Hidden phases and colossal insulator-metal transition in single-crystalline \( T-Nb_2O_5 \) thin films accessed by lithium intercalation

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Abstract

Fast migration of lithium (Li)-ions in oxide materials is fundamental to the operation of Li-ion batteries\textsuperscript{1-10}. The intercalation of Li-ions into oxides can further lead to emergent electronic property changes\textsuperscript{11-16}. Some of the fastest Li\textsuperscript{+}-ion conductors are 4d oxides, and of these, the niobium oxide polymorph $T$-Nb\textsubscript{2}O\textsubscript{5}\textsuperscript{17} is especially interesting with its two-dimensional fast ion migration channels\textsuperscript{6-10}. However, the growth of single-crystalline $T$-Nb\textsubscript{2}O\textsubscript{5} films is challenging due to its stability over only a limited synthesis temperature window, the existence of many other polymorphs\textsuperscript{18}, and its large orthorhombic unit cell\textsuperscript{19}. Here, we first demonstrate the epitaxial growth of single domain $T$-Nb\textsubscript{2}O\textsubscript{5} thin films, critically with the ion channels oriented perpendicular to the film’s surface. We show that the insertion of just a small amount of Li using ionic liquids results in conversion of the initially insulating film to a metallic state with a colossal change in resistivity of almost eleven orders of magnitude. In situ experiments, in conjunction with theoretical calculations, reveal a series of transitions between distinct crystal and electronic structures as the lithium content is systematically increased. These include hidden phases that have not previously been identified. Furthermore, replacing the Au electrode with a Li-oxide electrode allows for a significant reduction of the gate voltage at which metallization takes place. Our study opens a new path towards the exploration of hidden phases and the development of novel electrochemically controlled electronic devices.
Introduction

The control of the electronic properties of materials via voltage biasing forms the cornerstone of many electronic applications. Substantial efforts have been recently directed to enable the electric-field control of these properties, including insulator-to-metal transitions by using ionic liquid gating (ILG) of oxides. These electronic transitions are mostly induced by the electrochemical intercalation of $O^2-$ or $H^+$ ions, which can sometimes be sluggish, poorly controlled or involve electrolyte degradation. Alternatively, intercalation of $Li^+$ ions into oxides can provide fast ion diffusion and emergent electronic property changes. While fast migration of lithium (Li)-ions in oxide materials is fundamental to the operation of Li-ion batteries, comparatively little has been done to uncover the correlation between the structure and electronic properties via Li intercalation into oxides. This is mostly because of the technical difficulties associated with measurements on powdered samples: powders cannot be readily densified, particularly if they are metastable. Therefore, there are potentially a wealth of oxide materials showing fast and reversible Li intercalation with hidden electronic properties that have yet to be discovered. Moreover, these Li-containing materials can potentially be used as gate electrodes, where, during the electrochemical gating, Li is removed or inserted from these materials within the electrolyte stability window, allowing potential control of the operation voltages.

$T-Nb_2O_5$ is a promising anode material for applications in fast-charging batteries or electrochemical capacitors/pseudocapacitors. Fast Li-ion diffusion in $T-Nb_2O_5$ is enabled by its crystal structure, consisting of pillared two-dimensional layers with very low steric hindrance for intralayer Li ion diffusion (Fig. 1a and Supplementary Fig. 1). Moreover, $T-Nb_2O_5$ is a $d^0$ insulator, and Li-ion intercalation is expected to increase the electronic conductivity by populating the Nb 4$d$ conduction band levels (Fig. 1b), making $T-Nb_2O_5$ a promising candidate for electronic applications. However, since the discovery of $T-Nb_2O_5$ in 1941, single-domain thin films – required for fast electrochemical gating – have not been successfully prepared, likely due to its large orthorhombic unit cell ($Pbam$; $a = 6.175 \ \text{Å}$, $b = 29.175 \ \text{Å}$, and $c = 3.930 \ \text{Å}$), its metastability, and the existence of many Nb$_2$O$_5$ polymorphs that are close in energy.

Here, we present a detailed study of the electronic properties of $T-Nb_2O_5$ in conjunction with the unexplored phase transitions that occur during Li-ion intercalation. Single-domain epitaxial $T-Nb_2O_5$ films were synthesised here for the first time, providing rapid Li-ion diffusion...
along oriented pathways and enabling electronic property measurements in the absence of grain boundaries or conductive additives. Li-containing ionic liquid gating (Li-ILG) experiments were performed on the \(7\text{-}\text{Nb}_2\text{O}_5\) thin films, resulting in colossal insulator–metal transitions with an increase in conductivity of about 11 orders-of-magnitude during the early stages of Li insertion. Multiple phase transitions, including a monoclinic and tetragonal distortion, are observed by \textit{in situ} X-ray diffraction (XRD) experiments and rationalized with the help of density-functional theory (DFT) calculations. Furthermore, a tuneable metallization voltage and low-voltage operation is demonstrated by altering the chemical potential of the gate electrode via the use of lithiated counter electrodes.

**Results**

Pulsed laser deposition (PLD) was used to optimize the growth conditions of \(7\text{-}\text{Nb}_2\text{O}_5\) thin films on (001)- and (110)-oriented substrates of \(\text{LaAlO}_3\) (LAO), \((\text{La}_{0.18}\text{Sr}_{0.82})(\text{Al}_{0.59}\text{Ta}_{0.41})\text{O}_3\) (LSAT), and \(\text{SrTiO}_3\) (STO). Various polymorphs including the \(TT\text{-}, T\text{-}, B\text{-},\) and \(H\text{-}\text{Nb}_2\text{O}_5\) phases were identified by XRD depending on the growth temperature (Supplementary Fig. 2a) with \(7\text{-}\text{Nb}_2\text{O}_5\) (180) forming as a single phase for growth temperatures between 600 and 650 °C. Cross-sectional scanning transmission electron microscopy (STEM) is used to obtain high angle annular dark field (HAADF) images and fast Fourier transformation (FFT) patterns (Fig. 1c-1i). These methods established that single crystalline \(7\text{-}\text{Nb}_2\text{O}_5\) (180) thin films could be epitaxially grown on (110)-oriented substrates, but that twin domains, rotated in-plane by 90° with respect to each other, were formed when using (001)-oriented substrates, as previously observed for growth on STO (001). Reflection high-energy electron diffraction (RHEED) patterns and XRD phi scans confirmed this finding (see Supplementary Section 1). The anisotropic in-plane geometry of the (110)-oriented substrates likely prohibits the formation of twin domains. However, both the twin-domain and single-domain thin films contain vertically oriented two-dimensional 4g layers (the green dashed lines in Fig. 1e and 1g) that are ideal for Li ion transport.

Li intercalation in epitaxial \(7\text{-}\text{Nb}_2\text{O}_5\) single-domain thin films deposited on LSAT (110) substrates was characterized electrochemically in a typical Li-ion battery configuration using Li metal as the anode/reference electrode and LP57 (1M LiPF\(_6\) in EC/EMC 3/7) as the electrolyte (see methods and Supplementary Fig. 6). Under galvanostatic cycling at high current densities between 1.43 and 14.3 A/g (7C–70C, assuming a capacity of 201.7 mAh g\(^{-1}\), i.e., 1
electron reduction per Nb$_2$O$_5$), the expected voltage versus capacity profile for the T-Nb$_2$O$_5$ thin film is obtained with reversible capacities ranging from 130 – 80 mAh/g (Fig. 2a and 2b) demonstrating Li insertion with excellent high-rate performance in accord with previous reports$^8$. Note that Li intercalation was also demonstrated by cyclic voltammetry for 16, 80, and 160 nm thick films (Fig. 2c and Supplementary Fig. 7).

To measure the change in electronic properties upon Li intercalation, T-Nb$_2$O$_5$ electronic devices for Li-ionic liquid gating (Li-ILG) were fabricated (Figure 2d and Supplementary Fig. 8a). Hall devices were fabricated from T-Nb$_2$O$_5$ films with Au/Ru as the gate electrode, while the resistance was measured by a 4-point probe method. The devices were gated using conventional ionic liquids (ILs) including DEME-TFSI, EMIM-TFSI, and 0.3 M Li-TFSI in EMIM-TFSI (Li-IL) (Fig. 2f). During gating, the gate voltage ($V_g$) was swept between 3 V and -2 V at a sweep rate of 16 mV/s. Gating with the pure ILs does not lead to any noticeable changes in resistivity, whereas gating with Li-IL induces metallization at positive gate voltages. This contrasts with ionic liquid gating of oxide films such as VO$_2$, WO$_3$, and SrCoO$_{2.5}$, all of which show metallization in the absence of Li ions due to oxygen or hydrogen ion migration$^{20-25}$. Figure 2g shows temperature-dependent resistivity (RT) curves at different gate voltages. Before placing the Li-IL onto the device, we first measured RT curves of pristine T-Nb$_2$O$_5$ films using a high resistance meter (Supplementary Fig. 9), obtaining a room temperature resistivity of the T-Nb$_2$O$_5$ film of $\approx$2.78 × 10$^8$ ohm cm, which is even higher than values reported for amorphous or polycrystalline T-Nb$_2$O$_5$ that range from 10$^4$ to 10$^7$ ohm-cm$^{28,29}$. When the IL is placed on the device surface, the resistivity drops to $\sim$10$^{-1}$ ohm-cm due to current flow between the source and drain contacts through the IL itself. For simplicity, all resistivities are calculated using the film thickness and the channel size (65 × 30 μm$^2$). Notably, the resistivity after metallization is $\approx$2 × 10$^{-3}$ ohm cm, which is $\approx$11 orders of magnitude smaller than that of the pristine T-Nb$_2$O$_5$. Such a colossal insulator-metal transition is remarkable compared to the previously reported metallization by an ILG$^{20-25}$ (See Supplementary Fig. 10 and Table 1). This insulator-metal transition occurs after insertion of fewer than 0.25 Li$^+$ per Nb$_2$O$_5$ formula unit (Fig. 2h).

The effect of the substrate and film thickness are summarized in Supplementary Fig. 11. In short, all films grown on (001)- and (110)-oriented substrates show good metallization behaviour owing to vertical ionic transport channels. For thicknesses ranging from 16 to 160 nm with sufficiently slow voltage sweep rates, the resistivity at 3 V is close to 10$^{-3}$ ohm cm,
demonstrating that the insulator-metal transition happens in the bulk of the material. This is further confirmed by hard X-ray absorption near-edge structure (XANES) measurements (Supplementary Fig. 12). Nb K-edge XANES revealed a shift to lower energy upon gating to positive potentials, indicating reduction of the Nb oxidation state in the bulk of the thin film, in line with prior work on a polycrystalline sample\textsuperscript{30}. When we performed high voltage gating (Supplementary Fig. 13), the resistivity increased as the gating voltage was increased above 4.5 V, indicating the onset of a metal to insulator transition. However, at about 6 V an irreversible electronic transition occurred. The observed voltage-dependent carrier concentration, mobility, and resistivity changes are summarized in Fig. 2h.

The working voltage of a Li-ion battery cell depends on the difference in chemical potential between the cathode and the anode\textsuperscript{5}. To exploit this, the Au/Ru gate electrode was replaced by conventional Li-containing electrode materials, namely LiFePO\textsubscript{4} (LFP), LiCoO\textsubscript{2} (LCO), and Li\textsubscript{3}Nb\textsubscript{2}O\textsubscript{5} (LNbO). The Li intercalation potentials in these materials are ≈ 3.5, 4.0 and 1.8 V vs. Li\textsuperscript{+}/Li for LFP, LCO, and LNbO, respectively, these potentials all within the electrochemical stability range of the IL used in this study. The fabrication process is described in Supplementary Section 4, and the $V_g$-dependent resistivity (RV) curves with different gate electrodes are shown in Supplementary Fig. 17 and Fig. 2g. The critical metallization voltage ($V_c$) is defined from the peak of the normalized $d\rho/dV$ curves. The chemical potential ($V$ vs. Li/Li\textsuperscript{+}) dependent $V_c$ plot (Supplementary Fig. 17c) shows that $V_c$ tends to decrease as the potential difference between the gate electrode and $T$-Nb\textsubscript{2}O\textsubscript{5} decreases. Notably, the LNbO gate electrode leads to the lowest $V_c$ value of ≈0.54 V in addition to symmetric resistivity changes between the LNbO gate electrode and Nb\textsubscript{2}O\textsubscript{5} channel (Fig. 2i). Such potential control of $V_c$ is not possible with conventional ILG based on proton insertion or oxide ion loss, because the $V_c$ will be determined by the more poorly determined electrochemical process that occurs at the counter (gate) electrode (including double layer formation, electrolyte degradation and oxygen evolution).

To understand how the observed electronic transitions are coupled with changes in the atomic structure, the structural evolution of bulk polycrystalline $T$-Nb\textsubscript{2}O\textsubscript{5} was studied during lithiation via \textit{operando} laboratory XRD and synchrotron-based XRD (SXRD experiments). During Li-ion intercalation, continuous shifts of the Bragg reflections were observed together with two phase transitions at lithiation states corresponding to approximately $x$=0.8 and $x$=1.8 in Li$_x$Nb$_2$O$_5$, respectively (Fig. 3a, 3b and Supplementary Fig. 18). SXRD (Fig. 3c,
Supplementary Fig. 19 and Table 2) shows that at the first transition approximately 75 % of the powder has undergone a monoclinic ($m$-) distortion ($\gamma \approx 94^\circ$) of the orthorhombic ($o$-) $T$-Nb$_2$O$_5$ structural model without a significant change in the Nb framework (Supplementary Fig. 19 and Table 2). The second phase transition corresponds to the formation of a new tetragonal ($t$-) Li-rich layered rock salt determined by SXRD (Fig 3d, Supplementary Fig. 20 and Supplementary Table 3). Having resolved the structures in the Li–Nb$_2$O$_5$ pseudobinary phase diagram, Rietveld refinement of the structure model against the operando XRD dataset was conducted to obtain the cell parameter variation presented in Fig. 3b (and Supplementary Figs. 21 and 22).

The evolution of the XRD patterns of a $T$-Nb$_2$O$_5$/LSAT (110) thin-film device were then measured to monitor the structural changes during gating and relate them to changes in resistivity (Fig. 3e). A Au/Ru gate electrode was used for simplicity in device fabrication (Supplementary Fig. 23). Between 0–3 V gating voltages, there was no noticeable change in the XRD patterns, with the (180) reflection position barely changing, while the source–drain current ($I_{SD}$) started to increase at $\approx 2$ V. This indicates, in agreement with the XRD of the powder, that the insulator–metal transition, which occurs in the range Li$_x$Nb$_2$O$_5$ ($0.2 < x \leq 0.8$, see Fig. 2h), is not associated with a structural phase transition. From 3.5 to 4 V, the (180) peak shifted abruptly toward lower angles indicating transition to the monoclinic phase, as confirmed by reciprocal space mapping (Supplementary Fig. 25), without any effect on $I_{SD}$. As shown in Supplementary Fig. 24, From 4 V to $-1$ V, the (180) peak and $I_{SD}$ returned to their original values, showing the reversibility of the structural and electronic changes. At 6 V, concomitantly with the irreversible decrease of $I_{SD}$, an amorphization of the film was observed, as evidenced by a decrease of the (180) peak intensity and by TEM (Supplementary Fig. 26), indicating a degradation of the thin film under harsh reducing conditions. Note that the tetragonal phase observed by operando SXRD of a polycrystalline sample was not seen in thin films, possibly because the domains of the new phase are too small to be seen by XRD, or that possibly there is clamping effect of the substrate, which hinders this phase change and drives the amorphization.

Overall, combining the various structural and electronic measurements, 4 different regimes are defined as a function of Li content ($x$ in Li$_x$Nb$_2$O$_5$) in the thin films: (i) pristine orthorhombic insulator for $x = 0$ (ii) orthorhombic metal for $0.2 \leq x < 0.8$, (iii) monoclinic metal for $0.8 \leq x < 1.8$, and (iv) an insulating state for $x > 1.8$, which is amorphous or highly disordered, as depicted in Fig. 2h and 4a.
The evolution of the structural and electronic properties of $T$-Nb$_2$O$_5$ as a function of Li interstitial concentration was also investigated via ab initio studies. Here, we designed a new simulation model (Fig. 4b) for pristine $T$-Nb$_2$O$_5$ (Nb$_{16.8}$O$_{42}$) by eliminating the fractional occupancy of Nb and the resulting charge imbalance (see Supplementary Section 6.1), the calculations yielding a DFT-derived band gap of $\approx$2.3 eV (Fig. 4c). Next, we studied the energetic and kinetic properties of Li interstitials in our model unit cell of $[T$-Nb$_2$O$_5]$. We found that Li interstitials located in the 4g layer atop two-coordinated oxygen atoms have a marginally stronger binding energy ($\Delta E_b = -2.06$ eV, defined in Methods) than that of the other sites (see Supplementary Section 6.2). Then, we investigated Li diffusion on the minimum-energy path from this site to sites atop neighboring O atoms (Fig. 4g) and found an activation barrier of $E_a = 0.26$ eV. Since the diffusion barriers and energy differences for Li at different sites are both small, the incorporated Li ions are likely not trapped in fixed locations and easily diffuse through the material, in good agreement with our experiments.

To avoid spurious interactions between periodic images in the small $c$ direction, we model low Li concentrations using supercells. With one extra Li inserted in an $(a \times b \times 3c)$ super cell, the band gap is found to be greatly decreased (Fig. 4d) from 2.3 eV (in $[T$-Nb$_2$O$_5]$) to 0.3 eV (in Li$_{0.04}$[$T$-Nb$_2$O$_5$]), because a new filled defect band just below the Fermi energy is induced by this Li interstitial (see Supplementary Fig. 27b). After that, the material becomes metallic once a second extra Li is intercalated into our $(a \times b \times 3c)$ super cell, as shown in Fig. 4e, because the newly induced band crosses the Fermi energy (see Supplementary Fig. 28c). Our results indicate that the conductivity of the $T$-Nb$_2$O$_5$ structure is sensitive to Li insertion, where even low Li concentrations can make the semiconducting $T$-Nb$_2$O$_5$ material metallic.

Finally, we investigated the differential binding energy ($\Delta E_b$) as a function of Li interstitial concentration in our $[T$-Nb$_2$O$_5]$ model (Supplementary Section 6.2). For low Li concentrations ($x \lesssim 0.4$), the obtained $\Delta E_b$ fluctuates around -2 eV (-1.95 eV - -2.24 eV) (see Figure 4h). At higher concentrations, the binding energy gradually decreases but remains above 1.5 eV until at least $x = 1$. Our $\Delta E_b$ results agree with experimental findings that the initial onset potential of $\approx$2 V ($vs.$ Li$^+$/Li) is required to initiate the lithiation process for $T$-Nb$_2$O$_5$. The experimentally observed high Li capacity of single-crystal $T$-Nb$_2$O$_5$ material is also reflected in our DFT calculations. Moreover, we found that at high Li concentration, a phase transformation from orthorhombic to monoclinic is energetically favorable. Figure 4i shows the energetic
evolution of the Li$_{1.08}$-$[T$-Nb$_2$O$_5$] as a function of tilt angle varying from 90° to 92.5°. The monoclinic phase with a tilt angle about 91.4° is more stable than the orthorhombic phase by 0.44 meV per atom and is consistent with other metastable configurations of Li$_{1.08}$-$[T$-Nb$_2$O$_5$] (see Supplementary Fig. 29 and 30). Entropy corrections from room temperature (300 K) phonons will also stabilize the monoclinic phase by an additional 0.58 meV per atom (for a total free-energy difference of 1.02 meV/atom) compared with the orthorhombic phase. For comparison, we also considered monoclinic distortions of the unlithiated [T-Nb$_2$O$_5$] unit cell (Fig. 4i) and found that the orthorhombic phase is more stable. Therefore, the calculations predict that T-Nb$_2$O$_5$ will undergo a phase transition from orthorhombic to monoclinic at a high concentration of Li interstitials, in agreement with our experimental findings.

In conclusion, we have grown epitaxial single crystalline T-Nb$_2$O$_5$ thin films with vertically formed two-dimensional layers that provide paths for fast ionic migration. These films enable the measurement of a colossal insulator-metal transition with a change in resistivity of 11 orders of magnitude upon lithium insertion and concomitant n-doping. Two new structural phases in the Li-Nb$_2$O$_5$ phase diagram were discovered: a monoclinic distortion of orthorhombic T-Nb$_2$O$_5$ with approximate composition Li$_x$Nb$_2$O$_5$ (0.8 ≤ x < 1.8) and a tetragonal Li-rich layered structure (x > 1.8). For the thin film, the sequential phase transformations from an orthorhombic insulator, to an orthorhombic metal, to a monoclinic metal, to a degraded insulating phase were seen, without the formation of the tetragonal phase. The low activation energy of Li-ion migration in addition to the nearly constant differential binding energy with increasing Li-concentrations provide for fast ionic diffusion. Defect electronic states near the Fermi energy from Li-ion migration lead to abrupt changes in resistivity. Finally, we show that tuneable and low voltage operation with chemical potential control can be achieved by using Li-containing gate electrodes. This work showcases a synergistic experiment-theory approach to explore hidden phase transitions via ionic intercalation beyond typical charge storage and for the development of new types of ionically channelled devices.
Methods

**Film growth.** A reflection high energy electron diffraction (RHEED)-assisted pulsed laser deposition (PLD) system using a 248 nm KrF excimer laser was employed to optimize the growth conditions of Nb$_2$O$_5$ thin films by varying the growth temperature from 500 to 900 °C. The laser fluence, oxygen partial pressure ($p_{O_2}$), and repetition rate were 1 J cm$^{-2}$, 10 mT, and 6 Hz, respectively. The optimized growth temperature of $T$-Nb$_2$O$_5$ thin films was $\approx$620 °C. The heating and cooling rate were 30 and 10 °C/min, respectively. Substrates of STO (001), LSAT (001), LAO (001), STO (110), LSAT (110), and LAO (110) were used to study substrate orientation dependent domain structures. For gate electrode potential control, LFP and LCO thin films were grown on LSAT (110) substrates by varying $p_{O_2}$ at room temperature. The laser fluence and repetition rate were 1 J cm$^{-2}$ and 6 Hz, respectively. The optimal $p_{O_2}$ was 1 mT and 10 mT for the LFP and LCO thin films, respectively, as determined by XPS characterization.

**Ionic liquid gating device fabrication.** Standard photo-lithographic techniques were used to fabricate ionic liquid gating devices. Substrates with a size of 5×5 mm$^2$ were used. A $T$-Nb$_2$O$_5$ channel with a size of 65 × 30 μm$^2$ was etched and then Ru (5 nm) and Au (70 nm) layers were successively deposited using ion beam sputtering (SCIA coat 200) for both the gate electrode and channel contacts. The ionic liquid covered both the $T$-Nb$_2$O$_5$ and the gate electrode. For the gate electrode potential control, Li-containing oxides were deposited on top of the Au/Ru gate electrode.

For the LNbO gate electrode device fabrication, both channel and gate were etched, and then Au (70 nm)/Ru (5 nm) layers were deposited to make channel and gate contacts. Then, the reference electrode (LFP) was deposited using pulsed laser deposition. After the device fabrication, Li ions are moved from the LFP to the gate electrode by ILG to make L NbO gate electrode. Then, the gating was applied to the Nb$_2$O$_5$ channel using the LNbO gate electrode.

For the *in situ* XRD measurements of the thin films, a $T$-Nb$_2$O$_5$ channel with a size of 2 × 2 mm$^2$ was etched, then Au (70nm)/Ru(5 nm) layers were deposited for the gate electrode and channel contacts. The device was then attached using double-sided tape to a specially designed sample holder. The IL was placed on the device surface, and then Kapton film was attached to reduce the thickness of the IL. Resistance and $\theta$–$2\theta$ scans were measured during *in situ* ILG.
Thin film characterization. 0–20 scans, phi scans, and in situ XRD on the thin films were carried out using a Bruker d8 Discovery X-ray diffractometer with Cu-Kα radiation. RSM measurements were performed using a Ga jet x-ray source (λ=1.34 Å) and a six-circle diffractometer equipped with a Pilatus 100 K pixel detector. HAADF-STEM imaging was performed using a JEOL ARM200F with a spherical aberration corrector (CEOS GmbH) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Scientific) was conducted for Li-containing oxides. The film surface was gently cleaned by cluster ion etching prior to the measurement.

Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI), and Li-IL were used for the ILG. For the Li-IL, a lithium bis(trifluoromethanesulfonil)imide (Li-TFSI) powder was dissolved in the EMIM-IL at 50 °C for 2 h to achieve a solution of molality 0.3 mol kg⁻¹. Each IL was dried in a vacuum chamber (10⁻⁶ mbar) at 105 °C for at least 10 h prior to use.

Transport measurements of the ionic liquid gating devices were carried out in a physical property measurement system (Quantum Design). Gate voltages were applied using Keithley 2450A source meters. For the resistance measurements, a constant current of 1 µA was applied using a Keithley 6221 current source, and the voltage was measured by a Keithley 2182A nanovoltmeter. The gate voltage is applied between the gate electrode and the T-Nb₂O₅ channel, while monitoring the resistance of the channel. The substrate is insulating, thus the voltage is applied through IL, resulting in Li-ion migration from gating. The resistance of the pristine T-Nb₂O₅ thin films was measured by a high resistance meter (B2985A, KEYSIGHT). 1000 data points were averaged at each temperature in a probe station. Li-ILG of thin films for the ex situ XRD, STEM, and XANES measurements was carried out using a polytetrafluoroethylene (PTFE) boat with a gold plate (the gate electrode) covered with the Li-IL.

Nb K-edge X-ray absorption spectra were acquired at the CLÆSS beamline at the ALBA synchrotron. The synchrotron radiation emitted by a wiggler source was monochromatized using a double crystal Si (311) monochromator, while higher harmonics were rejected by proper choice of angles and coatings of the collimating and focusing mirrors. The samples were mounted in a liquid nitrogen cryostat, and the spectra were recorded in fluorescence mode at 80 K by means of a multichannel silicon drift detector. The sample normal and the fluorescence detector were at 60 and 90 degrees with respect to the incoming beam.
respectively. The fluorescence detector dead time was kept around 4.5 % at 19,600 eV for both samples for a better comparison.

**Operando powder XRD.** Free-standing electrodes for in situ XRD measurements with coupled electrochemistry was prepared by mixing 90 wt. % T-Nb$_2$O$_5$ powder, 5 wt. % Polytetrafluoroethylene (PTFE) binder, 5 wt. % carbon black (Timcal SuperP). The mixed powder was pressed and rolled onto a flat surface to give a homogenous film. The film was formed into a disc with a diameter of 13 mm and dried in a Buchi oven at 100 °C under dynamic vacuum (10$^{-2}$ mbar) for 12 h before transferring into an argon filled glovebox. A customised electrochemical cell equipped with a Be window was used to prepare cells for in situ XRD. The 70 μL of LP57 electrolyte (1 M LiPF$_6$, ethylene carbonate (EC)/ethyl methyl carbonate (EMC) 3/7, SoulBrain MI) was added to the film followed by 16 mm glass fiber separator. Battery cycling was conducted on a Land cycler at room temperature between open circuit voltage and 0.005 V at C/30 rate. The C-rate was defined based on a theoretical reversible capacity of 175 mAh/g. In situ XRD data were collected at 300 K on a Panalytical Empyrean diffractometer equipped with a Ni filter using Cu–Kα radiation (λ = 1.5406 Å) in Bragg-Bentano geometry.

**Electrochemical characterization.** For electrochemical cycling of thin films in a pouch cell, the samples were deposited on non-conducting LSAT substrates giving highly oriented single crystalline films. For the current collector, Au was deposited/patterned on the surface of the thin film. The Cu tab was connected on the gold pattern (Supplementary Fig. 6). The other components of cell, anode, electrolyte, and separator were the same as those used for the in situ powder XRD experiments. For cyclic voltammetry experiments, three different scan rates of 0.1, 0.5, and 1.0 mV/s, were used. Galvanostatic charge discharge was also performed with current densities of 14.28, 7.14, 3.57, and 1.43 A/g.

**Theoretical calculations.** The first-principles calculations use density functional theory with a plane-wave basis set, as implemented in the QUANTUM ESPRESSO (QE) package$^{32}$. Ultrasoft pseudopotentials$^{33}$ along with Perdew, Burke, Ernzerhof (PBE) exchange correlation (XC)$^{34}$ functional were used. Dispersion interactions are accounted for using the Grimme DFT-D3 method$^{35}$. Phonon calculations are performed using the DFT-D2 scheme due to technical computational considerations in performing this type of calculations using QE. The DFT+U method$^{36-38}$, with $U$=6.0 eV, is applied to account for d-electron localization on the Nb atoms$^{39}$. The plane wave kinetic-energy cutoff for wave functions is set at 40 Ry, with the cutoff for charge density being ten times larger. The Brillouin zone is sampled using a 6×1×8 Monkhorst-
Pack mesh for the unit cell of unlithiated $[T\text{-}\text{Nb}_2\text{O}_5]$ (Li$_4$Nb$_{16}$O$_{42}$ in our model, see the introduction in Supplementary Section 5.1). The $2a \times b \times 2c$ and $a \times b \times 3c$ super cells of $T\text{-}\text{Nb}_2\text{O}_5$ are sampled with a $3 \times 1 \times 4$ k-point mesh. We modeled the diffusion of one Li in the unit cell of $T\text{-}\text{Nb}_2\text{O}_5$ by the nudged elastic band method with climbing image (CI-NEB)\textsuperscript{41,42}. The free-energy profile of the most favorable diffusion pathway has been shown in Fig. 4f.

The differential binding energy ($\Delta E_b$) of each Li interstitial reaction in the $[T\text{-}\text{Nb}_2\text{O}_5]$ model (as shown in Fig. 4g) was calculated as:

$$\Delta E_b = E(\text{Li}_x\text{-}[T\text{-}\text{Nb}_2\text{O}_5]) - E(\text{Li}_{x'}\text{-}[T\text{-}\text{Nb}_2\text{O}_5]) - 0.5(x-x') \times n_{\text{Nb}} E(\text{Li}) (n_{\text{Nb}} = 16.8 \text{ or } 67.2)$$

where $n_{\text{Nb}}$ indicates the number of Nb atoms in the cell, and $0.5(x-x') \times n_{\text{Nb}}$ is the number of extra Li atoms intercalated into the material. $E$ indicates the DFT energies of the compositions calculated from \textit{ab initio} studies. The reference energy of $E(\text{Li})$ is calculated from bulk Li metal. The energy of $[T\text{-}\text{Nb}_2\text{O}_5]$ is calculated from our unit cell model of Li$_4$Nb$_{16}$O$_{42}$ and super cell of Li$_{16}$Nb$_{64}$O$_{168}$, respectively. All possible interstitial sites for each Li atom were considered and the site providing the most negative $\Delta E_b$ is the most energetically favorable location for that atom (these sites are shown in Supplementary Fig. 29). Such arrangement of interstitial Li is iteratively used as a starting configuration for the higher concentration simulations.

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**Author contributions.** H.H., Q.J., C.P.G, and S.S.P.P. conceived the project. H.H. grew thin films. H.H. and A.S. fabricated ILG devices. H.H. performed transport measurements. Q.J. and F.N.S. contributed to electrochemical measurements. Q.J., F.N.S., and K.J.G. analysed powder structures. H.H. and H.L.M. analysed thin film structures. S.Y.N. and J.P. performed TEM. L.S.
carried out XANES. Z.J., A.M.S., A.K. performed DFT calculations. H.H. was the lead researcher. C.P.G, A.M.R., and S.S.P.P. supervised the project. H.H., Q.J, Z.J., C.P.G, A.M.R., and S.S.P.P. wrote the manuscript with contributions from all authors.

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Fig. 1. Structure of epitaxial $T$-$\text{Nb}_2\text{O}_5$ thin films. a, Schematic showing Li-ion migration into $T$-$\text{Nb}_2\text{O}_5$. The black, red, and green spheres denote Nb, O, and Li ions, respectively. The grey and navy polyhedra denote distorted octahedra (NbO$_6$) and pentagonal bipyramids (NbO$_7$), respectively. The grey and yellow planes represent the 4h and 4g layers, respectively. The loosely packed two dimensional 4g layer provides for fast Li-ion transport. b, Nb 4$d$ orbital state changes from d$^0$ to d$^1$ due to electron doping via Li intercalation. c, Cross-sectional HAADF-STEM image of a $T$-$\text{Nb}_2\text{O}_5$ thin film grown on a LAO (001) substrate viewed along LAO [100], revealing the presence of two structural domains. d-e, Magnified STEM images of each domain labelled in (e), showing two domains of $T$-$\text{Nb}_2\text{O}_5$ [001] and [810], respectively. Overlaid yellow and grey spheres represent Nb and O atoms, respectively. Green dashed lines represent the vertical ionic transport channels (4g layers) viewed from $T$-$\text{Nb}_2\text{O}_5$ [810]. f-g, STEM images of $T$-$\text{Nb}_2\text{O}_5$ thin film grown on a LSAT (110) substrate viewed along the LSAT [001] and [110] directions, respectively. h-i, FFT patterns of a single crystalline film grown on LSAT (110) along $T$-$\text{Nb}_2\text{O}_5$ [001] and [810], respectively.
Fig. 2. Electrochemical and electronic properties of $T$-$Nb_2O_5$ thin films. a, Galvanostatic discharge-charge curves and b, Specific capacity obtained at each cycle at different current rates for a 40 nm thick film of $T$-$Nb_2O_5$/LSAT (110). The specific capacity was calculated from the exposed part of the film. Note that an irreversible capacity is observed at the lowest current densities, which is attributed to corrosion of parts of the device. c, Cyclic voltammogram recorded at different scan rates (0.1, 0.5 and 1.0 mV/s); the second cycle of each cycling rate is shown here. Schematics of ILG devices with d, Au/Ru gate electrode (top image) and e, Li-Nb$_2$O$_5$ gate electrode (bottom image). G represents gate electrode. Blue spheres denote Li-ion migrations from gating. f, Gate voltage ($V_g$) dependent resistivity and leakage current curves for several ILs (Li-IL, DEME-TFSI, and EMIM-TFSI). g, Temperature-dependent resistivity curves at different gate voltages. h, $V_g$ dependent carrier concentration ($n$), Li composition ($x$), mobility ($\mu$), and resistivity ($\rho$) curves from Hall measurements at 200 K for Li$_x$Nb$_2$O$_5$. Multi-step transitions are shown with increasing $V_g$, i.e., (i) orthorhombic insulator (white regime) (ii) orthorhombic metal (blue), (iii) monoclinic metal (red), and (iv) insulating state (grey). The carrier concentration suddenly increases, and the mobility starts to decrease at $\approx 4$ V, indicating carrier scattering at high Li concentration. The Li concentrations are obtained from Hall measurements, assuming that each Li atom creates one charge carrier. i, $V_g$ dependent $\rho$ and $I_g$ curves for the 16 nm thick $T$-$Nb_2O_5$/LSAT(110) device using the Li-Nb$_2$O$_5$ gate electrode. The symmetric resistivity changes are observed with very low gate voltages.
Fig. 3. Multi-step structural phase transitions of T-Nb$_2$O$_5$ via Li-ion intercalation. a, Operando XRD data for bulk T-Nb$_2$O$_5$ until the deep discharge potential of 0.005 V vs. Li with C/30 scan rate for electrochemical cycling. “Be” indicates peaks from the Be window of the in situ cell along with an intense peak at ≈52°. Horizontal yellow dashed lines indicate the boundary of the structural phase transition. b, c-lattice parameter as a function of x in Li$_x$Nb$_2$O$_5$. Grey dots represent the average c parameter obtained from the (002) reflection in SXRD data (Supplementary Fig. 14). Blue, red, and green dots denote the c parameter of the o-, m-, and t-phases, respectively, extracted from Rietveld refinement of the operando XRD data. The purple line is the voltage curve obtained during the Galvanostatic discharge-charge measurement. Color zone highlights four regions i) pristine orthorhombic (o-) phase from Li$_0$Nb$_2$O$_5$ to Li$_{0.8}$Nb$_2$O$_5$ (white), ii) a 25/75 % mixture of the orthorhombic (o-)/monoclinic (m-) phases from Li$_{0.8}$Nb$_2$O$_5$ to Li$_{1.8}$Nb$_2$O$_5$ (pink), iii) progressive disappearance of the o- and m- phase mixture to the benefit of the tetragonal (t-) phase from Li$_{1.8}$Nb$_2$O$_5$ to Li$_3$Nb$_2$O$_5$ (green), iv) no change of the XRD pattern from Li$_3$Nb$_2$O$_5$ to Li$_4$Nb$_2$O$_5$ (grey). c, left panel: SXRD patterns (red) of ex situ Li$_{1.6}$Nb$_2$O$_5$ together with simulated patterns of the Pbam and P21/m, in black and blue, respectively. right panel: SXRD pattern and Rietveld refinements of m-Li$_{1.6}$Nb$_2$O$_5$. Red circles, black line, and grey line represent the observed, calculated and difference patterns, respectively. d, Rietveld refinement of an operando SXRD pattern measured at 5 mV using the tetragonal (t-) phase described in Table S2. The operando cell produces a large background together with peaks marked *. Green circles, black line and grey line represent the observed, calculated and difference patterns, respectively. Blue vertical bars represent the Bragg position. e, In situ XRD
Fig. 4. Electronic and structural phases of $T\text{-}\text{Nb}_2\text{O}_5$ via Li intercalation. a. Composition dependent electronic and structural phase diagram of $T\text{-}\text{Nb}_2\text{O}_5$ thin films via Li intercalation. The reversibility of the phase transitions is also presented. b. Orthorhombic model system ($\text{Li}_4\text{Nb}_{16}\text{O}_{42}$) was employed to simulate the conventional unlithiated unit cell of $T\text{-}\text{Nb}_2\text{O}_5$ ($\text{Nb}_{16.8}\text{O}_{42}$, shown in Supplementary Fig. 22), where 4 Li are added per cell to replace the charge of the fractionally distributed 0.8 Nb atom/cell in the 4g layer. This $\text{Li}_4\text{Nb}_{16}\text{O}_{42}$ model for $T\text{-}\text{Nb}_2\text{O}_5$ is considered unlithiated and referred to as $[T\text{-}\text{Nb}_2\text{O}_5]$ throughout. c. Total density of states (DOS) of the $[T\text{-}\text{Nb}_2\text{O}_5]$ model unit cell. d. and e. Total DOS with one and two extra Li intercalated in the ($a \times b \times 3c$) super cell of our simulation model, (i.e. $\text{Li}_{0.08}\text{[T-Nb}_2\text{O}_5]$ and $\text{Li}_{0.08}\text{[T-Nb}_2\text{O}_5]$) f. Total density of states (DOS) of our monoclinic $\text{Li}_{1.08}$-$[T\text{-}\text{Nb}_2\text{O}_5]$ structure. g. Diffusion performance of the one extra Li in the $\text{Li}_{0.12}$-$[T\text{-}\text{Nb}_2\text{O}_5]$ primitive unit cell including free-energy profile and diffusion barrier ($E_a$). h. The evolution of differential binding energy ($\Delta E_b$) for low-concentration Li interstitials in the supercell ($2a \times b \times 2c$) and high-concentration Li interstitials in the primitive unit cell of $[T\text{-}\text{Nb}_2\text{O}_5]$. i. The relative energy evolution of two lithiation states ($[T\text{-}\text{Nb}_2\text{O}_5]$ and $\text{Li}_{1.08}\text{[T-Nb}_2\text{O}_5]$) as a function of axis angle tilt from 90° to 92.5°.