

Article

Topochemical stabilization and single-crystal transformations of a metastable 2D γ' -V₂O₅ intercalation cathode

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SUMMARY (150 words max)

The atomistic design of positive electrode materials requires understanding of (i) how guest cations diffuse through an intercalation host to fill empty interstices and (ii) the distortions of the host lattice induced as a result of ion intercalation. Here, we report the use of topochemistry to access single-crystals of a metastable 2D van der Waals solid, γ' -V₂O₅, and examine its single-crystal-to-single-crystal transformations upon lithiation up to γ -LiV₂O₅. High-resolution single-crystal diffraction provides an atomistic view of preferred interstitial sites occupied by Li ions and distortions of the 2D lattice in an extended solid-solution lithiation regime, which stands in stark contrast to the thermodynamic α -V₂O₅ phase. These results illustrate the potential of metastable compounds with reconfigured atomic connectivity to unlock lithiation pathways and mechanisms that are profoundly different from their thermodynamic counterparts. The study furthermore demonstrates the viability of combining topochemical modification with single-crystal diffraction to image intercalation phenomena with atomic resolution.

Keywords: Intercalation Chemistry, Energy Storage, Topochemistry, Cathodes, 2D materials, Diffusion Pathways, Single-crystal-to-single-crystal

INTRODUCTION

In Li ion batteries that are the mainstay of modern electrochemical energy storage, Li ions are intercalated and de-intercalated from transition metal oxide cathodes during discharging and charging of the battery.^{1,2} The insertion of Li ions within interstitial sites is key to accessing the redox capacity of transition metals (and for ensuring that redox reactions are not just limited to surfaces).^{3–5} Li ion insertion inevitably perturbs the structure of the host lattice; in some cases (e.g., LiCoO₂),⁶ the inserted ions are accommodated through extended solid-solution regimes wherein interstitial sites are sequentially filled while essentially preserving the host crystal lattice. In other cases (e.g., LiFePO₄ and α -V₂O₅)^{7,8} lithiation triggers a series of

The bigger picture (1000 characters max)

The ability to grow proteins as single crystals paved the way to the determination of high-resolution structures, enabling the design of targeted approaches to modulate protein function. In intercalation electrodes used in energy storage, the insertion of cations and their transport through the crystal lattice brings about a dynamical modulation of structure that remains poorly understood. Much present knowledge of diffusion pathways is derived from mapping of lithiation inhomogeneities using electron and X-ray microscopy at larger length scales (yielding particle- and electrode-level information), ensemble nuclear magnetic resonance spectroscopy studies of local ion dynamics, or rely on density functional theory calculations (prone to substantial inaccuracies for strongly correlated systems). We demonstrate here *single crystal intercalation chemistry* wherein

structural phase transformations.^{9–11} Deciphering lithiation mechanisms, the specific interstitial sites occupied by Li ions, lithiation-induced modification(s) of the crystal structure of the host lattice, and the coupling of Li ion diffusion to specific phonon modes¹² is of pivotal importance to materials design and for tuning the thermodynamics and kinetics of ion insertion.¹³ In particular, atomistic design of electrode materials requires a clear understanding of (i) how guest cations diffuse through the structure to fill empty available interstices; and (ii) the long-range transformations that intercalating ions induce in the host lattice away from equilibrium. In this article, we use single-crystal-to-single-crystal transformations to first stabilize a metastable van der Waals bonded γ' -V₂O₅ phase, and then to topochemically insert Li ions at various stoichiometries between the layers up to a stoichiometry of γ -LiV₂O₅. We thus obtain high-resolution crystallographic “snapshots” with Ångstrom resolution depicting Li-ions located not just at the most stable interstitial sites but traversing diffusion pathways between these sites.

Diffusion pathways traversed by cations in electrodes have been mapped at relatively coarse mesoscale levels using electron and X-ray microscopy and have illuminated the role of particle morphologies and interconnectivity.¹⁴ Ensemble nuclear magnetic resonance spectroscopy studies have provided insights into local ion dynamics.¹⁵ However, with the exception of a few studies combining X-ray and neutron diffraction to locate cation sites,^{16–18} the dynamical modulation of the structure of intercalation hosts upon lithiation remains poorly understood. Much of our current knowledge comes from first-principles density functional theory calculations, which are prone to substantial inaccuracies for strongly correlated systems and often do not precisely capture entropic contributions to site preferences and structure types. Single-crystal diffraction holds promise for high-resolution structure solutions that identify the site preferences of inserted cations with atomic resolution,¹⁹ but has seldom been applied to electrode materials given challenges in growing macroscopic single-crystals and achieving topochemical ion insertion in a manner that mimics the ‘far-from-equilibrium’ processes operational within a battery. In this article, we demonstrate the stabilization of single-crystals of γ' -V₂O₅, a metastable V₂O₅ polymorph comprising stacked 2D puckered sheets held together by van der Waals interactions. While electrochemical cycling of γ' -V₂O₅ powders has been previously investigated,^{20–22} this represents the first success with stabilizing single crystals, which enables atomic resolution mapping of individual metastable crystal domains, investigation of site preferences and mapping of diffuse electron density reflecting diffusion pathways at discrete stages of Li ion intercalation, while simultaneously tracking intercalation-induced periodic distortions of the lattice structure of the intercalation host again with Ångstrom resolution. Unlike powder XRD methods that have been indexed on the basis of 10–20 reflections, the 17,000+ reflections in single-crystal X-ray diffraction allow for unambiguous identification of Li sites with spatial resolution down to 0.77 Å.

Metastable polymorphs with atomic connectivity substantially reconfigured from thermodynamic minima provide a rich diversity of structures and chemical bonding motifs.^{23–25} From the perspective of energy storage, such compounds afford opportunities for tuning ion transport through reconfiguration of diffusion pathways, for instance, confining cations within frustrated coordination environments.^{8,26} 2D van der Waals materials provide a vast palette for exploring metastable configurations given their relatively shallow potential energy surfaces and low barriers to restacking, exfoliation, and twisting.^{27–29} Such compounds provide a diverse range of diffusion pathways, an abundance of interstitial sites arrayed between layers, limited distortion of the host structure upon intercalation/deintercalation of Li ions, and opportunities to engineer van der Waals heterostructures.^{30–33} In this work, we report the stabilization of single-crystals of a 2D metastable γ' -V₂O₅ phase and explore its single-crystal transformations at multiple stages of Li ion intercalation, enabling delineation of high-resolution electron density maps of cation occupancies during layer filling.

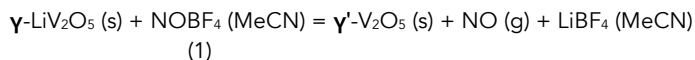
Single-crystal topochemical transformations performed using chemical lithiation reagents at room temperature provide a view of sites occupied by inserted cations that capture ‘out-of-equilibrium’ processes not accessible from ternary crystals ($\text{Li}_x\text{V}_2\text{O}_5$) prepared by direct synthesis wherein due to high synthesis temperatures, intercalated cations are able to locate within lowest energy sites.³⁴

RESULTS AND DISCUSSION

Single-Crystals of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ are Topochemically Delithiated and Lithiated in Sequence

Single-crystals of $\gamma\text{-LiV}_2\text{O}_5$ were synthesized as described in the Experimental section. **Figure 1** tracks the results of single-crystal delithiation and lithiation in the $\text{Li}-\gamma\text{-V}_2\text{O}_5$ system, with accompanying digital photographs of crystals (Figure 1A—E, F, top row); atomic structures delineating unit cell boundaries (Figure 1A—E, middle row); and a plot of lattice parameters and unit cell volume as a function of Li stoichiometry (Figure 1A—E, bottom row). These parameters as well as other crystallographic and topochemical information are also presented in **Table S1** in the Supporting Information.

Figure 1A shows optical images of the lustrous black crystals of $\gamma\text{-LiV}_2\text{O}_5$ (Structure A) with approximately rectangular cross-sections alongside the crystal structure viewed down the *b*-axis. Slow topochemical delithiation of $\gamma\text{-LiV}_2\text{O}_5$ was accomplished by treatment with NOBF_4 as per:



Leached single-crystals of $\gamma'\text{-V}_2\text{O}_5$ (Structure B) retain excellent crystallinity and exhibit almost complete de-lithiation for small crystals ($<300\text{ }\mu\text{m}$). The completeness of the leaching process is indicated by the transformation to a translucent yellow appearance caused by oxidation of V^{4+} to V^{5+} (**Figure 1B**, top panel); the total absence of electron density corresponding to Li atoms in the structure refined from high-resolution single-crystal XRD (Figure 1B, middle panel); and the substantial distortion of lattice parameters and diminution in unit cell volume (**Figure 1B**, lower panel). ICP-MS results acquired for an ensemble of crystals is shown in Table S22. The top-right panel of Figure 1B shows a low-magnification image of an ensemble of larger crystals, which are characterized by a variously dappled or striped appearance—dark regions in the otherwise bright-yellow crystals correspond to remnant $\text{Li}_x\text{V}_2\text{O}_5$ phases; the residual lithium content derives from incomplete leaching of Li ions from the centers of the largest crystalline domains owing to the extremely long diffusion path lengths. Such inhomogeneities and slow diffusion kinetics also induce strain gradients that account for the substantial cracking of the largest crystals. Inhomogeneous phase boundaries and diffusion-derived strain gradients are an inherent challenge facing effective single-crystal-to-single-crystal transformations.^{35–37} Further topochemical transformations have been performed for homogeneously deintercalated small ($<300\text{ }\mu\text{m}$) single-crystals of $\gamma'\text{-V}_2\text{O}_5$.

While the structure of $\gamma'\text{-V}_2\text{O}_5$ has previously been inferred from Rietveld refinement of powder X-ray diffraction patterns,³⁸ this is the first report of the isolation of metastable $\gamma'\text{-V}_2\text{O}_5$ in the form of single-crystals (shown in **Figure 1B**). Based on high-resolution structure solutions, the unit cell volume is substantially decreased from $370.1\text{ }\text{\AA}^3$ to $354.4\text{ }\text{\AA}^3$, a 4.2% reduction in volume, upon delithiation of $\gamma\text{-LiV}_2\text{O}_5$ to stabilize metastable $\gamma'\text{-V}_2\text{O}_5$. This loss can be entirely attributed to the removal of Li atoms from the galleries between the layers and the subsequent shrinkage along the *c*-axis to reduce void space. A minor expansion (2.4%) is observed along the *a*-direction as the layers of VO_5 square pyramids “un-buckle”. The decrease of unit cell volume despite the small increase in the *a* parameter is a direct consequence of the

2D nature of the structure, which in the absence of Li ions is held together primarily by van der Waals interactions. **Figure 2** contrasts the thermodynamically stable polymorph, orthorhombic α -V₂O₅ (panel A) with that of the metastable γ' -V₂O₅ (panel B).

Structural Distortions in Stable and Metastable Layered V₂O₅ are Calculated from High-resolution Single-Crystal XRD

Owing to the symmetry of the unit cell and configuration of VO₅ polyhedra, γ' -V₂O₅ contains two crystallographically distinct vanadium sites, whereas α -V₂O₅ contains a singular vanadium site. The average separation between extended layer centroids is shown with a dashed blue line in **Figure 2**; this value is equivalent to the length of the *c* lattice parameter in α -V₂O₅, and *c*/2 in γ' -V₂O₅ and γ -LiV₂O₅. **Figure 2E** tracks the expansion of this metric for interlayer separation across a selection of polymorphs, which stretches from 4.342Å in α -V₂O₅ to 4.996Å in γ' -V₂O₅ (Structure B), and continues to expand with topochemical Li ion insertion between layers to 5.243Å in γ -Li_{0.5}V₂O₅ (Structure D) and 5.325Å in γ -Li_{1.0}V₂O₅ (Structure E). The shortest inter-layer V—O distance in γ -LiV₂O₅ (Structures A and E) is 3.053Å (shown as a red dashed line in Figure 2A—D). The equivalent bond in the fully delithiated Structure B shrinks to 2.692Å, which is almost short enough to constitute a quasi-octahedral arrangement around this V atom, corner-sharing with the opposite-facing square pyramid; and is even shorter than the quasi-octahedral bond distance in α -V₂O₅, which is 2.753Å. For reference, 2.5Å is “long” for a true V—O bond, with an upper limit estimated to be 2.7Å.³⁹ AFM analysis of a crystal of exfoliated γ' -V₂O₅ is shown in **Figure 1G**. **Figure 3A** shows the results of cleavage energies calculated from density functional theory (DFT) in order to contextualize the interlayer binding forces of the metastable γ' -V₂O₅ phase in comparison to the thermodynamic α -V₂O₅ polymorph, and to graphene, a model van der Waals solid, that both similarly undergo Li intercalation phenomena. The energy required to cleave layers of γ' -V₂O₅ to an interlayer separation of 10Å from a starting interlayer separation of 4.996Å is 0.1035 J/m², which is significantly lower as compared to the corresponding value of 0.2076 J/m² for α -V₂O₅; both values are notably lower than the cleavage energy required to separate individual graphene layers from graphite (0.3405 J/m²) calculated using the same exchange-correlation functional and van der Waals correction). This substantial reduction in cleavage energy relative to other layered insertion materials highlights the capacity for topochemically-accessed metastable materials with emptied layers to have substantially lower activation energies for mechanical cleavage as well as diffusion and for creation of stacked van der Waals heterostructures with precisely tunable diffusion pathways.

The relatively slow transformation kinetics in single-crystals, owing to their large diffusion path lengths relative to powders and nanomaterials,^{14,19} provides the opportunity to isolate metastable structures at intermediate lithiations whose structure can be difficult to resolve from *operando* powder XRD experiments; in the case of γ' -V₂O₅, only lattice trends have been examined and scarce little is known about atom positions and site occupancies.^{19,20,22} We have used topochemical transformations of γ' -V₂O₅ single-crystals to access two intermediate γ -Li_xV₂O₅ phases (Figs. 1C and D) as well as a “filled” γ -LiV₂O₅ phase (Fig. 1E), herein referred to as Structures C, D, and E, respectively. High-resolution structures provide a detailed perspective of the site preferences of Li ions and the concomitant distortion of the γ' -V₂O₅ square pyramids. We observe that the space group and atomic positions in the unit cell remain identical, and only the Li atomic occupancy and lattice parameters are modulated in tandem (traced in Figure 1A—E). The unit cell volume is increased to 363.5Å³ in Structure C at 0.41 Li, then to 367.9Å³ in Structure D at 0.50 Li. With lithiation, O—Li—O bridges become the principle means of connectivity across layers; the shortest interlayer V—O distance in Structure D stretches to 2.971Å (Fig. 2C). The angle of “puckering” across the V1 and V2 square pyramids becomes more

acute with increasing lithiation (and subsequent shrinkage of the *a*-axis). The puckering angle changes dramatically from 120.1° to 118.1° to 114.9° with increasing lithiation from γ -V₂O₅ to γ -Li_{0.50}V₂O₅ to γ -LiV₂O₅, respectively (Figure 1, Structures B, D, and E). This trend is shown in Figure 2E in comparison to the essentially unpuckered α -V₂O₅ structure, where the angle across corner-sharing square pyramids is almost exactly 180°.

During lithiation, the Li ions that are inserted between V₂O₅ layers are observed in all measured crystals to occupy a single 6-coordinate insertion site within the structure. Both Structure C (~41% Li occupancy) and Structure D (~50% Li occupancy) refined to the same *Pnma* unit cell as the empty (Structure B) and filled (Structures A and E) structures, with a random distribution of Li modeled as partial occupancy at the six-coordinated interlayer site, which we will refer to as the “A” site for Li ions in the structure. The favorability of randomly-distributed Li in the structure is reflective of the strong energetic preference for this 6-coordinated site (as shown in Figure 3). A second putative “B” site with tetrahedral coordination in a plausible intermediate position has been derived from the electron density map of Structure C (shown in Figure 4) where fewer than half of A-sites are occupied, and its energetics relative to a structure where only A-sites are occupied have been calculated with DFT (Figure 3B).

DFT Elucidates Energies for Layer Cleavage, Site Occupancy, and Ion-by-Ion Filling Configurations

Using the partial atomic occupancy data provided by single-crystal experiments as a basis, DFT calculations have also been performed to understand the evident preference for random site-filling over ordering phenomena such as staging, and glean further insight into local perturbations induced by individual Li-ions given that the single crystal structure solution represents an averaged view of an entire domain that has been trapped outside of thermodynamic equilibrium and may be undergoing dynamic effects at the local level. The energetics of layer-by-layer site-filling in a relaxed superstructure of the γ -V₂O₅ lattice, shown in Figure 3C, is analyzed in comparison to more disordered configuration of lattice occupancies. The configurations that correspond to an ordered staging phenomenon, where alternating layers are filled preferentially, are represented by configurations 8 and 9 for γ -Li_{0.25}V₂O₅, 12 and 13 for γ -Li_{0.375}V₂O₅, and 17 for γ -Li_{0.5}V₂O₅. Disordered configurations were found in all cases to be energetically similar or more favorable at each stoichiometry. These results corroborate well with ensemble crystallographic data (Figure 1) that by contrast give an average view of the overall crystal domain at each extent of lithiation, and are consistent with a preference for random Li distribution across local environments. These results further reflect that maintaining optimal separation of inserted Li ions (and accompanying local structure perturbations) is energetically more preferable as compared to a configuration with alternating distorted and undistorted layers as would be expected from stage ordering and superlattice formation. Upon lithiation, as also shown in Figures 2C and D, the Li-O bonds transform the 2D lattice to a 3D interconnected structure.

DFT has also been used to analyze the energetic preference of the tetrahedral “B” site identified from the high-resolution electron density map of Structure C. The observation of this site only in the γ -Li_{0.41}V₂O₅ structure and its relatively minor contribution to the total electron density compared to the stable six-coordinate A-site, suggests that it is an intermediate position that is filled transiently by Li-ions diffusing through the open *ab* plane of the structure to fill A-sites, which are very stable relative to an empty structure (Figure 3C). DFT calculations performed on relaxed unit cells where a single B-site is occupied support this hypothesis: Figure 3B shows the energy of unit cells containing one filled B-site, relative to unit cells of the same total Li-content containing only filled A-sites at adjacent positions. At very low levels of lithiation, when nearly all A-sites are empty and diffusion can be

expected to be highest, an occupied B-site is slightly preferred (by about 78 meV/unit cell), and this slight preference is maintained when some, but not all adjacent A-sites are filled (slightly less stable, at about 26 meV/unit cell relative to an A-only structure). Such an “intermediate” structure, where some-but-not-all A-sites are filled and the B-site is very slightly stabilized, corresponds well to Structure C from which the B-site is experimentally derived (shown in detail in **Figure 4**). When all adjacent A-sites are filled however, necessarily closing off potential diffusion routes and corresponding to a structure with total Li occupancy of 0.5, the B-site ceases to be favored and instead corresponds to a higher energy unit cell by nearly 140 meV; and correspondingly, an electron density peak is not observed at this position in Structure D. The observation of the B-site only in the intermediately-lithiated crystal highlights the potential for high-resolution diffraction of metastable crystals to provide insights into preferred diffusion pathways that may not be observable in equilibrium structures.

Treatment of γ -V₂O₅ single-crystals with 1.0 molar equivalents of *n*-BuLi effects a virtually perfect return of the crystal structure to that of the precursor material prepared using solid-state reaction conditions. The pristine Structure A exhibits a solved unit cell volume of 370.11 Å³ at 110K, while the fully re-lithiated Structure E has a nearly identical unit cell volume of 370.15 Å³. The similarity between Structure A and Structure E is further reflected in the values of the refined Li site occupancies; the final occupancy of Li at the A-site in both structures is best refined at 100%. The transformations described here thus represent a complete topochemical “cycling” of the material from full occupancy in crystals of Structure A, to zero occupancy in crystals of Structure B, and finally back to full occupancy in crystals of Structure E. The absence of irreversible structural changes or indicators of topochemical deformation by high-resolution XRD reflects the thermodynamic stability of the fully-lithiated γ -LiV₂O₅ structure and the robustness of the γ -V₂O₅ framework.

Notably, previous studies have shown that the γ -Li_xV₂O₅ phase is characterized by a much wider solid solution region than demonstrated here (0.0 < x < 2.0) before it is irreversibly transformed to the amorphous quasi-rock salt structured ω -phase.^{40,41} However, attempts to lithiate large single crystals of γ -V₂O₅ beyond x = 1 in Li_xV₂O₅ resulted in cracking and exfoliation of the crystals in a distinctive, accordion-like fashion as shown in Figure 1F. Due to the observed decrease in crystal quality at these high levels of lithiation, it is no longer possible to obtain single-crystal XRD. Since at x = 1 the lowest energy Li ion sites are shown to be fully occupied, additional higher energy sites are necessarily occupied at x > 1. The filling of these additional sites likely drives an intercalation-induced structural transformation that contributes to the total loss of crystal integrity.

A “Lithium’s-Eye View” of the 2D Layered γ -V₂O₅ Structure

At intermediate extents of lithiation (Structures C and D), the highly-resolved view provided by single-crystal XRD also allows for analysis of the F_o - F_c structure-factor maps for peaks and troughs of electron density, further providing insights into the diffusion behavior of topochemically inserted Li ions at resolutions entirely unattainable from powder XRD. The residual electron density map for Structure C, which has a comparatively low average Li content of about 0.4 Li per V₂O₅, includes a peak at an intermediate site located between principle six-coordinated “A” sites. While too small and diffuse a region of electron density to refine stably as a partially-occupied Li site, its position at a four-coordinate tetrahedral position correlates with previous DFT calculations that predicted a 4-coordinate intermediate between stable 6-coordinate sites; the electron density distribution thus indicates low-energy diffusion proceeding along an octahedral—tetrahedral—octahedral pathway.^{23,42} **Figure 4** shows the structure-factor map (positive residual indicated by a green mesh) in this crystallographic region in relation to the surrounding V₂O₅ framework and partially-occupied A-sites in Structure C. Notably, this peak also resides in the main void space between A-sites along both *b*- and *a*-

axes, suggesting that two-dimensional diffusion within the *ab*-plane is plausible in the γ' -V₂O₅ structure. Furthermore, DFT-calculated energies shown in **Figure 3B** confirm that this position is stabilized by ca. 20–80 meV at low total occupancies by empty adjacent A-sites when diffusion between void spaces to fill available interstices is most favorable. In another metastable polymorph, ζ -V₂O₅, Li ions are accommodated in a plethora of adjacent intercalation sites with closely spaced energetics and a substantial amount of diffuse electron density is observed in intermediate positions.¹⁹

In stark contrast, the vast majority of Li electron density in γ' -V₂O₅ is concentrated at the single 6-coordinated A-site, even at intermediate extents of lithiation. This is likely due to the ease of diffusion between these stable sites, which thus gives rise to an extended solid-solution intercalation regime from $x = 0$ –1 in Li_xV₂O₅. The openness of the layered γ' -V₂O₅ structure (highlighted in **Figure 4**) allows comparatively easy hopping between thermodynamically stable insertion sites without the cations dwelling for long in intermediate positions. It is worth noting that γ' -V₂O₅ is metastable; however, being only ca. 6 meV above hull as compared to α -V₂O₅,²⁹ it is within the range accessible at finite temperatures $k_B T$ and thus can be stabilized under ambient conditions; albeit only indirectly via topochemical routes.⁴³ DFT calculations show that the total energy of γ' -V₂O₅ is 0.36 eV/f.u. greater as compared to α -V₂O₅ (Fig. 3A). However, the fully-lithiated γ -LiV₂O₅ structure is the thermodynamic minimum in the phase diagram for the Li-V-O system at these stoichiometries. This explains the seamless transformation of single-crystals in this study back to the fully-lithiated γ -LiV₂O₅ phase and the extended solid-solution intercalation mechanism with relatively minor lattice distortions at each point of lithiation.

The results demonstrate that unlike its thermodynamically stable counterpart α -V₂O₅, which is a canonical phase-separating material,⁸ intercalated Li ions are accommodated in γ' -V₂O₅ through a solid-solution mechanism across an extended range of lithiation. The mechanism is furthermore quite distinct from another metastable polymorph, 1D tunnel-structured ζ -V₂O₅, where increasing concentrations of Li ions are accommodated through extensive cation reordering and the sequential occupancy of interstitial sites.²⁹

Conclusions

Topochemically modifying single-crystals of γ -LiV₂O₅ has allowed us to stabilize single-crystals of a 2D metastable polymorph of V₂O₅. The van der Waals solid comprises stacked layers of highly puckered V₂O₅ with up–down–up–down orientations of edge- and corner-sharing VO₅ square pyramids that fold and unfold at angles ranging from 114.9°–120.1° as a function of lithiation. The layered structure defines a vast abundance of interlayer interstitial sites that can accommodate Li ions. Single-crystal-to-single-crystal topochemical transformations have been realized at a series of points across the Li-V₂O₅ phase diagram, enabling the use of single-crystal X-ray diffraction to elucidate the site preferences of inserted Li ions and the accompanying lattice distortion at Ångström resolution. The open structure of the γ' -V₂O₅ intercalation host allows for continuous Li ion diffusion into highly-stable octahedral sites with random distribution suggesting a solid-solution lithiation mechanism from $x = 0$ to at least 1 in Li_xV₂O₅. A six-coordinated site is found to be strongly energetically favored across this range and is fully occupied in γ -LiV₂O₅; further lithiation brings about structural transformations that shear the layers with respect to each other resulting in exfoliation into accordion-like morphologies. Electron density maps indicate a tetrahedral position at a plausible intermediate site between 6-coordinated sites, supporting facile pathways for Li ion diffusion available across the *ab*-plane, and DFT calculations confirm that this position is slightly stabilized on the order of 100 meV/unit cell at low levels of total lithiation when adjacent A-sites are empty and diffusion between these low-lying A-sites is most

energetically favorable. The continuity of site-occupancy changes, minimal structural distortion, and the complete reversibility of transformation in the layered Υ -V₂O₅ structure stands in contrast to the series of intercalation-induced transformations required to accommodate Li ions in the thermodynamically stable polymorph, α -V₂O₅, and the extensive cation-reordering mechanism observed in 1D tunnel-structured ζ -V₂O₅. This comparison highlights the potential advantages of open 2D polymorphs in rendering accessible extensive solid-solution ranges, as required for reducing phase separation, non-uniform stress gradients, and enabling high-rate electrochemistry.^{14,44} More generally, the results illustrate the potential of metastable compounds with reconfigured atomic connectivity to unlock lithiation pathways and mechanisms that are profoundly different from their thermodynamic counterparts. In providing an atomistic view of the layered orthorhombic Υ -V₂O₅ system, this study also demonstrates the viability of combining topochemistry with single-crystal XRD in order to image intercalation phenomena at atomic resolution. These results in conjunction with mapping of Li-ion diffusion pathways in ζ -V₂O₅ with a substantially different structural motif and pattern of extended atomic connectivity,¹⁹ illustrates the generalizability of this approach. Topochemical transformations of large single crystals are particularly relevant to rigid extended frameworks, crystal lattices exhibiting high Li-ion diffusivity, and lattices that undergo relatively modest structural distortions upon insertion of guest cations. Powders of intercalation compounds with a variety of chemical and structural compositions have been long known to be amenable to cation insertion by topochemical reagents;⁴⁵ to the extent that any species can be isolated as large high-quality single-crystals, then, it is likely that transformations of the sort discussed herein may be effected under reaction conditions that favor insertion/removal over reconstitution and are slow enough so as to develop large stress gradients inevitably introduced across extremely long diffusion paths. Achieving topochemical single-crystal-to-single-crystal transformations to generalize the applicability of this method thus requires (1) availability of high-quality single crystals; (2) identifying conditions wherein insertion or leaching reactions are strongly preferred over dissolution/recrystallization or oxygen evolution; and (3) careful control of Li diffusion kinetics across millimeter-sized dimensions to ensure structural integrity of the single crystals as they undergo lattice expansion and contraction. Given the great diversity of polymorphs within the V₂O₅ family and other transition metal oxide systems, we expect that topochemical routes for the modification of large single-crystals will provide a means of atomic scale mapping of diffusion pathways and structural transformations in intercalation materials.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Sarbajit Banerjee (banerjee@chem.tamu.edu).

Materials availability

All materials generated in this study are available from the lead contact.

Data and code availability

The crystallographic information files (CIF files) generated by the refinements of all structures in this study and including structure factors have been deposited in the Cambridge Structural Database and are available for access with deposition numbers 2084509, 2084510, 2084511, 2084512, and 2084513 for Structures A, B, C, D, and E, respectively.

γ -LiV₂O₅ was first synthesized as a powder using a solvothermal process. Stoichiometric amounts of LiOH (Sigma Aldrich, 98%) and V₂O₅ (Sigma Aldrich, 99.6%) and 86 mL of EtOH were added to a PTFE-lined stainless steel autoclave (Parr, 125 ml capacity) and allowed to react for 72 h at 210°C. The resulting black powder was filtered and allowed to dry under air overnight. The powder was ground and further annealed at 600°C in a tube furnace under a flow of Ar gas for 12 h to remove any residual moisture. The as-obtained powder was shown to be phase-pure by powder X-ray diffraction. To obtain large crystals, powder γ -LiV₂O₅ product was ball-milled again, sealed in quartz ampoules under vacuum, and then melted at 800°C and cooled at a rate of 2°C/h in a programmable furnace (Thermo Scientific, Lindberg Blue M with UT150 controller) to obtain large, lustrous black block-shaped single crystals.

It is important to note that under the synthetic conditions used to obtain the powder samples, γ -LiV₂O₅ is observed to be the only stable phase. Despite the mixture of phases in the melt, the large single crystals measured were observed to be phase-pure γ -LiV₂O₅. Topochemical de-intercalation of Li-ions to access crystals of γ' -V₂O₅ was effected by treating them with 1.5M equivalents of NOBF₄ (Alfa Aesar, 98%) in dry acetonitrile (ca. 0.01M solution) for 24 h. The leaching of Li ions and corresponding oxidation of tetravalent vanadium to pentavalent vanadium caused a drastic change in appearance from lustrous black to translucent yellow (**Figure 1**); cracks are observed along the blocks in a layer-like habit, reflecting the 2D nature of the V₂O₅ structure.

Topochemical lithiation was performed by treating 50 mg of γ' -V₂O₅ crystals with 0.25, 0.50, and 1.0 molar equivalents of LiI (Alfa Aesar, 99%) dissolved in acetonitrile (results of ICP-MS elemental analyses are shown in Table S22 of the supporting information). Small differences between Li content in individual measured crystals and average Li content in bulk samples measured by ICP-MS suggest some inhomogeneity across crystal domains, likely due to variety in diffusion path lengths; however, it should be noted that each solved crystal structure reported in this study corresponds to a single domain at each Li content. DFT calculations of various possible site-filling regimes shown in **Figure 3** support the notion that a given crystal domain at each total lithiation corresponds to a disordered solid-solution regime.

At molar ratios above 1.0 Li per V₂O₅, large cracks appear within the crystals, which are fractured into accordion-like morphologies (highlighted in the optical images in Figure 1). Beyond this point there was substantial loss of diffraction intensity and severe twinning during attempts to collect further single-crystal structures. The γ' -V₂O₅ single crystals were also mechanically exfoliated onto a clean silicon wafer by the classical scotch tape method. The resulting extremely thin 2D flakes were characterized by tapping mode AFM with a silicon cantilever (AC240TS-R3, nominal spring constant 2 N/m) using an MFP-3D Infinity AFM instrument (Asylum Research, an Oxford Instrument Company, CA).

Single-crystal diffraction data was collected on a BRUKER Quest X-ray diffractometer utilizing the APEX3 software suite, with X-Ray radiation generated from a Mo- λ ps X-ray tube (K_{α} = 0.71073Å). All crystals were placed in a cold N₂ stream maintained at 110K. Following unit cell determination, extended data collection was performed using omega and phi scans. Data reduction, integration of frames, merging, and scaling were performed with the program APEX3, and absorption correction was performed utilizing the program SADABS.^{46,47} Structures were solved using intrinsic phasing, and least-squares refinement for all structures was carried out on F^2 . Structural refinement, the calculation of derived results, and generation of electron density maps were performed using the SHELXTL package of computer programs, ShelXle, and Olex2.⁴⁸⁻⁵⁰ Crystallographic Information Files pertaining to structures used in this study have been deposited in the Cambridge Structural Database and are available for access with deposition numbers 2084509, 2084510,

2084511, 2084512, and 2084513 for Structures A, B, C, D, and E, respectively. The atomic labeling scheme used for structures in this study is shown in **Figure S1** in the Supporting Information; and crystallographic and refinement information is listed in **Tables S2—S21** in the Supporting Information.

Total energies of relaxed atomistic structures were calculated using first-principles DFT,^{51,52} as implemented in the Vienna ab initio simulation package (VASP). The exchange-correlation energy functional was modeled using the GGA with the Perdew-Burke-Ernzerhof (PBE) form.⁵³ Considering the strongly correlated 3d electrons of vanadium, a Hubbard parameter U was applied to the PBE functional in the approach proposed by Dudarev et al.,⁵⁴ with $U_{\text{eff}} = 3.0$ eV and D3 van der Waals corrections utilized. Atomic structures were derived from the refined CIF files obtained from single-crystal X-ray diffraction and comprised a $1 \times 1 \times 2$ supercell containing 4 layers, and were fully relaxed. In the cleavage energy calculation, the bulk layered materials (V_2O_5 and graphite) are gradually separated by inserting additional interlayer distance in the van der Waals gap at the middle of the cell. The atomic positions are fully relaxed, while keeping the total cell length along the normal direction of the van der Waals plane fixed. Periodic boundary conditions are applied as the van der Waals gap is located at the middle of the cell, and at the cell boundary the system is treated periodically. To understand the energetically preferred site for Li in layered V_2O_5 , DFT total energy calculations have been performed for different configurations with Li at different interstitial sites. Specifically, a supercell of $1 \times 1 \times 2$ atoms with 4 atomic layers was examined the model a low Li-ion intercalation scenario. Total energies were calculated with the periodic boundary condition, at a specific Li concentration, to represent the infinite V_2O_5 crystal with a certain amount of Li atoms intercalated in practice. In this case, the supercell is also treated periodically to model alternating intercalation patterns.

SUPPLEMENTAL INFORMATION

Document S1, containing Figure S1 and Tables S1—S22, consisting of atomic labeling scheme details, crystal structure topochemical synthesis and refinement information, selected atomic and bond data, and ICP-MS information.

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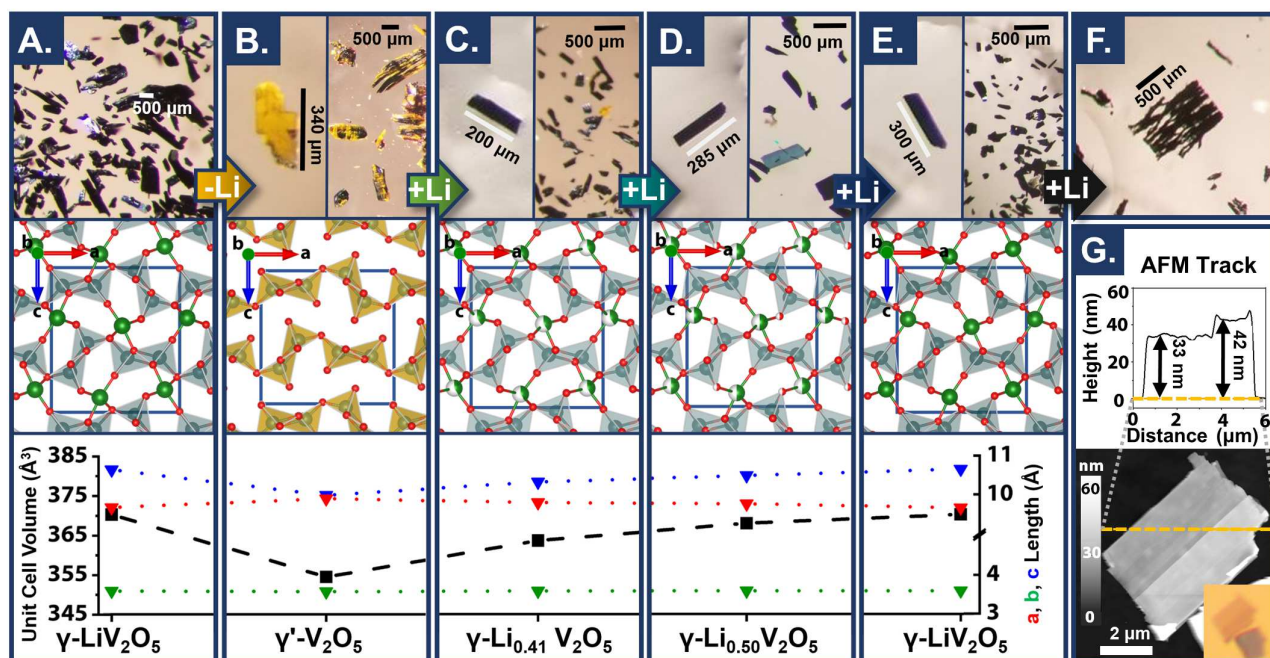
AUTHOR CONTRIBUTIONS

J.V.H.: Conceptualization, methodology, investigation, writing- draft preparation and editing, visualization. J.L.A.: Conceptualization, methodology, investigation, writing-draft preparation. B.Z.: Software, formal analysis, investigation. D.K.: Investigation. N.B.: Validation. Q.T.: Supervision, funding acquisition. X.Q.: Supervision. S.B.: Supervision, funding acquisition, project administration, writing- reviewing and editing.

DECLARATION OF INTERESTS

The authors declare no competing interests.

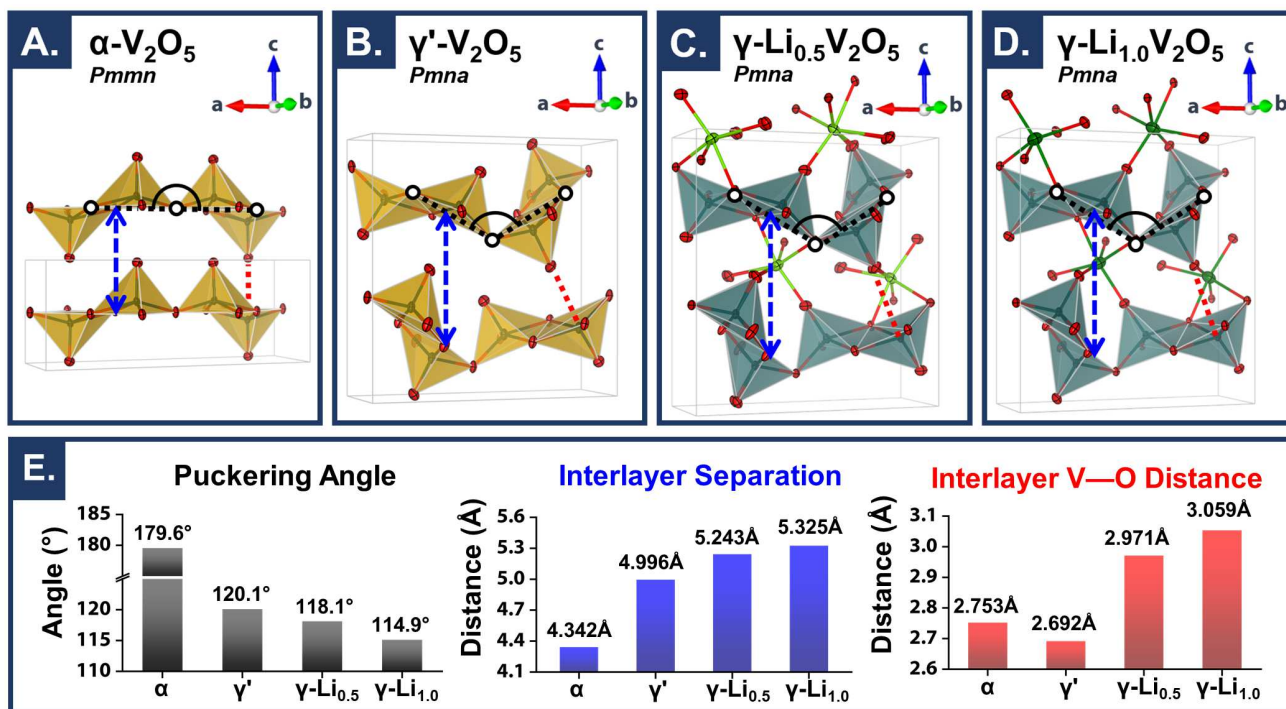
Figure 1. Sequence of Topochemical Delithiation and Lithiation in Single-



Crystals of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$.

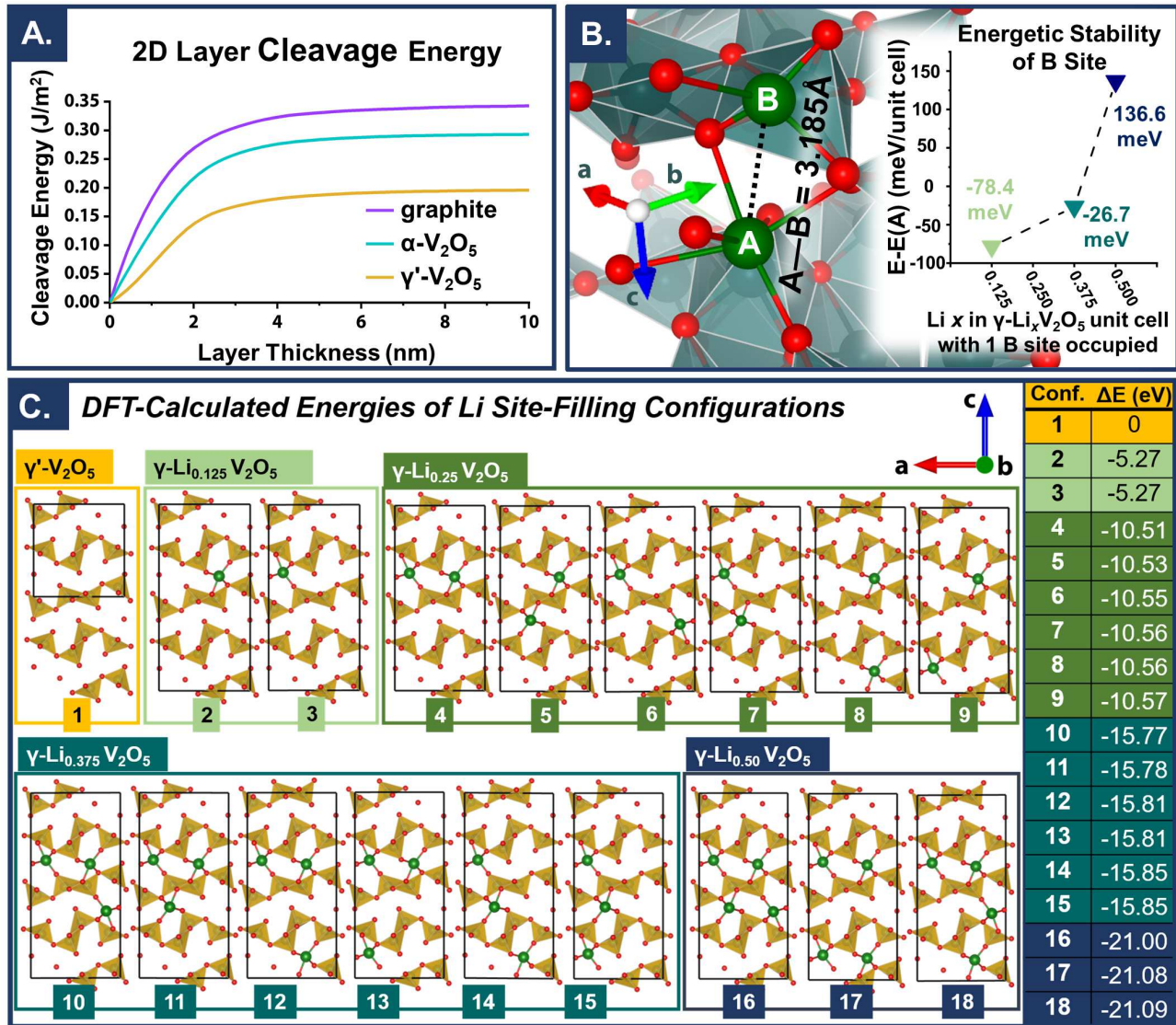
(A—E, F, top row) Digital photographs of single-crystals used in this study, tracking changes in color and habit upon topochemical transformation. The photographs highlight transformation from lustrous black blocks (panel A) to translucent yellow blocks with visible layers and defects arising from leaching Li ions from the layered $\gamma'\text{-V}_2\text{O}_5$ structure (panel B). Intermediate lithiation of $\gamma'\text{-V}_2\text{O}_5$ produces black plates that have a metallic blue hue when sufficiently thin (panels C and D); full re-lithiation yields irregular black plates with substantial edge damage but retaining single-crystalline integrity (panel E). Lithiation above 1 equivalent partially-exfoliates the crystals, which show an accordion-like habit (panel F). Left-hand panels in the top row of B, C, D, and E show crystals used for diffraction experiments. (A—E, middle row) Atomic structures of crystals used in this study as refined from single-crystal X-ray diffraction at 110K, viewed down the *b*-axis to show extended layers, with unit cell boundaries indicated by blue lines. Key: Red = Oxygen; Teal = Vanadium; Green = Lithium. Partial site occupancy of Li indicated with partially-shaded spheres. VO_5 square pyramids shaded in gray for lithiated structures (structures A, C, D, and E) and yellow for empty $\gamma'\text{-V}_2\text{O}_5$ (structure B). (A—E, bottom row) Lattice parameters *a* (red triangles), *b* (green triangles), *c* (blue triangles), and Volume (black squares) of *Pmna* unit cell from refined single-crystal structures at 110K. Left axis = unit cell volume; Right axis = lattice parameter length. (G) AFM height map image of a $\gamma'\text{-V}_2\text{O}_5$ single crystal (structure B) exfoliated to a thickness of ca. 40 unit cells; showing clear steps along the crystal surface. An optical image of the same crystal is shown as a lower-right inset. Crystal surface height as a function of distance across this crystal is shown in the top half of the panel (indicated by a dashed yellow line).

Figure 2. Structural Distortions in Thermodynamically Stable and Metastable Layered V_2O_5 Polymorphs as Calculated from Single-Crystal XRD.



(A—D) Perspective view of the structure of (A) thermodynamically stable α - V_2O_5 , (B) topochemically deintercalated γ' - V_2O_5 , (C) topochemically re-lithiated γ - $Li_{0.5}V_2O_5$, and (D) topochemically re-lithiated γ - $Li_{1.0}V_2O_5$ derived from single-crystal XRD data at 110K; highlighting the angle of puckering across corner-sharing VO_5 polyhedra in each structure (black line), average layer separation measured by the length of the c lattice parameter in α - V_2O_5 and $c/2$ in γ' - V_2O_5 and γ - $Li_xV_2O_5$ (dashed blue line), and quasi-octahedral interlayer V—O bond distance (dashed red line). Key: Red = Oxygen; Teal = Vanadium; Light green = Lithium at 50% occupancy; Dark green = Lithium at 100% occupancy. All thermal ellipsoids shown at 80% probability. Space groups listed below structure names; unit cell boundaries shown as solid gray lines. (E) Comparison of select crystallographic data in the structures shown in panels (A—D) in order to highlight trends as a function of lithiation and as compared to the thermodynamic α - V_2O_5 structure.

Figure 3. DFT-Calculated Energies for Layer Cleavage, Site Occupancy, and Ion-by-Ion Layer Filling Configurations in Layered V_2O_5 .



(A) Comparison of DFT-calculated layer cleavage energy as a function of vacuum thickness; and total energy per formula unit for orthorhombic γ' - V_2O_5 relative to stable orthorhombic α - V_2O_5 ; with calculated cleavage energy values for graphite also shown. (B) Perspective view comparing 6-coordinate A-site and 4-coordinate B-site identified in Structure C of this study in context of the γ' - V_2O_5 framework, with interatomic distance (3.185 Å) shown; alongside a plot of DFT-calculated energies for relaxed unit cells where one B-site is filled, and any other sites in the unit cell correspond to filled adjacent A-sites, showing how the B-site is effectively stabilized by adjacent empty A-sites. (C) DFT-calculated energies of a sequence of Li site-filling configurations performed on a $1 \times 1 \times 2$ relaxed-volume supercell model of the γ' - V_2O_5 structure, in order to compare relative stabilities of various possible ion-by-ion site-filling configurations. The number of Li atoms inserted into each configuration, and hence the average stoichiometry represented by each configuration, is color-coded according to: Yellow = empty γ' - V_2O_5 ; light green = γ - $Li_{0.125}V_2O_5$ (one Li atom); dark green = γ - $Li_{0.25}V_2O_5$ (two Li atoms); teal = γ - $Li_{0.375}V_2O_5$ (three Li atoms); blue = γ - $Li_{0.50}V_2O_5$ (four Li atoms). Energies relative to the empty configuration 1 are listed on the right-hand side, in increasing order of stability.

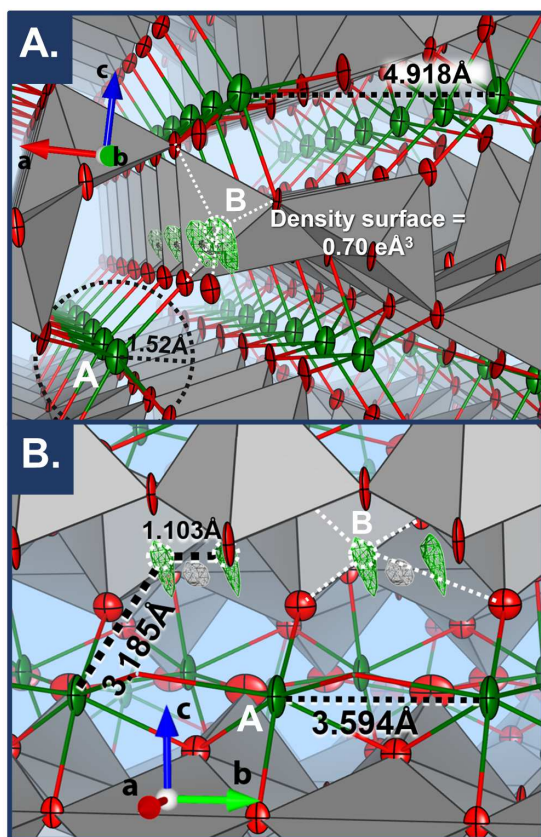


Figure 4. A "Lithium's-Eye View" of the 2D Layered γ' - V_2O_5 Structure

(A) Perspective views of extended atomic layers of partially-intercalated Structure C, viewed down the *b*-axis to emphasize interstitial sites accessible to intercalating Li ions. Key: Red = Oxygen, Green = Lithium, Gray polyhedra = VO_5 . All thermal ellipsoids shown at 50% probability. Li atomic site occupancy is 41%. Residual electron density surface derived from F_o-F_c structure factor map in the final refinement of Structure C is shown at select locations, with a white dotted circle around the peak of electron density at a tetrahedral "B" position between principle 6-coordinate Li "A" sites and mirrored along the *b*-direction. Green mesh = positive density; gray mesh = negative density. A- and B-sites are labeled in white. The atomic radius of Li (1.52Å) is labeled and indicated by a dotted gray circle. The nearest Li—Li distance in the *a*-direction (4.918Å) is highlighted. (B) The same structure, viewed down the *a*-axis, with important distances highlighted, including the nearest Li—Li distance in the *b*-direction (3.594Å), the A-site to B-site distance (3.185Å), and the distance between adjacent B-sites (1.103Å). O atoms bridging Li atoms are omitted for clarity.

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Supporting Information for:

Topochemical stabilization and single-crystal transformations of a metastable 2D γ' -V₂O₅ intercalation cathode

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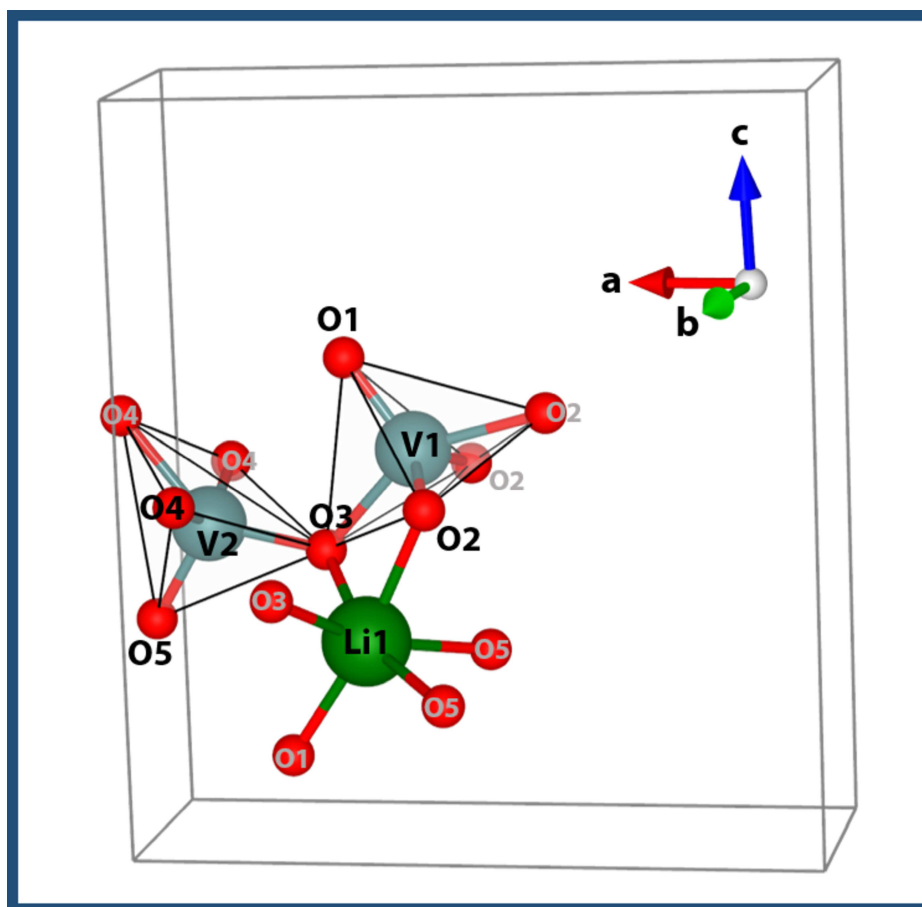
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Figure S1. Atomic labeling scheme used for structures in this study. The anisotropic unit for the Pnma unit cell general to all structures in this study is shown, with the atom labels (in black) used for crystallographically unique atoms. O1 and O5 are axially-coordinated O atoms in the square pyramids for V1 and V2, respectively; O2 and O4 are the equatorially-coordinated O atoms for V1 and V2, respectively; and O3 is the corner-sharing oxygen at the “joint” of the two polyhedra. Additional atoms created by symmetry are also shown in order to complete the local coordination environments around V1, V2, and Li1, with these labels in gray. The unit cell boundaries are indicated by a solid gray line.



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Table S1: Crystal structure topochemical information and refinement results summary. Listed are the structural formula and space group for each structure (A, B, C, D, and E) referred to in this study; the topochemical reagents used to modify each crystal from its preceding state as described in the Experimental section of the main paper; the lattice parameters of the orthorhombic unit cell; the final ShelX least-squares refinement residual (R%) of each structure; and the deposition number of each structure in the Cambridge Structural Database (CSD).

Structure Formula and (Space group)	Topochemical Reagent	Unit Cell Lattice Parameters				Final R%	CSD #
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)		
A. γ -LiV ₂ O ₅ (<i>Pnma</i>)	n/a	9.674	3.595	10.642	370.184	1.5	2084509
B. γ' -V ₂ O ₅ (<i>Pnma</i>)	1.5 eq. NOBF ₄ (MeCN)	9.903	3.581	9.993	354.418	3.4	2084510
C. γ -Li _{0.41} V ₂ O ₅ (<i>Pnma</i>)	0.25 eq. LiI (MeCN)	9.797	3.594	10.324	363.552	6.3	2084511
D. γ -Li _{0.5} V ₂ O ₅ (<i>Pnma</i>)	0.5 eq. LiI (MeCN)	9.759	3.594	10.487	367.904	2.3	2084512
E. γ -LiV ₂ O ₅ (<i>Pnma</i>)	1.0 eq. LiI (MeCN)	9.661	3.597	10.651	370.150	1.8	2084513

Tables for Structure A

Table S2. Crystal data and structure refinement for γ -LiV₂O₅ (Structure A): 5462a. CSD deposition number 2084509.

Identification code	5462a	
Empirical formula	Li O ₅ V ₂	
Formula weight	188.82	
Temperature	110.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 9.6743(6) Å	$\alpha = 90^\circ$
	b = 3.5954(2) Å	$\beta = 90^\circ$
	c = 10.6427(6) Å	$\gamma = 90^\circ$
Volume	370.18(4) Å ³	
Z	4	
Density (calculated)	3.388 Mg/m ³	
Absorption coefficient	4.932 mm ⁻¹	
F(000)	356	
Crystal size	0.108 x 0.083 x 0.077 mm ³	
Theta range for data collection	2.845 to 40.260°.	
Index ranges	-16 ≤ h ≤ 17, -6 ≤ k ≤ 6, -19 ≤ l ≤ 19	
Reflections collected	13242	
Independent reflections	1268 [R(int) = 0.0265]	
Completeness to theta = 25.242°	91.70%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3489 and 0.2045	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1268 / 0 / 50	
Goodness-of-fit on F²	1.16	
Final R indices [I > 2σ(I)]	R1 = 0.0149, wR2 = 0.0348	
R indices (all data)	R1 = 0.0152, wR2 = 0.0350	
Extinction coefficient	0.064(4)	
Largest diff. peak and hole	0.514 and -0.497 e.Å ⁻³	

Table S3. Atomic coordinates ($\times 10^4$), occupancies, and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-LiV}_2\text{O}_5$ (Structure A): 5462a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	Occupancy	Uiso
V(1)	6239(1)	2500	5011(1)	1	5(1)
V(2)	9338(1)	2500	4000(1)	1	5(1)
O(1)	7218(1)	2500	6239(1)	1	9(1)
O(2)	5735(1)	-2500	4510(1)	1	6(1)
O(3)	7590(1)	2500	3650(1)	1	6(1)
O(4)	9403(1)	-2500	4538(1)	1	8(1)
O(5)	10185(1)	2500	2694(1)	1	11(1)
Li(1)	6643(3)	-2500	2772(2)	1	17(1)

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-LiV}_2\text{O}_5$ (Structure A): 5462a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U11	U22	U33	U23	U13	U12
V(1)	4(1)	4(1)	6(1)	0	0(1)	0
V(2)	4(1)	4(1)	6(1)	0	0(1)	0
O(1)	9(1)	10(1)	8(1)	0	-2(1)	0
O(2)	5(1)	5(1)	8(1)	0	1(1)	0
O(3)	5(1)	7(1)	7(1)	0	0(1)	0
O(4)	9(1)	4(1)	11(1)	0	-4(1)	0
O(5)	8(1)	15(1)	10(1)	0	3(1)	0
Li(1)	18(1)	21(1)	12(1)	0	3(1)	0

Table S5. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\gamma\text{-LiV}_2\text{O}_5$ (Structure A): 5462a.

Atoms	Bond Length	Atoms	Bond Length
V(1)-O(1)	1.6143(7)	V(2)-O(3)	1.7316(7)
V(1)-O(2)	1.9371(3)	V(2)-O(4)	1.8876(2)
V(1)-O(2)#1	1.9763(7)	V(2)-O(4)#3	1.9760(7)
V(1)-O(2)#2	1.9371(3)	V(2)-O(4)#2	1.8876(2)
V(1)-O(3)	1.9512(7)	V(2)-O(5)	1.6138(7)

Atoms	Bond Angle	Atoms	Bond Angle
O(1)-V(1)-O(2)	111.723(19)	O(4)-V(2)-O(4)#3	74.98(2)

O(1)-V(1)-O(2)#2	111.723(19)	O(4)#2-V(2)-O(4)#3	74.98(2)
O(1)-V(1)-O(2)#1	110.99(3)	O(4)-V(2)-O(4)#2	144.49(4)
O(1)-V(1)-O(3)	102.00(3)	O(5)-V(2)-O(3)	108.09(3)
O(2)#2-V(1)-O(2)#1	80.09(2)	O(5)-V(2)-O(4)#3	111.42(4)
O(2)-V(1)-O(2)#1	80.09(2)	O(5)-V(2)-O(4)	104.13(2)
O(2)-V(1)-O(2)#2	136.26(4)	O(5)-V(2)-O(4)#2	104.13(2)
O(2)-V(1)-O(3)	87.96(2)	V(1)-O(2)-V(1)#4	136.26(4)
O(2)#2-V(1)-O(3)	87.96(2)	V(1)-O(2)-V(1)#1	99.91(2)
O(3)-V(1)-O(2)#1	147.01(3)	V(1)#4-O(2)-V(1)#1	99.91(2)
O(3)-V(2)-O(4)#3	140.49(3)	V(2)-O(3)-V(1)	119.64(3)
O(3)-V(2)-O(4)#2	95.61(2)	V(2)#4-O(4)-V(2)#3	105.02(2)
O(3)-V(2)-O(4)	95.61(2)	V(2)-O(4)-V(2)#3	105.02(2)
		V(2)-O(4)-V(2)#4	144.49(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 x,y+1,z #3 -x+2,-y,-z+1 #4 x,y-1,z

Tables for Structure B

Table S6. Crystal data and structure refinement for γ' -V₂O₅ (Structure B): 5822a. CSD deposition number 2084510.

Identification code	5822a	
Empirical formula	O5 V2	
Formula weight	181.88	
Temperature	110.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 9.9031(9) Å	$\alpha = 90^\circ$
	b = 3.5813(3) Å	$\beta = 90^\circ$
	c = 9.9932(9) Å	$\gamma = 90^\circ$
Volume	354.42(5) Å ³	
Z	4	
Density (calculated)	3.409 Mg/m ³	
Absorption coefficient	5.149 mm ⁻¹	
F(000)	344	
Crystal size	0.102 x 0.045 x 0.037 mm ³	
Theta range for data collection	2.896 to 30.496°.	
Index ranges	-13 ≤ h ≤ 14, -5 ≤ k ≤ 5, -14 ≤ l ≤ 14	
Reflections collected	6205	
Independent reflections	612 [R(int) = 0.0273]	
Completeness to theta = 25.242°	98.40%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3368 and 0.2172	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	612 / 0 / 43	
Goodness-of-fit on F ²	1.346	
Final R indices [I > 2σ(I)]	R1 = 0.0342, wR2 = 0.0857	
R indices (all data)	R1 = 0.0343, wR2 = 0.0857	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.333 and -0.863 e.Å ⁻³	

Table S7. Atomic coordinates (x 10⁴), occupancies, and equivalent isotropic displacement parameters (Å²x 10³) for γ' -V₂O₅ (Structure B): 5822a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	Occupancy	Uiso
V(1)	1240(1)	2500	148(1)	1	6(1)
V(2)	4296(1)	2500	1028(1)	1	6(1)
O(1)	2102(4)	2500	-1187(3)	1	11(1)
O(2)	718(3)	-2500	379(3)	1	7(1)

O(3)	2557(3)	2500	1407(3)	1	8(1)
O(4)	4362(3)	-2500	433(4)	1	9(1)
O(5)	5036(4)	2500	2437(4)	1	13(1)

Table S8. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for γ' - V_2O_5 (Structure B): 5822a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U11	U22	U33	U23	U13	U12
V(1)	4(1)	3(1)	10(1)	0	0(1)	0
V(2)	4(1)	3(1)	10(1)	0	1(1)	0
O(1)	11(2)	11(2)	10(2)	0	1(1)	0
O(2)	6(1)	3(1)	12(1)	0	2(1)	0
O(3)	4(1)	9(2)	12(1)	0	1(1)	0
O(4)	8(1)	4(1)	14(2)	0	3(1)	0
O(5)	9(2)	19(2)	11(2)	0	-3(1)	0

Table S9. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for γ' - V_2O_5 (Structure B): 5822a.

Atoms	Bond Length	Atoms	Bond Length
V(1)-O(1)	1.584(4)	V(2)-O(3)	1.763(3)
V(1)-O(2)#1	2.009(3)	V(2)-O(4)#2	1.8878(11)
V(1)-O(2)	1.8781(10)	V(2)-O(4)	1.8878(11)
V(1)-O(2)#2	1.8781(10)	V(2)-O(4)#3	1.974(3)
V(1)-O(3)	1.812(3)	V(2)-O(5)	1.587(4)

Atoms	Bond Angle	Atoms	Bond Angle
O(1)-V(1)-O(2)#2	104.60(10)	O(4)-V(2)-O(4)#3	75.16(10)
O(1)-V(1)-O(2)	104.60(10)	O(4)#2-V(2)-O(4)#3	75.16(10)
O(1)-V(1)-O(2)#1	107.41(16)	O(4)-V(2)-O(4)#2	143.1(2)
O(1)-V(1)-O(3)	101.35(17)	O(5)-V(2)-O(3)	105.09(17)
O(2)#2-V(1)-O(2)	144.90(19)	O(5)-V(2)-O(4)#2	105.26(11)
O(2)-V(1)-O(2)#1	76.51(10)	O(5)-V(2)-O(4)	105.26(11)
O(2)#2-V(1)-O(2)#1	76.51(10)	O(5)-V(2)-O(4)#3	110.21(17)
O(3)-V(1)-O(2)#1	151.24(15)	V(1)#4-O(2)-V(1)#1	103.50(10)
O(3)-V(1)-O(2)#2	96.47(11)	V(1)-O(2)-V(1)#4	144.90(19)
O(3)-V(1)-O(2)	96.47(11)	V(1)-O(2)-V(1)#1	103.49(10)

O(3)-V(2)-O(4)	95.82(11)	V(2)-O(3)-V(1)	123.64(19)
O(3)-V(2)-O(4)#3	144.70(16)	V(2)-O(4)-V(2)#4	143.1(2)
O(3)-V(2)-O(4)#2	95.83(11)	V(2)-O(4)-V(2)#3	104.84(10)
		V(2)#4-O(4)-V(2)#3	104.84(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 x,y+1,z #3 -x+1,-y,-z #4 x,y-1,z

Tables for Structure C

Table S10. Crystal data and structure refinement for γ -Li_{0.41}V₂O₅ (Structure C): 5564a. CSD deposition number 2084511.

Identification code	5564a	
Empirical formula	Li _{0.41} O ₅ V ₂	
Formula weight	184.74	
Temperature	110.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 9.7976(17) Å	$\alpha = 90^\circ$
	b = 3.5940(6) Å	$\beta = 90^\circ$
	c = 10.3245(18) Å	$\gamma = 90^\circ$
Volume	363.55(11) Å ³	
Z	4	
Density (calculated)	3.375 Mg/m ³	
Absorption coefficient	5.021 mm ⁻¹	
F(000)	349	
Crystal size	0.072 x 0.048 x 0.023 mm ³	
Theta range for data collection	2.866 to 27.613°.	
Index ranges	-12<=h<=10, -4<=k<=4, -13<=l<=13	
Reflections collected	4973	
Independent reflections	491 [R(int) = 0.0800]	
Completeness to theta = 25.242°	100.00%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3130 and 0.1724	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	491 / 0 / 50	
Goodness-of-fit on F ²	1.238	
Final R indices [I>2sigma(I)]	R1 = 0.0635, wR2 = 0.1721	
R indices (all data)	R1 = 0.0678, wR2 = 0.1751	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.535 and -1.375 e.Å ⁻³	

Table S11. Atomic coordinates ($\times 10^4$), occupancies, and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-Li}_{0.41}\text{V}_2\text{O}_5$ (Structure C): 5564a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	Occupancy	Uiso
V(2)	4316(2)	2500	1008(2)	1	16(1)
V(1)	1234(2)	2500	78(2)	1	14(1)
O(4)	4380(7)	-2500	459(8)	1	19(2)
O(2)	738(6)	-2500	417(7)	1	15(1)
O(3)	2568(7)	2500	1360(7)	1	21(2)
O(1)	2126(8)	2500	-1201(7)	1	24(2)
O(5)	5088(8)	2500	2366(9)	1	40(2)
Li(1)	3360(50)	2500	-2710(50)	0.410(0)	24(17)

Table S12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-Li}_{0.41}\text{V}_2\text{O}_5$ (Structure C): 5564a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U11	U22	U33	U23	U13	U12
V(2)	2(1)	12(1)	33(1)	0	2(1)	0
V(1)	2(1)	13(1)	27(1)	0	0(1)	0
O(4)	8(3)	3(3)	46(5)	0	8(3)	0
O(2)	2(3)	17(4)	27(4)	0	-1(2)	0
O(3)	6(3)	28(4)	29(4)	0	2(3)	0
O(1)	12(3)	32(5)	27(4)	0	4(3)	0
O(5)	5(3)	73(7)	40(5)	0	-7(3)	0
Li(1)	20(20)	10(20)	50(30)	0	0(20)	0

Table S13. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\gamma\text{-Li}_{0.41}\text{V}_2\text{O}_5$ (Structure C): 5564a.

Atoms	Bond Length	Atoms	Bond Length
V(1)-V(1)#4	3.017(2)	V(2)-V(2)#1	3.058(3)
V(1)-V(1)#5	3.017(2)	V(2)-V(2)#2	3.058(3)
V(1)-O(2)	1.894(2)	V(2)-O(4)	1.885(3)
V(1)-O(2)#5	1.998(6)	V(2)-O(4)#2	1.981(8)
V(1)-O(2)#3	1.894(2)	V(2)-O(4)#3	1.885(3)
V(1)-O(3)	1.861(7)	V(2)-O(3)	1.751(7)
V(1)-O(1)	1.583(8)	V(2)-O(5)	1.593(9)

Atoms	Bond Angle	Atoms	Bond Angle
V(2)#2-V(2)-V(2)#1	71.97(8)	O(3)-V(1)-Li(1)#7	49.5(8)
O(4)-V(2)-V(2)#1	109.9(2)	O(1)-V(1)-V(1)#5	113.5(2)
O(4)-V(2)-V(2)#2	38.8(2)	O(1)-V(1)-V(1)#4	113.5(2)
O(4)#2-V(2)-V(2)#2	36.63(6)	O(1)-V(1)-O(2)#5	108.7(4)
O(4)#2-V(2)-V(2)#1	36.63(6)	O(1)-V(1)-O(2)	107.2(2)
O(4)#3-V(2)-V(2)#2	109.9(2)	O(1)-V(1)-O(2)#3	107.2(2)
O(4)#3-V(2)-V(2)#1	38.8(2)	O(1)-V(1)-O(3)	101.8(4)
O(4)#3-V(2)-O(4)#2	75.5(2)	O(1)-V(1)-Li(1)#7	125.0(8)
O(4)-V(2)-O(4)#2	75.5(2)	O(1)-V(1)-Li(1)#6	125.0(8)
O(4)#3-V(2)-O(4)	144.8(5)	Li(1)#6-V(1)-V(1)#4	77.6(8)
O(3)-V(2)-V(2)#2	124.75(19)	Li(1)#7-V(1)-V(1)#4	121.1(9)
O(3)-V(2)-V(2)#1	124.75(19)	Li(1)#7-V(1)-V(1)#5	77.6(8)
O(3)-V(2)-O(4)#3	95.4(2)	Li(1)#6-V(1)-V(1)#5	121.1(9)
O(3)-V(2)-O(4)#2	142.2(3)	Li(1)#6-V(1)-Li(1)#7	75.6(12)
O(3)-V(2)-O(4)	95.4(2)	V(2)-O(4)-V(2)#2	104.5(2)
O(5)-V(2)-V(2)#2	113.0(2)	V(2)#8-O(4)-V(2)	144.8(5)
O(5)-V(2)-V(2)#1	113.0(2)	V(2)#8-O(4)-V(2)#2	104.5(2)
O(5)-V(2)-O(4)	104.4(3)	V(1)-O(2)-V(1)#8	143.2(4)
O(5)-V(2)-O(4)#3	104.4(3)	V(1)-O(2)-V(1)#5	101.6(2)
O(5)-V(2)-O(4)#2	111.5(4)	V(1)#8-O(2)-V(1)#5	101.6(2)
O(5)-V(2)-O(3)	106.3(4)	V(1)#8-O(2)-Li(1)#7	93.5(4)
V(1)#5-V(1)-V(1)#4	73.13(7)	V(1)-O(2)-Li(1)#7	93.5(4)
O(2)#3-V(1)-V(1)#4	40.47(18)	V(1)#5-O(2)-Li(1)#7	129.5(13)
O(2)-V(1)-V(1)#5	40.47(18)	V(2)-O(3)-V(1)	122.6(4)
O(2)#5-V(1)-V(1)#5	37.96(6)	V(2)-O(3)-Li(1)#6	119.2(11)
O(2)#3-V(1)-V(1)#5	111.69(19)	V(2)-O(3)-Li(1)#7	119.2(11)
O(2)-V(1)-V(1)#4	111.69(19)	V(1)-O(3)-Li(1)#7	91.1(13)
O(2)#5-V(1)-V(1)#4	37.96(6)	V(1)-O(3)-Li(1)#6	91.1(13)
O(2)#3-V(1)-O(2)#5	78.4(2)	Li(1)#6-O(3)-Li(1)#7	107(2)
O(2)-V(1)-O(2)#5	78.4(2)	V(1)-O(1)-Li(1)	175.8(14)
O(2)#3-V(1)-O(2)	143.2(4)	V(2)-O(5)-Li(1)#2	115.8(12)
O(2)#5-V(1)-Li(1)#7	109.3(9)	V(2)-O(5)-Li(1)#1	115.8(12)
O(2)-V(1)-Li(1)#6	118.2(7)	Li(1)#1-O(5)-Li(1)#2	97.9(17)
O(2)#5-V(1)-Li(1)#6	109.3(9)	V(1)#9-Li(1)-V(1)#10	75.6(12)
O(2)#3-V(1)-Li(1)#6	46.3(7)	O(2)#9-Li(1)-V(1)#10	40.2(7)
O(2)#3-V(1)-Li(1)#7	118.2(7)	O(2)#9-Li(1)-V(1)#9	40.2(7)
O(2)-V(1)-Li(1)#7	46.3(7)	O(2)#9-Li(1)-O(3)#10	77.3(15)
O(3)-V(1)-V(1)#4	126.95(16)	O(2)#9-Li(1)-O(3)#9	77.3(15)
O(3)-V(1)-V(1)#5	126.95(16)	O(2)#9-Li(1)-O(5)#2	82.5(14)
O(3)-V(1)-O(2)#3	92.8(2)	O(2)#9-Li(1)-O(5)#1	82.5(14)
O(3)-V(1)-O(2)	92.8(2)	O(3)#10-Li(1)-V(1)#9	102.5(18)
O(3)-V(1)-O(2)#5	149.4(3)	O(3)#9-Li(1)-V(1)#10	102.5(18)
O(3)-V(1)-Li(1)#6	49.5(8)	O(3)#9-Li(1)-V(1)#9	39.4(7)
O(1)-Li(1)-O(3)#10	95.2(15)	O(3)#10-Li(1)-V(1)#10	39.4(7)
O(1)-Li(1)-O(3)#9	95.2(15)	O(3)#9-Li(1)-O(3)#10	107(2)
O(1)-Li(1)-O(5)#1	105.8(17)	O(3)#10-Li(1)-O(5)#2	159(2)
O(1)-Li(1)-O(5)#2	105.8(17)	O(3)#9-Li(1)-O(5)#2	73.5(4)

O(5)#2-Li(1)-V(1)#10	119.5(19)	O(3)#10-Li(1)-O(5)#1	73.5(4)
O(5)#1-Li(1)-V(1)#10	64.4(8)	O(3)#9-Li(1)-O(5)#1	159(2)
O(5)#2-Li(1)-V(1)#9	64.4(8)	O(1)-Li(1)-V(1)#10	134.4(12)
O(5)#1-Li(1)-V(1)#9	119.5(19)	O(1)-Li(1)-V(1)#9	134.4(12)
O(5)#1-Li(1)-O(5)#2	97.9(17)	O(1)-Li(1)-O(2)#9	167(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 -x+1,-y,-z #3 x,y+1,z
#4 -x,-y+1,-z #5 -x,-y,-z #6 -x+1/2,-y+1,z+1/2
#7 -x+1/2,-y,z+1/2 #8 x,y-1,z #9 -x+1/2,-y,z-1/2
#10 -x+1/2,-y+1,z-1/2

Tables for Structure D

Table S14. Crystal data and structure refinement for γ -Li_{0.50}V₂O₅ (Structure D): 5552. CSD deposition number 2084512.

Identification code	5552	
Empirical formula	Li _{0.50} O ₅ V ₂	
Formula weight	185.35	
Temperature	110.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 9.7596(4) Å	$\alpha = 90^\circ$
	b = 3.59430(10) Å	$\beta = 90^\circ$
	c = 10.4879(4) Å	$\gamma = 90^\circ$
Volume	367.90(2) Å ³	
Z	4	
Density (calculated)	3.346 Mg/m ³	
Absorption coefficient	4.962 mm ⁻¹	
F(000)	350	
Crystal size	0.102 x 0.062 x 0.041 mm ³	
Theta range for data collection	2.851 to 47.737°	
Index ranges	-20 ≤ h ≤ 20, -7 ≤ k ≤ 5, -21 ≤ l ≤ 21	
Reflections collected	16966	
Independent reflections	1913 [R(int) = 0.0421]	
Completeness to theta = 25.242°	97.70%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3587 and 0.2371	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1913 / 0 / 52	
Goodness-of-fit on F ²	1.285	
Final R indices [I > 2σ(I)]	R1 = 0.0231, wR2 = 0.0534	
R indices (all data)	R1 = 0.0251, wR2 = 0.0541	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.747 and -0.899 e.Å ⁻³	

Table S15. Atomic coordinates ($\times 10^4$), occupancies, and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-Li}_{0.50}\text{V}_2\text{O}_5$ (Structure D): 5552. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	Occupancy	Uiso
V(1)	6236(1)	-2500	42(1)	1	5(1)
V(2)	9317(1)	-2500	1001(1)	1	5(1)
O(2)	5735(1)	2500	419(1)	1	6(1)
O(1)	7152(1)	-2500	-1216(1)	1	12(1)
O(3)	7569(1)	-2500	1337(1)	1	10(1)
O(4)	9384(1)	2500	443(1)	1	11(1)
Li(1)	6625(6)	2500	2253(5)	0.500(0)	11(1)
O(5)	10101(1)	-3011(4)	2335(1)	1	10(1)

Table S16. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-Li}_{0.50}\text{V}_2\text{O}_5$ (Structure D): 5552. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U11	U22	U33	U23	U13	U12
V(1)	4(1)	4(1)	7(1)	0	-1(1)	0
V(2)	4(1)	4(1)	7(1)	0	0(1)	0
O(2)	6(1)	5(1)	8(1)	0	-1(1)	0
O(1)	14(1)	13(1)	8(1)	0	1(1)	0
O(3)	4(1)	18(1)	6(1)	0	0(1)	0
O(4)	12(1)	4(1)	16(1)	0	9(1)	0
Li(1)	13(2)	12(2)	10(2)	0	-3(2)	0
O(5)	8(1)	10(1)	11(1)	0(1)	-3(1)	0(1)

Table S17. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\gamma\text{-Li}_{0.50}\text{V}_2\text{O}_5$ (Structure D): 5552.

Atoms	Bond Length	Atoms	Bond Length
V(1)-V(1)#1	3.0093(3)	V(2)-V(2)#4	3.0683(3)
V(1)-V(1)#2	3.0093(3)	V(2)-V(2)#5	3.0683(3)
V(1)-O(2)#1	1.9834(9)	V(2)-O(3)	1.7415(9)
V(1)-O(2)#3	1.9040(3)	V(2)-O(4)#5	1.9747(10)
V(1)-O(2)	1.9040(3)	V(2)-O(4)#3	1.8911(3)
V(1)-O(1)	1.5935(11)	V(2)-O(4)	1.8911(3)
V(1)-O(3)	1.8809(9)	V(2)-O(5)	1.6060(12)

Atoms		Bond Angle		Atoms		Bond Angle	
V(1)#2-V(1)-V(1)#1		73.340(9)		O(3)-V(2)-O(4)#5		141.63(5)	
O(2)#1-V(1)-V(1)#2		38.328(8)		O(3)-V(2)-O(4)		95.55(3)	
O(2)#1-V(1)-V(1)#1		38.328(8)		O(3)-V(2)-O(4)#3		95.55(3)	
O(2)#3-V(1)-V(1)#2		40.24(2)		O(4)#3-V(2)-V(2)#4		38.43(3)	
O(2)-V(1)-V(1)#1		40.25(2)		O(4)-V(2)-V(2)#4		109.26(3)	
O(2)#3-V(1)-V(1)#1		111.35(3)		O(4)#5-V(2)-V(2)#5		36.528(8)	
O(2)-V(1)-V(1)#2		111.35(3)		O(4)-V(2)-V(2)#5		38.43(3)	
O(2)-V(1)-O(2)#1		78.57(3)		O(4)#3-V(2)-V(2)#5		109.26(3)	
O(2)-V(1)-O(2)#3		141.43(5)		O(4)#5-V(2)-V(2)#4		36.528(8)	
O(2)#3-V(1)-O(2)#1		78.57(3)		O(4)#3-V(2)-O(4)		143.72(6)	
O(1)-V(1)-V(1)#1		115.19(3)		O(4)-V(2)-O(4)#5		74.96(3)	
O(1)-V(1)-V(1)#2		115.19(3)		O(4)#3-V(2)-O(4)#5		74.96(3)	
O(1)-V(1)-O(2)#3		108.43(3)		O(5)-V(2)-V(2)#5		117.12(5)	
O(1)-V(1)-O(2)		108.43(3)		O(5)-V(2)-V(2)#4		108.77(5)	
O(1)-V(1)-O(2)#1		110.02(5)		O(5)-V(2)-O(3)		106.89(6)	
O(1)-V(1)-O(3)		102.09(5)		O(5)-V(2)-O(4)		111.21(6)	
O(3)-V(1)-V(1)#1		125.14(2)		O(5)-V(2)-O(4)#5		111.22(6)	
O(3)-V(1)-V(1)#2		125.14(2)		O(5)-V(2)-O(4)#3		98.29(6)	
O(3)-V(1)-O(2)#3		91.57(3)		V(1)-O(2)-V(1)#1		101.43(3)	
O(3)-V(1)-O(2)#1		147.89(4)		V(1)-O(2)-V(1)#6		141.43(5)	
O(3)-V(1)-O(2)		91.57(3)		V(1)#6-O(2)-V(1)#1		101.43(3)	
V(2)#4-V(2)-V(2)#5		71.707(8)		V(2)-O(3)-V(1)		122.10(5)	
O(3)-V(2)-V(2)#4		124.35(2)		V(2)-O(4)-V(2)#5		105.04(3)	
O(3)-V(2)-V(2)#5		124.35(2)		V(2)#6-O(4)-V(2)		143.72(6)	
				V(2)#6-O(4)-V(2)#5		105.04(3)	

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x+1,-y-1,-z #3 x,y-1,z
#4 -x+2,-y-1,-z #5 -x+2,-y,-z #6 x,y+1,z

Tables for Structure E

Table S18. Crystal data and structure refinement for γ -LiV₂O₅ (Structure E): 5551. CSD deposition number 2084513.

Identification code	5551	
Empirical formula	Li O ₅ V ₂	
Formula weight	188.82	
Temperature	110.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 9.6612(4) Å	$\alpha = 90^\circ$
	b = 3.5970(2) Å	$\beta = 90^\circ$
	c = 10.6514(5) Å	$\gamma = 90^\circ$
Volume	370.15(3) Å ³	
Z	4	
Density (calculated)	3.388 Mg/m ³	
Absorption coefficient	4.933 mm ⁻¹	
F(000)	356	
Crystal size	0.127 x 0.105 x 0.048 mm ³	
Theta range for data collection	2.846 to 45.312°.	
Index ranges	-19 ≤ h ≤ 19, -7 ≤ k ≤ 5, -21 ≤ l ≤ 21	
Reflections collected	15681	
Independent reflections	1706 [R(int) = 0.0361]	
Completeness to theta = 25.242°	98.50%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3555 and 0.2260	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1706 / 0 / 49	
Goodness-of-fit on F ²	1.157	
Final R indices [I > 2σ(I)]	R1 = 0.0181, wR2 = 0.0429	
R indices (all data)	R1 = 0.0206, wR2 = 0.0442	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.780 and -0.715 e.Å ⁻³	

Table S19. Atomic coordinates ($\times 10^4$), occupancies, and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for γ -LiV₂O₅ (Structure E): 5551. $U(eq)$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	Occupancy	Uiso
V(1)	1240(1)	2500	4986(1)	1	5(1)
V(2)	4340(1)	2500	5999(1)	1	5(1)
O(1)	2222(1)	2500	3760(1)	1	9(1)
O(2)	-734(1)	2500	4506(1)	1	6(1)

O(3)	2592(1)	2500	6352(1)	1	6(1)
O(4)	5594(1)	2500	4537(1)	1	8(1)
O(5)	5190(1)	2500	7304(1)	1	10(1)
Li(1)	3357(3)	2500	2229(2)	1	16(1)

Table S20. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\gamma\text{-LiV}_2\text{O}_5$ (Structure E): 5551.
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U11	U22	U33	U23	U13	U12
V(1)	3(1)	5(1)	6(1)	0	0(1)	0
V(2)	3(1)	5(1)	6(1)	0	0(1)	0
O(1)	8(1)	11(1)	8(1)	0	2(1)	0
O(2)	5(1)	6(1)	8(1)	0	-1(1)	0
O(3)	4(1)	8(1)	7(1)	0	0(1)	0
O(4)	8(1)	5(1)	10(1)	0	3(1)	0
O(5)	7(1)	14(1)	9(1)	0	-2(1)	0
Li(1)	15(1)	21(1)	11(1)	0	3(1)	0

Table S21. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\gamma\text{-LiV}_2\text{O}_5$ (Structure E): 5551.

Atoms	Bond Length	Atoms	Bond Length
V(1)-O(1)	1.6144(8)	V(2)-O(3)	1.7296(7)
V(1)-O(2)	1.9742(7)	V(2)-O(4)#3	1.8882(3)
V(1)-O(2)#1	1.9405(3)	V(2)-O(4)#4	1.8882(3)
V(1)-O(2)#2	1.9405(3)	V(2)-O(4)	1.9735(7)
V(1)-O(3)	1.9553(7)	V(2)-O(5)	1.6143(8)

Atoms	Bond Angle	Atoms	Bond Angle
O(1)-V(1)-O(2)#2	111.93(2)	O(4)#3-V(2)-O(4)	74.95(2)
O(1)-V(1)-O(2)	111.04(4)	O(4)#4-V(2)-O(4)#3	144.53(4)
O(1)-V(1)-O(2)#1	111.93(2)	O(4)#4-V(2)-O(4)	74.95(2)
O(1)-V(1)-O(3)	102.05(4)	O(5)-V(2)-O(3)	108.07(4)
O(2)#1-V(1)-O(2)	80.15(2)	O(5)-V(2)-O(4)#3	104.09(2)
O(2)#2-V(1)-O(2)#1	135.89(4)	O(5)-V(2)-O(4)	111.52(4)
O(2)#2-V(1)-O(2)	80.15(2)	O(5)-V(2)-O(4)#4	104.09(2)

O(2)#1-V(1)-O(3)	87.75(2)	V(1)#2-O(2)-V(1)#1	135.89(4)
O(2)#2-V(1)-O(3)	87.75(2)	V(1)#1-O(2)-V(1)	99.85(2)
O(3)-V(1)-O(2)	146.91(3)	V(1)#2-O(2)-V(1)	99.85(2)
O(3)-V(2)-O(4)#4	95.66(2)	V(2)-O(3)-V(1)	119.41(4)
O(3)-V(2)-O(4)	140.41(3)	V(2)#4-O(4)-V(2)	105.05(2)
O(3)-V(2)-O(4)#3	95.66(2)	V(2)#4-O(4)-V(2)#3	144.53(4)
		V(2)#3-O(4)-V(2)	105.05(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1 #2 -x,-y+1,-z+1 #3 -x+1,-y+1,-z+1

#4 -x+1,-y,-z+1

Table S22. ICP-MS information and sample data. Listed are the molecular formula and label of the solved topochemical single-crystal structures in this study; Sample IDs for bulk samples of topochemically-treated crystals tested with ICP-MS, from which the individually solved crystals were drawn; Li:V₂ molar ratios based on refined single-crystal XRD data from individual single-crystals in this study; Li:V₂ molar ratios in bulk samples calculated from Li⁷ and V⁵¹ analyte concentrations determined with a PerkinElmer NexION 300D ICP-MS instrument using a Sc⁴⁵ internal standard.

Solved Single Crystal Formula	Bulk Sample ID ¹	Refined Single-Crystal Li:V ₂ (mol/mol)	ICP-MS Calculated Bulk Li:V ₂ (mol/mol)
γ'-V ₂ O ₅ (B)	JLA-11 gamma-V ₂ O ₅	0.0	0.19 ²
γ-Li _{0.41} V ₂ O ₅ (C)	JLA-7 gamma-LiV ₂ O ₅	0.41	0.38
γ-Li _{0.50} V ₂ O ₅ (D)	JLA-4 gamma-LiV ₂ O ₅	0.50	0.46
γ-Li _{1.0} V ₂ O ₅ (E)	JLA-11 gamma-LiV ₂ O ₅	1.0	1.1

¹Samples were prepared for ICP-MS by digesting 1-2 mg of topochemically-treated single-crystals in concentrated nitric acid, then diluting in Milli-Q-purified H₂O until estimated concentrations were in a suitable (ca. 10-100 ppb) range.

²PXRD analysis of bulk samples indicated the presence of remnant Li_xV₂O₅ and unreacted Li₂V₃O₈ in this sample.