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Los Angeles

Dynamic Structural and Electronic Analyses of
Electrochemically Lithiated Ternary Vanadium Niobium Oxides

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Science
in Materials Science and Engineering

by

Alan Louis Pierrat

2026

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2026

ABSTRACT OF THE THESIS

Dynamic Structural and Electronic Analyses of Electrochemically Lithiated Ternary Vanadium Niobium Oxides

by

Alan Louis Pierrat

Master of Science in Materials Science and Engineering

University of California, Los Angeles, 2026

Professor Bruce S. Dunn, Chair

Four vanadium niobate compounds were selected as candidates for lithium-ion battery anode materials: $\text{VNb}_9\text{O}_{25}$, $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, VNbO_4 , and $\text{V}_7\text{Nb}_6\text{O}_{29}$. Each compound possesses a different V to Nb ratio, oxidation state of V, and structures which were first experimentally synthesized and verified. Electrochemical testing, structural probing, and electrical modeling enable for the analysis of the dynamic behavior of (de)lithiation and the ultimate identification of $\text{V}_4\text{Nb}_{18}\text{O}_{55}$ as the optimal vanadium niobate among the four compositions. This compound possesses a maximum reversible capacity of 257 mAh g^{-1} at C/10, well over its theoretical capacity of 214 mAh g^{-1} , assuming one-electron redox. Its uncompromising performance at higher rates further indicates promise in further studying the vanadium niobium oxide system. Although the other three compounds fall short of their theoretical performances, they still serve as useful systems for

understanding the tunable redox activities of the two similar transition metals, which better informs the search for the optimal vanadium niobium oxide.

The thesis of Alan Louis Pierrat is approved.

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University of California, Los Angeles

2026

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INTRODUCTION

The search for better lithium-ion battery anode materials to address the growing demand for energy storage materials in grid storage, electric vehicles, and consumer electronics has turned to materials beyond traditional graphite. [2] This search has culminated in the exploration of materials that operate at higher potential versus the Li/Li^+ redox couple and therefore above the lowest unoccupied molecular orbital (LUMO) of the electrolyte species, hindering the formation of an unstable solid-electrolyte interphase (SEI). Additionally, the demand for materials that remain stable after repeated cycling and that can reversibly accommodate rapid diffusion of lithium ions continues to grow.

In attempting to overcome poor ionic diffusion and electronic limitations in bulk electrode materials, nanosizing has become a major modification of interest. The increased surface area of nanoscale electrode materials allows for reduction in diffusion lengths and greater exposure to interfacial Faradaic reactions. [3] However, an increased interfacial energy can lead to high surface passivation from increased Li^+ diffusion into the region. A form of this passivation occurs as growth of a SEI, which will form over a larger area within nanostructured materials and in a more unpredictable fashion due to their variable energy landscape. A SEI generally consumes Li^+ in its formation while partially inhibiting the diffusion of Li^+ ions thereafter. This can result in a high loss of capacity over many cycles and at higher rates, especially in systems where SEI may continually break down and reform. [4]

Therefore, an alternative to nanosizing involves modifying the bulk host structure. These modifications attempt to increase the rate performances and reversible capacities of bulk electrode materials without tuning size or porosity. [5]

Theoretical Background

Studies of bulk structures are often focused on defect engineering, where various synthesis strategies can be used to induce structural changes that can be used to enhance ionic and electronic transport. Two such products of defect engineering include Wadsley-Roth (W-R) shear structures and tetragonal tungsten bronzes (TTBs) (**Figure 1-1**). Both provide corner- and edge-sharing polyhedra which create unique, tunable geometries based on the nature of the transition metal centers and their oxidation states.

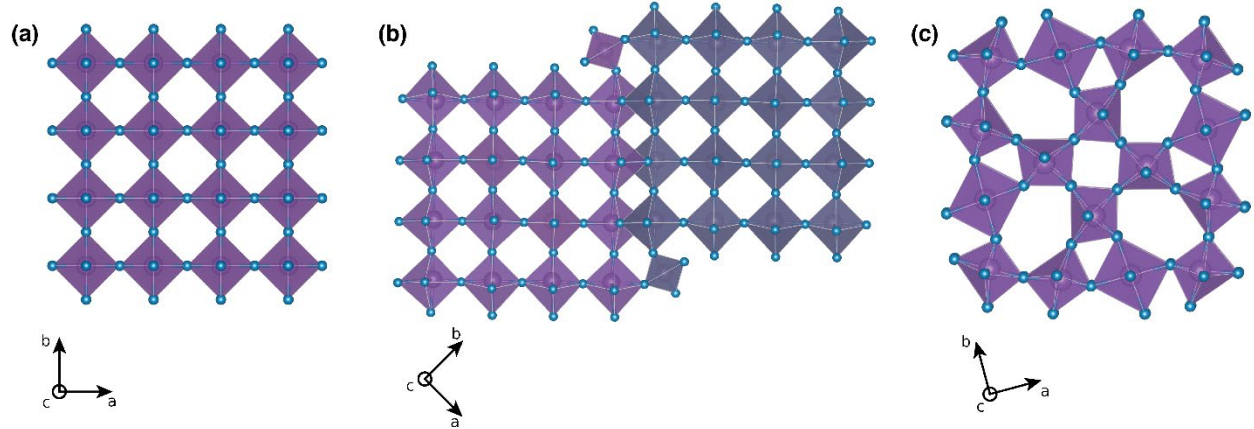


Figure 1-1. 2D visualization of a (a) ReO_3 structure [6-10], (b) Wadsley-Roth shear phase with $4 \times 4 \times \infty$ blocks from TiNb_2O_7 [11], and (c) simplified tetragonal tungsten bronze derived from potassium tantalum niobate [12], recreated in VESTA. [13]

Wadsley-Roth shear structures were originally derived from a perovskite-like ReO_3 structure. [6-10] Prototypical ReO_3 possesses only corner sharing ReO_6 octahedra with the angles of the octahedra 180° with respect to one another and within the same plane (**Figure 1-1a**). This highly symmetric framework contains large open channels that can accommodate lithium but which are especially prone to collapse or phase transition when Li^+ ions are locked in available sites. [5]

In attempting to stabilize ReO_3 -type materials during lithiation and de-lithiation, a modification of symmetry in which structures contain “crystallographic shear planes” was first observed by Wadsley and Roth in titanium and tungsten niobates. [14, 15] Rather than purely corner-sharing octahedra, the namesake Wadsley-Roth phase can possess edge-sharing polyhedra in infinitely long $n \times m$ block structures. The shear boundaries of these blocks (**Figure 1-1b**) stabilize the resulting structure while preserving large cavities that can accommodate the rapid insertion of lithium without accumulating substantial structural damage. [11, 16] These features do not relate to mechanical shear, as they are an intrinsic structural feature of each phase, tuned through careful element choice and synthesis techniques.

While W-R phases and TTBs possess similar corner- and edge-sharing features, TTBs can accommodate a larger variety of channel geometries due to the effective rotation of polyhedra along the c-axis (**Figure 1-1c**). [12] Prototypical tetragonal tungsten bronze consists of solely corner-sharing octahedra that form channels with triangular and pentagonal cross-sections due to a 45° rotation of octahedra in a central 2×2 block. [17] The incorporation of additional polyhedral geometries, including tetrahedral (ML_4) and pentagonal bipyramidal (ML_7), within both corner- and edge-sharing polyhedral arrangements, allows for the formation of many different TTB substructures. [18]

While the formation of W-R and TTB phases is the core to our overall study, other geometries remain of interest as they can provide metrics for comparison. For example, a common, rutile-type geometry consisting of the same transition metal species is of particular interest. In bulk rutile-type frameworks, Li transport is severely limited, as seen in the well-studied TiO_2 [19]. Investigations into nanosized rutile phases of various transition metal oxides, such as NbO_2 , point to significant morphologically derived performance improvements, as previously mentioned [20]. Hence, our study attempts to understand the properties of a bulk

rutile-type transition metal oxide with a similar composition and bulk morphology to the W-R and TTB phases of interest.

To understand the preference of corner- versus edge-sharing polyhedra, Pauling's rules can be employed; central atoms with a lower oxidation state favor vertex sharing. [21] Conversely, those with higher oxidation states experience higher electrostatic repulsion with neighboring central atoms, encouraging corner sharing polyhedral arrangements, resulting in larger corner-sharing block features or equivalents in the final structure. Therefore, our work on the ternary V-Nb-O system seeks to understand the structural and electronic effects of varying vanadium's oxidation state in pristine materials while maintaining a stable Nb^{5+} oxidation state.

Transition metals exhibit reversible redox due to flexible electron occupation within their d orbitals. When hybridized with 2p orbitals of oxygen atoms, this leads to a sharing of electron density. [22] This sharing is highly affected by the TM atom species and the resulting geometry of the polyhedral arrangements. For instance, tetrahedral arrangements have closer metal-ligand distances than octahedral arrangements due to less ligand-ligand repulsion. This leads to a higher crystal field stabilization energy (CFSE) for an octahedral arrangement compared to a tetrahedral one. [23]

When lithium atoms diffuse within channel regions between polyhedra, their charges create localized distortions in electron densities. These distortions can interact with the d-orbitals of central transition metal atoms, lowering their oxidation states when lithium gives up an outer electron. Further lithiation leads to delocalization of electron densities, first along edge-sharing sites, which has been confirmed to cause an insulator-to-metal transition in Magnéli phases. [24]

These phases exhibit 1D crystallographic shear, representing a simplified modification from parent ReO_3 structures.

Hence, we believe that these findings may be applied to other phases with 2D crystallographic shear, notably W-R phases and some TTBs. Part of the research reported here is dedicated to understanding insulator-to-metal transitions within the four studied vanadium niobate compounds by virtue of experimental verification with synchrotron techniques and computational verification with partial density-of-state (pDOS) calculations.

Finally, while much electrode research focuses on one transition metal, our work studies two, V and Nb. Introducing several metals within a compound alters the site preference of different metals as a function of block size in W-R phases. [11] Furthermore, block size can be modified by the metal to oxygen ratio in the compound; a larger ratio yields more corner sharing connections and results in larger blocks. Although TTBs do not use block descriptors, the same principles of corner sharing apply; the geometries of channel regions are therefore significantly affected by the ratio of metal to oxygen in the compound. Additionally, the MO_7 polyhedra that are allowed in TTBs further complicates the site preferences of each transition metal in a ternary system.

Ternary Vanadium Niobium Oxide System

To better understand the interplay of electrochemical activity, structure, and electronic behavior, four vanadium niobium oxides were synthesized using sol-gel and solid-state methods. In their pristine forms, the four compounds— $\text{VNb}_9\text{O}_{25}$, $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, VNbO_4 , and $\text{V}_7\text{Nb}_6\text{O}_{29}$ —have been shown in previous works to possess a consistent Nb^{5+} with variations in vanadium oxidation states respectively: V^{5+} , V^{5+} , V^{3+} , V^{4+} . [2], [25-27]

In the list of the vanadium niobates indicated above, there is a consistent increase in the ratio between vanadium and niobium. This ratio offers the opportunity to study the effect of replacing a transition metal center with another with similar properties (given their relative locations on the periodic table). Naturally, the increase of vanadium within each material leads to the formation of polyhedra with stronger nuclear attraction to surrounding polyhedra due to vanadium's smaller ionic size and higher electronegativity; this allows for metastable phases with “anion-deficient nonstoichiometry” in VNbO_4 and $\text{V}_7\text{Nb}_6\text{O}_{29}$ for increasing V:Nb ratios. [5]

Given that two phases of interest, $\text{VNb}_9\text{O}_{25}$ and $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, possess Nb^{5+} and V^{5+} in their pristine states, the presence of second order Jahn-Teller (J-T) distortions from the instability of d^0 cations is possible. [28] However, as soon as either transition metal is reduced, second order J-T distortions are replaced with their ordinary counterpart, leading to increasingly reduced d^1 , d^2 , and d^3 configurations. Second order J-T distortions are more likely to occur in smaller cations since they are subject to larger changes in orbital energies during oxidation, making V^{5+} a suitable candidate. In an octahedrally coordinated V^{5+} , the local symmetry would be reduced as the cation drifts from its geometric center, lowering the energy of empty d orbitals, sometimes to the point of mixing in energy with occupied p orbitals. [29] Subsequent reduction of the V^{5+} eliminates the possibility of second order distortions. In Nb^{5+} , second order J-T distortions are predicted to occur in KNbO_3 and TiNb_2O_7 . [30], [31] However, their occurrence in these two compounds is dependent on a heavily distorted local geometry.

Vanadium oxidation states can range from 5+ to 2+, representing a wide window in which vanadium ions can be incorporated into niobium oxides without phase segregation. The three-electron redox potential of vanadium also accounts for larger capacities compared to those capable if assuming only single-electron redox. To study this, our work focuses on probing the

oxidation states of both central transition metals using ex-situ XAS at different points of lithiation and characterizing any structural information and modifications. Our collaborators further used computational modeling of (de)lithiation within these four structures to validate our experimental findings. [32]

Previous works predicted the unit cell parameters and accompanying structures of each of the four vanadium niobates of interest. A table of unit cell parameters is presented in **Table 1-1** while cross-sectional unit cell visualizations are in **Figure 1-2**.

Table 1-1. *Unit cell parameters of the four vanadium niobates, from literature. [27], [33-35]*

	VNb₉O₂₅	V₄Nb₁₈O₅₅	VNbO₄	V₇Nb₆O₂₉
a (Å)	15.92376	17.35490	6.57181	11.82077
b (Å)	15.92376	17.69770	6.68754	11.82077
c (Å)	3.85301	3.97052	3.06093	3.80816
$\alpha = \beta = \gamma = 90^\circ$	90	90	90	90
Volume (Å³)	976.99232	1219.51278	134.52476	532.11653

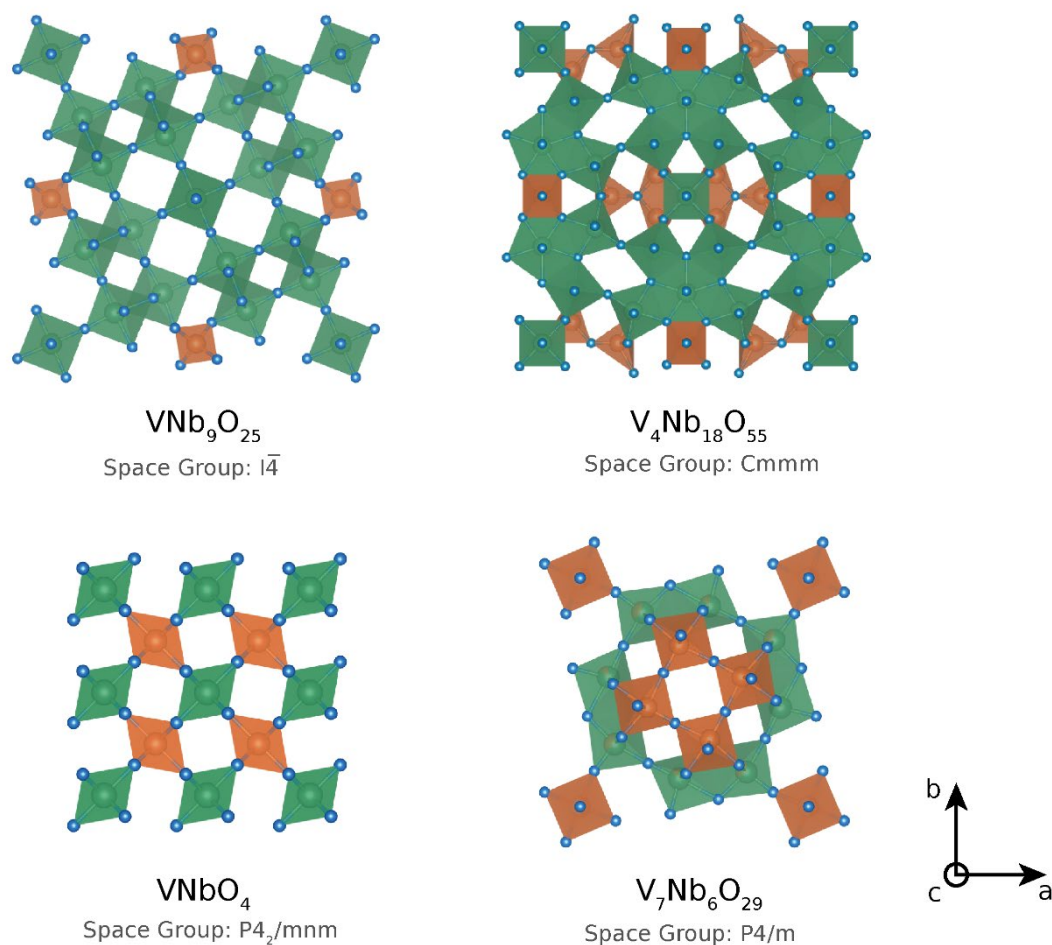


Figure 1-2. 2D projections of the four vanadium niobates along the *c*-axis, recreated using VESTA. [13], [27], [33-35]

The large distribution in unit cell volumes is directly linked to the high differences in symmetry of the four structures. High-symmetry $P4_2/\text{mm}$ allows for a reduction in the unit cell parameters of VNbO_4 which cannot be realized in lower-symmetry Cmmm of $\text{V}_4\text{Nb}_{18}\text{O}_{55}$. In this case, more atoms need to be included to create the smallest repeating unit.

$\text{VNb}_9\text{O}_{25}$ ($I\bar{4}$) is a W-R phase which has only NbO_6 octahedra that are corner and edge sharing with other NbO_6 octahedra. Vanadium only exists in tetrahedral geometries and only shares corners with NbO_6 octahedra. NbO_6 octahedra that exclusively share corners make up the

$3 \times 3 \times \infty$ block region. At the corners of blocks are corner sharing VO_4 tetrahedra.

Crystallographic shear in this phase is realized as the edge sharing of NbO_6 octahedra in neighboring $3 \times 3 \times \infty$ blocks, identical to the geometry of TiNb_2O_7 (**Figure 1-1b**).

$\text{V}_4\text{Nb}_{18}\text{O}_{55}$ is a tetragonal tungsten bronze (TTB) with space group $Cmmm$, which possesses a mix of NbO_7 (pentagonal bipyramidal) and NbO_6 (octahedral) coordination. NbO_7 polyhedra are edge-sharing with NbO_6 octahedra and VO_6 octahedra. VO_4 tetrahedra are exclusively edge sharing with NbO_6 octahedra and possess both corner- and edge-sharing sites with themselves. Octahedra of both types are exclusively corner sharing with like octahedra.

VNbO_4 ($P4_2/mnm$) possesses a rutile-type structure with V and Nb ideally alternating perfectly in transition-metal occupancy. Octahedra are edge sharing parallel to the b-axis and corner sharing parallel to the c-axis. In **Table 1-1**, a doubled unit cell is shown for better scaling with respect to the other compounds.

The second W-R phase, $\text{V}_7\text{Nb}_6\text{O}_{29}$ ($P4/m$), consists of only NbO_6 and VO_6 octahedra. In creating the structure, *Lawrance et al.* predicted shared occupancy in certain sites, notably those with a Nb preference that share corners to form the $3 \times 3 \times \infty$ block region of $\text{V}_7\text{Nb}_6\text{O}_{29}$. [27] Crystallographic shear is realized in each $3 \times 3 \times \infty$ block where NbO_6 octahedra share edges with those of equivalent neighboring blocks. VO_6 is in $2 \times 2 \times \infty$ blocks that share edges with NbO_6 in $3 \times 3 \times \infty$ blocks. Unit cell corners also consist of purely VO_6 corner-sharing octahedra. These octahedra fit in the centers of the $3 \times 3 \times \infty$ blocks, which is visible when the unit cell is expanded in the a and b directions.

In the syntheses of these four compounds, we show the feasibility of tuning vanadium and niobium fractions to create stable and metastable vanadium niobate compounds, based on the

high solubility of vanadia within niobia. Successful synthesis was verified using the following characterization methods.

TECHNICAL BACKGROUND

Ordinary and Operando X-Ray Diffraction

Ordinary powder X-ray diffraction (pXRD) operates best when particles are scattered in random orientations. These crystalline particles diffract incident X-ray radiation when oriented appropriately, producing a spectrum when the incident beam's angle is shifted with respect to the sample and when the intensity of the diffraction is recorded. The resulting relation was determined by William Bragg.

$$n\lambda = 2d \sin(\theta) \quad (1)$$

n is an integer multiple of the wavelength of the X-ray, λ . d represents the interplanar spacing between lattice planes, and θ represents the angle of the incident beam with respect to the sample's plane.[36]

Operando XRD uses the same operating principle as regular XRD but incorporates another parameter, the amount of lithium in the material. Alignment with the electrode is crucial to track the structural changes during (de)lithiation. Additionally, other diffraction peaks are detected from elements within the pouch cell, such as those corresponding to aluminum from the aluminized mylar or the aluminum current collector. These peaks are consistent in position and intensity throughout various scans, serving as good reference points to align the operando spectra with respect to each other. However, they are ignored in further analysis since they do not come from the active material of interest. Peaks that do shift during (de)lithiation can be tracked and used to quantify changes in lattice parameter and to understand the active material's recoverability. [37] Those peaks that disappear or appear can be used to understand phase changes which may occur in some systems.

UV-Visible Spectroscopy and Tauc Analysis

UV-Visible (UV-Vis) spectroscopy operates by sending an incident beam containing a range of wavelengths to a target sample. In reflection, the sensor captures reflected radiation which can then be used to recreate a spectrum for each compound.

Conducting UV-Vis in reflectance allows for the inference of the optical band gap of materials which exhibit an absorbance “edge” in the range of wavelengths. This can be performed using a Tauc analysis as presented in the following equation:

$$(\alpha \cdot h\nu)^{\frac{1}{\gamma}} = B(h\nu - E_g) \quad (2)$$

h represents Planck’s constant, while ν represents the frequency of the incident photon. B is a proportionality constant, and γ is a factor representing the transition type, with a value of $\frac{1}{2}$ for direct allowed transitions and 2 for indirect allowed transitions. [38] Experimentally determining the absorption parameter α from a diffuse reflectance value obtained from a powder sample first requires conversion. Therefore, we arrive at the Kubelka-Munk formulism, where the Kubelka-Munk value $F(R_\infty)$ can be substituted for α in Equation 2:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (3)$$

The resulting Tauc relation can be plotted as energy (determined from wavelength) versus the left portion of **Equation 2**. The linear region can be extrapolated to the x-axis, which represents the experimentally determined optical band gap of the material. [38]

Raman Spectroscopy

Raman spectroscopy is one method that attempts to capture the vibrational modes of bonded atoms which can reveal structural insights. In bulk solids, the vibrational modes of

certain bonds are coupled with neighboring ones depending on local geometry, distorting their vibrational character and causing differences in the perceived Raman shift and peak intensities. [39] Therefore, complex compounds with different polyhedral orientations such as the vanadium niobium oxides of interest, can yield Raman spectra which can be difficult to parse.

When light of a known wavelength strikes a sample, an excited photon of the same energy can leave the sample and be captured by a detector. This phenomenon is an elastic collision, known as Rayleigh scattering. Raman scattering works on the principle of inelastic scattering, where the emitted photon from the sample is no longer the same wavelength as the incident photon. [40]

Since atomic bonds are spring-like, they vibrate or resonate at certain frequencies which depend on the atom species and surrounding bonds. An incident photon will be energized by the vibration, creating an electron transition to a higher virtual energy level. When the electron returns to its ground state, a photon of higher energy than the incident radiation is emitted, known as anti-Stokes scattering. When the incident photon imparts part of its energy into a molecule, it loses energy when re-emitted, in a phenomenon known as Stokes scattering. [41]

A Raman detector captures the emitted photons, which can be constructed into a spectrum depending on the captured wavelength (converted into Raman shift, cm^{-1}). Peaks in the Raman spectrum correspond to specific Raman-active vibrational modes in the compound of interest; intense peak deconvolution and fitting often need to be done to understand the orbital interactions to which each peak can be associated. [41]

Galvanostatic Cycling with Potential Limitation (GCPL)

Supplying a constant current to a battery cell over a constant period, calculated by limiting the potential window in which that cell can cycle and considering the active material's mass reveals useful electrochemical information of the redox mechanisms in the cell. First, this measurement reveals insight into the capacity of a cell when charged and discharged, and any discrepancies between the two. Second, the c-rate (or current density value) can be changed to study the rate capabilities of the active material. The degradation of the active material can also be witnessed when cycling is repeated hundreds or even thousands of times. Third, the shapes of voltage profiles versus time can be observed, where potential plateaus may indicate multi-phase domains. [42]

Cyclic Voltammetry (CV)

Instead of supplying a constant current, a constant voltage ramp (or voltage sweep) can be applied to the battery cell. This creates a current response which can be quantified for each voltage point in the system. The resulting relation yields interesting insights as to the redox potentials of the active material, as quantified by observing peaks in the CV curve. Additionally, the shapes of these curves can be analyzed to better understand the reaction reversibility.

Time varying voltage (sweep rate, v) and current (I) in a cyclic voltammogram are described by a power law relationship:

$$I = av^b \quad (4)$$

a is a numerical constant, while the value of b must reside between 0.5 and 1. The value of b (b -value) approaches 1 for more capacitor-like responses and is closer to 0.5 if semi-infinite diffusion limits the kinetics of the redox process. [43] This analysis can be performed on redox

peaks at several voltage sweep rates to obtain more data points for a more accurate determination of b .

The shapes of features in CV can also be used to determine more information about the system. For example, a box-like CV region indicates capacitor-like behavior, often corroborating b -value findings. The peak anodic and cathodic currents in an ideal reversible system should have a ratio of magnitudes of 1.0. Additionally, their profiles may be broader and their peaks slightly shifted in voltage due to uncompensated resistance. [44]

X-Ray Absorption Spectroscopy

X-ray absorption spectra are based on the sharp increases in absorption at specific incident X-ray wavelengths, which directly correlate to their energies. This absorption edge corresponds to the energy required for a core electron to become ejected into the LUMO or to the unbound continuum state, leaving a core hole behind which is then filled in relaxation. This leads to a sharp absorption of the incident energy at a narrow set of wavelengths, known as the absorption edge. [45]

This absorption edge is named after the energy levels from which the electron transitions. The K-edge refers to the transition of an electron from the 1s orbital, and the L-edge refers to the transition of an electron from the 2s or 2p orbitals. L-edge spectra are captured at lower energies and have a higher resolution and are of special interest due to their ability to capture $2p \rightarrow d$ electronic transitions, which are essential in understanding metal-ligand interactions.[46]

In our work, we focus on the X-ray absorption near edge structure (XANES), which is approximately 50 eV above the absorption edge and provides information in coordination,

oxidation state, and electronic structure, which is essential for our understanding of the (de)lithiation mechanisms of the four vanadium niobates. [45]

Entropic Potential

The entropic potential of a system represents the sum of vibrational, configurational, and electronic components. This analysis can provide insight into the different intercalation mechanisms of lithium into an electrode material.

Notably, *Baek et al.* associated four different trends in total entropic potential and open circuit voltage versus lithium concentration in an electrode with the following mechanisms. [47] The first mechanism, lithium intercalation into a solid solution is characterized by a decrease in entropic potential and OCV of the cell with increasing lithium concentration. The second mechanism, ion ordering within a homogeneous solid solution, is characterized by a fluctuation of entropic potential in the shape of a tilde. The third mechanism, a first order phase transition with a two-phase coexistence, is revealed by a constant OCV and entropic potential. The last mechanism, a two-phase coexistence due to a stable intermediate phase, is associated with plateau regions in both OCV and entropic potential, separated by discontinuities (step-like features). [47]

Density of States

Computational work was performed by collaborators at UCLA to validate optical bandgap measurements determined experimentally using Tauc analysis based on partial density of states calculations. [32] Additionally, DFT was used to model changes in the unit cells of each

vanadium niobate during lithiation, along with changes in their electronic structures, as represented in partial density of states (DOS) calculations.

The band edges of a density of states provide especially important insight into the electronic properties of a material and will therefore serve as the focus of our studies. In a standard DOS plot versus energy, the Fermi level is normalized at 0 eV. Below the Fermi energy are the occupied states (valence band), and above the Fermi energy are the unoccupied states (conduction band). In a semiconductor, the region between the occupied and unoccupied states is the bandgap. In metals, this region becomes blurred, since there can be a continuum of states from the valence band that become occupied and are hence below the Fermi level. Negative DOS values correspond to spin-down states while positive DOS values correspond to spin-up states. [31]

Discrepancies in spin symmetry yield valuable insight into specific orbital occupation, while peak intensities and overlap correspond to specific orbital energy degeneracies. Combining these can yield important supporting information for the lithiation mechanisms of our four vanadium niobates.

METHODS

Synthesis of Vanadium Niobates

Two overarching synthesis techniques were explored: solid-state and sol-gel synthesis. Both techniques were successful in synthesizing $V_4Nb_{18}O_{55}$, while a sol-gel synthesis was employed for VNb_9O_{25} and $VNbO_4$ and a solid-state technique was used for $V_7Nb_6O_{29}$. A sol-gel approach lowered the necessary synthesis temperature for the preservation of reduced vanadium phases, given the incorporation of complexing agents. Furthermore, this lowered the likelihood of vanadium dioxide sublimation during annealing.

All syntheses were performed using unmodified commercially available precursors. Phase purity and crystallinity were validated using ordinary and high-resolution X-ray diffraction and appropriate refinement.

Sol-gel synthesis of $V_4Nb_{18}O_{55}$ and VNb_9O_{25}

$V_4Nb_{18}O_{55}$ was synthesized using the sol-gel method from a modified published method. [48] This involved the synthesis of a sol from 20.0 mg of ammonium metavanadate (NH_4VO_3 , Sigma-Aldrich $\geq 99.0\%$), 344 mg of ammonium niobium oxalate ($C_4H_4NNbO_9 \cdot XH_2O$, Sigma-Aldrich 99.99%, $X \approx 6.5$), and 33.5 mg of oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$, Sigma-Aldrich $\geq 99\%$) fully dissolved into 6 mL of de-ionized water at $80^\circ C$. 197 mg of citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, Thermo Fisher $\geq 99\%$) was then dissolved before mixing was stopped. The solution was left to gel overnight before drying at $180^\circ C$ for 2 hours. The mixture was transferred to an alumina crucible and annealed in air at $650^\circ C$ for 24 hours with a heating rate of $5^\circ C \text{ min}^{-1}$.

The method was adopted for $\text{VNb}_9\text{O}_{25}$, adjusted to achieve the appropriate molar ratios of V and Nb. The same quantity of ammonium metavanadate (NH_4VO_3 , Sigma-Aldrich $\geq 99.0\%$) was used, adding 688 mg of ammonium niobium oxalate ($\text{C}_4\text{H}_4\text{NNbO}_9 \cdot \text{XH}_2\text{O}$, Sigma-Aldrich 99.99%, $X \approx 6.5$) and 32.5 mg of oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich $\geq 99\%$) to dissolve in de-ionized water at 80°C . 359 mg of citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Thermo Fisher $\geq 99\%$) was added to promote gelation, which was performed under the same conditions as for $\text{V}_4\text{Nb}_{18}\text{O}_{55}$. In this synthesis, the resulting powder was instead annealed at 780°C using the same ramp rate for 24 hours in air.

Solid-state synthesis of $\text{V}_4\text{Nb}_{18}\text{O}_{55}$

A solid-state synthesis of $\text{V}_4\text{Nb}_{18}\text{O}_{55}$ was conducted by mixing stoichiometric ratios of vanadium (v) oxide (V_2O_5 , Sigma, $\geq 99.6\%$) and niobium (v) oxide ($\text{TT-Nb}_2\text{O}_5$). The annealing time and conditions were identical to that created using the sol-gel method.

Sol-gel synthesis of VNbO_4

Two similar sol-gel synthesis routes were proposed for VNbO_4 , using slightly different precursors but achieving equivalent functional chemistries before annealing. These were heavily inspired by a method from published literature. [49] The first involved stirring 144 μL of niobium ethoxide ($\text{Nb}(\text{OCH}_2\text{CH}_3)_5$, Sigma-Aldrich) in 32 mL of ethanol until a clear solution was obtained. 160 mg of vanadium (iii) 2,4 pentanedionate ($\text{C}_{15}\text{H}_{21}\text{O}_6\text{V}$, Thermo Fisher 97%) was then added, turning the solution brown. Then, 221 mg of oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich $\geq 99\%$) was dissolved before adding 193 mg of citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Thermo Fisher Scientific $\geq 99\%$). Stirring was stopped after full

dissolution and the solution was left to gel and dry overnight at 80°C in air. The gel was dried and ground similarly to those synthesized in sol-gel $V_4Nb_{18}O_{55}$ and VNb_9O_{25} . However, the powder was annealed at 700°C for 12 hours in argon with a heating rate of 5°C min⁻¹. The powder was then ground and stored under vacuum.

$VNbO_4$ was also synthesized using niobium chloride ($NbCl_5$, Thermo Fisher Scientific $\geq 99.9\%$) and 2M ammonia in ethanol (Sigma-Aldrich) instead of niobium (v) ethoxide ($Nb_2(OC_2H_5)_{10}$, Sigma-Aldrich $\geq 99.5\%$). This created the ammonia salt NH_4Cl , which would be entirely thermally decomposed below the annealing temperature of 700°C into gaseous NH_3 and HCl and purged. Therefore, the system was functionally equivalent, since the $NbCl_5$ dissociates and forms niobium (v) ethoxide in ethanol. Although it is not possible to calculate the pH of a non-aqueous system, the dissociation of ammonia in ethanol should effectively raise pH to that necessary for condensation to occur. 124 mg of niobium (v) chloride was dissolved in 32 mL of ethanol until a yellow solution was obtained. Then, 2 mL of ammonia solution 2.0 M in ethanol was added dropwise, until the solution turned clear. The remaining procedure was identical to that of the above sol-gel process.

Solid-state synthesis of $V_7Nb_6O_{29}$

A published solid-state synthesis method first proposed by *Belnap* for the synthesis of $V_7Nb_6O_{29}$ was modified. [50] Stoichiometric quantities of niobium (II) oxide (NbO , Alfa Aesar), vanadium (V) oxide (V_2O_5 , Sigma, $\geq 99.6\%$), and niobium (V) oxide ($TT-Nb_2O_5$) were ground and pelletized under 100 MPa with a two-minute dwell. Niobium (V) oxide precursor quantities were adjusted for a target of 29.6 rather than 29 for each mol of the compound for oxygen loss during annealing. The pellet was inserted into a quartz ampoule which was sealed under dynamic

vacuum. The ampoule was then annealed at 650°C for 10 hours with a 5°C min⁻¹ ramp step followed by a 1°C min⁻¹ to 850°C for 16 hours before cooling to room temperature at 5°C min⁻¹. The resulting powder was also stored under vacuum.

Materials Characterization

Scanning electron microscopy (SEM) was conducted using the Nova NanoSEM 230's secondary electron detectors (ETD and TLD) equipped with energy dispersive X-ray spectroscopy (EDS). Samples were sonicated within ethanol to create a suspension before casting onto stainless steel sheets or directly onto aluminum stubs to reduce charging effects under high accelerating voltages.

Raman spectroscopy was conducted using a inVia Renishaw confocal Raman microscope with a 514 nm green laser in the 0-1200 cm⁻¹ range.

UV-Vis spectroscopy was performed using the Agilent Cary 4000 UV-Vis spectrometer, from 300 to 1250 nm.

Ordinary X-ray diffraction θ -2 θ scans were conducted using the PANalytical X'Pert Pro with Cu K α_1 source and nickel filter from 8 to 80° 2 θ with an incident slit of 1 mm and a step size of 0.0334225° with a dwell of 50.8 seconds per step.

Powders samples were also sent to the Stanford Synchrotron Radiation Lightsource (SSRL) for high resolution XRD by collaborators from SLAC. [51], [52] XAS measurements for V K-edge, Nb K-edge, and L₃-edge were collected at beamline 4-3 at SSRL. Additional characterization details from experiments conducted by collaborators will be included in the published manuscript.[1]

Electrochemical Analyses

Two-electrode SUS204 CR2032 coin cells were constructed for electrochemical testing, including voltametric and galvanostatic techniques. 10mm lithium metal coins (Sigma-Aldrich 99.9%) were used as the reference electrode and anode in half cell configurations. 16-mm diameter glass fiber was used as a separator with 1M LiPF₆ EC/DMC v/v (LP30, Sigma-Aldrich) electrolyte. Slurries for each compound were cast using a 250 μ m doctor blade height onto carbon-coated aluminum foil. The doctor blade height was increased to 750 μ m to increase active material loading for operando studies ($\sim 5\text{mg cm}^{-2}$). Electrodes were air-dried for 3 hours at 70°C under light vacuum before they were then punched into 10mm diameter circular electrodes and weighed.

For V₄Nb₁₈O₅₅ and VNb₉O₂₅, water-based slurries were made from first mixing 80 wt % active material, 5 wt. % C65 carbon, and 5 wt. % multi-walled carbon nanotubes (MWCNTs) until uniform. Then, 5 wt. % carboxy methylcellulose (CMC, 10 g L⁻¹ in water) was mixed before 5 wt. % styrene butadiene-rubber (SBR, 100 g L⁻¹ in water) was quickly mixed before immediately casting. After punching, electrodes were further dried at 80°C overnight before cell construction.

For oxygen- and moisture-sensitive VNbO₄ and V₇Nb₆O₂₉, a non-aqueous method was employed from mixing an equivalent ratio of active material and carbon, substituting the CMC and SBR for n-methyl 2-pyrrolidone (NMP) solvent and polyvinylidene fluoride (PVDF) binder in NMP (40 g L⁻¹). After punching, electrodes were dried for 4 hours at 100°C before cell construction.

Voltametric techniques were operated on the BioLogic VMP-300 potentiostat, while galvanostatic techniques were operated on the Neware BTS 4000 battery tester. All

electrochemical tests were conducted between the 1.0-3.5 V potential window versus Li/Li⁺. Electrodes intended for ex-situ XAS were transferred to the BioLogic VMP-300 potentiostat for potential holds (chronoamperometry steps) to stabilize the structures at various potentials. These were used to examine the redox mechanisms present in each compound in the following XAS workflow.

For operando XRD experiments, 3.5 cm by 3 cm pouch cells were constructed using 113 μm thick aluminized mylar. Two nickel tabs were first attached and sealed onto the mylar before attaching 10 mm electrodes with 114 μm Kapton tape. 1M LiPF₆ in 30/70 EC/DEC was used to minimize X-ray absorption and for better wetting of the Celgard 2500 separator which was cut to size.

Entropic potential experiments performed by collaborators at UCLA used the BioLogic VSP-300 on previously constructed coin half cells. [53] A galvanostatic intermittent titration (GITT) based method was adopted at 20°C, where current pulses at C/20 were held for 30 minutes before cells were relaxed for 120 minutes. Then, the cell temperature was modified in 5°C intervals between 15°C and 25°C, using a cold plate (TE Technology, CP-121). The cell potential was recorded after the cell reached within $\pm 0.1^\circ\text{C}$ of the temperature of the cold plate, and the OCV drifted by less than 1 mV h⁻¹.

Computational Analyses

Partial density of states (pDOS) calculations were performed by collaborators at UCLA, using the Vienna Ab initio Simulation Package (VASP), with additional details to be included in the published manuscript. [32] [1] The ground states of each vanadium niobate were predicted by creating 50 lithiated configurations at different concentrations: pristine (X=0), X=0.25, 0.5, and

0.75, with more details to be published. [1] Accompanying structural information of each of the compounds per lithium concentration was also provided.

RESULTS AND DISCUSSION

Structural Characterization

The morphological characteristics of each vanadium niobate from SEM are presented in **Figure 4-1**. Each formed rod-like features of approximately 1 μm in length except for VNbO_4 (**Figure 4-1c**), which consistently formed a mix of nanoscale features (around 100 nm in size) and some more bulk ones. EDS analysis confirmed that the atomic for V and Nb for each of the compounds was within 5% of the theoretical values, as presented in the top right of each image.

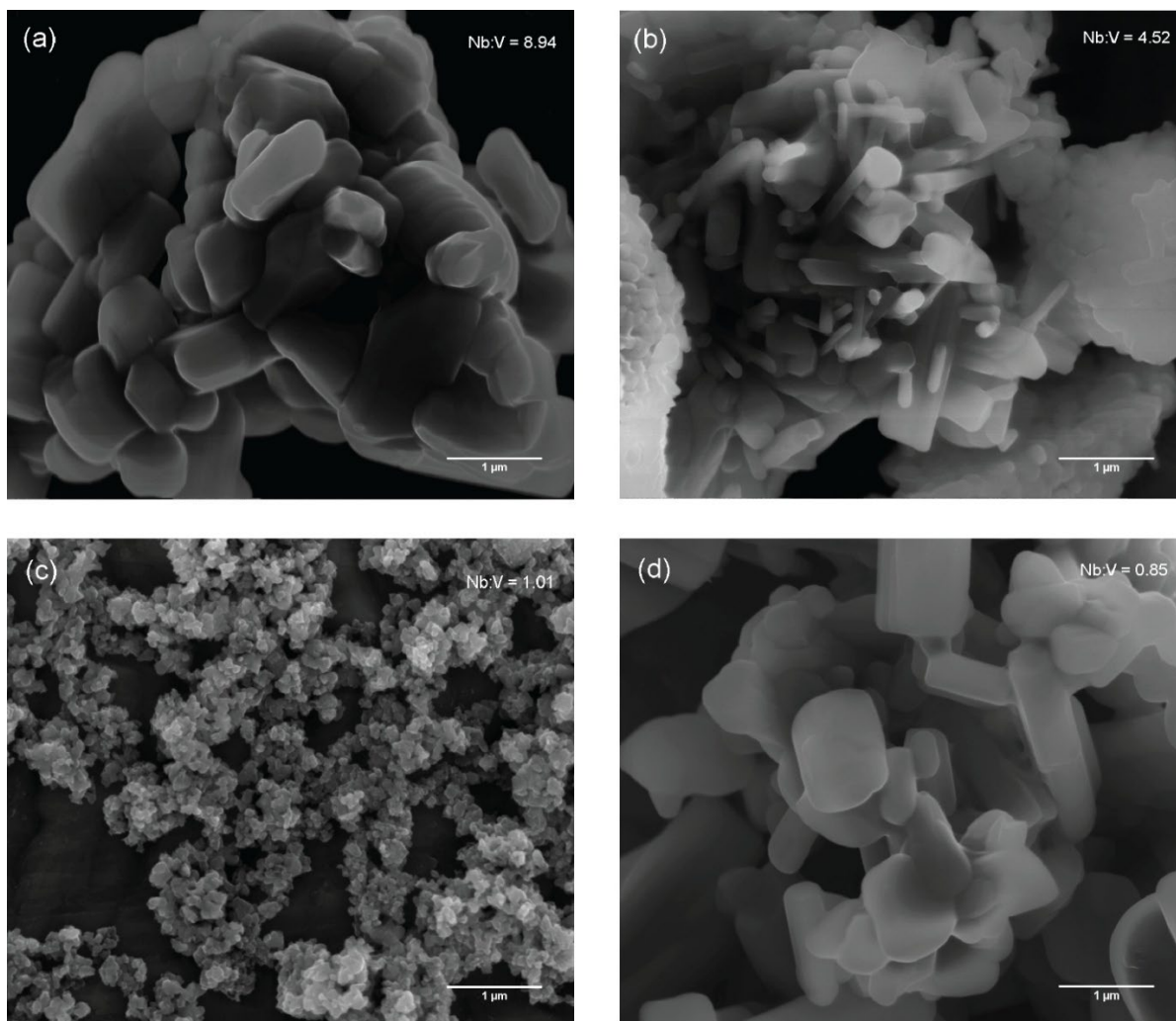


Figure 4-1. SEM images of (a) $\text{VNb}_9\text{O}_{25}$, (b) $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, (c) VNbO_4 , and (d) $\text{V}_7\text{Nb}_6\text{O}_{29}$, with corresponding insets representing the atomic ratios of Nb to V calculated by EDS. [54]

Ordinary X-ray diffraction was first used to confirm phase purity (**Figure 4-2**). Subsequently, collaborators at SLAC performed high-resolution X-ray diffraction (HR-XRD) from a synchrotron source. [51] All synthesis routes performed yielded phase pure products except for a minor secondary phase in $\text{V}_7\text{Nb}_6\text{O}_{29}$ indicating the ability to use different synthesis techniques to yield the same products.

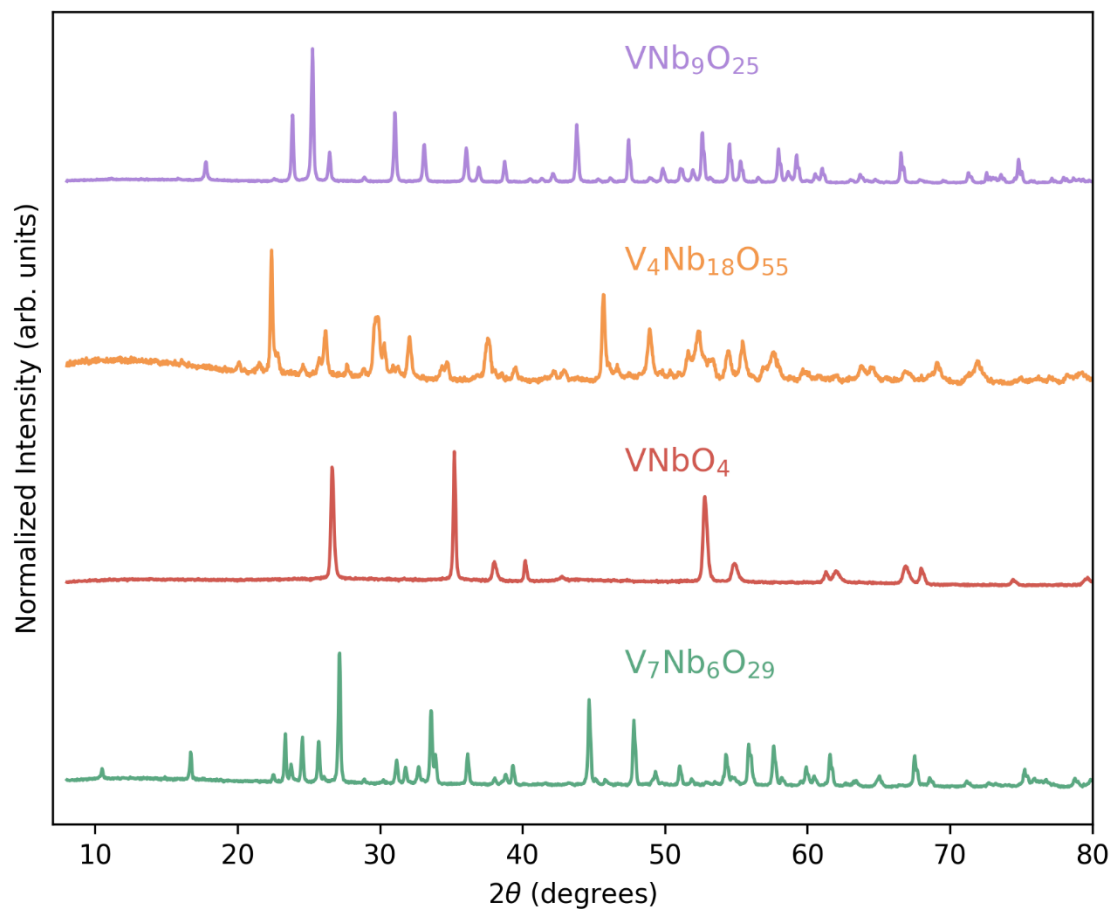


Figure 4-2. Ordinary X-ray diffraction of the four vanadium niobates.

High resolution X-ray diffraction (HR-XRD) was used to verify the phase purity of each compound and calculate their lattice parameters. Analyzing the spectra of VNb₉O₂₅ (**Figure 4-3**), V₄Nb₁₈O₅₅ (**Figure 4-4**), VNbO₄ (**Figure 4-6**), and V₇Nb₆O₂₉ (**Figure 4-7**) allow for the determination of other present phases, if any. Unit cell information is presented in **Table 4-1**.

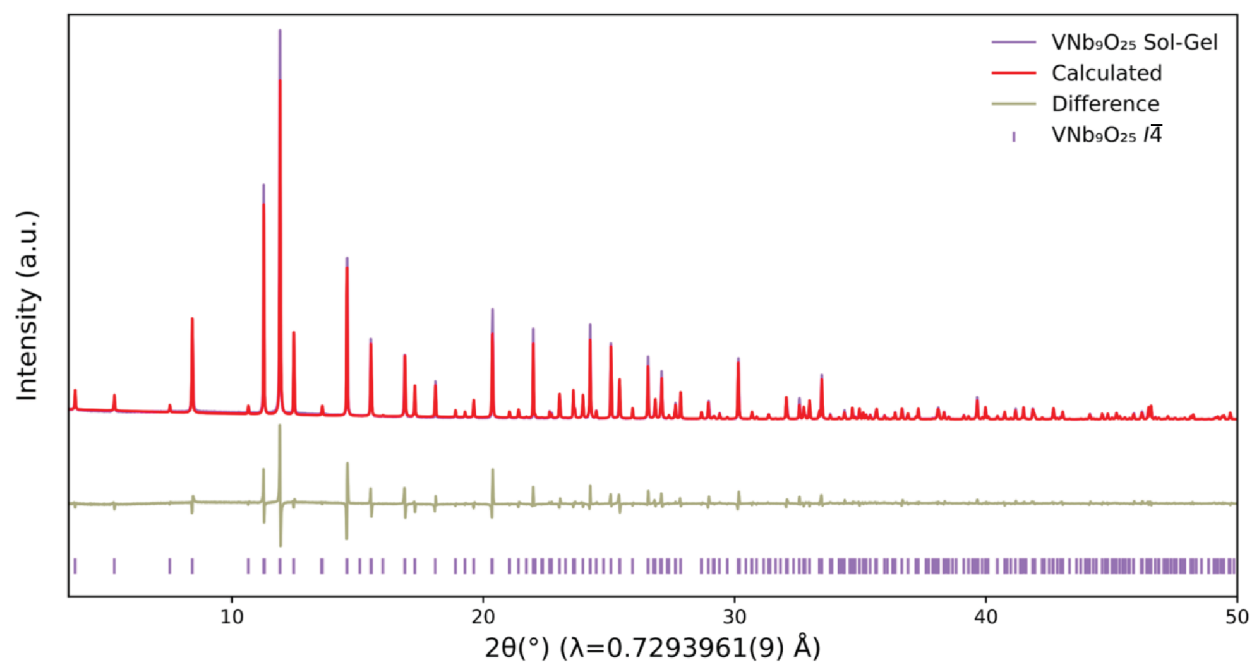


Figure 4-3. High resolution X-ray diffraction (HR-XRD) spectra of sol-gel $\text{VNb}_9\text{O}_{25}$, performed by Gugulethu Nkala. [51]

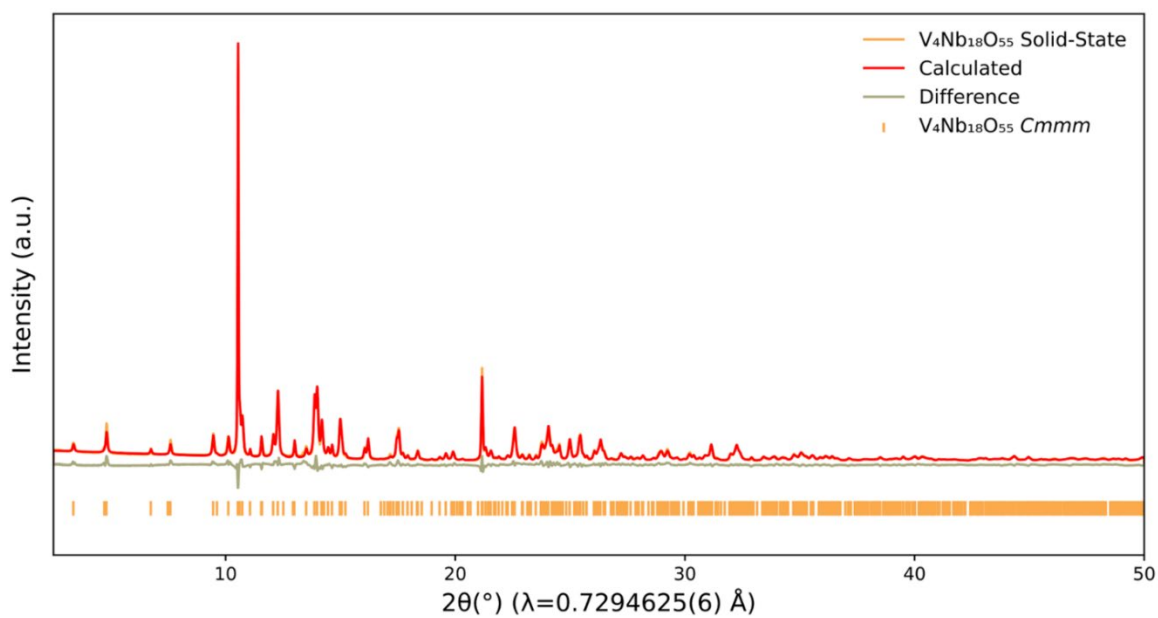


Figure 4-4. High resolution X-ray diffraction (HR-XRD) spectra of solid-state $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, performed by Gugulethu Nkala. [51]

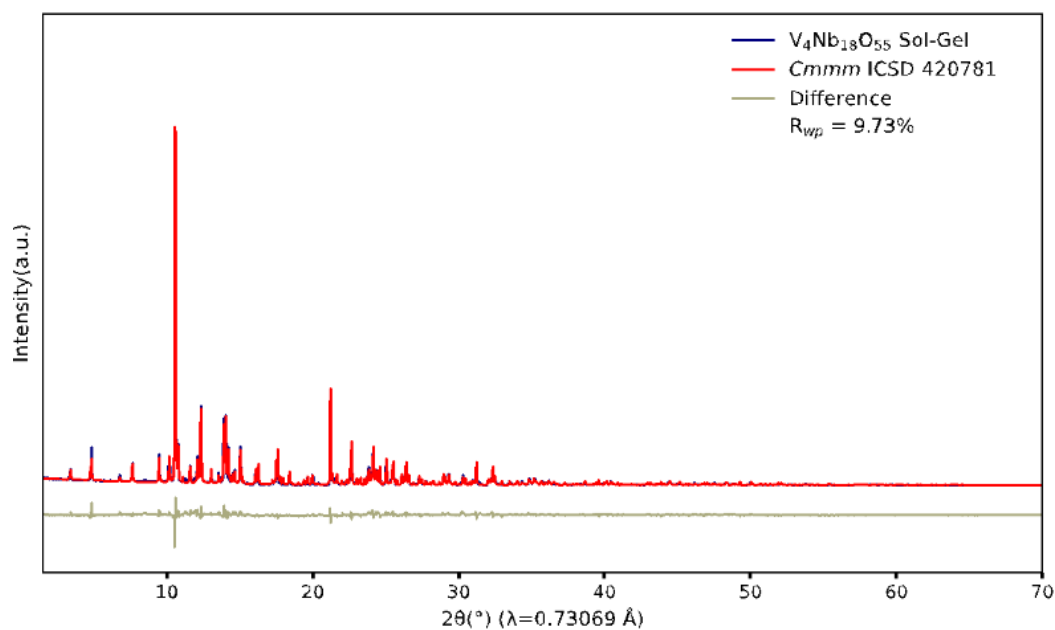


Figure 4-5. High resolution X-ray diffraction (HR-XRD) spectra of sol-gel $V_4Nb_{18}O_{55}$, performed by Gugulethu Nkala. [51]

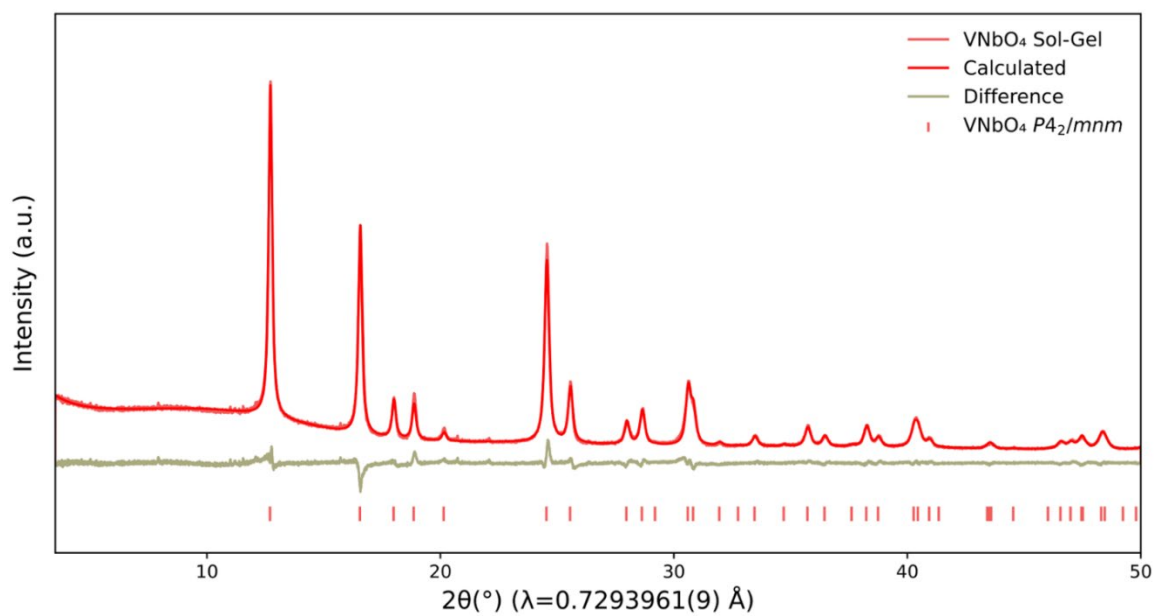


Figure 4-6. High resolution X-ray diffraction (HR-XRD) spectra of sol-gel $VNbO_4$, performed by Gugulethu Nkala. [51]

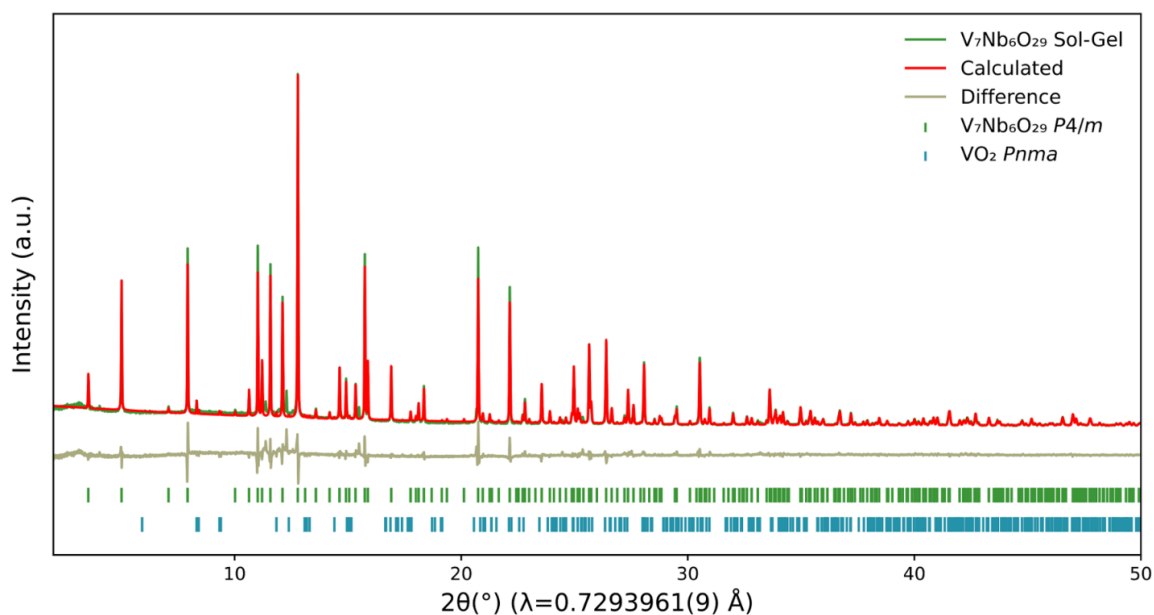


Figure 4-7. High resolution X-ray diffraction (HR-XRD) spectra of solid-state $V_7Nb_6O_{29}$, performed by Gugulethu Nkala. [51]

Table 4-1. Unit cell parameters of the four vanadium niobates, from HR-XRD refinement, performed by Gugulethu Nkala. [51]

	VNb_9O_{25}	$V_4Nb_{18}O_{55}$	$VNbO_4$	$V_7Nb_6O_{29}$
a (Å)	15.716	17.393	4.665	11.809
b (Å)	15.716	17.702	4.665	11.809
c (Å)	3.825	3.973	3.019	3.798
$\alpha = \beta = \gamma = 90^\circ$	90	90	90	90
Volume (Å³)	944.821	1223.250	65.700	529.641

VNb_9O_{25} was determined as phase pure from its HR-XRD spectra which matches well with reference data (**Figure 4-3**).

Both synthesis techniques of $V_4Nb_{18}O_{55}$ produced phase-pure products, albeit with slightly different morphologies (**Figure 4-4, 4-5**). These were only distinguishable using HR-XRD, where sol-gel crystallite size was determined from peak broadening to be larger on average than solid-state crystallite size. This distinction was attributed to different nucleation in the two synthesis methods, where an organic sol-gel with well-mixed precursors would be more likely to nucleate $V_4Nb_{18}O_{55}$ in a homogeneous fashion, while a solid-state method would prefer heterogeneous nucleation at the edges of existing particles, where diffusion occurs.

Phase-pure $VNbO_4$ was synthesized successfully using both variants of the discussed sol-gel technique (**Figure 4-6**). The broad peak widths indicate a smaller crystallite size compared to the other compounds, corroborating the nanosized particles seen under SEM (**Figure 4-1c**).

The lattice parameters of each compound determined from HR-XRD and presented in **Table 4-1** generally agreed within 1.5% to those presented in **Table 1-1** except for those for $VNbO_4$. This was partially attributed to the nanosized $VNbO_4$ particles, which experience more lattice compression due to surface stress. However, given the magnitude of this discrepancy, it is also likely that the predicted structure provided by *Ding et al.* is not a good fit for our synthesized phase. [26]

$V_7Nb_6O_{29}$ was synthesized successfully with small amounts of a secondary phase, attributed to paramontroseite $VO_2(P)$ ($Pbmn$). [55] This phase was virtually undetectable in ordinary X-ray diffraction. Additional peaks at the shoulders of the main diffraction peaks were associated with differences in site occupancy due to the vanadium-deficiency caused by the formation of the secondary phase. A niobium excess would, in fact, remove some cation disorder in the system, possibly introducing some of the superlattice peaks that were not present in

Lawrance et al.'s predicted structure due to their disappearance in a more disordered structure. [27]

Raman Spectra

Raman spectra were captured for each of the vanadium niobates to better understand their structural arrangements (**Figure 4-8**). The spectrum for each compound agreed with those found in literature [34], [49], [56]. However, no reference was found for $V_7Nb_6O_{29}$, making conclusions about these systems difficult.

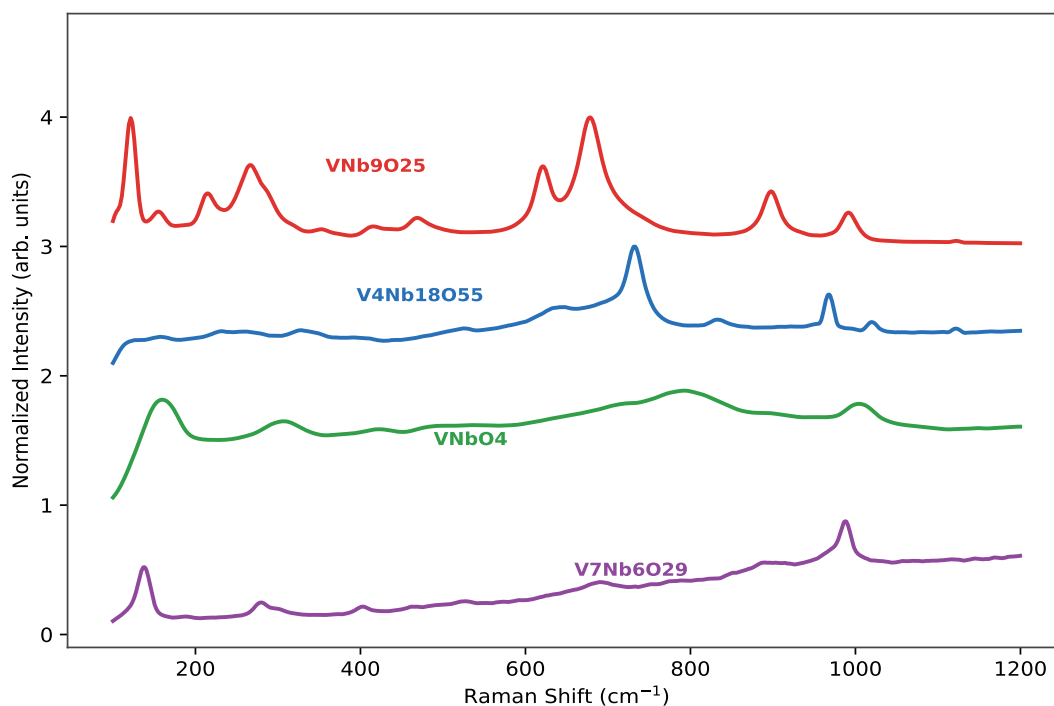


Figure 4-8. Raman spectra of the four vanadium niobates over a Raman shift of 0-1200 cm^{-1} , performed by Andrea Zambotti. [54]

In VNb_9O_{25} , the spectra are likely dominated by Nb-O and Nb-O-Nb contributions due to the 1:9 ratio between V and Nb. Given the non-centrosymmetric structure of the $(I\bar{4})$ space

group, the compound has no inversion symmetry. Hence, there are vibrational modes that can be both IR- and Raman-active. The other three vanadium niobates possess centrosymmetric structures in the following space groups: *Cmmm*, *P4₂/mnm*, and *P4/m*. Their vibrational modes therefore follow the rule of mutual exclusion, forbidding the Raman activity of modes that are also IR-active. [57] This finding corroborates the fewer number of peaks in those spectra compared to the spectrum of VNb₉O₂₅.

The Raman spectrum of VNbO₄ has broader peak widths than the spectra of the other compounds, which corroborate the XRD and SEM methods' determination of nanocrystalline material.

Although each compound agreed well with other experimentally determined Raman spectra, computational work would need to be performed to index the Raman peaks, due to the complexity of these compounds. This work would yield more certain structural determination for each compound and possibly help reveal the existence of or the amount of cation disorder in each system due to different V-O versus Nb-O bond behavior.

Experimental Electronic Analysis

To estimate the optical bandgaps of the four vanadium niobates, Tauc plots were generated from UV-Visible spectroscopic data, following the steps illustrated in **Equations 2** and **3**. Collaborators at UCLA provided estimates as to the bandgap nature of the four compounds: V₄Nb₁₈O₅₅ was the only predicted material to have a direct bandgap, while the other three vanadium niobates were predicted to have an indirect bandgap. [32] The Tauc plots for the four vanadium niobates are represented in **Figure 4-9**.

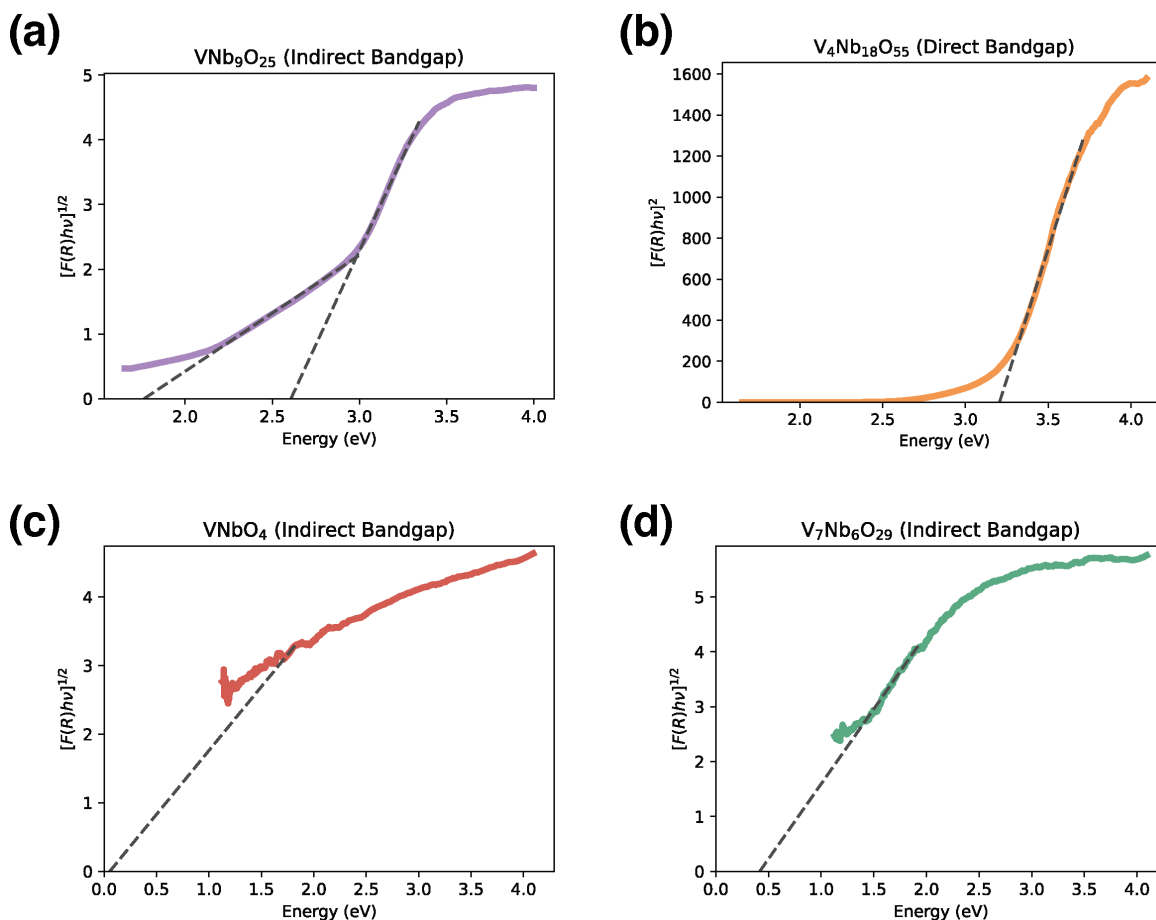


Figure 4-9. Tauc plots for (a) $\text{VNb}_9\text{O}_{25}$, (b) $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, (c) VNbO_4 , and (d) $\text{V}_7\text{Nb}_6\text{O}_{29}$ derived from UV-Vis performed from 300-1250 nm in reflectance.

The Tauc plot of $\text{VNb}_9\text{O}_{25}$ possesses an inflection point (**Figure 4-9a**), leading to the calculation of two separate bandgaps. Its two effective bandgap energies were calculated as 1.76 eV and 2.61 eV. The inflection point was associated with an energy level within the bandgap. The optical bandgap energy of $\text{V}_4\text{Nb}_{18}\text{O}_{55}$ was calculated to be 3.21 eV. For VNbO_4 and $\text{V}_7\text{Nb}_6\text{O}_{29}$, optical bandgap energies were difficult to predict since both exhibited high absorptivity over the entire wavelength range, making it difficult to decouple noise from true reflectance in the linear region. Both were still predicted to be highly conductive and thus have

bandgaps near 0 eV. However, no reliable absorption edge was resolvable within the measured range.

Electrochemical Performance

Given the wide range of potentials that the two transition metals in each compound operate, a 1.0-3.5 V potential window versus Li/Li⁺ was chosen for electrochemical testing. These were first motivated from literature search of these materials and used for initial cyclic voltammetry experiments. [2], [26], [27], [48] Accompanying b-value analyses were also performed to better understand the charge storage kinetics of the four vanadium niobates. These values follow the power law relationship that was discussed in **Equation 4**.

Voltage Profiles, Rate Performances, and Long-term Cycling

The four vanadium niobates were cycle tested at various constant currents, using equivalently constructed and loaded electrodes, as detailed in the methods. **Figure 4-10** displays voltage profiles from the first discharge and first charge of each vanadium niobate at 1C after formation cycling. **Figure 4-11** displays both charge and discharge capacities of the four compounds at different c-rates.

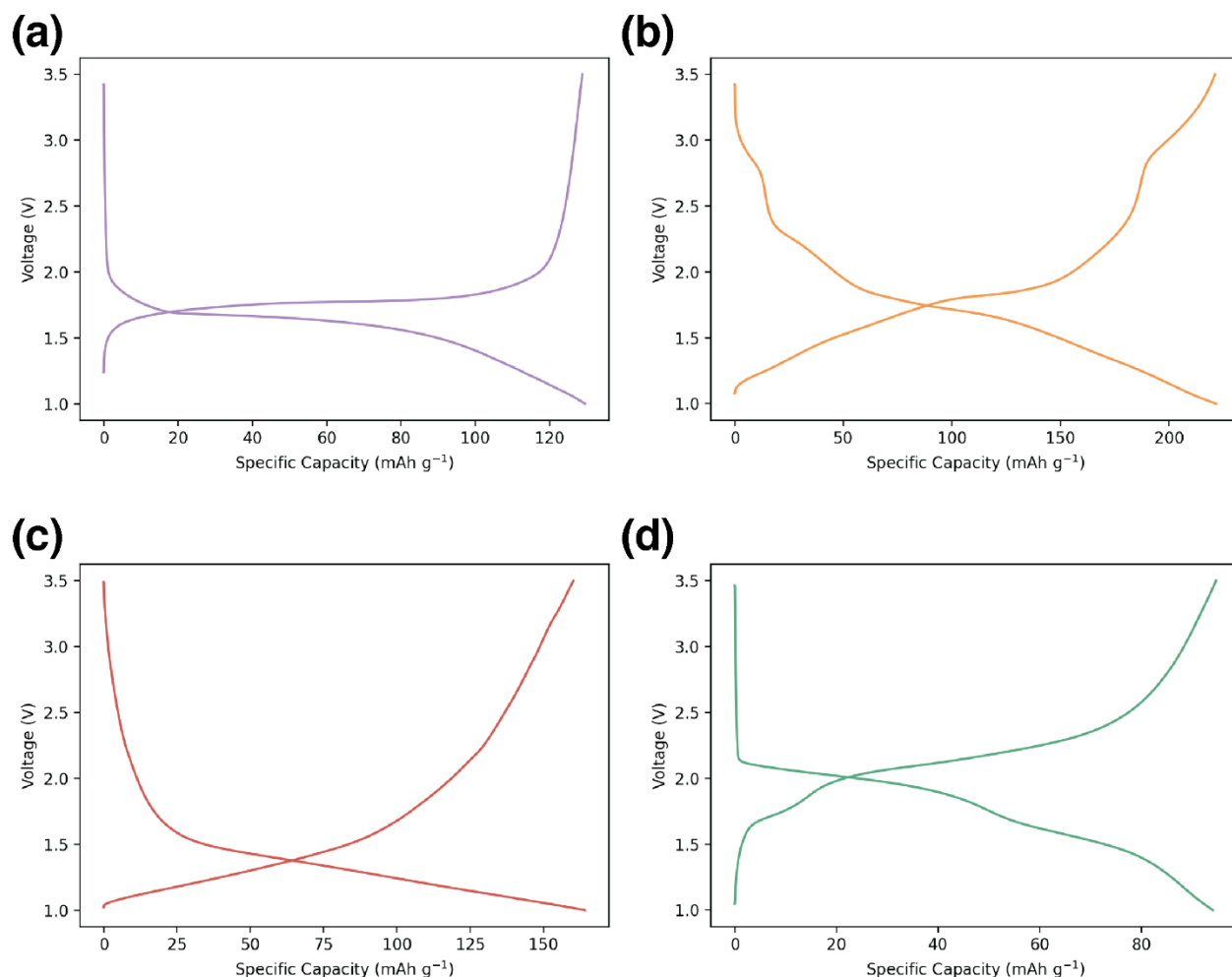


Figure 4-10. Voltage profiles at 1C of (a) VNb₉O₂₅, (b) V₄Nb₁₈O₅₅, (c) VNbO₄, and (d) V₇Nb₆O₂₉ within the 1.0-3.5 V vs. Li/Li⁺.

Distinct plateaus in VNb₉O₂₅'s voltage profile between 1.5 and 2.0 V were attributed to a likely first-order phase transformation which was highly reversible based on the symmetry of the discharge and charge profiles (**Figure 4-10a**). Operando HR-XRD was subsequently used to confirm this finding. The gently sloping profiles of each of the other vanadium niobates were attributed to lithium insertion within a solid solution over most of the potential range, which was subsequently confirmed using studies of entropic potential. The asymmetric profiles observed in

$V_7Nb_6O_{29}$ (**Figure 4-10c**) were associated with an asymmetry in the Li^+ migration barrier during discharging versus charging.

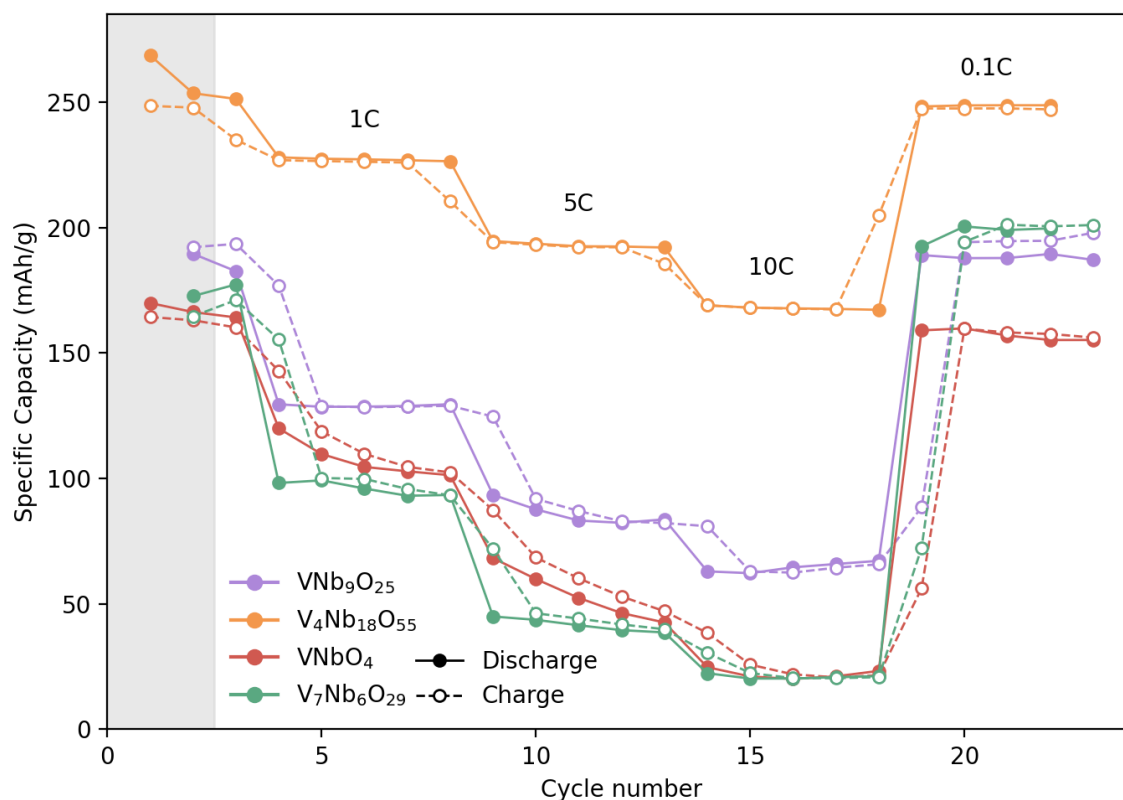


Figure 4-11. Rate capabilities of the four vanadium niobates cycled within the 1.0-3.5 V vs. Li/Li^+ potential range.

Each vanadium niobate showed excellent capacity retention after cycling at high currents; however, $V_4Nb_{18}O_{55}$ stood out as the material with the highest specific capacity at each c-rate, with a reversible capacity of 257 mAh g^{-1} at C/10 and 184 mAh g^{-1} at 10C. $V_4Nb_{18}O_{55}$'s performance at reduced currents further exceeded its theoretical capacity of 214 mAh g^{-1} (assuming one electron redox per transition metal). This was therefore attributed to possible

multi-electron redox of transition metal species within an open structure, which will be confirmed using XAS characterization and DFT computations in following sections.

The other compounds only exhibited maximal capacities that were below 70% of their theoretical values at the lowest c-rates. $V_7Nb_6O_{29}$ and $VNbO_4$ suffered from severe transport limitations at 10C, causing capacity to collapse to approximately 22 mAh g⁻¹. The poor rate capability of $VNbO_4$ was partially attributed to the carbon content in the active material, which surrounded each of the nanostructures as a product of the organic synthesis and likely frustrated the intercalation of Li^+ into active sites within the $VNbO_4$. Additionally, large distortions within the denser frameworks of both $VNbO_4$ and $V_7Nb_6O_{29}$ during lithiation likely led to diffusional barriers for Li^+ . Coupling these effects likely exceeded the rate performance benefit induced by the nanoscale nature of $VNbO_4$.

Each vanadium niobate was also subjected to continuous charge and discharge cycles in the same potential range, as presented in **Figure 4-12**.

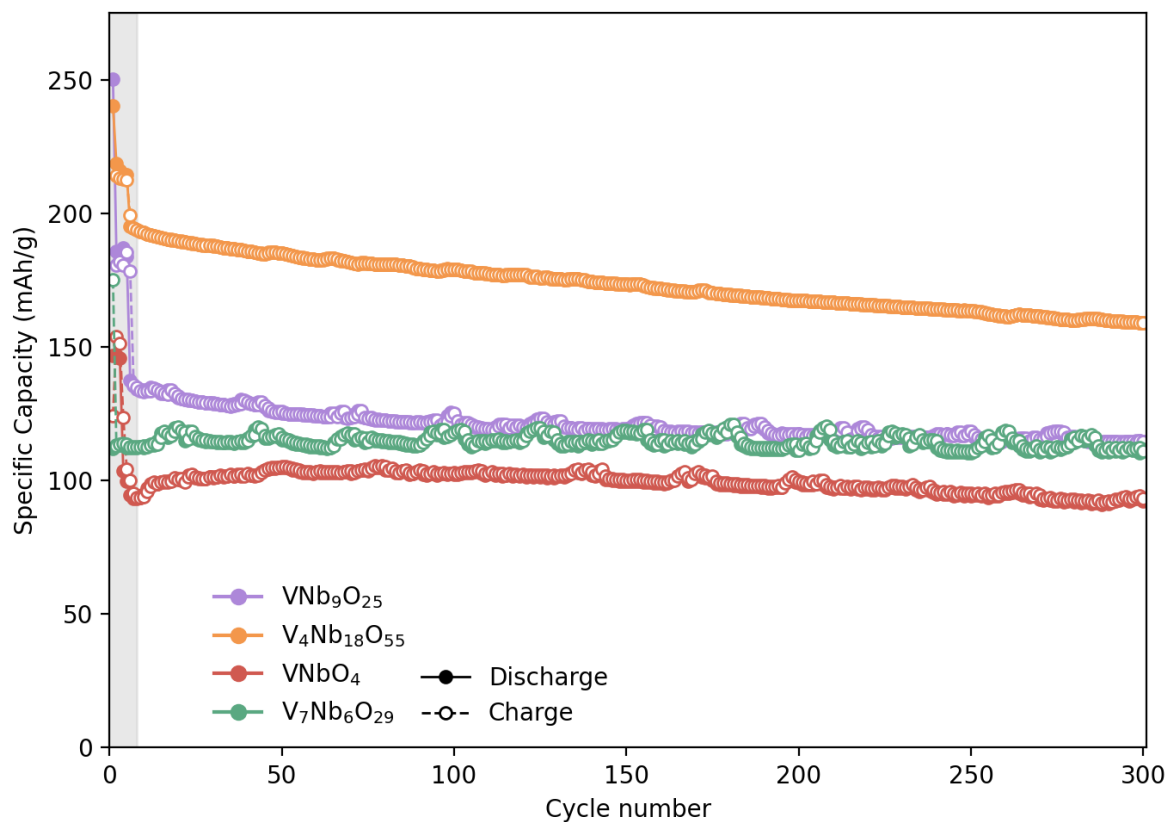


Figure 4-12. Extended cycling over 300 cycles within the 1.0-3.5 V vs. Li/Li^+ potential range of the four vanadium niobates.

Each compound exhibited at least 80% of their initial discharge capacity (after formation cycling) over 300 cycles when cycled at 1C. Moreover, $\text{V}_4\text{Nb}_{18}\text{O}_{55}$'s capacity was less sensitive to daily temperature fluctuations than the other vanadium niobates, suggesting its possible use in more sensitive environments.

Cyclic voltammograms of the four vanadium niobates are plotted in **Figure 4-13**.

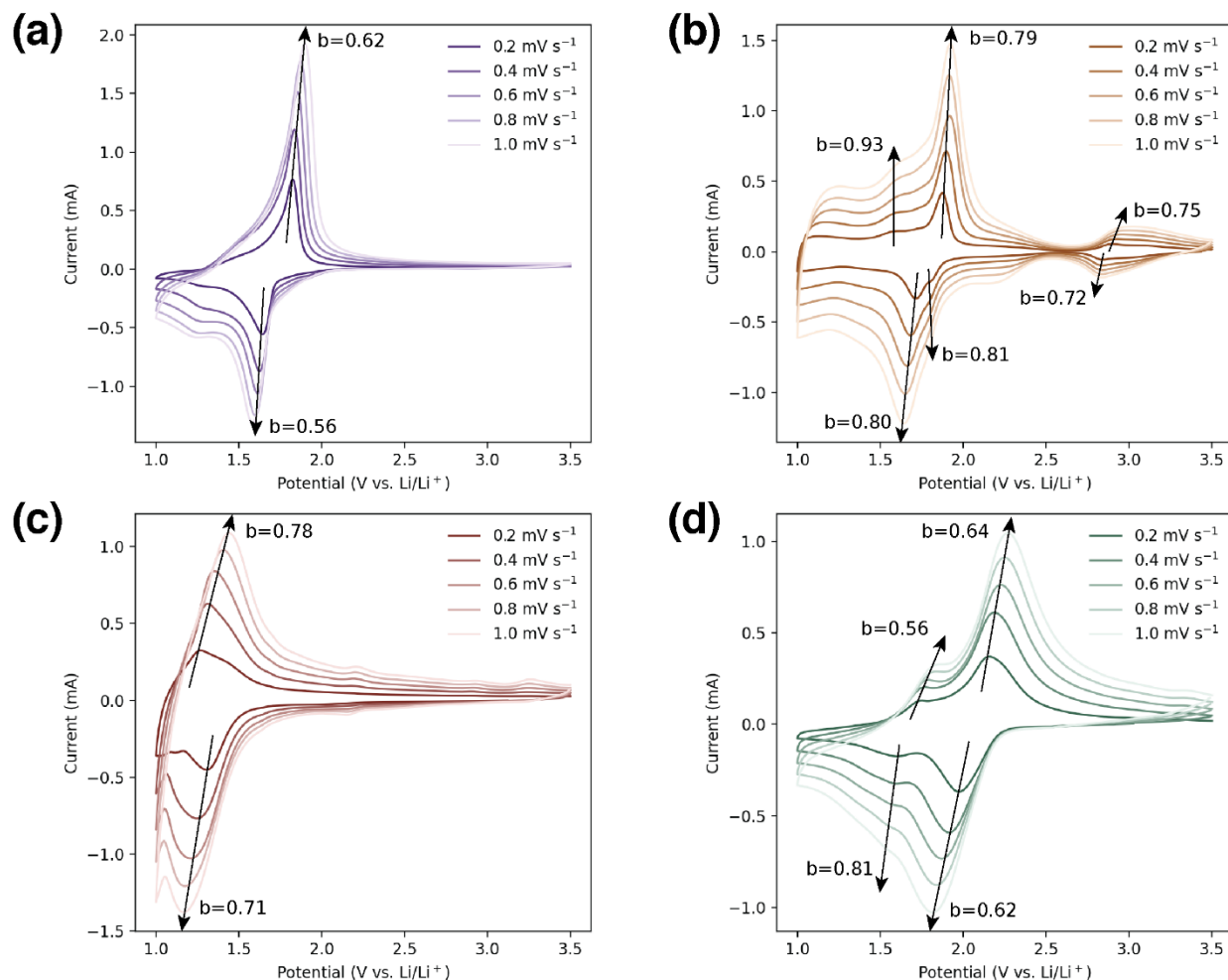


Figure 4-13. Cyclic voltammograms of (a) $\text{VNb}_9\text{O}_{25}$, (b) $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, (c) VNbO_4 , and (d) $\text{V}_7\text{Nb}_6\text{O}_{29}$ within the 1.0-3.5 V vs. Li/Li^+ with peak identification for b -value analysis. [54]

The cyclic voltammograms revealed significant redox activity in each of the vanadium niobates below 2.5 V vs. Li/Li^+ . The redox peaks further agreed well with the position of inflection points in the voltage profiles of each compound (**Figure 4-10**). $\text{VNb}_9\text{O}_{25}$ underwent a phase transition, as evidenced by a very different cathodic current peak position compared to

subsequent cycles. The voltametric profiles of $\text{V Nb}_9\text{O}_{25}$ at different current sweeps showed very sharp peaks and a diminished current from 2.0 to 3.0 V, indicating little redox activity or lithium insertion outside of the 1.0 to 2.0 V range. The sharpness of the peaks also indicates very ordered lithium insertion within well-defined crystallographic sites. The cathodic and anodic b-values were calculated to be 0.56 and 0.62, respectively. Given the proximity of these values to 0.5, the charge storage mechanism of $\text{V Nb}_9\text{O}_{25}$ is dominated primarily by diffusion-controlled processes into the bulk of the active material.

$\text{V}_4\text{Nb}_{18}\text{O}_{55}$ was the only phase that showed some isolated reversible redox activity above 2.7 V vs. Li/Li^+ . For the primary redox peaks in $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, cathodic and anodic b-values were calculated as 0.80 and 0.79, respectively. The shoulder peaks had cathodic and anodic values of 0.81 and 0.93. The ternary peaks above the 2.5 V vs Li/Li^+ region had cathodic and anodic b-values of 0.75 and 0.72. Many of these values fall within the middle of allowable b-values. Hence, this region of potentials falls within a finite diffusion region. [58] Increased lithiation of the material leads to a higher b-value of 0.93 which approaches $b=1$. This suggests the possibility of an insulator-to-metal transition near 1.6 V, where electronic conduction allows for instant redox reactions at the electrode surface due to faster electron transfer through the bulk material.

V NbO_4 exhibited broader redox peaks than the other compounds, attributed to sluggish electron transfer kinetics. Given the high carbon fraction in the resulting compound, we expect poorly graphitized (amorphous) carbon to both increase the IR drop of the system and increase the capacitance of the system. This is likely why there is not perfectly zero current even with very little or no redox activity as we approach 3.5 V. Cathodic and anodic b-values were 0.71 and 0.78, respectively, indicating the likelihood of finite diffusion determining the kinetics. [58]

$V_7Nb_6O_{29}$ exhibited broad redox peaks at various scan rates, with a maximum b-value (cathodic) of 0.81 at 1.5 V, with the other peaks at higher voltages having b-values near 0.6. Therefore, similar conclusions can be drawn for $V_7Nb_6O_{29}$ as for $V_4Nb_{18}O_{55}$. At higher lithium concentrations, the material likely undergoes an insulator-to-metal transition, causing a significant increase in capacitor-like charge storage over diffusion limitations. The broad peaks with shallow sloping were associated with the cation disorder in the system, which agrees with the fact that this is the only phase with confirmed cation disorder.

Rate Performance of Niobium-Deficient $V_4Nb_{18}O_{55}$

A comprehensive study of compositional variations in sol-gel $V_4Nb_{18}O_{55}$ was performed, following attempts to reach the 4:18 ratio of vanadium to niobium. Ammonium niobium oxalate precursor was hydrated with an unknown amount of water which, although determinable using thermogravimetric analysis (TGA), still required optimization to achieve the final correct ratio. X-ray diffraction of niobium-deficient $V_4Nb_{18}O_{55}$ revealed no significant differences in phase. Only EDS data provided insight into the discrepancy of this ratio. The excess vanadium likely substitutes niobium in octahedrally coordinated NbO_6 sites, although there has been no reported evidence of shared occupancy within the structure. Furthermore, since the phase consists of fully oxidized V^{5+} and Nb^{5+} , the ratio of transition metal to oxygen remained constant.

Electrochemical cycling data was performed for each composition after three formation cycles at C/10 until the desired V:Nb ratio of 4:18 was reached, as presented in **Figure 4-14**.

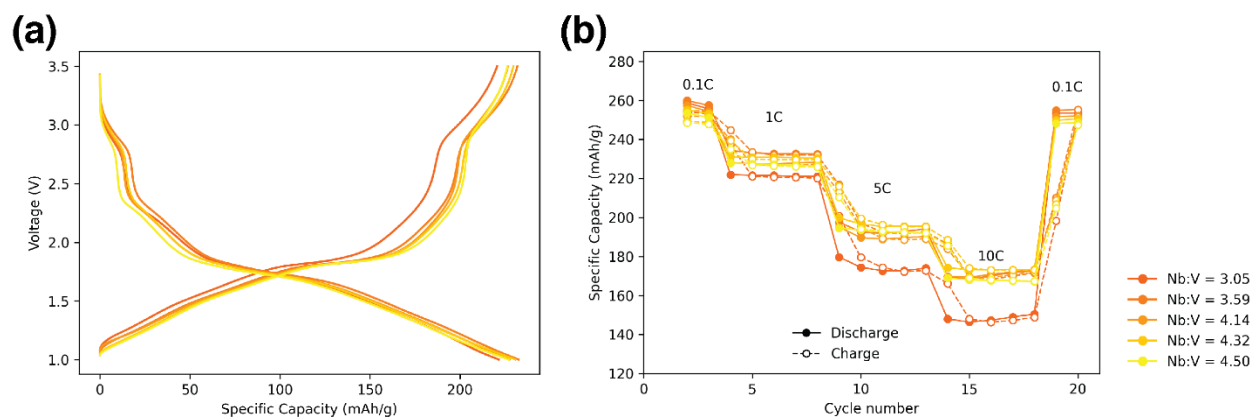


Figure 4-14. (a) Voltage profiles at 1C and (b) rate capabilities of several niobium-deficient $V_4Nb_{18}O_{55}$ compositions.

The overall increase of niobium fraction within the compound increased the rate capability of the compound, suggesting that the ideal $V_4Nb_{18}O_{55}$ composition previously determined represents a good optimization of a V^{5+} and Nb^{5+} compound. Niobium deficiency in $V_4Nb_{18}O_{55}$, although insignificant enough to cause a change in the overall structure of the compound, still led to decreases in performance at higher rates. No changes were observed in the shapes of the voltage profiles, indicating similar lithiation mechanisms for each compound.

At a Nb to V ratio of 3.05, discharge capacities at 10C were reduced by about 30 mAh g⁻¹, while the discrepancy decreased at slower rates. However, all five compositions still showed excellent capacity retention after 10C, returning to within five percent of their initial C/10 capacities. Interestingly, the $V_4Nb_{18}O_{55}$ compound with the ideal Nb:V ratio underperformed slightly compared to the other compositions at lower rates. The ideal composition had a maximum recoverable discharge capacity of 248 mAh g⁻¹ at C/10 while the vanadium rich composition of Nb:V of 3.59 exhibited a maximum recoverable discharge capacity of 255 mAh g⁻¹. These findings were attributed to increased vanadium redox in vanadium-excess samples,

likely in preferentially edge-sharing octahedra that were inaccessible to lithium ions at higher rates. This geometry preference is further supported by vanadium's stronger nuclear attraction to oxygen atoms in neighboring polyhedra due to its smaller atomic size than niobium. These findings would indicate the presence of asymmetric cation disorder in $V_4Nb_{18}O_{55}$, driven by the substitution of niobium with vanadium in compounds with excess vanadium content, especially in edge-sharing polyhedra.

X-Ray Absorption Near-Edge Structure and Operando X-Ray Diffraction

Operando XRD diffraction and X-Ray absorption spectroscopy (XAS) at the K-edge of vanadium and the K- and L_3 -edges of niobium were performed to better understand the structural changes and redox behavior of the four vanadium niobium oxides. The following data are divided into their respective compounds for clarity. Operando data is presented in **Figure 4-14**, while ex-situ XAS of vanadium K-edge is presented in **Figure 4-15**. ex-situ XAS of the niobium K-edge and L_3 -edge are presented in **Figure 4-16**.

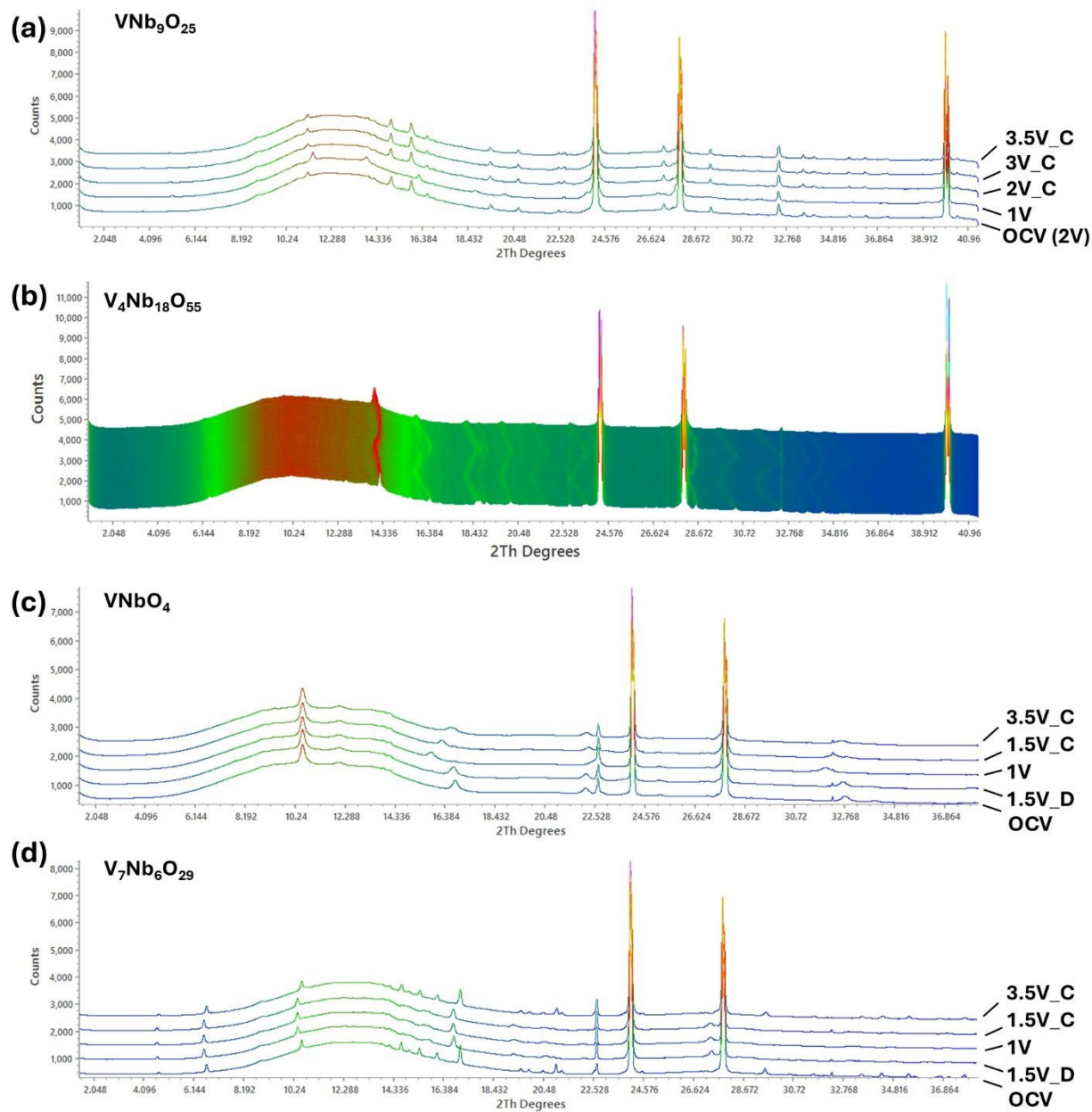


Figure 4-15. High resolution operando XRD patterns of (a) $\text{VNb}_9\text{O}_{25}$, (b) $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, (c) VNbO_4 , and (d) $\text{V}_7\text{Nb}_6\text{O}_{29}$ taken after precycling, performed by Gugulethu Nkala. [51]

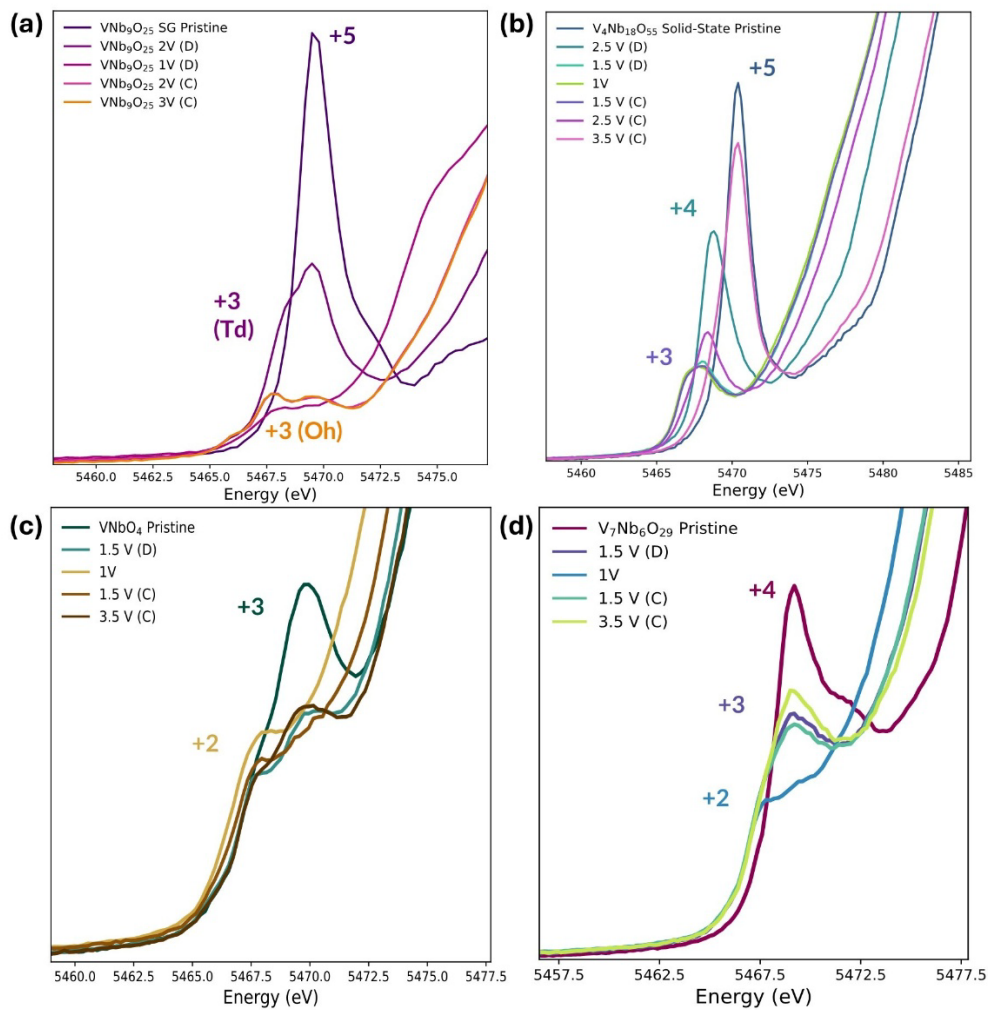


Figure 4-16. XANES of vanadium K-edge extracted from ex-situ XAS samples of (a) $\text{VNb}_9\text{O}_{25}$, (b) $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, (c) VNbO_4 , and (d) $\text{V}_7\text{Nb}_6\text{O}_{29}$, performed by Gugulethu Nkala. [51]

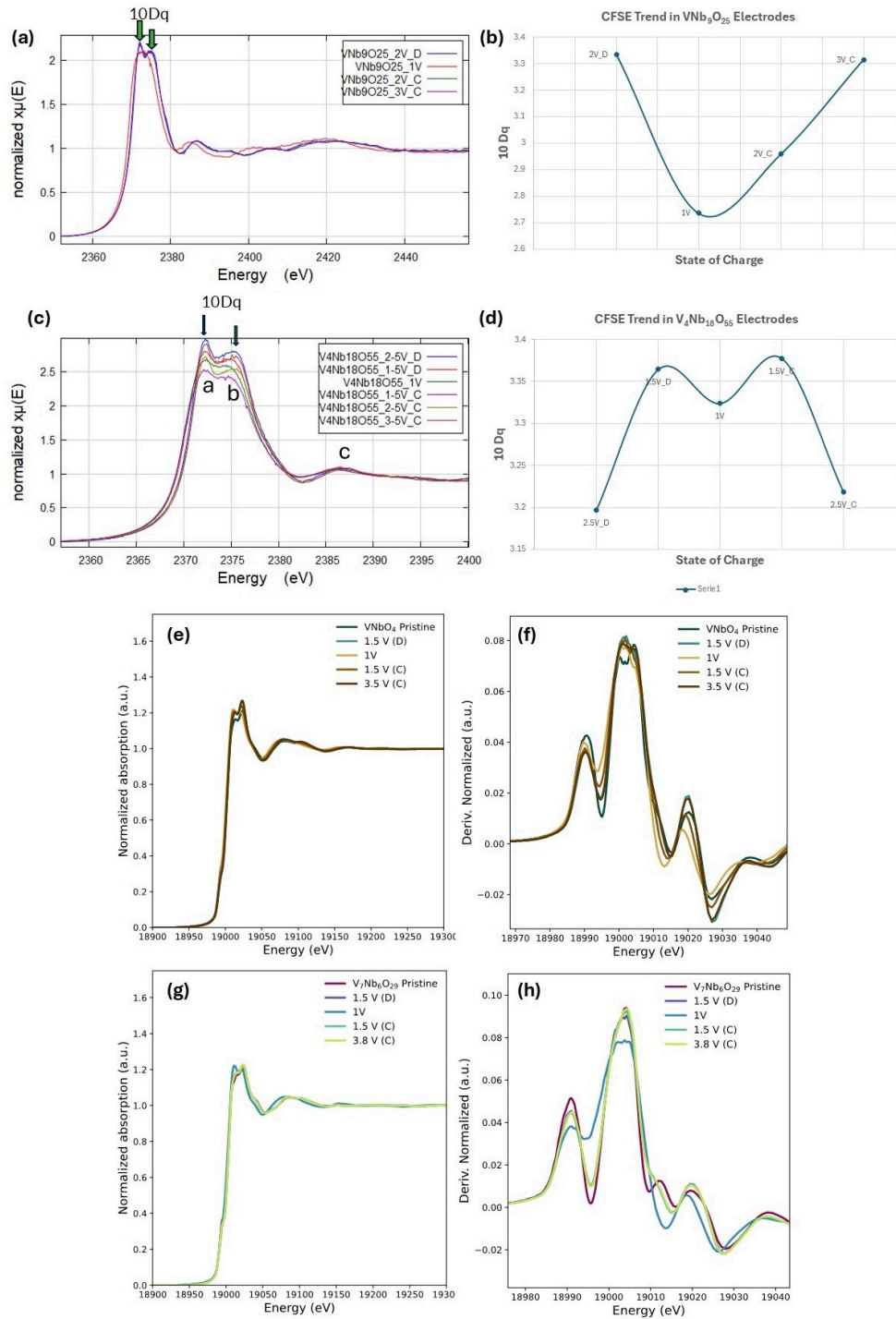


Figure 4-17. Niobium XAS L3-edge spectra of (a) VNb_9O_{25} and (b) accompanying $10 Dq$ values calculated as a function of voltage for VNb_9O_{25} , (c) $V_4Nb_{18}O_{55}$, (d) $10 Dq$ values calculated as a function of voltage. Niobium XAS K-edge spectra of (e) $VNbO_4$ and (f) its corresponding near edge region, and (g) $V_7Nb_6O_{29}$ and (h) its corresponding near-edge region. [51]

Pristine VNb₉O₂₅, possessing a (*I* $\bar{4}$) space group confirmed using HR-XRD, exhibited a phase transition into the P-4 space group, confirmed by the disappearance of peaks at 14.9°, 15.8°, and 16.6° 2 θ and the appearance of peaks at 11.4°, 13.8°, and 16.3° 2 θ upon lithiation to 1.0 V (**Figure 4-14a**). On de-lithiation to 2.0 V, the *I* $\bar{4}$ space group was fully regained in the reversal to the previous peaks. Strong peak alignment with the pristine VNb₉O₂₅ indicates highly reversible lithiation.

As previously discussed, the intensity of the Vanadium K-edge pre-edge peak decreases in intensity with decreasing oxidation state and a leftward shift to lower energies. Both were observed in VNb₉O₂₅, consistent with the reduction of V⁵⁺ in the pristine sample to V³⁺ at 2 V during lithiation (**Figure 4-15a**). Further lithiation led to a shift from a semi-resolved doublet to a weak triplet, characteristic of a change in local geometry from tetrahedral to octahedral without a change in the vanadium's oxidation state. De-lithiation to 3 V was not sufficient to reverse the change in local geometry or of the oxidation state of the vanadium back to 5+. This was likely due to the increased redox potential of vanadium which possesses a purely tetrahedral geometry in the initial structure. This pins the lithium in sites adjacent to vanadium polyhedra, further contributing to the capacity loss exhibited after the first cycle.

In the niobium L₃-edge pre-edge XAS, a 10 Dq parameter was calculated for different lithiation steps (**Figure 4-16a, b**). A decrease of 10 Dq during lithiation evidenced a reduction in niobium's oxidation state, likely from 5+ to 4+. Nb⁵⁺ was only recovered after de-lithiating to 3 V. Therefore, niobium redox occurs reversibly in VNb₉O₂₅, while vanadium redox does not. ~40 mAh g⁻¹ was therefore attributed to irreversible vanadium redox after the first discharge cycle, given an initial discharge capacity of 225 mAh g⁻¹ and subsequent discharge capacities of around

185 mAh g⁻¹ with a constant current method. While Li is traditionally lost in SEI formation, it was likely also trapped in interstitial sites that kept vanadium in a reduced V³⁺ state even though the structure returned to $I\bar{4}$ after de-lithiation.

V₄Nb₁₈O₅₅

The operando XRD and XAS data for V₄Nb₁₈O₅₅ corroborated the electrochemical findings of the highest observed capacity regardless of charge/discharge rate and over long-term cycling. Notably, over the entire voltage regime, although distortions in the lattice were observed, there was no observed phase change from the compound's original *Cmmm* space group (**Figure 4-14b**).

The highly recoverable and reversible redox of vanadium from 5+ to 3+ further contributed to its higher capacity compared to the other three compounds (**Figure 4-15b**). However, since the entire V⁵⁺ peak was not restored in intensity, an estimated 2.5 Li⁺ per V₄Nb₁₈O₅₅ was determined as lost within the structure. This accounted for a loss of about 24 mAh g⁻¹. The observed capacity loss from the first lithiation to second lithiation (288 mAh g⁻¹ to 210 mAh g⁻¹) was therefore attributed to the irreversibility of the vanadium redox. 78 mAh g⁻¹ can be attributed to the V⁵⁺ to V³⁺ transition. Fully de-lithiated V₄Nb₁₈O₅₅ therefore contains vanadium with a formal charge of 4.4+.

Therefore, the Nb L₃-edge data presented in **Figure 4-16c, d** were used to calculate 10 Dq values for different levels of lithiation. An initial increase of 10 Dq accompanying lithiation from 2.5 V to 1.5 V was unexpected, given the estimated reduction of Nb⁵⁺ to Nb⁴⁺. This would decrease the 10 Dq value, since metal-ligand interaction is reduced when the central metal ion is less charged. We therefore associate this increase in 10 Dq with the structure accommodating the

insertion of Li-ions, which compress niobia polyhedra, reducing Nb-O bond distances. The subsequent decrease of 10 Dq into a local minimum at 1 V was associated with ion ordering within the compound, which may be responsible for the onset of a tilde shape in the entropic potential right near 1.0 V OCV (**Figure 4-17b**). Since Nb⁵⁺ to Nb⁴⁺ reduction accounts for 175 mAh g⁻¹, while 210 mAh g⁻¹ was observed, a formal charge of 3.8+ for the niobium centers can be calculated, so incomplete Nb⁴⁺ to Nb³⁺ reduction is predicted to occur.

VNbO₄

From operando XRD studies, VNbO₄ exhibited no phase change during cycling within the entire potential range (1.0 – 3.5 V vs Li/Li⁺), maintaining its *P4₂/mnm* space group (**Figure 4-14c**). Peak shifts to initial 2-theta indicate strong reversibility in the lithiation process, which agree well with the insights presented by Ding et al. [26]

From the vanadium K-edge XAS in **Figure 4-15c**, the decrease in intensity of the V³⁺ peak during lithiation to 1.5 V was attributed to the local environment of the V³⁺ changing from a distorted octahedral to a regular (more symmetric) octahedral one. In a centrosymmetric octahedron, 3d—4p orbital mixing becomes forbidden, preventing 1s → 3d transitions. [59] Significant overlap of vanadium's 3d orbital and oxygen's 2p donor orbitals was therefore reduced, increasing ionic behavior in the octahedra. This resulted in a low-amplitude doublet, representative of t_{2g} and e_g peaks.

The leftward shift of the peak upon further lithiation to 2 V and the loss of the doublet was attributed to a V³⁺ to V²⁺ transition. The triplet (t_{2g}) orbital of vanadium, while previously occupied by 2 electrons, becomes half filled with three electrons upon reduction. The addition of additional electrons hence faces an energy barrier in the t_{2g} orbital, removing its contribution in

the pre-edge spectra. The e_g peak therefore dominates the pre-edge profile of V^{2+} , as visualized in our spectra.

Upon de-lithiation to 1.5V, V^{3+} was partially restored, as evidenced by the rightward shift of the e_g peak and the appearance of a partial doublet (**Figure 4-15c**). Further de-lithiation to 3.5 V led to a weak triplet, indicative of a restoration of a distorted octahedral environment but one that is less distorted than in the pristine compound. A significant but not total recovery of the V^{3+} oxidation state was proposed due to the peak alignment of the e_g peak with that of the pristine compound, but the degree of this recovery is indeterminable. The doublet spacing remained far larger than the width of the intense broad peak in the pristine $VNbO_4$, further supporting the more regular octahedral environment in the de-lithiated (to 3.5 V) cycled compound compared to the pristine compound.

To better understand the niobium redox activity, XAS was performed on the K-edge of niobium in $VNbO_4$ (**Figure 4-16e, f**). In pre-edge features, the peak shift between pristine and lithiated (to 1V) was measured to be ~ 2.3 eV. However, due to Kunzl's law, a full Nb^{5+} to Nb^{4+} would cause a shift of 3.2 eV. [60] Therefore, incomplete Nb^{5+} reduction was suggested, corresponding to $0.72 e^-$ per niobium center. Since V^{3+} to V^{2+} reduction was predicted to account for 129 mAh g^{-1} and the first discharge capacity was 225 mAh g^{-1} , the remaining capacity was attributed to incomplete Nb^{5+} to Nb^{4+} reduction with $0.74 e^-$ per niobium center. These values can be extrapolated to a formal charge of niobium between +4.26 and +4.41.

$V_7Nb_6O_{29}$

Operando XRD performed on $V_7Nb_6O_{29}$ revealed that no phase transition occurred during (de)lithiation within the entire potential range from the original P4/m space group (**Figure**

4-14d). Although the reduction of peak intensity and broadening behavior was observed for 14° and $16^\circ 2\theta$, these changes remained completely reversible. This likely arose due to $V_7Nb_6O_{29}$'s $2 \times 2 \times \infty$ blocks expanding at different rates than $3 \times 3 \times \infty$ blocks present in the compound. Additional shared occupancy in the cation disordered framework would also contribute to preferentially reduced vanadium over niobium, leading to hyperlocal distortions distributed randomly across lattice sites. The resulting microstrains collectively would broaden XRD peaks and reduce their intensities during increased lithiation.

From the pre-edge region of vanadium K-edge XAS in $V_7Nb_6O_{29}$ presented in **Figure 4-15d**, the pristine compound's initial vanadium oxidation state of $4+$ was reduced to $3+$ during lithiation to 1.5 V and $2+$ during lithiation to 1 V. However, the $4+$ oxidation state was unrecoverable even after de-lithiation to 3.5 V, as determined by peak intensity and slight leftward shift relative to the $4+$ peak. Pre-edge peaks seem to consist of narrow, highly overlapping peaks, which split further during vanadium reduction. These close peaks likely correspond to t_{2g} and e_g orbitals, the distance of which correspond inversely to the distance of the V-O bond. Therefore, further reduction of the vanadium led to likely increased V-O bond distance and therefore less vanadium 3p and oxygen 2p orbital overlap. The resulting increase in ionic behavior of the V-O bond further led to very weak energy peak intensities in the V^{2+} oxidation state. Like in $VNbO_4$, when vanadium is reduced to V^{2+} , the 3d orbital becomes half-filled, further reducing the intensity of the t_{2g} peak and the overall intensity in the pre-edge region. The doublet still present could indicate that vanadium still exists in a distorted octahedral geometry even at the $2+$ oxidation state. Given the initial discharge capacity of 190 mAh g^{-1} at C/10, a vanadium formal charge of +2.6 can be ascribed to the fully lithiated state.

From the Nb K-edge XAS in **Figure 4-16g, h**, no conclusive Nb^{5+} to Nb^{4+} reduction could be determined since no significant peak shift was observed. This agrees with the reported work by Lawrance et al. However, while Lawrance et al. reason that heavy distortion within NbO_6 octahedra limits Nb redox activity, niobium's 5+ oxidation state allows it to be subject to second order J-T distortions. [27] These often can lead to the opposite effect; Nb d orbitals shift to lower energies (closer to the Fermi level), increasing their chance of occupancy and hence redox. The magnitude of this will be confirmed in following pDOS studies.

Entropic Potential

The open circuit voltage $U_{\text{ocv}}(x,T)$ and the entropic potential $\partial U_{\text{ocv}}(x,T)/\partial T$ were plotted for several compositions of lithium in each vanadium niobate (**Figure 4-17**). Several regions were ascribed to different lithiation mechanisms dependent on the effective lithium concentration in each compound. Plateau-like regions in entropic potential can oftentimes be difficult to analyze, since they could hide combined positive and negative entropy contributions rather than representing true plateaus. Additionally, the entropic potential consists of vibrational, configurational, and electronic components, which are difficult to decompose.

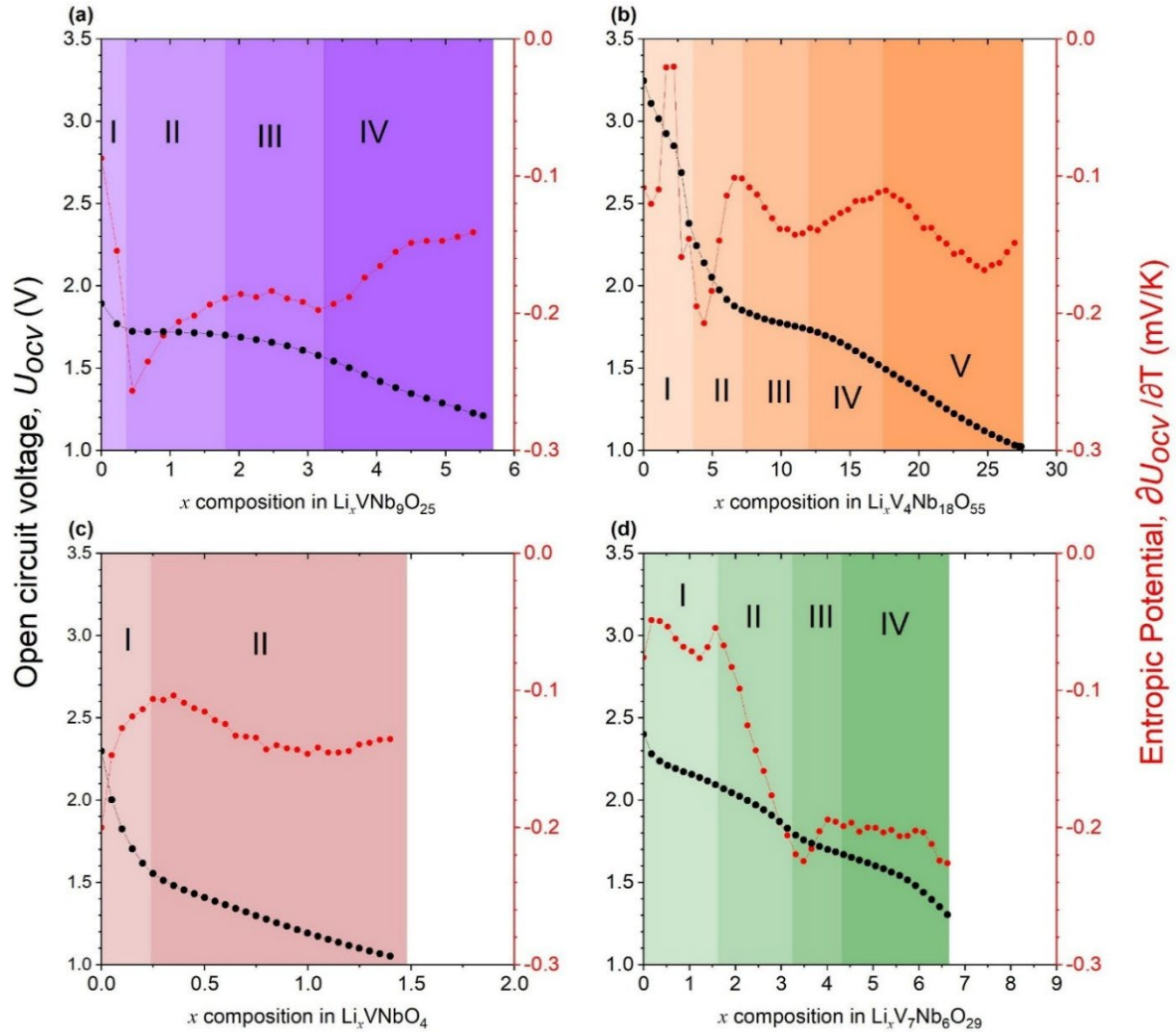


Figure 4-18. Entropic potential $\partial U_{ocv}(x,T)/\partial T$ and OCV (U_{ocv}) of (a) VNb_9O_{25} , (b) $V_4Nb_{18}O_{55}$, (c) $VNbO_4$, and (d) $V_7Nb_6O_{29}$, created by Nicolas Leport. [53]

The entropic potential of VNb_9O_{25} was split into four different regions (**Figure 4-17a**). A monotonic decrease of both U_{ocv} and $\partial U_{ocv}(x,T)/\partial T$ in region I was ascribed to a solid-solution-like lithium intercalation process. U_{ocv} then plateaued in region II while $\partial U_{ocv}(x,T)/\partial T$ increased, likely due to a first-order phase transformation process and subsequent two-phase

region coexistence. The potential plateau at ~ 1.7 V was within the region of the phase transformation that was observed in operando XRD experiments from a $I\bar{4}$ to $P\bar{4}$ structure (**Figure 4-14a**). In region III, a decrease of both U_{OCV} and $\partial U_{OCV}(x,T)/\partial T$ indicated another solid-solution-like regime, however only within the new phase. In region IV, the monotonic decrease in U_{OCV} and the logarithmic increase in $\partial U_{OCV}(x,T)/\partial T$ was attributed to possible insulator-metal transition, due to the artificial creation of a plateau from negative contributions from the configurational entropic potential and positive contributions from the electronic entropic potential. [61]

For $V_4Nb_{18}O_{55}$, the entropic potential was split into five distinct regions (**Figure 4-17b**). In region I, a monotonic decrease in U_{OCV} and a local maximum in $\partial U_{OCV}(x,T)/\partial T$ were attributed to the reduction of V^{5+} to V^{4+} , as confirmed by XAS in the equivalent potential range (**Figure 4-15b**). In region II, a steep decrease in U_{OCV} and a tilde-shaped fluctuation in $\partial U_{OCV}(x,T)/\partial T$ were consistent with ion ordering within a solid solution. [47] The ensuing decrease of both U_{OCV} and $\partial U_{OCV}(x,T)/\partial T$ in region III further indicated ion intercalation in the solid solution. The local maximum in entropic potential between regions II and III were further attributed to the reduction of V^{4+} to V^{3+} . In regions IV and V, overall monotonic changes in both U_{OCV} and $\partial U_{OCV}(x,T)/\partial T$ were ascribed to ion intercalation in the solid solution like before. However, the local maximum between regions IV and V was associated with the reduction of Nb^{5+} to Nb^{4+} . In the tail end of region V, $\partial U_{OCV}(x,T)/\partial T$ exhibited a local minimum, likely due to a beginning saturation of lithium within available sites that causes an initial reduction of configurational entropy in the system and a subsequent rise due to crowding and a higher number of delocalized electrons contributing to an increased electronic entropic contribution. Nb^{4+} to

Nb³⁺ reduction could also occur, which would account for Nb's formal charge of +3.8, as determined from the XAS.

VNbO₄ exhibited only two regions, the first region displaying a decrease in U_{ocv} and an increase in $\partial U_{ocv}(x,T)/\partial T$ (**Figure 4-17c**). These were attributed to the change in site symmetry of vanadium, on average going from a distorted octahedral to a more symmetric octahedral geometry as revealed in XAS of the Vanadium K-edge (**Figure 4-15c**). U_{ocv} and $\partial U_{ocv}(x,T)/\partial T$ both decreased on average in region II. Consistent with equivalent regions in the other vanadium niobates, this was attributed to lithium intercalation in a solid solution. However, a slight reversal of trend was also observed for the entropic potential at high lithium compositions (approaching 1 Li per transition metal), like that observed in V₄Nb₁₈O₅₅. The local maximum in $\partial U_{ocv}(x,T)/\partial T$ was consistent with the transition of vanadium's oxidation state from 3+ to 2+ in the XAS.

V₇Nb₆O₂₉ exhibited four distinct regions, the first displaying a decrease in U_{ocv} and an inverted tilde-shaped fluctuation in $\partial U_{ocv}(x,T)/\partial T$ (**Figure 4-17d**); this likely indicated a frustration in ion ordering in a solid solution, which is consistent with the cation disorder present in this W-R phase. [47] Cation disorder and geometric constraints in the W-R phase are responsible for creating a large distribution of energies in sites available for lithium insertion. The shallow-sloping, continually decreasing U_{ocv} indicated solid-solution behavior for the entire 1.0 – 3.5 V vs. Li/Li⁺ potential range; this was consistent with the operando XRD, where no phase change was observed. A tilde-shaped fluctuation was also identified in region III, consistent with ion ordering. Regions II and IV, which showed consistent decreases in both U_{ocv} and $\partial U_{ocv}(x,T)/\partial T$ were again associated with lithium intercalation in the solid solution. The local maximum of $\partial U_{ocv}(x,T)/\partial T$ between regions I and II was attributed to V⁴⁺ to V³⁺ redox,

while the local maximum between regions III and IV was attributed to V^{3+} to V^{2+} redox as determined through comparison with the V K-edge XAS (**Figure 4-15d**).

Partial Density of States and Structural Predictions

Unit cell parameters were determined for each pristine compound based on energetic calculations (**Table 4-2**). Each parameter fell within 2% of theoretical values from literature (**Table 1-1**). Additionally, lithium intercalation energies were also predicted for the four compounds at the same points of lithiation (**Figure 4-18**).

Structural predictions and partial density of state (pDOS) calculations were performed for each compound at various points of lithiation (0, 0.25, 0.5, and 0.75 Li^+) for each compound (**Figure 4-19, 4-20, 4-21, 4-22**). In the pDOS, green peaks correspond to Nb d-orbitals, orange peaks correspond to V d-orbitals, and red peaks correspond to O p-orbitals. The subsequent analysis attempts to correlate features seen in operando XRD, XAS, and electrochemical experiments to those in the electronic band structures of the compounds. However, since important accompanying data were not provided, such as Bader charge analysis, concrete conclusions are difficult to draw.

Table 4-2. Unit cell parameters of the four vanadium niobates predicted from DFT, performed by Supriti Dutta. [32]

	VNb₉O₂₅	V₄Nb₁₈O₅₅	VNbO₄	V₇Nb₆O₂₉
a (Å)	15.97	17.67	6.60	11.98
b (Å)	15.97	18.18	6.78	11.93
c (Å)	3.86	3.89	3.08	3.84
$\alpha = \beta = \gamma = 90^\circ$	90	90	90	90
Volume (Å³)	984.35	1256.51	137.82	549.62

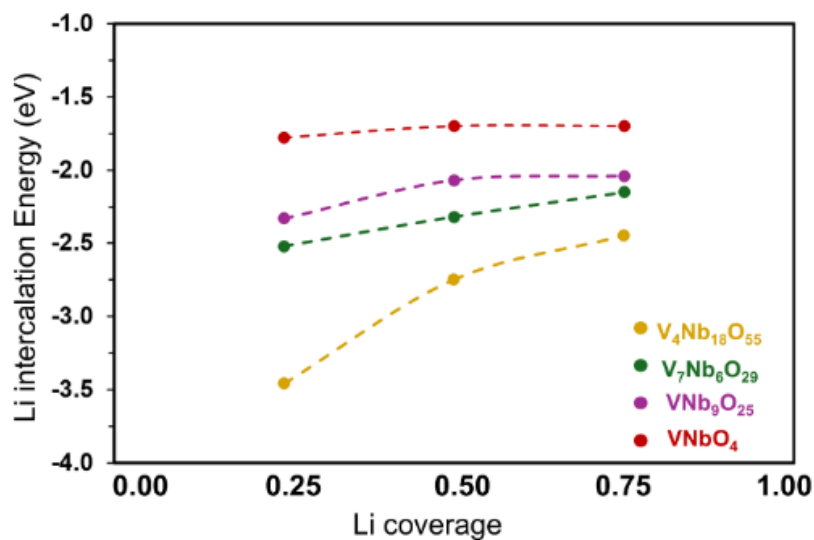


Figure 4-19. Li^+ intercalation energies with respect to lithium insertion for the four vanadium niobates, created by Supriti Dutta. [32]

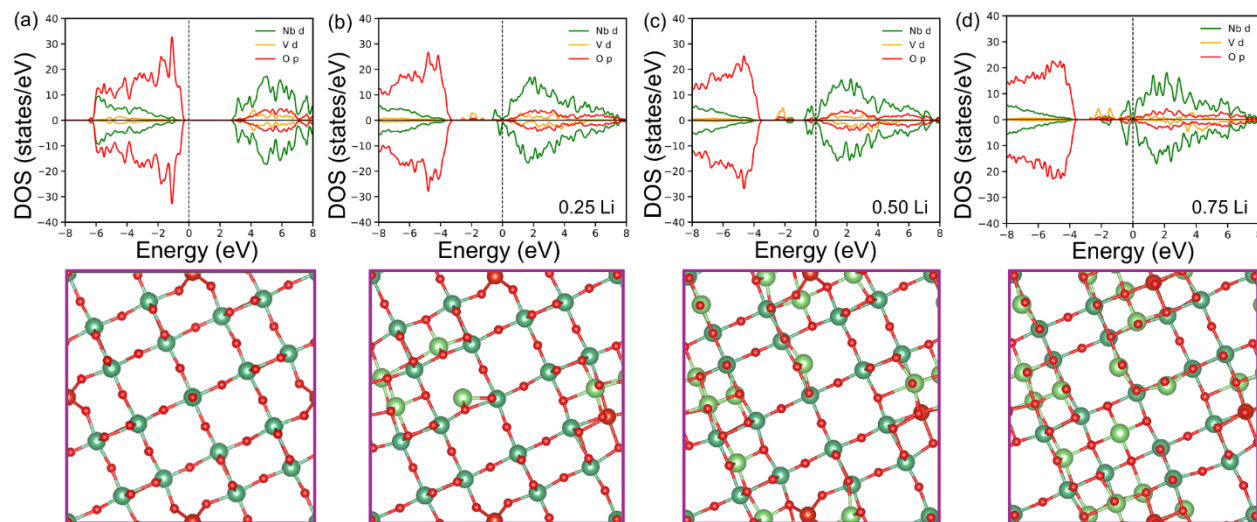


Figure 4-20. *Partial Density of States (pDOS) and predicted structures of $V_4Nb_{18}O_{55}$ for (a) pristine, (b) $X=0.25 Li^+$ per unit, (c) $X=0.50 Li^+$ per unit, (d) $X=0.75 Li^+$ per unit, created by Supriti Dutta. [32]*

Pristine VNb_9O_{25} possesses a very distinct energy gap between occupied O p-states and unoccupied Nb states. No states were observed within the energy gap of the pristine compound, differing slightly from the Tauc analysis of the optical bandgap. In the Tauc analysis, there were predicted states within the gap, which we see upon lithiation at $X=0.25$ in the pDOS. The experimental UV-Vis prediction of the existence of these states in the pristine compound could have resulted from defects or dislocations in the experimentally synthesized compound which are not encapsulated in the simulation of the pristine compound.

Upon lithiation to $X=0.25 Li$, corresponding to $2.5 Li^+$ per unit and an OCV of 1.7 V, V d states and O p spin-up states form in the previous band gap. These corroborate the reduction of V^{5+} to V^{3+} that was exhibited in the vanadium K-edge XAS beginning at 2 V. Nb d-states which

cross the Fermi level are highly symmetric, likely indicating Nb-Nb dimerization and a coupled Nb^{5+} to Nb^{4+} reduction, which is probable given the high concentration of niobium relative to vanadium centers in the compound. Additionally, Nb-Nb dimerization has been shown to exist in similar W-R phase $\text{PNb}_9\text{O}_{25}$, while Ti-Nb dimer-like interactions have been shown in TiNb_2O_7 . [2], [31] The phase transition of $\text{VNb}_9\text{O}_{25}$ from $I\bar{4}$ to $P\bar{4}$ at this accompanying voltage is determined to occur from a distortion of the placement of the Nb in the NbO_6 octahedron at the center of the $3\times 3\times\infty$ block. Given the open channels surrounding the corner sharing center octahedron, it is easy for lithium ions to diffuse through these channels, albeit asymmetrically, causing an interaction that can be visualized in **Figure 4-19b** accompanying the pDOS calculation.

Upon lithiation to $X=0.5$ Li, corresponding to 5 Li^+ per unit, high spin-symmetry of the Nb d-states likely indicates stronger hybridization within the Nb-Nb dimer. The appearance of additional Nb d-states within the former energy gap, energetically near the vanadium d-states corresponding to V^{3+} , is likely associated with Nb^{3+} ; however, no previous experimental explanation can confirm this. The level of lithiation corresponds to 1.3 V OCV within region 4 of the entropic potential, but there is no further lithiation in entropic potential experiments to better understand the further effects.

Upon lithiation to $X=0.75$ Li, corresponding to 7.5 Li^+ per unit, the OCV corresponds to a region beyond what was calculated in entropic potential. Therefore, substantial conclusions are hard to draw; however, we can assume that this corresponds to an OCV of approximately 1V, based on OCV trends versus lithiation. From the 0.50 Li to 0.75 Li, an increase in peak separation of V d-state peaks within the former energy gap can be attributed to an increase in crystal field stabilization energy that we witness when vanadium changes from an octahedral to

tetrahedral environment. These peaks therefore correspond to the t_{2g} and e_g orbitals. Since the crystal field splitting of an octahedral environment is 2.25 times that of a tetrahedral environment, we can visually confirm that this is indeed the case from the pDOS.

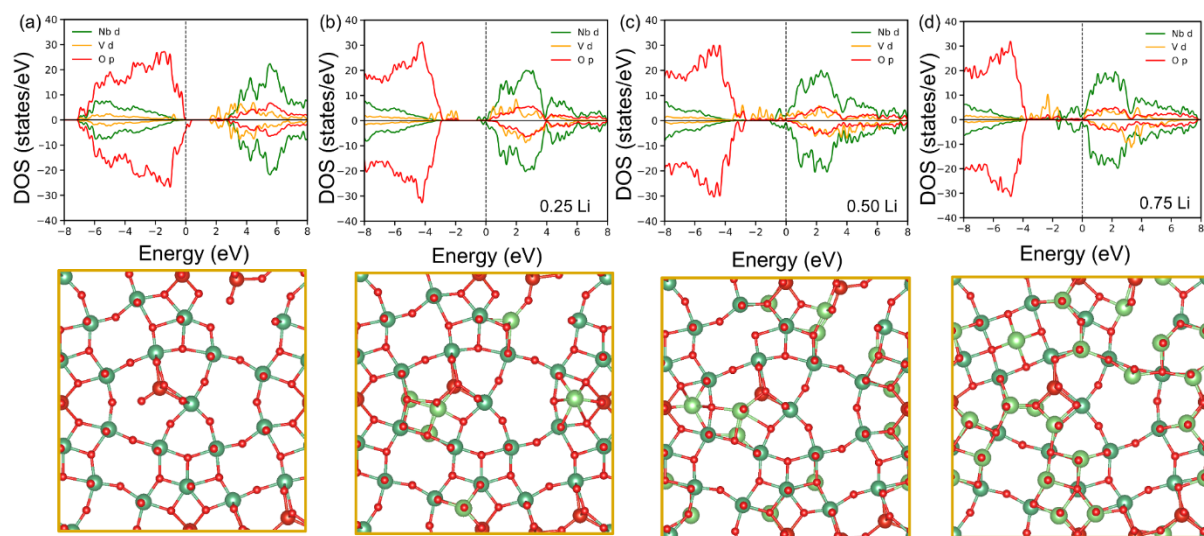
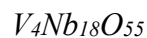


Figure 4-21. *Partial Density of States (pDOS) and predicted structures of VNb_9O_{25} for (a) pristine, (b) $X=0.25 Li^+$ per unit, (c) $X=0.50 Li^+$ per unit, (d) $X=0.75 Li^+$ per unit, created by Supriti Dutta. [32]*

In the pristine $V_4Nb_{18}O_{55}$, oxygen p-states dominate the valence band. There also exist occupied states above the fermi level. Unoccupied vanadium states exist close to the fermi level; however, there is an energy gap between the occupied states (valence band) and unoccupied states (conduction band). This gap corresponds approximately to the material's bandgap.

At $X=0.25 Li$, which corresponds to $5.5 Li^+$ per unit, vanadium spin-up states become occupied; this is reflective of a preferential reduction of V due to electron localization on V d-

states. This indicates definitive V redox activity which corresponds to an OCV decrease to 1.9 V and a complete reduction of vanadium from V^{5+} to V^{4+} , which is confirmed in the vanadium K-edge XAS. Some niobium d-states also shift below the Fermi level, indicating that they begin to become occupied, and contribute to an increase in electronic conduction of the phase. Increased d—p hybridization splitting in NbO_6 octahedra likely causes the shift of O p-states away from the Fermi level and results in the occupation of some Nb d-states. This interaction further corresponds to structural contraction during lithiation where Nb-O bond distances become shorter; this was reflected in L_3 -edge Nb data, where $10Dq$ values increase from 2.5 V to 1.9 V. It is therefore difficult to confirm, however, whether this represents the onset of niobium reduction.

When lithiated to $x=0.5$ Li, which corresponds to 11 Li^+ per unit and an OCV of 1.75 V, niobium d states exhibit higher spin symmetry than vanadium d-states. This, coupled with the 18 Nb sites versus 4 V sites per unit makes it difficult to understand the onset of Nb redox and may indicate the formation of Nb-Nb or V-Nb dimer-like pairs. This would yield a more complex, delocalized Nb redox dependent on covalent bonding. Overlap of Nb and V d-state peaks at -1 eV during increased lithiation further support an explanation of hybridization between Nb and V.

When lithiated to $x=0.75$, consistent with 16.5 Li^+ per unit and an OCV of 1.6 V, the intensities of Nb d-state peaks grow along with those of spin-polarized V d-state peaks. The spin symmetry of Nb d orbitals also increases, suggesting redox of Nb^{5+} down to Nb^{3+} (d^2), where low-spin pairing of d-electrons is favored. This is also explained in the Nb L_3 -edge XAS, where a calculated local maximum of $10 Dq$ at 1.6 V reflects shorter Nb-O bonds in more symmetric NbO_6 octahedra. This leads to increased Nb d and O p orbital overlap, strengthening the ligand field. Furthermore, this remains consistent with the local minimum in entropic potential at approximately 1.1 V, which can be associated with the reduction of Nb^{4+} to Nb^{3+} . High spin Nb^{4+}

(d^1) has 2-fold spin degeneracy while Nb^{3+} (d^2) has 3-fold degeneracy, causing an ensuing rise in entropic potential during this reduction. The formal charge of Nb was calculated to be 3.8 from Nb L₃-edge XAS, suggesting that reduction to Nb^{3+} must at least partially occur.

VNbO₄

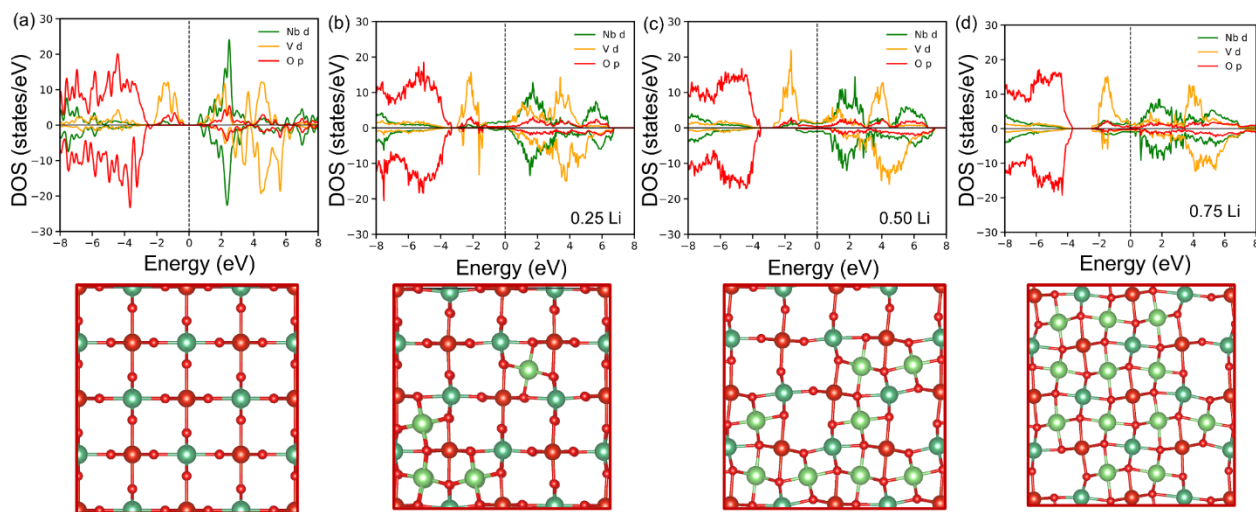


Figure 4-22. *Partial Density of States (pDOS) and predicted structures of VNbO₄ for (a) pristine, (b) $X=0.25 \text{ Li}^+$ per unit, (c) $X=0.50 \text{ Li}^+$ per unit, (d) $X=0.75 \text{ Li}^+$ per unit, created by Supriti Dutta. [32]*

In the pristine VNbO_4 , the energy gap between the unoccupied and occupied orbitals is already less than 1 eV. This agrees well with the trends from Tauc analysis, where VNbO_4 exhibited the smallest optical bandgap of the four compounds. The occupied V d-states agree well with the overall V^{3+} oxidation state, which seems to produce a high-spin configuration, given the lack of spin-symmetry. Substantial peak overlap near the valence band edge between occupied V d-states and O p-states indicates strong hybridization between the d- and p-orbitals.

Since some occupied Nb d-states are also visualized in the same region as the previous two peaks, there are some Nb-O and Nb-V interactions in the compound. This therefore distorts the CFSE that we would measure when probing either the vanadium or niobium edges in XAS. This could be responsible for the singular, wide peak that we see in the vanadium K-edge XAS, where crystal field splitting is not sufficient to resolve the t_{2g} and e_g peaks in the octahedral field. Furthermore, given the existence of occupied high-spin Nb d-states near the band edge, some Nb must be Nb^{4+} , likely lowering the formal charge of Nb below 5, as predicted in the pristine compound.

At $X=0.25$, which corresponds to $0.5 Li^+$ per unit, the OCV is approximately 1.55 V, corresponding to the area between regions I and II of the entropic potential. The local maximum in this region was associated with the onset of reduction of V^{3+} to V^{2+} . V^{2+} can only exist in a high-spin configuration since it possesses a half-filled d-orbital. Polarization of occupied Nb d-states likely indicates the reduction of Nb^{5+} to Nb^{4+} , consistent with ... Given the continuum of states within the previous energy gap, the material has undergone an insulator-to-metal transition.

Complete reduction of V^{3+} to V^{2+} was likely complete around 1.5 V, supported by the ex-situ XAS of the vanadium K-edge. At $X=0.5$ ($1 Li^+$ per unit) which corresponds to an OCV of 1.4 V, we expect vanadium to be fully reduced to V^{2+} , given the intensity of the V d-state peaks and their high polarization and that the d-orbitals of vanadium become half-filled so the electrons must have parallel spins. These account for the asymmetry of the vanadium d-states throughout the different energies. With further lithiation, we also get a higher trapping of lithium ions in certain sites, which agrees well with a dense rutile-type phase. This can be visualized well in the predicted structure at $X=0.5$ and $X=0.75$ and is well complemented by a slight increase in magnitude of lithium intercalation energy upon higher lithiation.

At $X=0.75$, which corresponds to 1V OCV and 1.5 Li^+ per unit, there exists more symmetry in the occupied V d-states and Nb d-states. Given the 1:1 V:Nb ratio, there is a possibility for V/Nb hybridization, the latter of which would cause peak overlap of occupied V and Nb d-states. We witness this in both positive and negative DOS, indicating some direct or facilitated hybridization of the two species. Since vanadium's d-electrons are purely high-spin, there would be no penalty in flipping the spin of the Nb d electron during hybridization. [62] This corroborates a possible explanation of hybridization between Nb and V metal centers, considering the perfectly alternating V and Nb occupancies in the pristine structure. V-V and Nb-Nb hybridization are less likely to occur, given that there are no neighboring octahedra of the same TM species in the pristine compound.

$V_7\text{Nb}_6\text{O}_{29}$

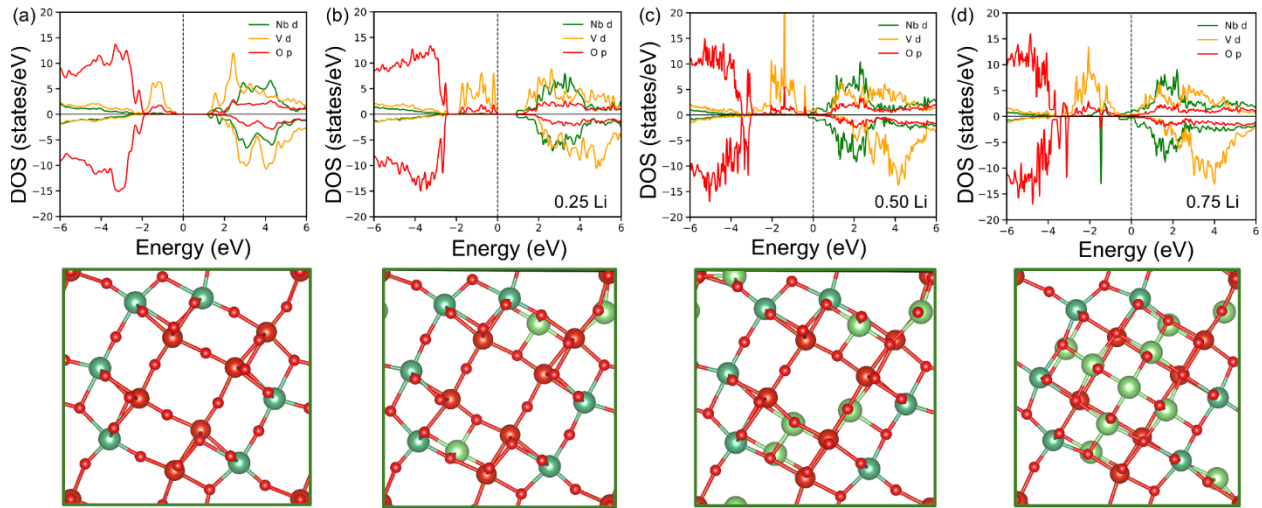


Figure 4-23. Partial Density of States (pDOS) and predicted structures of $V_7\text{Nb}_6\text{O}_{29}$ for (a) pristine, (b) $X=0.25 \text{ Li}^+$ per unit, (c) $X=0.50 \text{ Li}^+$ per unit, (d) $X=0.75 \text{ Li}^+$ per unit, created by Supriti Dutta. [32]

Pristine $V_7Nb_6O_{29}$ exhibits a clear energy gap and possesses occupied vanadium d-states. The high polarization of the d-states near the Fermi level are consistent with V^{4+} . The existence of a narrow energy gap agrees well with the reduced vanadium niobate phase having a smaller bandgap.

After lithiating to $X=0.25$, corresponding to $3.25 Li^+$ per unit, a notable expansion in the energies of the occupied vanadium d-states and oxygen p-states toward the Fermi level occurs. This corresponds to an OCV of 1.8 V and falls between regions II and III of the entropic potential curve. A V^{4+} to V^{3+} reduction also fully occurs by 1.5 V from the vanadium K-edge XAS, likely accounting for the increase in peak magnitude of the occupied vanadium d-states.

An insulator to metal transition occurs after lithiation to $X=0.5$ which corresponds to $6.5 Li^+$ per unit, where some Nb d-states become occupied. The notable increase in the intensity of occupied V d-state peaks is associated with the reduction of V^{3+} to V^{2+} , which corresponds well to the completely reduced V^{2+} in the vanadium K-edge XAS, given the voltage of 1.3 V which falls squarely between the V^{3+} and V^{2+} regions.

At $X=0.75$, which corresponds to $9.75 Li^+$ per unit, entropic potential data were no longer captured. However, the OCV can be extrapolated to approximately 1 V, corresponding to the full reduction of vanadium to V^{2+} . The increased occupation of Nb d-states could indicate redox behavior of Nb, although this disagrees with the work of Lawrance et al. and cannot be fully confirmed using Nb K-edge XAS data. However, given that the redox activity of vanadium occurs during low lithiation and that Nb d-states do not become occupied until deep lithiation of the material, there could be hybridization between V and Nb, where respective octahedra share edges. Both transition metals exist at close concentrations in this reduced phase, so Nb electronic

activity could be closely linked to that of V. Since V is a more electronegative species, during hybridization with Nb, V could still hold onto d-electrons more strongly. This would affect the formal charge of vanadium more strongly than that of Nb and make it difficult to uncouple the redox activity of Nb in this phase. This is further corroborated by the overlap of the Nb and V d-states that we see starting at $X=0.5$. Alternatively, no Nb redox behavior (pure Nb^{5+}), significant enough distortions in NbO_6 octahedra reported by Lawrance et al. could lead to second order J-T distortions, which could be significant enough to cause interactions between Nb d-orbitals and O p-orbitals that are observed in the pDOS. Expectedly, distortions become more prevalent during lithiation, as ions further distort octahedra.

CONCLUSIONS AND FURTHER WORK

Four vanadium niobium oxides were synthesized, characterized, and studied using electrochemical methods to better understand their redox mechanisms. Each adopts distinct structural features: $V_4Nb_{18}O_{55}$ possesses a tetragonal tungsten bronze framework, VNb_9O_{25} and $V_7Nb_6O_{29}$ are Wadsley-Roth shear phases, and $VNbO_4$ is rutile-like. Even with these differences, however, redox activity in each of these compounds was generally limited to under 2.5 V vs. Li/Li^+ . The only compound which exhibited significant activity above 2.5 V vs. Li/Li^+ was $V_4Nb_{18}O_{55}$, which also had the highest capacity of the four compounds at 257 mAh g⁻¹, exceeding the theoretical one-electron capacity of the compound at 214 mAh g⁻¹.

Where these compounds exhibit significant differences is during the lithiation process; as captured by operando XRD experiments and XAS. Even with nearly equivalent Nb^{5+} oxidation states, their V oxidation states were variable. These variabilities and the structures of these compounds led to high lithium trapping within the sites of VNb_9O_{25} and to a lesser extent $VNbO_4$ and $V_7Nb_6O_{29}$, degrading their usable capacities after the first cycle. $V_4Nb_{18}O_{55}$ exhibited the highest recoverability of the V^{5+} oxidation state upon de-lithiation, likely due to its variable, open channel geometry.

The consistently higher specific capacity of $V_4Nb_{18}O_{55}$ at various charge/discharge rates with a high degree reversibility indicates its promise as a commercial electrode material. Additionally, the flexibility in increasing the proportion of earth-abundant vanadium over niobium in $V_4Nb_{18}O_{55}$ without creating additional phases or significantly reducing performance indicates promise for possible commercial applications.

Additionally, the mix of low temperature organic sol-gel synthesis routes and solid-state synthesis routes allowed for the facile creation of various structurally distinct vanadium niobates

with different vanadium oxidation states. Hence, this ternary system provides a promising avenue for future research activity in Li-ion anode materials beyond graphite.

However, further research would be valuable for exploring applications of this study to other ternary or multi-component transition metal oxide systems. Due to the focus on probing niobium and vanadium with various techniques, other transition metals are excluded, by design. While the effect of structure and local geometry on the redox behavior of these transition metals has proven fruitful, the multi-dimensionality of this work makes it difficult to understand if the same findings can be applied to other systems, even with changes tweaks in composition, structure, or oxidation state. Fundamentally, this system provides data that is better to be consolidated with data of the same nature from as many other compounds as possible, after which computational methods can be used to predict stable, desirable electrode materials. This is one of the core goals of the DMREF grant, of which this project is a part.

REFERENCES

- [1] “Exploring the Electrochemical Lithiation of Vanadium Niobates”.
- [2] M. B. Preefer *et al.*, “Multielectron Redox and Insulator-to-Metal Transition upon Lithium Insertion in the Fast-Charging, Wadsley-Roth Phase $\text{PNb}_9\text{O}_{25}$,” *Chem. Mater.*, vol. 32, no. 11, pp. 4553–4563, May 2020, doi: 10.1021/acs.chemmater.0c00560.
- [3] E. Uchaker and G. Cao, “Mesocrystals as electrode materials for lithium-ion batteries,” *Nano Today*, vol. 9, no. 4, pp. 499–524, Aug. 2014, doi: 10.1016/j.nantod.2014.06.004.
- [4] V. Jabbari, V. Yurkiv, M. G. Rasul, A. H. Phakatkar, F. Mashayek, and R. Shahbazian-Yassar, “In situ formation of stable solid electrolyte interphase with high ionic conductivity for long lifespan all-solid-state lithium metal batteries,” *Energy Storage Mater.*, vol. 57, pp. 1–13, Mar. 2023, doi: 10.1016/j.ensm.2023.02.009.
- [5] K. J. Griffith, K. M. Wiaderek, G. Cibir, L. E. Marbella, and C. P. Grey, “Niobium tungsten oxides for high-rate lithium-ion energy storage,” *Nature*, vol. 559, no. 7715, pp. 556–563, Jul. 2018, doi: 10.1038/s41586-018-0347-0.
- [6] T. I. Dyuzheva, N. A. Bendeliani, and S. S. Kabalkina, “Compressibility and polymorphism of Re O_3 at pressures up to 30 GPa,” *Dokl. Akad. Nauk SSSR*, vol. 298, pp. 100–102, 1988.
- [7] C. Tzuenshi and P. Trucano, “Lattice parameter and thermal expansion of Re O_3 between 291 and 464 K,” *J. Appl. Crystallogr.*, vol. 11, pp. 286–288, 1978.
- [8] J. E. Jorgensen, D. J. Jorgensen, B. Batlogg, J. P. Remeika, and J. D. Axe, “Order parameter and critical exponent for the pressure- induced phase transitions in Re O_3 ,” *Phys. Rev. Ser. 3 B - Condens. Matter* 181978-, vol. 33, pp. 4793–4798, 1986.

- [9] D. Colaitis, C. Lecaille, D. Lebas, and J. D. Axe, “Precisions sur les parametres cristallins et sur l’indexation des raies Debye and Scherrer des oxydes ReO_2 et ReO_3 ,” *Rev. Chim. Miner.*, vol. 9, pp. 709–716, 1972.
- [10] K. Meisel, “Rheniumtrioxyd III. Mitteilung: Ueber die Kristallstruktur des Rheniumtrioxyds,” *Z. Fuer Anorg. Allg. Chem. 1950 DE*, vol. 207, pp. 121–128, 1932.
- [11] C. P. Koçer, K. J. Griffith, C. P. Grey, and A. J. Morris, “Cation Disorder and Lithium Insertion Mechanism of Wadsley–Roth Crystallographic Shear Phases from First Principles,” *J. Am. Chem. Soc.*, vol. 141, no. 38, pp. 15121–15134, Aug. 2019, doi: 10.1021/jacs.9b06316.
- [12] Q. Simon *et al.*, “Nanorods of Potassium Tantalum Niobate Tetragonal Tungsten Bronze Phase Grown by Pulsed Laser Deposition,” *Chem. Mater.*, vol. 25, no. 14, pp. 2793–2802, Jun. 2013, doi: 10.1021/cm401018k.
- [13] K. Momma and F. Izumi, “it VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data,” *J. Appl. Crystallogr.*, vol. 44, no. 6, pp. 1272–1276, Dec. 2011, doi: 10.1107/S0021889811038970.
- [14] R. S. Roth and A. D. Wadsley, “Mixed oxides of titanium and niobium: the crystal structure of $\text{TiNb}_{24}\text{O}_{62}$ ($\text{TiO}_{2.12}\text{Nb}_2\text{O}_5$),” *Acta Crystallogr.*, vol. 18, no. 4, pp. 724–730, Apr. 1965, doi: 10.1107/S0365110X65001664.
- [15] R. S. Roth and A. D. Wadsley, “Multiple phase formation in the binary system Nb_2O_5 – WO_3 . I. Preparation and identification of phases,” *Acta Crystallogr.*, vol. 19, no. 1, pp. 26–32, Jul. 1965, doi: 10.1107/S0365110X65002712.

- [16] A. R. Patterson *et al.*, “Rapid and Reversible Lithium Insertion in the Wadsley–Roth-Derived Phase $\text{NaNb}_3\text{O}_{10}$,” *Chem. Mater.*, vol. 35, no. 16, pp. 6364–6373, Aug. 2023, doi: 10.1021/acs.chemmater.3c01066.
- [17] O. Aalling-Frederiksen, M. Juelsholt, A. S. Anker, and K. M. Ø. Jensen, “Formation and growth mechanism for niobium oxide nanoparticles: atomistic insight from in situ X-ray total scattering,” *Nanoscale*, vol. 13, no. 17, pp. 8087–8097, May 2021, doi: 10.1039/d0nr08299f.
- [18] J.-Y. KIM and Y.-I. KIM, “Local structure and dielectric behavior of tetragonal tungsten bronzes β - SrTa_2O_6 and β' - SrTa_2O_6 ,” *J. Ceram. Soc. Jpn.*, vol. 123, no. 1437, pp. 419–422, 2015, doi: 10.2109/jcersj2.123.419.
- [19] S. Bach, J. P. Pereira-Ramos, and P. Willman, “Investigation of lithium diffusion in nano-sized rutile TiO_2 by impedance spectroscopy,” *Electrochimica Acta*, vol. 55, no. 17, pp. 4952–4959, Jul. 2010, doi: 10.1016/j.electacta.2010.03.101.
- [20] P. Chithaiah, R. C. Sahoo, J. H. Seok, S. U. Lee, H. S. S. R. Matte, and C. N. R. Rao, “ NbO_2 a Highly Stable, Ultrafast Anode Material for Li- and Na-Ion Batteries,” *ACS Appl. Mater. Interfaces*, vol. 15, no. 39, pp. 45868–45875, Sep. 2023, doi: 10.1021/acsami.3c08694.
- [21] R. J. Gillespie, “Fifty years of the VSEPR model,” *Coord. Chem. Rev.*, vol. 252, no. 12, pp. 1315–1327, 2008, doi: <https://doi.org/10.1016/j.ccr.2007.07.007>.
- [22] J. Suntivich *et al.*, “Estimating Hybridization of Transition Metal and Oxygen States in Perovskites from O K-edge X-ray Absorption Spectroscopy,” *J. Phys. Chem. C*, vol. 118, no. 4, pp. 1856–1863, Jan. 2014, doi: 10.1021/jp410644j.
- [23] M. W. Barsoum, *Fundamentals of Ceramics*, 2nd ed. CRC Press, 2003.

- [24] D. I. Khomskii, *Transition Metal Compounds*. Cambridge: Cambridge University Press, 2014. doi: 10.1017/CBO9781139096782.
- [25] I. D. Johnson *et al.*, “Probing Mg Intercalation in the Tetragonal Tungsten Bronze Framework V₄Nb₁₈O₅₅,” *Inorg. Chem.*, vol. 59, no. 14, pp. 9783–9797, Jul. 2020, doi: 10.1021/acs.inorgchem.0c01013.
- [26] X. Ding, J. Lin, H. Huang, B. Zhao, and X. Xiong, “Competitive Redox Chemistries in Vanadium Niobium Oxide for Ultrafast and Durable Lithium Storage,” *Nano-Micro Lett.*, vol. 15, no. 1, p. 195, Aug. 2023, doi: 10.1007/s40820-023-01172-9.
- [27] E. A. Lawrence *et al.*, “Reversible Electrochemical Lithium Cycling in a Vanadium(IV)- and Niobium(V)-Based Wadsley–Roth Phase,” *Chem. Mater.*, vol. 35, no. 9, pp. 3470–3483, Apr. 2023, doi: 10.1021/acs.chemmater.2c03465.
- [28] H. B. Wedler, P. Wendelboe, and P. P. Power, “Second-Order Jahn–Teller (SOJT) Structural Distortions in Multiply Bonded Higher Main Group Compounds,” *Organometallics*, vol. 37, no. 18, pp. 2929–2936, Sep. 2018, doi: 10.1021/acs.organomet.8b00382.
- [29] D. Spada *et al.*, “FeNb₁₁O₂₉, anode material for high-power lithium-ion batteries: Pseudocapacitance and symmetrisation unravelled with advanced electrochemical and in situ/operando techniques,” *Electrochimica Acta*, vol. 393, p. 139077, Oct. 2021, doi: 10.1016/j.electacta.2021.139077.
- [30] V. Polinger, “Off-center instability of Nb⁵⁺ in KNbO₃ under ambient pressure,” *Chem. Phys.*, vol. 459, pp. 72–80, Sep. 2015, doi: 10.1016/j.chemphys.2015.07.028.

- [31] M. Saber, S. S. Behara, and A. Van der Ven, “Redox Mechanisms, Structural Changes, and Electrochemistry of the Wadsley–Roth $\text{Li}_x\text{TiNb}_2\text{O}_7$ Electrode Material,” *Chem. Mater.*, vol. 35, no. 22, pp. 9657–9668, Nov. 2023, doi: 10.1021/acs.chemmater.3c02003.
- [32] “The experiments and data shown in Figures 4-19 to 4-23 and Table 4-2 were performed by Supriti Dutta at UCLA.”
- [33] P. Villars and K. Cenzual, Eds., “ $\text{VNb}_9\text{O}_{25}$ ($\text{Nb}_9\text{VO}_{25}$ tet1) Crystal Structure: Datasheet from ‘PAULING FILE Multinaries Edition – 2022’ in SpringerMaterials (https://materials.springer.com/isp/crystallographic/docs/sd_1502552).” Springer-Verlag Berlin Heidelberg & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan. [Online]. Available: https://materials.springer.com/isp/crystallographic/docs/sd_1502552
- [34] C. Börrnert, W. Carrillo-Cabrera, P. Simon, and H. Langbein, “ $\text{V}_{2.38}\text{Nb}_{10.7}\text{O}_{32.7}$: A V_2O_5 – Nb_2O_5 mixed oxide tunnel structure related to the tetragonal tungsten bronzes,” *J. Solid State Chem.*, vol. 183, no. 5, pp. 1038–1045, May 2010, doi: 10.1016/j.jssc.2010.02.018.
- [35] C. Keller, “Über ternäre Oxide des Niobs und Tantals vom Typ ABO_4 ,” *Z. Für Anorg. Allg. Chem.*, vol. 318, no. 1–2, pp. 89–106, Sep. 1962, doi: 10.1002/zaac.19623180108.
- [36] T. E. Weirich, “A new paper-based approach for teaching Bragg’s law,” *Acta Crystallogr. Sect. E*, vol. 81, no. 12, pp. 1195–1199, Dec. 2025, doi: 10.1107/S2056989025010576.
- [37] J. Park, S. S. Park, and Y. S. Won, “In situ XRD study of the structural changes of graphite anodes mixed with SiO_x during lithium insertion and extraction in lithium ion

- batteries,” *Electrochimica Acta*, vol. 107, pp. 467–472, Sep. 2013, doi: 10.1016/j.electacta.2013.06.059.
- [38] P. Makuła, M. Pacia, and W. Macyk, “How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra,” *J. Phys. Chem. Lett.*, vol. 9, no. 23, pp. 6814–6817, Dec. 2018, doi: 10.1021/acs.jpcclett.8b02892.
- [39] O. Svitelskiy and J. Toulouse, “Translational and rotational mode coupling in disordered ferroelectric $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ studied by Raman spectroscopy,” *J. Phys. Chem. Solids*, vol. 64, no. 4, pp. 665–676, Apr. 2003, doi: 10.1016/S0022-3697(02)00369-4.
- [40] R. S. Das and Y. K. Agrawal, “Raman spectroscopy: Recent advancements, techniques and applications,” *Vib. Spectrosc.*, vol. 57, no. 2, pp. 163–176, 2011, doi: <https://doi.org/10.1016/j.vibspec.2011.08.003>.
- [41] G. Keresztury, J. Chalmers, and P. Griffith, “Raman spectroscopy: theory,” *Handb. Vib. Spectrosc.*, vol. 1, pp. 71–87, 2002.
- [42] A. J. Bard, L. R. Faulkner, and H. S. White, *Electrochemical Methods: Fundamentals and Applications*. Wiley, 2022. [Online]. Available: <https://books.google.com/books?id=eZ6HDAEACAAJ>
- [43] J. Wang, J. Polleux, J. Lim, and B. Dunn, “Pseudocapacitive Contributions to Electrochemical Energy Storage in TiO_2 (Anatase) Nanoparticles,” *J. Phys. Chem. C*, vol. 111, no. 40, pp. 14925–14931, Sep. 2007, doi: 10.1021/jp074464w.
- [44] F. Marken, A. Neudeck, and A. M. Bond, “Cyclic Voltammetry,” in *Electroanalytical Methods: Guide to Experiments and Applications*, F. Scholz, A. M. Bond, R. G. Compton, D. A. Fiedler, G. Inzelt, H. Kahlert, Š. Komorsky-Lovrić, H. Lohse, M. Lovrić, F. Marken,

- A. Neudeck, U. Retter, F. Scholz, and Z. Stojek, Eds., Berlin, Heidelberg: Springer Berlin Heidelberg, 2010, pp. 57–106. doi: 10.1007/978-3-642-02915-8_4.
- [45] M. Fehse and L. Stievano, “X-ray absorption spectroscopy—a beginner’s guide,” *J. Phys. Energy*, vol. 8, no. 2, p. 023003, 2026.
- [46] J. M. Kasper, T. F. Stetina, A. J. Jenkins, and X. Li, “Ab initio methods for L-edge x-ray absorption spectroscopy,” *Chem. Phys. Rev.*, vol. 1, no. 1, p. 011304, Dec. 2020, doi: 10.1063/5.0029725.
- [47] S. W. Baek, M. Saber, A. Van der Ven, and L. Pilon, “Thermodynamic Analysis and Interpretative Guide to Entropic Potential Measurements of Lithium-Ion Battery Electrodes,” *J. Phys. Chem. C*, vol. 126, no. 14, pp. 6096–6110, Apr. 2022, doi: 10.1021/acs.jpcc.1c10414.
- [48] S. Qian *et al.*, “Rapid and durable electrochemical storage behavior enabled by V₄Nb₁₈O₅₅ beaded nanofibers: a joint theoretical and experimental study,” *J. Mater. Chem. A*, vol. 6, no. 36, pp. 17389–17400, Sep. 2018, doi: 10.1039/c8ta05447a.
- [49] N. Ballarini *et al.*, “Reactivity of V/Nb mixed oxides in the oxidehydrogenation of propane under co-feed and under redox-decoupling conditions,” *4th Int. Symp. Group Five Compd. Bicenten. Meet.*, vol. 78, no. 1, pp. 353–364, Feb. 2003, doi: 10.1016/S0920-5861(02)00303-6.
- [50] J. R. Belnap, “Structural and Electrochemical Characterization of V₇Nb₆O₂₉: A Variation on Wadsley-Roth Phases for Lithium-Ion Battery Electrodes Using Earth-Abundant Metals,” M.S., The University of Utah, United States -- Utah, 2022. [Online]. Available: <https://www.proquest.com/dissertations-theses/structural-electrochemical-characterization-v-sub/docview/2784390967/se-2?accountid=14512>

- [51] “The experiments and analysis shown in Figures 4-3 to 4-7, Figures 4-15 to 4-17, and Table 4-1 were performed by Gugulethu Nkala at SLAC.”
- [52] K. H. Stone, M. R. Cosby, N. A. Strange, V. Thampy, R. C. Walroth, and C. Troxel Jr, “Remote and automated high-throughput powder diffraction measurements enabled by a robotic sample changer at SSRL beamline 2-1,” *J. Appl. Crystallogr.*, vol. 56, no. 5, pp. 1480–1484, Oct. 2023, doi: 10.1107/S1600576723007148.
- [53] “The experiments and analysis shown in Figure 4-18 were performed by Nicolas Leport at UCLA.”
- [54] “The experiments shown in Figures 4-1, 4-8, and 4-13 were partially performed by Andrea Zambotti at UCLA.”
- [55] Y. Zhang, W. Xiong, W. Chen, and Y. Zheng, “Recent Progress on Vanadium Dioxide Nanostructures and Devices: Fabrication, Properties, Applications and Perspectives,” *Nanomaterials*, vol. 11, no. 2, 2021, doi: 10.3390/nano11020338.
- [56] A. A. McConnell, J. S. Aderson, and C. N. R. Rao, “Raman spectra of niobium oxides,” *Spectrochim. Acta Part Mol. Spectrosc.*, vol. 32, no. 5, pp. 1067–1076, Jan. 1976, doi: 10.1016/0584-8539(76)80291-7.
- [57] P. F. Bernath, *Spectra of Atoms and Molecules*, 2nd ed. Oxford University Press, 2005.
- [58] M. Chagnot *et al.*, “Influence of Finite Diffusion on Cation Insertion-Coupled Electron Transfer Kinetics in Thin Film Electrodes,” *J. Electrochem. Soc.*, vol. 171, no. 1, p. 010527, Jan. 2024, doi: 10.1149/1945-7111/ad1d98.
- [59] A. Braun and E. I. Solomon, “Electronic Structure Contributions to the Reactivity of Mononuclear FeIV-Oxo Intermediates,” *Acc. Chem. Res.*, vol. 59, no. 2, pp. 209–220, Dec. 2025, doi: 10.1021/acs.accounts.5c00655.

- [60] C. Cartier, T. Hammouda, M. Boyet, O. Mathon, D. Testemale, and B. N. Moine, “Evidence for Nb²⁺ and Ta³⁺ in silicate melts under highly reducing conditions: A XANES study,” *Am. Mineral.*, vol. 100, no. 10, pp. 2152–2158, 2015, doi: doi:10.2138/am-2015-5330.
- [61] E. J. Zuras, F. Fauth, G. Rousse, and A. Grimaud, “Investigating Lithium Ordering and Electronic Evolutions in Wadsley–Roth Phases,” *J. Phys. Chem. C*, vol. 129, no. 7, pp. 3446–3456, Feb. 2025, doi: 10.1021/acs.jpcc.4c08417.
- [62] N. V. Korovina *et al.*, “Singlet Fission in a Covalently Linked Cofacial Alkynyltetracene Dimer,” *J. Am. Chem. Soc.*, vol. 138, no. 2, pp. 617–627, Dec. 2015, doi: 10.1021/jacs.5b10550.