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Nanoscale Depth and Lithiation Dependence of V$_2$O$_5$ Band Structure by Cathodoluminescence Spectroscopy

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Abstract

Vanadium pentoxide ($V_2O_5$) is a very well-known cathode material that has attracted considerable interest for its potential use in solid-state lithium-ion batteries. We pioneer the use of depth-resolved cathodoluminescence spectroscopy (DRCLS) to monitor the changes in the electronic structure of lithiated $V_2O_5$ from the free surface to the thin film bulk several hundred nm below as a function of lithiation. DRCLS measurements of $V_2O_5$ interband transitions are in excellent agreement with density functional theory (DFT) calculations. The direct measure of $V_2O_5$’s electronic band structure as a function of lithiation level provided by DRCLS can help inform solid state battery designs to further withstand degradation and increase efficiency. In particular, these unique electrode measurements may reveal physical mechanisms of lithiation that change $V_2O_5$ irreversibly, as well as methods to mitigate them in solid-state batteries.

Keywords: depth-resolved cathodoluminescence spectroscopy, Li-ion battery, thin films, atomic layer deposition, vanadium oxides
Introduction

Research into sustainable energy technologies continues to gain importance as technologists learn more about how human activity impacts global warming and as society seeks more environmentally friendly energy sources. In line with this technological demand is the development of more efficient energy storage techniques including advanced materials for batteries. In particular, lithium-ion batteries have the potential to play a significant role in the solution of environmental problems, for example, in electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs).\textsuperscript{1,2} In large part, they are attractive due to their high energy density compared to other rechargeable batteries.\textsuperscript{3}

Considerable efforts have been dedicated to developing each component of the battery system—anode materials,\textsuperscript{4} electrolytes,\textsuperscript{5} and cathode materials\textsuperscript{6,7}—and to gaining a better fundamental understanding of the interfacial processes that govern the electrochemical performance of the system.\textsuperscript{5} The thermodynamic properties of a given electrode material—in particular the reversibility of the intercalation and deintercalation reactions, the material’s capability to change valence states, and the amount of available space it has to hold the ions—determine the material’s lithium-ion storage capacity.\textsuperscript{8,9} The anode materials have higher lithium-ion storage capacities than all known cathode materials.\textsuperscript{10} Therefore, one of the primary factors to address in order to develop lithium-ion batteries with higher energy densities is the capacity of the cathode to store lithium-ions.\textsuperscript{9}

Vanadium oxide (V$_2$O$_5$) is an interesting cathode material for lithium-ion batteries because of its high theoretical capacity of 440 mA h g$^{-1}$ for storing three lithium ions per unit V$_2$O$_5$, or 294 mA h g$^{-1}$ for two lithium ions per unit V$_2$O$_5$.\textsuperscript{11} Other advantages include its low cost and easy synthesis.\textsuperscript{12} However, several issues present challenges to its widespread use in such contexts. For example, V$_2$O$_5$’s low lithium ion diffusion coefficient of $10^{-12}$ to $10^{-13}$ cm$^2$ s$^{-1}$ into the matrix\textsuperscript{13} and its moderate electrical conductivity of $10^{-2}$ to $10^{-3}$ S cm$^{-1}$ limit its intercalation capacity and charge/discharge rate.\textsuperscript{14,15} Another problem involves the irreversible phase transformations associated with lithiation of V$_2$O$_5$.\textsuperscript{16,17,18}

The bulk structure of Li$_x$V$_2$O$_5$ with $0 < x < 3$ is well understood.\textsuperscript{16,19,20,21,22} Pristine V$_2$O$_5$’s structure consists of pyramidal VO$_5$ square pyramids which share edges and corners. The structure can alternatively be thought of as distorted VO$_6$ octahedra with perovskite-like cavities into which ions such as Li can diffuse, \textit{i.e.}, intercalate between V$_2$O$_5$ lattice planes, making the material
attractive for chemical processes involved in lithium-ion batteries. \( \text{Li}_x\text{V}_2\text{O}_5 \) with \( x \leq 0.1 \) is termed \( \alpha\text{-V}_2\text{O}_5 \). As lithium is intercalated into the crystal structure, the layers increasingly distort or pucker. \( \text{Li}_x\text{V}_2\text{O}_5 \) with \( 0.35 \leq x \leq 0.7 \) is termed \( \varepsilon\text{-Li}_x\text{V}_2\text{O}_5 \) and \( \text{Li}_x\text{V}_2\text{O}_5 \) with \( 0.9 \leq x \leq 1 \) is termed \( \delta\text{-Li}_x\text{V}_2\text{O}_5 \). For lithiation with \( x \leq 1 \), the phase transitions that occur are reversible and there is little structural variation compared to pristine \( \text{V}_2\text{O}_5 \). However, upon the lithiation of more than one \( \text{Li}^+ \) per unit \( \text{V}_2\text{O}_5 \), a partially reversible phase transition to \( \gamma\text{-Li}_x\text{V}_2\text{O}_5 \) \( (1 < x \leq 2) \) occurs. If three \( \text{Li} \) per unit \( \text{V}_2\text{O}_5 \) are intercalated, a phase termed \( \omega\text{-Li}_3\text{V}_2\text{O}_5 \) forms. This particular phase transformations are considered irreversible as the structure does not resemble that of any other phase of \( \text{Li}_x\text{V}_2\text{O}_5 \), but rather that of rock salt.

\( \text{V}_2\text{O}_5 \) is also known to dissolve into liquid electrolytes during the battery operation at high voltage.\(^{23}\) These interfacial degradation mechanisms have a significant impact on battery performance because even a small amount of metal dissolution accompanied by surface reconstruction has a large effect over the course of many cycles.\(^{18}\) The exact role of the surface chemistry, oxygen vacancy formation and surface structural rearrangement are still subject to controversies due to the complex nature of these phenomena and the inherent limitations of the standard analytical tools.\(^{24-26}\)

The goal of this study is to probe how the electronic band structure of \( \text{V}_2\text{O}_5 \) changes with \( \text{Li} \) cycling as it is used as a battery cathode. We pioneer the use of depth-resolved cathodoluminescence spectroscopy (DRCLS) to monitor the changes in the \( \text{V}_2\text{O}_5 \) electronic structure as a function of lithiation and as a function of depth from the free surface to the thin film bulk several hundred nm below. The changes in the electronic band structure are measured and interpreted with reference to the reversible and irreversible structural changes that \( \text{V}_2\text{O}_5 \) undergoes over the course of lithiation to \( \text{Li}_x\text{V}_2\text{O}_5 \) with \( 0 \leq x \leq 2 \).

**Experimental Methods**

Pristine \( \text{V}_2\text{O}_5 \) samples were prepared by means of atomic layer deposition (ALD) according to Chen *et al.*’s method, using Si/SiO\(_2\) as a substrate material.\(^{27}\) A gold current-collector was deposited by DC sputtering with a thickness of 200 nm to avoid any interference of silicon peaks on the CL and Raman spectra. Fig. 1 contains illustrations of the ALD-grown \( \text{V}_2\text{O}_5 \) as well as the structural changes in the material as lithiation proceeds from \( \alpha\)- to \( \delta\)- to \( \gamma\text{-Li}_x\text{V}_2\text{O}_5 \). As shown in Fig. 1, all \( \text{V}_2\text{O}_5 \) samples obtained through ALD have a thickness of 500 nm, with the exception
of those analyzed in Fig. 3, for which the V$_2$O$_5$ layer is 200 nm thick. The film thickness was determined by contact profilometry and by scanning electron microscopy (SEM).

In order to obtain lithiated samples with approximately one and two Li ions per unit V$_2$O$_5$, corresponding to δ-LiV$_2$O$_5$ and γ-Li$_2$V$_2$O$_5$, respectively, V$_2$O$_5$ crystalline thin films were biased in solution with V$_2$O$_5$ as the working electrode, Li foil as the counter electrode, and 1 M LiClO$_4$ dissolved in polycarbonate solvent as the electrolyte (Fig. 1). Lithium ions were intercalated into the V$_2$O$_5$ by galvanostatic cycling inside an Ar-filled glovebox using a 2 electrodes beaker cell configuration, applying a current of 8 μA (film thickness 500 nm) or 3 μA (film thickness 200 nm); the cut-off voltage dictates the lithium content and was chosen accordingly to obtain the phase of Li$_x$V$_2$O$_5$ desired: 2.8 V for δ-LiV$_2$O$_5$ and 2.2 V for γ-Li$_2$V$_2$O$_5$, as shown in Fig. 1. To ensure a homogeneous repartition of the lithium within the δ-LiV$_2$O$_5$ and γ-Li$_2$V$_2$O$_5$, the voltage was maintained at the cut-off voltage until the current reached nearly zero μA, for approximately 5 and 10 hours, respectively. For the delithiated sample, the sample δ-LiV$_2$O$_5$ was brought back to 3.4V by galvanostatic cycling where the voltage was maintained at this value until the current reached nearly zero μA, for approximately 5 hours. Fig. 1 also shows images of the structure of each phase. After lithiation/delithiation, the samples underwent cleaning by means of extensive rinsing with propylene carbonate solvent inside the Ar-filled glovebox to ensure that no solid-electrolyte interface (SEI) layer was present on the surface.
Figure 1: The voltages applied in the beaker containing V$_2$O$_5$, Li foil, and 1 M LiClO$_4$ in PC electrolyte in order to obtain the four phases of V$_2$O$_5$ relevant to this study: α-, ε-, δ-, and γ-Li$_x$V$_2$O$_5$. In the upper-left is a picture of the sample obtained through ALD and in the lower-left, the electrochemical cell used for this study. Along the upper-right side are schematic diagrams of the structure of α-, δ-, and γ-Li$_x$V$_2$O$_5$. V atoms lie inside the nearest neighbor coordinating pyramids.

Raman spectroscopy was used to probe the local structure of the samples before and after lithiation. Raman spectroscopy measurements were recorded with a confocal "Labram" microscope system (Horiba Jobin Yvon USA) equipped with a 633 nm laser source (laser power adjusted to ≤ 1 mW, ~2 µm beam diameter) using a 50x microscope objective (Olympus America Inc.). To maximize the spectral quality, a 600 gr/mm grating with a 30 second exposure time for 20 repetitions was used. For each composition, 2 samples and 3 different areas were measured. To prevent variations in lithium content during measurement, the samples were placed in an air-tight cell compatible with the Raman system.

Cathodoluminescence spectroscopy (CLS) provides a new and potentially useful technique to measure electronic band structure inside and at the interfaces of battery electrodes such as V$_2$O$_5$ as well many other electronic materials. This technique involves focusing an electron beam with
energy of a few keV or less onto a specimen in UHV (background pressure ≤ 2×10⁻⁹ Torr). This incident electron beam generates a cascade of secondary electrons with successively lower energies due to plasmon energy loss and ultimately impact ionization that results in the creation of free electron-hole (e-h) pairs. These free carriers recombine either by electronic transitions between unoccupied conduction band and occupied valence band states or by transitions between defect or impurity states with levels inside the band gap and the conduction or valence band edges. These electronic transitions produce photons with energies characteristic of the material’s band structure, not only the band gap between highest occupied valence and lowest unoccupied conduction band but also between higher lying unoccupied states and occupied states at the valence band maximum. These photons are collected with optical lenses, dispersed with a monochromator and the spectra recorded with a charge-coupled detector (CCD). The ability to focus the electron beam enables CLS to probe band gaps, defects, and bound states in electronic materials and devices with sub-mm to nanoscale spatial resolution and over a wider energy range of excitation than photoluminescence spectroscopy, enabling studies of higher lying conduction bands. Because the electron beam cascade extends deeper into the solid with increasing incident beam energy, one can control the depth of excitation with nanoscale precision. The CLS technique used to measure electronic properties as a function of excitation depth is termed depth-resolved CLS or DRCLS. The ability of DRCLS to probe surfaces, sub-surface layers and their interfaces with nanoscale resolution can prove useful for the study of solid state batteries, which have nanoscale lateral and depth structure whose features can provide new information about electronic and structural changes involving in battery cycling.

With increasing electron beam energy $E_B$, the penetration depth of the incident electron beam increases. Accordingly, cathodoluminescence spectra characteristic of the electronic band structure for $E_B$ extending from 500 eV to 5 keV can be collected from depths of just a few nm to several hundred nm, respectively, inside the sample with depth resolution on a scale of tens of nanometers.

![Figure 2: Monte Carlo simulation produced with CASINO software showing the rate of e-h pair generation versus incident electron beam energy for α-V₂O₅.](image)
Fig. 2 shows penetration depths of an electron beam of a given energy in V₂O₅ calculated using Monte Carlo simulations generated by CASINO (monte CARlo SImulation of electroN trajectory in sOlids) software.²⁰ Besides E_B, parameters required for this simulation include density, atomic weight, and atomic number Z, of pristine V₂O₅.²¹ Because the maximum beam energy used for CL in this research was 3.0 kV, penetrating ~110 nm into the sample, there is no difference in these simulations between 200 nm and 500 nm V₂O₅ layers. These simulations can be used for lithiated V₂O₅ as well, since lithiation does not significantly affect the lattice density and beam penetration depth. Each DRCLS graph is the average of five spectra, each of which consists of 10 scans, where each scan lasts 20 seconds. Spectra from several spots on each sample were tested, and several samples of each lithiation level were tested; the data presented here are therefore repeatable.

Results

We acquired DRCL spectra as a function of depth for α-, δ-, and γ-Li₅V₂O₅. Fig. 3a shows DRCLS on pristine (α-) V₂O₅. For E_B = 0.5 kV, which corresponds to a maximum penetration (Bohr-Bethe) range (R_B) of ~10 nm in Fig. 2, Fig. 3a shows peak features at 1.8-2, 3.2, 3.6-3.7, and 4.0 eV. When E_B is increased to 1.0 kV, corresponding to R_B ≈ 40 nm, the broad feature around 2 eV exhibits three distinct features at 1.8, 1.9, and 2.0 eV. Higher energy features at ~3.1 eV, 3.6 eV, and 4.0 eV remain. With increasing E_B and excitation depth, the 1.8, 1.9, and 4.0 eV features increasingly dominate the spectra.

With lithiation to produce δ-Li₅V₂O₅ (applied voltage of 2.8 V in Fig. 1), DRCL spectra exhibit several changes. Fig. 3b shows that the features around 1.8-2.0 eV are suppressed at beam energies of 0.5 kV, although a shoulder still remains at 1.96 eV. In addition, evidence for broad emission at 2.45 eV appears with this near-surface excitation, more clearly visible in Fig. 3d. For E_B = 2.0 kV (R_B ≈ 60 nm), all photon emissions <3 eV are suppressed. Similar to the pristine (α-V₂O₅) spectra, the 4.0 eV feature dominates at deeper beam penetration depths, but the 1.8-2.0 eV feature is absent.
With lithiation to produce $\gamma$-Li$_2$V$_2$O$_5$ (applied voltage of 2.2 V in Fig. 1), Fig. 3c shows that even the 1.96 eV feature is no longer present for any penetration depth. The weak 2.45 eV feature from $\delta$-LiV$_2$O$_5$ in Fig. 3d remains for $E_B = 0.5$ kV, but is shifted to 2.5 eV. As $E_B$ increases to 3.0 eV, this trend continues: all spectral emissions except for the 4.0 eV feature disappear. The orbital nature of all peaks in Fig. 3 and their close alignment with DFT calculations are discussed below.
DRCL spectra also provide optical information to gauge the reversibility of lithiation. Fig. 4 shows the DRCL spectra of a sample prepared as $\delta$-LiV$_2$O$_5$ and then delithiated by galvanostatic cycling. The lithium content of the delithiated sample corresponds to $\varepsilon$-Li$_x$V$_2$O$_5$ with $0.1 < x < 0.3$. The 0.5 kV beam energy spectrum shows that the effects of lithiation are partially reversible. In particular, while lithiation suppressed the 1.8-2.0 eV feature, this feature returns upon delithiation, but only as a very narrow peak. Even so, this relatively small feature around 1.87 eV exhibits structural broadening suggestive of the multiple peaks in that spectral region for the 1.0 kV beam energy pristine spectrum from Fig. 3b.

Even though the suppression of the 1.8-2.0 eV peaks is indeed reversible when $\delta$-LiV$_2$O$_5$ is delithiated, the 2.45 eV feature from Fig. 3d remains at all excitation depths. In comparison, the $\delta$-LiV$_2$O$_5$ and $\gamma$-Li$_2$V$_2$O$_5$ near-surface spectra at $E_B = 0.5$ kV in Figs. 3b and 3c, respectively, show that lithiation introduced a 2.45 eV feature. Since this feature is not removed when the sample is delithiated, the effects of lithiation are therefore not entirely reversible. As in all pristine and lithiated V$_2$O$_5$ spectra with $E_B = 0.5$ kV, features at ~3.7 and 4.1 eV remain as well for delithiated Li$_x$V$_2$O$_5$.

At deeper beam penetration depths, the 2.5 eV feature remains prominent, unlike in the $\delta$-LiV$_2$O$_5$ spectrum in Fig. 3b, in which all emissions below 3 eV vanish. In addition, Fig. 4 shows a new strong 3.3 eV feature, clearly visible at $E_B = 1.0$ kV and 2.0 kV.
One physical mechanism that could change V₂O₅ with electrochemical cycling is chemical bonding between Li and O in the LiV₂O₅ scaffolds. Formation of Li-O bonds during Li intercalation could result in the formation of Li₂O and V₂O₄,¹²,³³ resulting in extraction of lattice oxygen from the V₂O₅ scaffold and formation of oxygen vacancies. In order to test whether such oxygen vacancies were present, we exposed both pristine and lithiated V₂O₅ to a remote oxygen plasma (ROP),³⁴ which has been shown to fill oxygen vacancies in ZnO,³⁴,³⁵ SrTiO₃,³⁶ and Ga₂O₃.³⁷ Remote exposure of samples to activated oxygen in a plasma avoids lattice damage due

![Figure 5: DRCL spectra of (a) pristine V₂O₅ before ROP treatment, (b) γ-Li₂V₂O₅ before ROP treatment, (c) pristine V₂O₅ after ROP treatment, and (d) γ-Li₂V₂O₅ after ROP treatment, with varying beam energy and penetration depth. Other than increasing near-surface CL intensity, ROP treatment does not change the spectra significantly, implying that oxygen vacancies are not present in lithiated V₂O₅ samples.](image)
to collisions with energetic oxygen atoms. Changes in DRCL spectra following ROP treatment might then be related to oxygen vacancies. Figs. 5a and 5c display the pre- and post-ROP DRCLS spectra respectively for pristine $V_2O_5$ with beam energies of 0.5, 1.5, and 3.0 kV. Here, ROP treatment of samples in a backfilled ultra-high vacuum chamber connected to a gas cavity linked to an RF reactor lasted for 1 hour. The pre-ROP CL spectrum in Fig. 5a appears slightly different from the pristine $V_2O_5$ spectrum at the same beam energy in Fig. 3a because it is from a different sample batch. Nevertheless, the Fig. 5a spectrum is clearly that of pristine $V_2O_5$.

A comparison of the pre- and post-ROP spectra shows that ROP treatment caused the $V_2O_5$ luminescence intensities in Fig. 5c to increase by nearly 2x for $E_B = 0.5$ kV. This is probably due to ROP cleaning the $V_2O_5$ surface, eliminating any adsorbates that could otherwise reduce substrate luminescence by non-radiative minority carrier recombination. Aside from this intensity difference, the ROP does not seem to have introduced, suppressed, or shifted any features in energy, confirming that the cleaning process performed with propylene carbonate removed any electrolyte residue or electrolyte surface degradation layer, i.e., solid electrolyte interphases (SEI).

Figs. 5b and 5d show the pre- and post-ROP CL spectra for $\gamma$-Li$_2$V$_2$O$_5$. As with pristine $V_2O_5$, the post-ROP $\gamma$-Li$_2$V$_2$O$_5$ CL spectrum intensity for $E_B = 0.5$ kV is much higher due to ROP surface cleaning. The only difference between the pre- and post-ROP $\gamma$-Li$_2$V$_2$O$_5$ spectra is the increase in intensity of the narrow 1.88 eV peak in the post-ROP spectrum, which is very weak in the pre-ROP spectrum. Note the strong resemblance of this 1.88 eV feature with that of the delithiated $V_2O_5$ CL spectrum at $E_B = 0.5$ kV in Fig. 4, both of which exhibit a sharp peak with a shoulder. In general, spectra from deeper excitation depths of both pristine $V_2O_5$ and $\gamma$-Li$_2$V$_2$O$_5$ show no significant differences between pre- and post-ROP CL spectra. This is consistent with ROP treatment depths extending only to 50-100 nm for other semiconductors. Therefore, other than increasing near-surface CL intensity, Fig. 5 displays no significant changes with ROP treatment, implying that oxygen vacancies are not present in lithiated $V_2O_5$ samples.

Intercalation of lithium within $\alpha$-V$_2$O$_5$ is considered to be an intercalation process. However, as discussed above, formation of Li$_2$O or V$_2$O$_4$ and, more generally, vanadate or oxide, during $V_2O_5$ battery operation, have been reported.$^{32,33,38}$ The origin of such degradation products can be potentially assigned to a conversion reaction:

$$Li_2V_2^5 + O_5 \rightarrow Li_2O + V_2^4 + O_4 \rightarrow Li_2O + V_2^2 + O_3 + \frac{1}{2}O_2(g) \quad (1)$$
Alternative explanations involve lithium concentration gradients/segregation resulting in phase mixtures\cite{32,39,40}. In order to test whether the lithiation and depth-dependent changes shown in Figs. 3-5 are due to a partial conversion reaction/lithium segregation, we took CL spectra of Li$_2$O powder, V$_2$O$_3$ powder, and V$_2$O$_4$ powder at $E_B = 0.5$ kV, shown in Fig. 6. Perhaps the most remarkable feature of the Li$_2$O spectrum (Fig. 6a) is its intensity—Li$_2$O luminesces at least two orders of magnitude more intensely than $\alpha$, $\varepsilon$-, $\delta$- or $\gamma$-Li$_x$V$_2$O$_5$. If Li$_2$O were present in lithiated samples in significant quantities, it would cause a substantial increase of the 2.5 and 3.1 eV features in DRCL spectra of lithiated V$_2$O$_5$ samples. There is evidence for an increase in intensity of these peaks in the delithiated V$_2$O$_5$ sample (Fig. 4), especially for $E_B = 1.0$ kV and $E_B = 2.0$ kV, for which CL spectra exhibit 2.5 eV and 3.3 eV peaks. However, whether the 3.3 eV peak visible in

Figure 6: DRCL spectra taken with $E_B = 0.5$ kV for (a) Li$_2$O powder, (b) V$_2$O$_3$ powder, and (c) V$_2$O$_4$ powder. Note the high intensity of the Li$_2$O CL spectrum. All peak features appear at energies present in various Li$_x$V$_2$O$_5$ CL spectra.
Fig. 4 and the 3.13 eV peak visible in Fig. 6a are the same peak is questionable. Regardless, the absence of any order-of-magnitude increase in the 2.5 eV and 3.3 eV CL peak intensities implies that Li$_2$O can only be present in lithiated samples in concentrations not exceeding 1%.

Conversely, V$_2$O$_4$ luminescence is significantly less than any other sample measured. The spectrum shown in Fig. 6c required 6x lower monochromator resolution to gather proportionally more light comparable or less than Figs. 6b or 3d spectra exhibit. Because of V$_2$O$_4$’s exceptionally weak luminescence, even significant amounts would not contribute significantly to lithiated V$_2$O$_5$ spectra. Nevertheless, V$_2$O$_4$’s peaks at ~2.0 eV and 4.05 eV bear strong resemblance to those of pristine V$_2$O$_5$ (Fig. 3a). V$_2$O$_4$ peaks at 2.5 eV and 3.22 eV resemble those of delithiated V$_2$O$_5$ (Fig. 4), and δ-LiV$_2$O$_5$ (Fig. 3b) also shares the 2.5 eV peak in common with V$_2$O$_4$, though very weakly.

As for V$_2$O$_3$ (Fig. 6b), the 2.54 eV peak and 3.18 eV peak are notable for the same reasons discussed for those peaks in V$_2$O$_4$ and Li$_2$O. A peak around 3.75 eV has been observed in α, ε-, δ- and γ-Li$_x$V$_2$O$_5$ spectra, and the shoulder around 2 eV is similar to those of α and δ-Li$_x$V$_2$O$_5$. Raman spectra of these various vanadium oxide phases can further refine these comparisons as discussed below.

**Discussion**

The optical transition energies measured by DRCLS are in excellent agreement with DFT energy bands calculated by Eyert and Höck. Fig. 7a shows the partial V$_{3d}$ t$_{2g}$ density of states (DOS) from their work with arrows to indicate cathodoluminescence transitions from these unoccupied conduction band states to the valence band E$_V$ maximum. This comparison of the optical emission peaks with conduction band density of states takes into account the flat V$_2$O$_5$ valence band maximum in k-space so that direct optical transitions need not involve a joint density of states involving both valence and conduction band structure. Table I compares the transition energies from Fig. 7a (left column) with the DRCLS peak energies of pristine V$_2$O$_5$ from Fig. 7b (right column). With the exception of a DFT 2.7 eV transition, weak evidence for which nevertheless appears at 2.5 – 2.6 eV in other α-V$_2$O$_5$ spectra, e.g., Fig. 3a, the energies of all five DRCLS peaks agree with the energies of the V$_{3d}$ t$_{2g}$ DOS transitions to within 0.1 eV.

Based on the DFT identifications of each peak, DRCLS features can be labeled quantum mechanically with their atomic orbital character, as shown in Fig. 7b. Based on these orbital labels, the set of peaks around 1.8-2.0 eV can be attributed to a hybridization of V 3d$_{x^2-y^2}$-O$_{2p_z}$/2p$_y$ states,
which are based on distortions of the VO₆ octahedra. This gives rise to the split-off conduction band in the 2.1 eV range. The electrons associated with these V 3dₓᵧ-OₓC 2pₓ/2pᵧ states are weakly bound, so that one expects these features around 1.8-2.0 eV to be sensitive to structural distortions associated with lithiation. Indeed, these features are suppressed in δ-LiV₂O₅ spectra (Fig. 3b), and
disappear completely in γ-Li$_2$V$_2$O$_5$ spectra (Fig. 3c). Furthermore, the three closely grouped features around 1.8-2.0 eV in Fig. 7b can be attributed to distortions of the VO$_6$ octahedra along the three crystallographic axes since the calculated partial O 2p DOS of V$_2$O$_5$ includes three closely spaced O$_c$ 2p$_x$, O$_c$ 2p$_y$, and O$_c$ 2p$_z$ peaks centered around 2 eV,$^{41}$ consistent with the orthogonal polarization dependence of three closely spaced absorption thresholds at 2.1-2.2 eV.$^{42}$ Note the very narrow 1.9 eV feature in the delithiated near-surface spectrum of Fig. 4, which may be related to one of the three VO$_6$ octahedra distortions resulting in square pyramids. Alternatively, the densities of states of the split-off band in both the Eyert & Höck$^{41}$ and the Bhandari et al.$^{44}$ densities of states exhibit just a single peak. Notwithstanding the three closely spaced and polarization-dependent absorption onsets report by Kenny et al.,$^{42}$ some contribution from the closely spaced valence band splitting cannot be excluded as a possibility. DFT calculations also predict V$_{3d}$ e$_g$ states starting at 5-7 eV, for which Fig. 7c provides only weak evidence due to our $\leq$ 6 eV CCD detector cutoff energy.

Optical absorption measurements of Kenny et al. provide additional evidence for the threefold, crystallographic nature of the split-off band.$^{42}$ Strong, fundamental absorption thresholds were reported at 2.15, 2.22, and 2.17 eV for light polarization fields E along bulk V$_2$O$_5$ crystal axes $a$, $b$, and $c$, respectively. Such polarization effects would not be expected for random defect distributions. Instead, defect absorption is reported at 1.24 and 1.49 eV whereas CL spectra here show no emissions at these energies. Extrapolated absorption edges exhibited direct forbidden and allowed intrinsic absorption edges between 2.35 eV and 2.45 eV, depending on crystal orientation, incident light polarization, and power law dependence modeled. Figures 3, 4, and 5 above also display 2.4 – 2.5 eV emissions consistent with a direct optical band gap. Hence, rather than defects, previous absorption spectra are consistent with the $\sim$1.9–2.1 eV split-off band in addition to 2.4 – 2.5 eV band-to-band absorption.

The nature of the split-off band itself has been of considerable interest. Eyert and Höck attributed the split-off band to weakly bound V 3d$_{xy}$ – O$_c$ 2p$_x$/2p$_y$ derived bands that separate from the main part of unoccupied conduction band states,$^{41}$ consistent with earlier work of Lambrecht et al. who found the split-off bands to be related to strong indirect V-V interactions across the bridge O atoms linking the double V-O chains in the crystal structure.$^{43}$ These conduction d states correspond to the V-d orbital making the fewest antibonding interactions with O and those only with O$_c$-p$_x$ but not with O-bridge p$_y$ orbitals, that is, V$_{3d}$ and O$_{2p}$ orbitals with the smallest $\pi$ overlap,
the absence of antibonding with bridge $p_y$ bonds\textsuperscript{44} and the smallest bonding-antibonding splitting\textsuperscript{41}.

Recent works\textsuperscript{39,45} combined DFT calculations with multimodal spectroscopies to probe the effect of lithium’s presence on the $\alpha$-$V_2O_5$ electronic structure. These studies revealed a strong impact of the lithium content on the DOS, with, from $\alpha$-$V_2O_5$ to $\delta$-$LiV_2O_5$, the reduction of the lowest split-off band $V\,3d_{xy}$ intensity and a shift of the $t_{2g}$ position toward higher energies. These effects are thought to be correlated with (1) lithium segregation, (2) lattice distortion and, (3) strong hybridization of the $V\,3d$ with the O\,2p.

In agreement with,\textsuperscript{39,45} the dramatic changes in the 1.8 – 2.1\,eV spectral regions of Figs. 3-5 with lithiation suggest that structural distortions play a major role in the degradation of $V_2O_5$ over the course of its use as a cathode material. This naturally leads to the question of whether lithium concentration gradients and/or new phase of V-O-Li bonding arises with lithiation, which is associated with the band structure changes observed. In order to address this issue, we acquired Raman spectra of the pristine and lithiated $V_2O_5$ samples ($\alpha$-, $\varepsilon$-, $\delta$-, and $\gamma$-$Li_xV_2O_5$) as well as several oxides ($Li_2O$, $V_2O_4$ and $V_2O_3$) that could form during lithiation (Fig. 8).\textsuperscript{32,33} Raman peak assignment for all of these compounds has been extensively discussed elsewhere.\textsuperscript{46,47,48,49,50,51} Due to the symmetry of the system, the peaks at 995\,cm$^{-1}$ and 143\,cm$^{-1}$ of $\alpha$-$Li_xV_2O_5$ are affected by the lithium intercalation more than all other peaks. The high-frequency peak at 995\,cm$^{-1}$ is associated with an out-of-plane vibration of the $V_2O_5$ layers: the stretching of the $V=O_{\text{apical}}$ symmetric bond. As a consequence of lithium insertion, $V=O_{\text{apical}}$ bonds lose their double-bond character and are elongated. This bond weakening is expected to lead to a shift toward lower frequency. On the other hand, the peak at 143\,cm$^{-1}$ is an indicator of the in-plane order as it is related to in-phase rotation. Any increase in the amount of disorder will result in a significant shift and/or decrease of intensity of these two signature peaks. Bhandari and Lambrecht provide a more recent, full DFT description of each infrared and Raman vibrational mode.\textsuperscript{52}

When the $V_2O_5$ is lithiated, Fig. 8a shows that the intensity of 143\,cm$^{-1}$ in-plane peak decreases, which is the first confirmation of the increase of disorder in the system. The out-of-plane vibration at 994\,cm$^{-1}$ shifts down with a nearly unshifted shoulder component for $\varepsilon$-$Li_xV_2O_5$, whereas for $\delta$-$LiV_2O_5$, it splits into two peaks which shift down significantly by over 50 and 170\,cm$^{-1}$. $\gamma$-$Li_xV_2O_5$’s peaks are shifted further down and exhibit severe broadening and splitting. The
increased splitting and shifting of this out-of-plane vibrational mode are consistent with the increased out-of-plane lattice distortion and bond elongation from \( \alpha \)- to \( \delta \)- to \( \gamma \)-Li\( _2 \)V\( _2 \)O\( _5 \) phase transitions pictured in Fig. 1.

Next, we compared these vibrational features with those of other Li-V-O compounds to identify which are similar to those of the lithiated V\( _2 \)O\( _5 \) samples (Fig. 8b). One should note that the Raman spectra of powder and film V\( _2 \)O\( _5 \) are in excellent agreement (Fig. 8a and 8b), confirming that similar grain-size powders of the Li oxides are representative of thin films as well. V\( _2 \)O\( _3 \) was eliminated as a possibility since its Raman spectra have no out-of-plane vibrational modes near 994 cm\(^{-1} \). Indeed, V\( _2 \)O\( _3 \) may not even be layered. On the other hand, Raman spectra for V\( _2 \)O\( _4 \) and Li\( _2 \)O bear more resemblance with those of pristine and lithiated V\( _2 \)O\( _5 \). There is one Li\( _2 \)O Raman frequency signature that overlaps with \( \alpha \)-, \( \varepsilon \)-, and \( \delta \)-Li\( _x \)V\( _2 \)O\( _5 \), but not \( \gamma \)-Li\( _2 \)V\( _2 \)O\( _5 \), which also rules out Li\( _2 \)O as a major degradation product correlated with extensive lithiation. The Raman spectrum of V\( _2 \)O\( _4 \) in Fig. 8b has nearly the same in-plane mode frequencies as that of V\( _2 \)O\( _5 \): a nearly unshifted 721 cm\(^{-1} \) mode, and two modes that bracket the 994 cm\(^{-1} \) modes. The origin of this similarity lies in the structure of V\( _2 \)O\( _4 \), where V\( ^{4+} \) is in a distorted octahedral environment of oxygen. As shown in Fig. 1, the intercalation of lithium into \( \alpha \)-V\( _2 \)O\( _5 \) is known to result in V\( ^{5+} \) to V\( ^{4+} \) reduction, elongation of V-O bonds, significant pyramidal chains, puckering, and rotation. Moreover, the pyramids can be described as octahedra distorted along the out-of-plane c-axis. The

![Figure 8: (a) The Raman spectra of V\( _2 \)O\( _5 \) thin film (orange) compared with that of \( \delta \)-Li\( _x \)V\( _2 \)O\( _5 \) (grey), \( \gamma \)-Li\( _x \)V\( _2 \)O\( _5 \) (green), and \( \varepsilon \)-Li\( _x \)V\( _2 \)O\( _5 \) (yellow). (b) Raman spectra of reference powders (V\( _2 \)O\( _5 \), V\( _2 \)O\( _4 \), V\( _2 \)O\( _3 \) and Li\( _2 \)O).](image-url)
absence of the two most intense peaks at 155 and 267 cm\(^{-1}\) shows that V\(_2\)O\(_4\) is not present as a significant phase in lithiated V\(_2\)O\(_5\) with a quantity below the detection limits of the Raman system.

The higher degree of octahedral distortion is also consistent with the changes in DRCL spectra evident both in Figs. 3-4 and in Fig. 6, which shows CL spectra for Li\(_2\)O powder, V\(_2\)O\(_3\) powder, and V\(_2\)O\(_4\) powder at \(E_B = 0.5\) kV. In agreement with their low or absent vibrational modes in the lithiated V\(_2\)O\(_5\) Raman spectra of Fig. 8, a comparison of these spectra’s features suggests that if the products of the conversion reaction Li\(_2\)O and V\(_2\)O\(_4\) form, it would only be as minor phases, possibly as inclusions that blend at the microscale with the primary phase. Thus, we propose that the lithiation of V\(_2\)O\(_5\) is associated with severe lattice distortion that is partially responsible for the changes in the electronic band structure observed through DRCLS and correlated with DFT-calculated energy bands. Additionally, the pre- and post-ROP CL spectra in Fig. 5 do not exhibit sub-band gap features typically observed for oxygen vacancies in oxide semiconductors,\(^{34-37}\) nor does ROP remove any pre-ROP features, providing strong evidence that lithiation does not cause oxygen vacancies. In general, then, the changes in the electronic band structure reported here, visible in Fig. 3, for example, can be explained by V\(_2\)O\(_5\) octahedral distortion rather than the formation of oxygen vacancies or secondary phases such as Li\(_2\)O and V\(_2\)O\(_4\).

**Conclusion**

DRCLS measurements of Li\(_x\)V\(_2\)O\(_5\)’s conduction bands to valence band transitions as a function of lithiation display excellent correlation with DFT-calculated conduction energy bands. The orbital nature of these bands enables the changes in the DRCL spectra with depth and lithiation to be explained by structural distortions of the VO\(_6\) octahedra rather than the presence of oxygen vacancies or formation of degradation products. The triplet of features around 1.8-2.0 eV corresponds to distortions of the V\(_2\)O\(_5\)’s structure along its three crystallographic axes. Delithiated V\(_2\)O\(_5\) spectra indicate that some changes associated with lithiation are reversible, whereas others are not. These changes in structure and bonding structural changes are associated with the changes in the electronic band structure detected by DRCLS. The depth-dependent electronic information presented here suggests that DRCLS can be a useful technique for probing electronic structure at V\(_2\)O\(_5\) surfaces and buried interfaces as well as to detect partial conversion reaction which is of utmost importance for the rational design of beyond lithium ion batteries cathode materials. In
turn, these measurements may improve our understanding and control of degradation processes during lithiation and battery cycling involving the electrolyte. Beyond these studies, we plan to investigate new methods of passivating the V₂O₅-electrolyte interface to minimize or prevent irreversible chemical and structural changes.

Conflicts of Interest
There are no conflicts to declare.

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V$_2$O$_5$ electronic band structure from cathodoluminescence reveals how lithiation creates octahedral distortion and not oxygen vacancies or conversion reactions.