard (HAXPES) X-rays, we are able to chemically distinguish and depth-resolve the interfacial phase transitions as a function of electrochemical lithiation. Core level analysis supports a straightforward two-phase reaction as the first lithium is intercalated. However, the intercalation of the first lithium is not yet completed when the second reaction begins, resulting in a pronounced lithium concentration gradient. Because of this limited ion diffusion, the ε-Li₁VOPO₄ phase is only formed near the surface of the equilibrated nanoparticles. This disruption of the kinetics is identified as a main contributor in limiting the realized capacity in our hydrothermally synthesized ε-VOPO₄. From inspection of the valence band region, we were able to monitor the evolution of ε-VOPO₄ after each full lithium insertion. Comparison with our hybrid density functional theory (DFT) calculations for ε-VOPO₄, ε-LiVOPO₄, and ε-Li₂VOPO₄ supports these assignments and reveals the nature of the lithium intercalation. Furthermore, the agreement between the measured valence band and density of states predicted by DFT demonstrates a methodology by which the computational methods can be assessed.

#### METHODOLOGY

Nanosized (average diameter ~100 nm) single crystals of ε-VOPO₄ were synthesized by the thermal decomposition of monoclinic H₃VOPO₄ and prepared as cathodes by combining the active material with carbon black (10 wt %) as a conductive additive and PVDF binder (10 wt %) in a mortar and pestle. NMP (1-methyl-2-pyrrolidinone, Aldrich) was added to create a paste, which was then laminated onto aluminum foil and vacuum-dried at 80 °C before use. The electrochemical properties were evaluated in a 2325-type coin cell with LiPF₆ electrolyte and lithium foil counter electrode. More detailed accounts of the synthesis and electrochemical properties of these cells are reported elsewhere.

After reaching various points on the first discharge/charge cycle, each cell was carefully disassembled under inert conditions (either He or Ar glovebox) to extract the cathodes for analysis. While in the glovebox, the cathode surfaces were washed with DMC (dimethyl carbonate) to remove the residual electrolyte, dried, and sealed in plastic. When possible (most in-house measurements), samples were mounted on the experimental sample holder prior to sealing and removing from the glovebox. The samples were removed from the sealed plastic and promptly transferred into the respective experimental chambers to minimize the exposure to air and moisture.

The lab-based (soft) XPS was performed using a Phi VersaProbe 5000 system with a monochromated Al Kα source and hemispherical analyzer at the Analytical and Diagnostics Laboratory (ADL) at

![Figure 1. Crystal structures of ε-VOPO₄ and corresponding lithiated LiVOPO₄ and Li₂VOPO₄ phases.](image)

<table>
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<th>phase</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (deg)</th>
<th>β (deg)</th>
<th>γ (deg)</th>
<th>V (Å³)</th>
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At 284.6 eV.21 The HAXPES measurements were performed at the bending magnet beamline X24A at the National Synchrotron Light Source (NSLS) using separate pieces of the same electrodes to ensure similar amounts of exposure. We noted no significant spatial variations across the electrodes in any photoemission experiments. An incident photon energy of ∼4 keV and takeoff angle (TOA) of ∼85° were employed to achieve the highest possible effective probing depth. The experimental chamber is equipped with a Scienta Electron Analyzer set to a pass energy of 200 eV operating in angular mode which results in a resolution comparable to the lab-based XPS. The binding energy scale for both the XPS and HAXPES were calibrated to the C 1s photomission peak for carbon black with adventitious hydrocarbons at 284.6 eV.21

Figure 2. O 1s and V 2p XPS core levels obtained for pure ε-VOPO₄ powder, a synthesized ε-VOPO₄ electrode with minimal exposure, and a ε-VOPO₄ electrode after an additional 30 min air exposure.

All calculations were performed using the periodic DFT code VASPT24,25 in which a plane-wave basis set describes the valence electronic states. The Perdew–Burke–Ernzerhof64 (PBE) gradient corrected functional was used to treat the exchange and correlation. The projector-augmented wave25,26 (PAW) method was used to describe the interactions between the cores [Li:He], [V:Ar], [O:He], and [P:He] and the valence electrons. To counteract the self-interaction error and the band gap errors inherent to standard DFT functionals such as the PBE functional, higher levels of theory must be used. In this study, we have used the screened hybrid density functional developed by Heyd, Scuseria, and Ernzerhof (HSE06),27,28 as implemented in the VASP code.29 HSE06 has been shown to yield improved decriptions of structure, band gap, and defect properties of a number of oxide semiconductors and battery materials.30

Adopting the nomenclature in which the lithiated phase is determined by the name of its delithiated form, structural optimizations of crystalline ε-VOPO₄12, ε-LiVOPO₄,11 ε-Li₂VOPO₄,10 Li₂O, and Li metal were performed using HSE06 at a series of volumes in order to calculate the equilibrium lattice parameters. In each case, the atomic positions, lattice vector, and cell angle were allowed to relax, while the total volume was held constant. The resulting energy volume curves were fitted to the Murnaghan equation of state to obtain the equilibrium bulk cell volume.47 This approach minimizes the problems of Pulay stress and changes in basis set which can accompany volume changes in plane wave calculations. The Pulay stress affects the stress tensor which is not used in obtaining the optimized lattice vectors, and hence this approach is significantly more accurate than using the stress tensor to perform constant pressure optimization. Convergence with respect to k-point sampling and plane wave energy cutoff were checked, and a cutoff of 750 eV and a k-point density of 0.2 k/Å⁺ were found to be sufficient. Calculations were deemed to be converged when the forces on all the atoms were less than 0.01 eV Å⁻¹.

These calculations can also be used to predict the open circuit voltage during battery operation. As pointed out by Ceder and co-workers,48 the average potential for intercalation between two compositions x₁ and x₂ can be obtained from the energy change in the reaction:

\[ \text{Li}_{x_1}\text{VOPO}_4 + (x_2 - x_1)\text{Li} \rightarrow \text{Li}_{x_2}\text{VOPO}_4 \]

We calculated the average potential to be 4.03 and 2.39 V for the first and second lithiation steps, respectively. This is in reasonable agreement with our electrochemical analysis.

### RESULTS AND DISCUSSION

**Examining Disassembled Cells.** To evaluate our methodology, we compared the core-level XPS spectra collected from nanosized ε-VOPO₄ in pure powder form to our electrodes after cell disassembly. Figure 2 shows the XPS spectra from three samples: the ε-VOPO₄ powder, an electrode with minimal exposure, and an electrode with an additional 30 min of exposure to air. Each spectrum includes three main features: the O 1s peak and the spin orbit split V 2p₁/₂ and V 2p₃/₂ peaks. The V 2p₁/₂ is further split into two components representing the 5⁺ (518.23 eV) and 4⁺ (517.01 eV) oxidation states. Due to the extreme surface sensitivity of XPS coupled with the redox active nature of these samples, it was found that significant partial reduction of the vanadium cation to the 4⁺ state occurs, which increases with duration of exposure. Along with this reduction, there is a concurrent increase in the O 1s feature at higher binding energy commonly attributed to adventitious surface oxygen. Both the V⁴⁺ and surface oxygen features are much less pronounced in the electrode with minimal exposure. This partial reduction is attributed to the additional chemistry involved in making the cathode slurry. The small V⁴⁺ contribution in the pure powder may be related to air exposure or it could represent a small amount of hydrogen remaining in the VOPO₄ framework from the sample growth resulting in a partial H⁺VOPO₄ phase. We conclude that limiting cathode atmospheric exposure after cell disassembly to <5 min is sufficient to accurately attribute any vanadium reduction in our experiments to lithium intercalation after electrochemical cycling.

**First Discharge/Charge Cycle.** Figure 3a shows the galvanostatic discharge–charge curve from 3.8 to 1.5 V for the first cycle of the ε-VOPO₄ cells at 0.082 mA/cm². The discharge voltage profile exhibits two plateaus, corresponding to the V⁵⁺/V⁴⁺ (∼3.8 V) and V⁴⁺/V³⁺ (starting at ∼2.5 V) redox couples. The calculated voltages for each step (dotted lines) show good agreement with the first cycle. The capacities for each lithium insertion here are similar to previous works, though notably, these are significantly lower than the theoretical lithium capacities, which are 165 and 331 mAh/g for the first and second lithium inclusion, respectively. The cells were stopped at different points along the first full cycle, labeled A–E (discharge) and F–I (charge). The surface of the control electrode A was exposed to the electrolyte and washed as the others were, even though it was not subjected to any electrochemical cycling, for best comparison.

The corresponding XPS spectra collected from each of these samples for the O 1s and V 2p core region are shown in Figure 3b. First, we note the stark changes in the V 2p₁/₂ over the first cycle. There is a general shift toward lower binding energy during discharge and back to higher binding energy during charging, consistent with reduction and subsequent oxidation of the vanadium cation. This correlates well with an increasing and
attenuation of the electrons originating from the composite cathode surface, i.e. the interface with the electrolyte, causing an

3c. Both of these features are in agreement with reported values representing lithium in Li$_2$O at 53.65 eV, almost 2 eV below the main peak of a foreign species at the cathode. This assignment is supported by the concurrent emergence of a distinct Li 1s core level obtained for electrodes D and E showing the main Li$_2$O peak (55.52 eV) and the appearance of the Li$_2$O peak (53.65 eV).

Figure 3. (a) First galvanostatic curve to 1.5 V typical of ε-VOPO$_4$ cells with labels A–I indicating stopping points where each cell was disassembled. (b) O 1s and V 2p XPS core levels obtained for ε-VOPO$_4$ electrodes after increasing amounts of discharge/charge. (c) Li 1s XPS core level obtained for electrodes D and E showing the main Li$_4$VOPO$_4$ peak (55.52 eV) and the appearance of the Li$_2$O peak (53.65 eV).

then decreasing intensity observed in the Li 1s core level. We note that the P 2p core level line shape (shown in Supporting Information) remained constant as a function of discharge and charge. This suggests that the PO$_4^{3-}$ groups are robust, confirming the stability of the PO$_4$ polyhedra. This is discussed further below.

Another distinct feature is the presence of a new peak centered at 528.28 eV below the main O 1s peak after discharge to 1.5 V (electrode E), indicated in Figure 3b. This peak is assigned to the O 1s core level in Li$_2$O, signifying the formation of a foreign species at the cathode. This assignment is supported by the concurrent emergence of a distinct Li 1s feature at 53.65 eV, almost 2 eV below the main peak representing lithium in Li$_4$VOPO$_4$ at 55.52 eV, shown in Figure 3c. Both of these features are in agreement with reported values for Li$_2$O.$^{49,50}$ Along with these changes in electrode E, there is a relative decrease in the intensity of the P 2p and V 2p features, as well as a slight decrease in the C 1s signal from the carbon black. This is ascribed to the formation of the Li$_2$O at the cathode surface, i.e. the interface with the electrolyte, causing an attenuation of the electrons originating from the composite cathode beneath. From these relative changes in intensity and the overall surface sensitivity of photoemission, we estimate the Li$_2$O layer to be <1 nm in thickness; however we do not expect this to be a uniform continuous film. Additional XPS measurements have ruled out air exposure as a possible origin of the Li$_2$O formation (refer to Supporting Information).

There have been reports of surface Li$_2$O formation as a solid-electrolyte interphase (SEI) constituent on electrode materials formed upon lithiation.$^{16,51,52}$ These reports all attribute this to a breakdown of the electrolyte. It is possible that this is the case here when considering the low operating voltage of the second lithium insertion. However, it is also possible that the Li$_2$O is a product of decomposition of the cathode material due to overdischarge, since the extended electrochemistry is not well-studied discharging past 2 V.$^{20}$ The similar LiFePO$_4$ is known to decompose to Li$_2$PO$_4$ and metallic Fe below 1 V, but the decomposition products of ε-VOPO$_4$ are not well-known.$^{53,54}$ Interestingly, the features associated with Li$_2$O are not present after charging. This is suggestive that the Li$_2$O layer is unstable on the Li$_4$VOPO$_4$ cathode surface; however the mechanism of this formation and decomposition is not studied here and warrants future investigation. Despite this interfacial species formation, the fully cycled electrode I displays nearly identical spectra as the nondischarged electrode A (shown in detail in the Supporting Information). This demonstrates the recovery capability of ε-VOPO$_4$ to the fully delithiated state, at least for the first cycle. This finding rules against the decomposition of the cathode material as the origin of the Li$_2$O.

Depth-Resolved Analysis. To further examine the interfacial chemistry as each lithium ion is inserted (approaching the Li$_4$VOPO$_4$ end point), we complement our XPS measurements with HAXPES to take advantage of the deeper probing depth. Estimated from the universal inelastic mean free path curve, 95% of V 2p$_{3/2}$ core level photoelectrons in XPS (KE ≈ 970 eV) derive from less than ~3 nm. However, in HAXPES, since the photoelectrons have greater kinetic energy (KE ≈ 3.5 keV), we are able to access information from up to ~12 nm below the surface.

Figure 4a shows the V 2p$_{3/2}$ core level obtained from XPS (left) and HAXPES (right) for electrodes A–E along the first discharge curve scaled such that the total area under each curve is equal to one. As in XPS, the HAXPES spectra of the noncycled electrode A and fully cycled electrode I display nearly identical oxidation state profiles, further indicating high reversibility when discharged to 1.5 V (shown in Supporting Information). Electrode A does show a slightly lower V$^{4+}$ weight in the HAXPES compared to the XPS spectra. However, this can be expected because the nanoparticle subsurface is likely less sensitive to the initial reduction from cathode synthesis. Following discharge, electrodes B and C show almost identical lineshapes between the XPS and HAXPES spectra indicating uniform lithium intercalation up until that point of the discharging process. After discharge to points D and E there is a pronounced lag of the vanadium cation reduction in the HAXPES signifying that the second lithium does not intercalate uniformly throughout the nanoparticle. Considering that photoemission is spatially averaging over many nanoparticles and the nanoparticles are in no particular orientation, we interpret this as a radial gradient of lithium with greater lithium concentration nearer the outer surface.

Peak fitting of the V 2p$_{3/2}$ region in both XPS and HAXPES was carried out for quantitative analysis of the vanadium reduction along the galvanostatic discharge curve. All fits were
performed including the O 1s and V 2p peaks concurrently after the removal of a Shirley-like background. Voigt lineshapes were used with Gaussian and Lorentzian contributions constrained to be the same for each unique peak across both (XPS/HAXPES) data sets. The fits revealed three discrete V 2p3/2 peaks at 518.23, 517.01, and 516.45 eV assigned to vanadium 5+, 4+, and 3+ oxidation states, respectively. The most reliable method of assigning oxidation states in XPS of vanadium oxides is the energetic separation from the main O 1s peak (531.1 eV). The separations and lineshapes observed in our spectra are in exceptionally good agreement with the vanadium oxide studies of Silversmit et al., although we note such precise agreement is likely fortuitous since we are comparing an oxide group to this oxyphosphate group. Nevertheless, the discrete energetic separations from the V5+ to the reduced counterparts should not deviate greatly from other systems.

The relative areas of each V 2p3/2 peak are plotted in Figure 4b for each electrode along the discharge curve. Aside from the exposure induced surface reduction, it is clear that there is no evidence of inhomogeneity of the lithium intercalation over the first ∼12 nm. This is consistent with a straightforward two-phase reaction from ε-VOPO4 to LiVOPO4 as previously suggested, with the vanadium almost entirely reduced to a 4+ oxidation state in both the surface and subsurface regions.

As the intercalation process proceeds toward the incorporation of the second lithium, i.e. from electrode C to E, there is a marked difference. The XPS shows a smooth crossover of the vanadium oxidation state from 4+ to 3+, while the HAXPES shows only relatively small changes across these electrodes. At the deepest discharge, while the vanadium oxidation state is almost exclusively 3+ within the first few nanometers of the surface, consistent with formation of Li2VOPO4, the subsurface probing of HAXPES indicates only about 30% formal valence of V3+. We estimate that there is only Li2VOPO4 present within the first 3–5 nm of the nanoparticles, since the majority of the HAXPES signal comes from nearer the surface, due to the exponentially decaying profile of the escaping photoelectrons. This is evidence of limited ion diffusion, i.e., a subsurface of Li1.5VOPO4 where 1 < x < 2, with less lithium toward the center of the nanoparticle.

The composition and spatial distribution of an average nanoparticle can be determined from our depth-resolved analysis. Figure 5 shows a cross-sectional schematic of a single ε-VOPO4 nanoparticle at key points along the first discharge curve. The theoretical capacity of 165 mAh/g for one full lithium intercalation (LiVOPO4) is indicated.
vanadium oxidation states, i.e., 5+, 4+, and 3+. To this point, the V 2p peak displays varying amounts of three distinct predictions allows for not only the identification of chemical structure but also accurate orbital assignment of distinct valence species. Furthermore, in the effort to understand cathode materials as they are (de)lithiated, the study of the structural evolution has routinely been of central focus, and these efforts have been remarkably successful. However, due to the strong electron correlation effects of the partially filled d states in the transition metals, a complete understanding cannot be obtained by the crystal structure alone. For example, the operating voltage, ion/ electron transport properties, and phase stability are each dictated by both the structural properties and the electronic states in the vicinity of the Fermi level. Therefore, direct comparison of the measured valence band with DFT predictions allows for not only the identification of chemical species but also accurate orbital assignment of distinct valence band features that can be monitored as a function of delithiation.

At the surface of the nanoparticles, each of the three vanadium oxidation states can be accessed using soft XPS. Here, an additional set of three electrodes have intentionally been discharged to each represent a distinct oxidation state. Figure 6a shows the valence band XPS spectra of these three electrodes (labeled 1–3), with the V 2p core level XPS shown in the inset. Additional core level XPS is shown in the Supporting Information (O 1s, V 2p, and Li 1s).

Due to the relatively little valence band structure seen for carbon black and low concentration of the binder, there is no significant spectral contamination. The prevalent valence band structure of these electrodes is very similar to that of the olivine LiMnPO4 and LiFePO4 systems and consists of two P 3s and 3p derived peaks at ~12 and 10 eV, along with a largely O 2p derived band centered at 6 eV below the Fermi level. Here, we do not observe evidence of any pyrophosphate contributions near 15 eV. This finding is consistent with the lack of any changes in the P 2p core level spectra. Instead, we consider this contribution at ~9 eV as a result of Li2O formation on the surface (Figure 3c).

To confirm our chemical assignments based on vanadium oxidation state, we compared our valence band spectra with the calculated electronic structure from DFT. Figure 6b shows the DFT predicted valence band spectra for ε-VOPO4 and its corresponding LiVOPO4 and Li2VOPO4 lithiated phases. These predictions are obtained by summing the orbital projected density of states after weighting by the corresponding photoionization cross-section and then convolving the sum with a Voigt profile (0.1 eV Lorentzian width, 0.5 eV Gaussian width) to match the experimental resolution. Also included are the predicted spectra for Li2O to account for a small amount of surface Li2O observed in the core level XPS only in the deepest discharged electrode 3. Our predicted Li2O line shape is in good agreement with experimental observations, and thus the large increase of spectral weight near 9 eV is not representative of any orbital rearrangements inherent to the Li2PO4 phase. We note that in our DFT, the Fermi level is at the valence band maximum. In Figure 6b, the predicted spectra were rigidly shifted to match the experimentally determined Fermi level.

The valence band spectra of the ε-VOPO4 end phases are in exceptional agreement with the electronic structure predictions, after the Li2O is considered. This agreement provides more conclusive evidence of reaching the LiVOPO4 and Li2VOPO4 end phases than the vanadium oxidation states alone. Common to all three phases in the DFT are a broad O 2p anion band spanning about 4–9 eV, and two sharper features near 10 and
The valence band maximum of these phases is highlighted by the additional feature above the O 2p states, respectively. The main difference between the V 3d states becoming more occupied with the insertion of each lithium. The nondischarged $\varepsilon$-VOPO$_4$ spectra do however deviate slightly from the predicted spectra in this region. There is some observed weight in the V 3d region that is not predicted by the DFT. This is explained by partial filling of the first unoccupied V 3d$^3$ state due to the tendency of the pristine material to reduce slightly from surface exposure inherent to the electrode processing, and it indeed correlates with the small amount of V$^{4+}$ observed in the V 2p$_{1/2}$ core level.

The difference spectra are included to highlight the evolution of the electronic structure after the first and second full lithium is intercalated, thus representing the

$$V^{5+}\text{OPO}_4^- + Li^+ + e^- \rightarrow LiV^{4+}\text{OPO}_4^-$$

and

$$LiV^{4+}\text{OPO}_4^- + Li^+ + e^- \rightarrow Li_2V^{3+}\text{OPO}_4^-$$

reactions, respectively. The addition of the first lithium is shown to cause significant changes to the valence band structure. There is an increase and slight redistribution of spectral weight in all the oxygen and phosphorus bonding states. This is attributed to the large change in crystal structure upon the transition from $\varepsilon$-VOPO$_4$ (Monoclinic $Cc$) to LiVOPO$_4$ (Triclinic $P\bar{1}$) along with an increase of octahedral symmetry leading to a ~7% contraction along the VO$_6$ chains all contributing to increased local bonding. This shows that the V=O bonds, especially along the VO$_6$ chains contribute to the stability of this structure. Along with these changes is a clear increase of the discrete V 3d$^1$ states about 1.5 eV above the top of O 2p band due to the electron transfer from the lithium to the vanadium cation.

After the second lithium is incorporated there is continued filling of the vanadium d states where a V 3 d$^3$ peak is observed above that of the V 3 d$^4$ states in both the DFT and XPS. After considering the contribution of the Li$_2$O (highlighted in red) to the difference spectra, there are only small changes in the deeper oxygen and phosphorus bonding states. This is likely because the VO$_6$ chains only contract an additional ~1.5% upon transitioning from LiVOPO$_4$ to Li$_2$VOPO$_4$ while the space group is preserved. Additional weight, however, is observed at the top of the O 2p band (~4 eV) as the V 3 d$^3$ states are filled, indicating that the electron transfer is largely shared by between the oxygen and vanadium. This covalent character should contribute to increased stability of this material upon lithiation.

Both the redox active vanadium 3 d$^1$ and 3 d$^2$ states are confirmed to lie well above the broad O 2p anion band rather than pinned in the O 2p band or below it. This is the preferred case for thermodynamic stability. Both of these redox active states are also sufficiently far below the Li$^+$/Li$^2$ potential such that they can both be accessed.

**CONCLUSIONS**

Our findings support a two-phase reaction from $\varepsilon$-VOPO$_4$ to LiVOPO$_4$, following a core−shell like structure. In our hydrothermally synthesized $\varepsilon$-VOPO$_4$, we find that the second lithium reaction begins before the full incorporation of the first lithium. This results in a pronounced lithium gradient within the nanoparticles, with the $\varepsilon$-Li$_2$VOPO$_4$ phase only forming near the surface. These assignments are supported by both the core level and valence band XPS as well as our hybrid DFT calculations. This restricted diffusion at the nanoparticle surface is sufficient to effect the macroscopic properties of the cathode material and thus could contribute to the relatively low capacities reported. This should be considered in order to achieve capacities closer to the theoretical limit.

Our observation of a Li gradient formation is quite different from the studies of Bianchini et al. where $\varepsilon$-LiVOPO$_4$ is used as the starting material and is shown to electrochemically reach the Li$_2$VOPO$_4$ phase in the bulk. Our findings indicate that using $\varepsilon$-VOPO$_4$ as a starting material may be intrinsically different (e.g., due to defects in the LiVOPO$_4$ phase) when electrochemically lithiating to Li$_2$VOPO$_4$. Such defects could be responsible for the disruption of the Li$^+$ kinetics or electronic transport and cause the Li gradient to occur.

Despite both the Li gradient and the surface formation of Li$_2$O, these cathodes exhibit full recovery to the delithiated $\varepsilon$-VOPO$_4$ state for the first full cycle. Furthermore, comparison with our hybrid-DFT calculations shows good agreement and confirms the orbital character of distinct valence band features. The evolution of the electronic structure provides insight into fundamental properties affecting the electrochemical performance of these cathodes.

**REFERENCES**


Initio total-energy calculations using a plane-wave basis set. Studies.

Orientation-Dependent Distribution of Subsurface Cation-Exchange of LiVPO4.


(52) Song, M.-S.; Kim, R.-H.; Baek, S.-W.; Lee, K.-S.; Park, K.; Benayad, A. Is Li4Ti5O12 a solid-electrolyte-interphase-free electrode material in Li-ion batteries? Reactivity between the Li4Ti5O12 electrolyte and electrolyte. J. Mater. Chem. A 2014, 2, 631−636.

(53) Yang, S.; Song, Y.; Ngala, K.; Zavalij, P. Y.; Whittingham, M. S. Performance of LiFePO4 as lithium battery cathode and comparison with manganese and vanadium oxides. J. Power Sources 2003, 119−121, 239−246. Selected papers presented at the 11th International Meeting on Lithium Batteries.


