Uniform second Li ion intercalation in solid state $\epsilon$-LiVOPO$_4$


Citation: Applied Physics Letters 109, 053904 (2016); doi: 10.1063/1.4960452
View online: http://dx.doi.org/10.1063/1.4960452
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/109/5?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
The role of electronic and ionic conductivities in the rate performance of tunnel structured manganese oxides in Li-ion batteries
APL Mater. 4, 046108 (2016); 10.1063/1.4948272

Li transport in fresh and aged LiMn$_2$O$_4$ cathodes via electrochemical strain microscopy

A high pressure x-ray photoelectron spectroscopy experimental method for characterization of solid-liquid interfaces demonstrated with a Li-ion battery system

Communications: Elementary oxygen electrode reactions in the aprotic Li-air battery

Pt metal- CeO$_2$ interaction: Direct observation of redox coupling between Pt $^0$ / Pt $^2+$ / Pt $^4+$ and Ce $^4+$ / Ce $^3+$ states in Ce 0.98 Pt 0.02 O 2 − δ catalyst by a combined electrochemical and x-ray photoelectron spectroscopy study
Uniform second Li ion intercalation in solid state $\epsilon$-LiVOPO$_4$

Linda W. Wangoh,1, Shawn Sallis,2 Kamila M. Wiaderek,3 Yuh-Chieh Lin,4 Bohua Wen,5 Nicholas F. Quackenbush,1 Natasha A. Chernova,5 Jinghua Guo,6 Lu Ma,3 Tianpin Wu,3 Tien-Lin Lee,7 Christoph Schlüeter,7 Shyue Ping Ong,4 Karen W. Chapman,3 M. Stanley Whittingham,8 and Louis F. J. Piper 1(2, a)

1Department of Physics, Applied Physics and Astronomy, Binghamton University, Binghamton, New York 13902, USA
2Materials Science and Engineering, Binghamton University, Binghamton, New York 13902, USA
3X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
4Department of NanoEngineering, University of California San Diego, 9500 Gilman Drive 0448, La Jolla, California 92037, USA
5NECES, Binghamton University, Binghamton, New York 13902, USA
6Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
7Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom

(Received 28 June 2016; accepted 22 July 2016; published online 4 August 2016)

Full, reversible intercalation of two Li$^+$ has not yet been achieved in promising VOPO$_4$ electrodes. A pronounced Li$^+$ gradient has been reported in the low voltage window (i.e., second lithium reaction) that is thought to originate from disrupted kinetics in the high voltage regime (i.e., first lithium reaction). Here, we employ a combination of hard and soft x–ray photoelectron and absorption spectroscopy techniques to depth profile solid state synthesized LiVOPO$_4$ cycled within the low voltage window only. Analysis of the vanadium environment revealed no evidence of a Li$^+$ gradient, which combined with almost full theoretical capacity confirms that disrupted kinetics in the high voltage window are responsible for hindering full two lithium insertion. Furthermore, we argue that the uniform Li$^+$ intercalation is a prerequisite for the formation of intermediate phases Li$_{1.50}$VOPO$_4$ and Li$_{1.75}$VOPO$_4$. The evolution from LiVOPO$_4$ to Li$_2$VOPO$_4$ via the intermediate phases is confirmed by direct comparison between O K–edge absorption spectroscopy and density functional theory. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4960452]

There is a demand for higher capacity, safer Li-ion battery (LIB) cathodes that are capable of reversibly intercalating more than one Li$^+$ per redox center whilst remaining compatible with existing LIB architecture. Vanadyl phosphates can reversibly intercalate more than one Li$^+$ per vanadium with the added benefit of better thermal and chemical stability than their layered oxide counterparts, thereby making them attractive.1, 2 In particular, $\epsilon$-VOPO$_4$ has a theoretical capacity of 332 mAh/g but the full two lithium ion capacity has not yet been achieved. Depth-profile studies of $\epsilon$-VOPO$_4$ as a function of discharge have shown that the second reaction occurs at the surface before the first lithium has been fully incorporated into the bulk.3 The inability to reach full capacity was explained in terms of not realizing the expected Li$_x$VOPO$_4$ endpoint phase within the bulk when starting from VOPO$_4$. In contrast, full incorporation of the second Li$^+$ can be achieved when starting from $\epsilon$-LiVOPO$_4$, with capacities reaching close to the theoretical limit of 165 mA h/g that can be retained upon extended cycling within the low voltage window (3.5–1.5 V).4 In addition, well-defined intermediate phases are observed under these conditions,5, 7 which are absent in the aforementioned studies of VOPO$_4$. Interestingly, when $\epsilon$-LiVOPO$_4$ is cycled over both voltage windows (4.5–1.5 V), rapid capacity fading is observed upon cycling in tandem with the smearing of plateaus associated with the intermediate phases.4 Taken together, these studies suggest that the loss of capacity and smearing of intermediate phases emanate from disrupted kinetics in the high voltage window, which is evident from a pronounced Li$^+$ gradient observed in the low voltage window. As a result, a Li$^+$ gradient is not expected to evolve for $\epsilon$-LiVOPO$_4$ when cycled within the low voltage window.

In this letter, we perform depth-profile analysis of solid state $\epsilon$-LiVOPO$_4$ electrodes cycled only within the low voltage (1.5–3.5 V) window to correlate Li–ion uniformity with well-defined intermediate phases as well as isolate the effects of disrupted kinetics in the high voltage window. We employ soft and hard x–ray photoelectron spectroscopy (XPS and HAXPES) together with complementary x–ray absorption near edge structure (XANES) to monitor changes in the vanadium oxidation state at the surface, subsurface, and bulk. Oxygen K-edge X–ray absorption spectroscopy (XAS) was also employed to confirm the formation of intermediate phases (i.e., Li$_{1.50}$VOPO$_4$ and Li$_{1.75}$VOPO$_4$) previously predicted by density functional theory (DFT).4 We report a uniform vanadium oxidation state at various stages of charge and discharge which reflects the lack of a pronounced Li$^+$ gradient. These data support our hypothesis that poorer kinetics in the high voltage window are responsible for the formation of a Li$^+$ gradient, which smears out plateaus associated with intermediate phases. Furthermore, our work highlights the need to address the kinetics in the high voltage
window in order to achieve the full theoretical capacity of reversible two Li\(^+\) intercalation that VOPO\(_4\) promises.

\(\varepsilon\)-LiVOPO\(_4\) was prepared via previously reported solid state synthesis and the phase purity confirmed by X-ray diffraction (Figure S1). Fabrication details of the \(ex\text{-}situ\) and \(operando\) electrodes can be found in supplementary material.

Surface studies were performed using monochromated Al K\(_\alpha\) XPS and XAS (TEY mode), which have an effective probing depth of 2–3 nm and 2–5 nm, respectively. While the subsurface and bulk studies were performed using HAXPES (with an effective probing depth of 5–20 nm) and XANES (measured in transmission mode), respectively. In addition, \(operando\) XANES employing the AMPIX cell was performed to account for differences between samples under equilibrium (\(ex\text{-}situ\)) and non-equilibrium (\(operando\)).

The corresponding electrochemical data for the LiVOPO\(_4\) electrodes are plotted in Fig. 1. The capacity of our electrodes reached 162 mA h/g, i.e., almost full theoretical capacity of 165 mA h/g, after the second Li\(^+\) insertion. Three plateaus are observed in our electrochemical curves (and associated derivative curves), consistent with the formation of intermediate states highlighted in previous studies. The set of electrodes used for \(ex\text{-}situ\) spectroscopy studies were disassembled at different voltages indicated in Fig. 1. We note that the electrochemical data of the LiVOPO\(_4\) electrodes within the AMPIX cell showed similar electrochemical performance (capacity and plateaus) to the disassembled cells.

The combination of the XPS, HAXPES, and XANES (both \(ex\text{-}situ\) and \(operando\)) was used to depth–resolve the vanadium oxidation state at various stages of discharge and charge (Figs. 2 and S2). The soft XPS was used to determine the vanadium oxidation states at the surface of the pristine LiVOPO\(_4\), Li\(_2\)VOPO\(_4\) and recovered LiVOPO\(_4\) occurring at the endpoints based on the relative energetic difference between the O 1s (531.8 eV) and V 2\(p_3/2\). As the reaction progresses, the initial vanadium oxidation state of V\(^{4+}\) for the pristine LiVOPO\(_4\) electrode progressively reduces to V\(^{3+}\) when discharged to 1.6 V (Li\(_2\)VOPO\(_4\)) and reversibly recovers to V\(^{4+}\) upon charging to 3.5 V (LiVOPO\(_4\)). The corresponding vanadium oxidation state of the subsurface was determined from the same analysis of the V 2\(p_{3/2}\) core-level measured by HAXPES. In Fig. 2, the HAXPES shows the same oxidation state as from XPS at all stages of discharge and charge. The V L edge XAS, which was measured simultaneously with the HAXPES, was used to further confirm the vanadium oxidation state at the surface, refer to Fig. S3(a). We note that in the case of the hydrothermally synthesized \(\varepsilon\)-VOPO\(_4\), the V\(^{3+}\) endpoint phase was only achieved at the surface. Finally, in Fig. 2(b) both \(ex\text{-}situ\) and \(operando\) V K edge XANES measurements show strong pre–edge peaks that are good indicators of bulk V\(^{4+}\) and V\(^{3+}\) oxidation states at the endpoints. The evolution of the XANES spectra is shown in supplementary information Figs. S2(a) and S2(b). Figure 2(b) reveals that the pristine LiVOPO\(_4\) pre–edge peak for both \(ex\text{-}situ\) and \(operando\) cases is centered around 5470 eV, as expected for the V\(^{4+}\) oxidation state. The dotted lines indicate the expected fractions of V\(^{3+}\) and V\(^{4+}\) at 1.50 and 1.75 Li.

**FIG. 1.** (Left) First cycle discharge/charge curve of electrochemically cycled \(\varepsilon\)-LiVOPO\(_4\) for both the \(ex\text{-}situ\) and \(operando\) cases. (Right) The associated derivative curves of the \(ex\text{-}situ\) case are shown alongside.

**FIG. 2.** Comparison of the (a) V 2\(p_{3/2}\) core–level (XPS and HAXPES) and (b) V K edge \(ex\text{-}situ\) and operando endpoints. (c) Summarized results of vanadium oxidation state from V K–edge (bulk) XANES and V 2\(p_{3/2}\) core–level (surface) XPS spectra of the cycled \(\varepsilon\)-LiVOPO\(_4\) electrodes. The vanadium is reducing from V\(^{4+}\) to V\(^{3+}\) upon discharge and back to V\(^{4+}\) when charged in both instances. The dotted lines indicate the expected fractions of V\(^{3+}\) and V\(^{4+}\) at 1.50 and 1.75 Li.
cases, the $V^{4+}$ oxidation state is recovered upon charging back to 3.5 V. The consistency across these multiple approaches and length-scales indicates uniform Li$^+$ intercalation and extraction within this voltage window.

To better illustrate the uniformity in the surface and bulk, fitting of the V 2p$_{3/2}$ and the V K edge pre-peak was performed at various stages of discharge and charge. (Fitted data are provided in supplementary material.) The inelastic background of XPS spectra was subtracted using a Shirley–like profile before fitting the V 2p$_{3/2}$ core–level. The surface V$^{4+}$ and V$^{3+}$ ratio for each electrode was then determined following a procedure described earlier, and is shown in Fig. 2(c). Representative end member XANES spectra were extracted using an algorithm based on Bayesian non–negative matrix factorization with volume constraints. They were then fit to the XANES data using least squares linear combination fitting to determine the bulk average vanadium oxidation state of the electrodes, also plotted in Fig. 2(c). The vanadium oxidation states of the surface and bulk are similar throughout the first low voltage cycle (Fig. 2(c)). This would suggest that lithium ion diffusion is uniform for solid state $\epsilon$–LiVOPO$_4$ within the low voltage window. This explains why almost full reversible capacity of 165 mA h/g is realized in this electrode.

Having established the quality of the $\epsilon$–LiVOPO$_4$ and uniform Li$^+$ distribution within our electrodes, we turn to the formation of intermediate phases with compositions of $\text{Li}_{1.5}$VOPO$_4$ and $\text{Li}_{1.75}$VOPO$_4$ that have been previously predicted from DFT. Figure 3(a) shows the O K edge XAS for selected voltages reflecting vanadium oxidation states expected for the four phases (i.e., Li$_x$VOPO$_4$ where $x = 1.00, 1.50, 1.75$, and 2.00). We have ruled out possible spectral contamination (refer to Fig. S3) to ensure that direct comparison with the O 2p partial density of states (PDOS) was valid. (Computational details are provided in supplementary material.) The O 2p PDOS in Fig. 3(a), obtained from raw O 2p in Fig. 3(b), was broadened by Gaussian (0.4 eV) and Lorentzian (0.3 eV) profiles to account for instrumental and lifetime broadening, respectively. The photon and binding energy axes were aligned by the O 1s binding energy. The evolution of the XAS spectra is reproduced by the DFT in Fig. 3(a). The O K-edge pre–edge region (528 eV–535 eV) reflects changes in V 3d $t_2g$ and $e_g$ orbital occupation with Li$^+$ insertion, as shown in Fig. 3(c). Feature A (~534 eV) is predominantly associated with the Li 2s orbital in Fig. 3(d). The features above 535 eV result predominantly from O 2p–P 3sp hybridized states, with minor contributions from O 2p–V 4sp hybridization. No major changes are observed in these regions confirming the robustness of the PO$_4^{3-}$ groups.

In summary, we correlated a uniform vanadium oxidation (and therefore Li$^+$) profile with the formation of intermediate phases in solid state $\epsilon$–LiVOPO$_4$ electrodes cycled within the low voltage (3.5–1.5 V) window. In addition, using O K-edge XAS and DFT, we confirmed the formation of the well-defined intermediate phases, $\text{Li}_{1.5}$VOPO$_4$ and $\text{Li}_{1.75}$VOPO$_4$. These data suggest that uniform Li$^+$ intercalation is a prerequisite for the formation of these intermediate phases. Our previous report of discharged $\epsilon$–VOPO$_4$ revealed a pronounced Li$^+$ gradient in the low voltage window, which was thought to originate from disrupted kinetics in the high voltage window. Other studies have shown that the electrochemistry of LiVOPO$_4$ does not degrade when cycling is restricted to the low voltage window. We argue that the uniform lithium ion insertion and extraction observed here is because we avoid the high voltage window. As a result, the depth-profile analysis of the first cycle shown here is considered to be representative of subsequent cycles. Taken together, our data reinforce the view that disrupted kinetics in the high voltage regime hinder the full two Li$^+$ capacity of $\epsilon$–VOPO$_4$ by forming a Li$^+$ gradient profile within the electrode. Therefore, a better understanding of the kinetics in the high voltage regime is required to realize the full two Li$^+$ capacity of VOPO$_4$.

![Fig. 3. (a) The O K edge XAS of the end points (pristine and 1.6 V) and intermediate phases of (2.35 V and 2.1 V) $\epsilon$–LiVOPO$_4$ plotted on a photon energy axis (top). Plotted underneath is the corresponding convoluted O 2p PDOS plotted against binding energy (bottom, 0 eV refers to the Fermi level). The two energy axes are different by the O 1s binding energy. The calculated spin up and spin down orbital and elementally resolved PDOS of (b) O p, (c) V d, and (d) Li s states of $\epsilon$–Li$_x$VOPO$_4$ ($x = 1.00, 1.50, 1.75$, and 2.00). The V d is broken down into the $e_g$ and $t_{2g}$ states.](image-url)
See supplementary material for details of the electrode fabrication, spectroscopy measurements and curve fitting analysis. Additional XRD, V K-edge XANES and V L-edge XAS analysis are also provided.

This work was supported as part of NECCES, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC0012583. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We thank Diamond Light Source for access to beamline I09 (SI12546) that contributed to the results presented here. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-05CH11231.