Supplementary information: Elucidating Structural Transformations in $Li_xV_2O_5$ **Electrochromic Thin Films by Multimodal Spectroscopies**

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Surface roughness of Li_xV₂O₅ as a function of lithiation.

Surface roughness as determined by atomic force microscopy is displayed in Figure 1. In agreement with the Raman response, the lithiation leads to a progressive amorphization of the phase.



Figure 1: Atomic force microscopy 3D images of $Li_xV_2O_5$ (x = 0; 1; 2) and associated roughness. Images are 5 microns by 5 microns with heights z in nm.

Crystal structure and associated electrochemistry of Li_xV₂O₅ polymorphs.

The effect of electrochemical intercalation of lithium on the vanadium oxides' crystallographic structures have been extensively studied since the seventies.¹ As depicted in Figure 2, the evolution of the long-range structure of $Li_xV_2O_5$ (0 < x < 2) during the lithium insertion process is generally accepted to occur via the following sequence $\gamma \rightarrow \delta \rightarrow \varepsilon \rightarrow \alpha$.^{1, 2} The α layered structure consists of infinite layers of alternating pairs of VO₅ pyramids connected by the edges and corners bound by van der Waals interactions. $\gamma \rightarrow \delta \rightarrow \epsilon \rightarrow \alpha$ phase transformations involve 1

substantial puckering, rotation and gliding of the VO₅ pyramids as well as an increase in interlayer spacing. However, these transitions are considered topotactic, i.e reversible structural modifications involving introduction of ions into a host structure, with a symmetry that remains orthorhombic (ε ; α : P mmn $\delta \rightarrow$: A mam $\gamma \rightarrow$: P nma). Hence, the transformation is fully reversible at low x (x \leq 1) and mostly reversible for higher value (1 \leq x \leq 2). To accommodate more than two lithium per unit cell, the system has to undergo a nonreversible phase transformation to a cubic rock salt structure where vanadium and lithium are randomly distributed within the same atomic crystallographic site,³ leading to a drastic decrease of the electrochemical performance. As this study focuses on diagnostics of standard battery operation degradation mechanisms rather than the total loss of structural integrity, intercalation involving more than two lithium will not be discussed further herein. Instead we will center our attention on the topochemical $\gamma \leftrightarrow \delta \leftrightarrow \varepsilon \leftrightarrow \alpha$ phase transformations with Li_xV₂O₅ (0 < x < 2) for a maximal theoretical capacity of 285 mAh/g.

Figure 2 shows the first galvanostatic charge of the $Li_xV_2O_5$ (0 < x < 2) thin film up to 2.2V at a ~C/25 rate, i.e., 25 hours for a charge. From high to low voltage, a first plateau is observed at 3.2V that corresponds to the formation of ε -Li_xV₂O₅, followed by a sharp potential drop near 3.1V up to 2.3V for δ -Li_xV₂O₅. The following lower voltage step is related to γ -Li_xV₂O₅ with 1 < x < 2. As seen in Figure 2, the amount of lithium inserted into the structure is directly correlated to the cut-off voltage applied during the electrochemical cycling of the Li_xV₂O₅ thin films.^{1, 2} 2.2 V vs. Li/Li⁺ is just below the second voltage plateau at 2.3V where the γ phase is expected to be formed. Hence, by fine-tuning the current applied, that governs the rate of lithium intercalation to match as closely as possible the chemical reaction kinetics, one will expect the homogeneous de-intercalation of approximately two lithium within the structure, to obtain a single-phase γ -Li₂V₂O₅ at 2.2V.¹ To support the discussion in the manuscript related to the possibility of a conversion reaction, the room temperature structure of Li₂O, V₂O₄ and V₂O₃ are displayed in Figure 3.



Figure 2: Representation of the crystallographic structure evolution of $Li_xV_2O_5$ as a function of the lithiation level as dictated by the electrochemistry



Figure 3: Representation of the crystallographic structure of Li₂O, V₂O₄ and V₂O₃ at room temperature.

Battery performance.

<u>Table 2</u>: Battery performance metrics (delivered capacity, internal resistance, and polarization) as a function of voltage range and cycling number.

Voltage range (V)	3.4-2.2 for two li ⁺ insertion		3.4-2.8 for one li ⁺ insertion	
Cycle number	0.5-1	5.5-6	0.5-1	5.5-6
Capacity delivered (mAh/g)	262	255	145	133
Polarization high cut-off voltage (ΔmV/hrs)	3	26	80	45
Polarization low cut-off voltage (ΔmV/hrs)	20	80	111	96
Internal Resistance high cut-off voltage (Ω)	350	2175	5500	4000
Internal Resistance low cut-off voltage (Ω)	1750	5000	12000	8950

Acknowledgments

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DESC0001160 (A.J., S.T. and G.W.R.) and by the NSF grant DMR-18-00130 (M.W. and L.B.). We also acknowledge the support of the Maryland Nanocenter.

References

(1) Delmas, C.; Cognac-Auradou, H.; Cocciantelli, J. M.; Ménétrier, M.; Doumerc, J. P., The $Li_xV_2O_5$ system: An overview of the structure modifications induced by the lithium intercalation. *Solid State lonics*, **1994**, *69*, 257-264.

(2) Baddour-Hadjean, R.; Safrany Renard, M.; Pereira-Ramos, J. P., Unraveling the structural mechanism of Li insertion in γ' -V₂O₅ and its effect on cycling properties. *Acta Materialia*, **2019**, *165*, 183-191.

(3) Christensen, C. K.; Sørensen, D. R.; Hvam, J.; Ravnsbæk, D. B., Structural Evolution of Disordered $Li_xV_2O_5$ Bronzes in V_2O_5 Cathodes for Li-Ion Batteries. *Chemistry of Materials*, **2019**, *31*, 512-520.