

Boise State University

ScholarWorks

Materials Science and Engineering Faculty
Publications and Presentations

Micron School for Materials Science and
Engineering

7-2022

Electrochemically Induced Amorphous-to-Rock-Salt Phase Transformation in Niobium Oxide Electrode for Li-Ion Batteries

Pete Barnes

Boise State University

Yunxing Zuo

University of California San Diego

Kiev Dixon

Boise State University

Dewen Hou

Boise State University

Sungsik Lee

Argonne National Laboratory

See next page for additional authors

Publication Information

Barnes, Pete; Zuo, Yunxing; Dixon, Kiev; Hou, Dewen; Lee, Sungsik; Ma, Zhiyuan; . . . and Xiong, Hui. (2022). "Electrochemically Induced Amorphous-to-Rock-Salt Phase Transformation in Niobium Oxide Electrode for Li-Ion Batteries". *Nature Materials*, 21, 795-803. <https://doi.org/10.1038/s41563-022-01242-0>

This document was originally published in *Nature Materials* by Springer Nature, Ltd. Copyright restrictions may apply. <https://doi.org/10.1038/s41563-022-01242-0>

Authors

Pete Barnes, Yunxing Zuo, Kiev Dixon, Dewen Hou, Sungsik Lee, Zhiyuan Ma, Justin G. Connell, Hua Zhou, Changjian Deng, Kassiopeia Smith, Eric Gabriel, Yuzi Liu, Olivia O. Maryon, Paul H. Davis, Haoyu Zhu, Yingge Du, Ji Qi, Zhuoying Zhu, Chi Chen, Zihua Zhu, Yadong Zhou, Paul J. Simmonds, Ariel E. Briggs, Darin Schwartz, Shyue Ping Ong, and Hui Xiong

Electrochemically-Induced Amorphous to Rock Salt Phase Transformation in Niobium Oxide Electrode for Li-Ion Batteries

Pete Barnes

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Currently at:

Energy Storage and Electric
Transportation Department
Idaho National Laboratory
Idaho Falls, ID

Yunxing Zuo

Department of NanoEngineering
University of California San
Diego
La Jolla, CA

Kiev Dixon

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Dewen Hou

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

and

Center for Nanoscale Materials
Argonne National Laboratory
Lemont, IL

Sungsik Lee

X-Ray Science Division
Argonne National Laboratory
Lemont, IL

Zhiyuan Ma

X-Ray Science Division
Argonne National Laboratory
Lemont, IL

Justin G. Connell

Joint Center for Energy Storage
Research and Materials Science
Division
Argonne National Laboratory
Lemont, IL

Hua Zhou

X-Ray Science Division
Argonne National Laboratory
Lemont, IL

Changjian Deng

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Kassiopeia Smith

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Eric Gabriel

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Yuzi Liu

Center for Nanoscale Materials
Argonne National Laboratory
Lemont, IL

Olivia O. Maryon

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Paul H. Davis

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Haoyu Zhu

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Yingge Du

Physical and Computational
Sciences Directorate
Pacific Northwest National
Laboratory
Richland, WA

Ji Qi

Energy Storage and Electric
Transportation Department
Idaho National Laboratory
Idaho Falls, ID

Zhuoying Zhu

Department of NanoEngineering
University of California San
Diego
La Jolla, CA

Chi Chen

Department of NanoEngineering
University of California San
Diego
La Jolla, CA

Zihua Zhu

Environmental Molecular
Sciences Laboratory
Pacific Northwest National
Laboratory
Richland, WA

Yadong Zhou

Environmental Molecular
Sciences Laboratory
Pacific Northwest National
Laboratory
Richland, WA

Paul J. Simmonds

Micron School of Materials
Science and Engineering
and
Department of Physics
Boise State University
Boise, ID

Ariel E. Briggs

Micron School of Materials
Science and Engineering
Boise State University
Boise, ID

Darin Schwartz

Department of Geosciences
Boise State University
Boise, ID

Shyue Ping Ong*

Department of NanoEngineering
University of California San Diego
La Jolla, CA
ongsp@eng.ucsd.edu

Hui Xiong*

Micron School of Materials Science and Engineering
Boise State University
Boise, ID
clairexiong@boisestate.edu
and
Center for Advanced Energy Studies
Idaho Falls, ID

Abstract

Intercalation-type metal oxides are promising negative electrode materials for safe rechargeable lithium-ion batteries due to the reduced risk of Li plating at low voltages. Nevertheless, lower energy and power density along with cycling instability remain bottlenecks for their implementation, especially for fast-charging applications. Here, we report a nanostructured rock-salt Nb₂O₅ formed through an amorphous-to-crystalline transformation during repeated electrochemical cycling with Li⁺. This electrode can reversibly cycle three lithium per Nb₂O₅, corresponding to a capacity of 269 mAh g⁻¹ at 20 mA g⁻¹, and retains a capacity of 191 mAh g⁻¹ at a high rate of 1 A g⁻¹. It exhibits superb cycling stability with a capacity of 225 mAh g⁻¹ at 200 mA g⁻¹ for 400 cycles, and a Coulombic efficiency of 99.93%. We attribute the enhanced performance to the cubic rock-salt framework, which promotes low-energy migration paths. Our work suggests that inducing crystallization of amorphous nanomaterials through electrochemical cycling is a promising new avenue for creating unconventional high-performance metal oxide electrode materials.

Increasing global energy demand has intensified the pursuit of high-performance, cost-effective, and sustainable energy storage technologies.¹ While rechargeable lithium-ion batteries (LIBs) are the current market leader, innovative battery materials created with novel processing techniques are needed to reach new performance benchmarks. Niobium oxides are promising negative electrode materials for rechargeable LIBs due to their rich redox chemistry (Nb⁵⁺ to Nb⁴⁺), chemical stability, and numerous meta-stable and stable polymorphs.²⁻⁸ The higher intercalation potential of Nb₂O₅ (~ 1.7 V vs. Li/Li⁺) relative to commercial graphite electrodes (< 0.3 V) makes it less susceptible to Li plating and electrolyte decomposition, and therefore, safer.⁸ However, sluggish Li⁺ diffusion, poor electrical conductivity (~3 x 10⁻⁶ S cm⁻¹),⁵ and low capacity have hindered the deployment of Nb₂O₅ electrodes.⁸⁻¹⁰ To address these issues, work has focused on increasing charge storage and transport properties by developing nanoarchitectures, and/or adding conductive materials (e.g., graphene and carbon-coatings).^{8,11-13}

Another strategy to improve the performance of Nb₂O₅ electrodes is to optimize the crystal structure for lithium ion intercalation. There are at least 12 different polymorphs of Nb₂O₅.⁵ Polymorphs of Nb₂O₅ previously studied as LIB negative electrodes include pseudohexagonal (TT-Nb₂O₅), orthorhombic (T-Nb₂O₅), and monoclinic (B, M, and H-Nb₂O₅).^{14,15} The average capacity of the most studied T-Nb₂O₅ electrodes is around 170 mAh g⁻¹,^{5,10,16} while a higher capacity of 227 mAh g⁻¹ has been reported for a monoclinic structure,⁶ which is beyond the theoretical capacity of 202 mAh g⁻¹ based on Li₂Nb₂O₅, i.e., one electron redox per Nb.

Currently, strategies for the synthesis of new intercalation metal oxide electrode materials include traditional ceramic processing by solid-state reactions, hydro(solvo)thermal processing, and ionothermal processing. However, metastable structures with unique properties cannot be easily obtained through such approaches. Recent works on other transition metal oxides have suggested that electrochemical cycling may present a new synthetic avenue to obtain novel structures and frameworks.¹⁷⁻²¹

The first demonstration of this phenomenon in transition metal oxide negative electrodes was with titanium dioxide nanotubes (TiO₂NT),¹⁸ wherein amorphous TiO₂NT underwent spontaneous phase transformation into a long-range ordered/short-range disordered cubic structure when cycled with Li⁺.¹⁸ Studies showed when Li⁺ reached a high concentration, atomic rearrangements were initiated within the material to minimize the energy, resulting in a cubic structure.^{18,19} Recently, a disordered rock-salt (DRX) Li_{3+x}V₂O₅ electrode obtained through electrochemically lithiating V₂O₅ to 1.5 V exhibited exceptional rate capability for fast-charging LIBs.²¹ Furthermore, it was also shown in a manganese oxide system that a tunnel-structured todorokite, which is common in nature but difficult to synthesize in the laboratory at room temperature, can be obtained through repeated electrochemical cycling from a layered MnO₂.²⁰

Here, we report an electrochemically-driven amorphous-to-crystalline (a-to-c) transformation of nanostructured Nb₂O₅ upon cycling with Li⁺, and demonstrate the insertion of three lithium into Nb₂O₅ (~ 1.5 electron redox per Nb). Amorphous Nb₂O₅ (*a*-Nb₂O₅) transformed spontaneously to a rock-salt structure (*RS*-Nb₂O₅) when the electrode was cycled to a potential of 0.5 V vs. Li/Li⁺, as identified by transmission electron microscopy (TEM) and synchrotron X-ray diffraction (sXRD). Density functional theory (DFT) calculations revealed that *RS*-Nb₂O₅ exhibits exceptionally high capacity for Li⁺ ions and low migration barriers for Li⁺ diffusion. Results from X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) indicated that the high capacity of *RS*-Nb₂O₅ was associated with its ability to go beyond the Nb⁵⁺/Nb⁴⁺ redox. In addition, the *RS* structure benefited from an increase in Li⁺ diffusivity and electrical conductivity compared to its amorphous counterpart, as shown by galvanostatic intermittent titration technique (GITT), peak force tunneling atomic force microscopy (PF-TUNA), and two-point probe conductivity measurement, which correlated closely with its rate performance. Electrochemically induced crystallization of nanomaterials therefore offers an innovative approach for the discovery of high energy/power and stable electrode materials that were previously inaccessible using conventional synthesis methods.

Characterization of As-Prepared Nanochanneled Nb₂O₅

As-prepared samples are consisted of vertically oriented nanochanneled niobium oxide (NCNO) electrically connected to a Nb current collector (Fig. 1 and Supplementary Fig.1). This particular nanoarchitecture facilitates fast access of the electrolyte to the active walls, as well as facile electron and ion transport for enhanced kinetics.²² Selected area electron diffraction (SAED) (Fig. 1d), XRD, and Raman spectroscopy (Supplementary Fig. 2) showed that the as-prepared NCNO was amorphous.

a-to-*c* Transformation of NCNO via Electrochemical Cycling

The as-prepared NCNO samples were subjected to electrochemical cycling between 3 V and 0.5 V vs. Li/Li⁺, and the voltage profiles and corresponding differential capacity (dQ/dV) plots for the electrode are shown in Fig. 2. The voltage profile of the initial discharge is characterized by a shallow, linear slope, which upon subsequent cycling develops a plateau-like feature centered around 1.67 V (Fig. 2a). The appearance of a plateau is indicative of an increased number of equivalent intercalation sites in a crystalline host material representing a first-order phase transition during intercalation/deintercalation,²³ which suggests an *a*-to-*c* phase transformation initiated by electrochemical cycling with Li⁺.

Fig. 2a exhibits a large hysteresis during the initial cycle, which may result from mechanical stress, thermodynamic entropic effects, activation polarization, nucleation barriers, and/or lattice distortions within the active material.²⁴⁻²⁸ A significant reduction in the hysteresis was observed on the 5th and 20th cycle. This demonstrates that the electrode self-improved its thermodynamic and kinetic properties through repeated Li insertion/extraction.

The corresponding differential capacity analysis is shown in Fig. 2b, which allows in-depth identification of phase evolution and self-improvement within the material upon electrochemical cycling. The results highlight the a-to-c phase transformation occurring below 1.1 V (blue dashed box in Fig. 2b). In the first cycle, the electrode exhibited a capacitor-like response within the majority of the potential window, consistent with previous work by Kim *et al.*,⁷ with the exception of below 1.1 V during lithiation. In this region, a cathodic peak developed around 0.78 V and continued to appear on the initial 3 cycles, which is associated with the a-to-c phase transformation. The corresponding anodic peak appeared near 2.31 V. The large peak-to-peak separation is consistent with the large hysteresis seen in Fig. 2a, suggesting initially high nucleation barriers and sluggish kinetics in the intermediate phase, as sluggish charge transfer kinetics cause greater separation of the cathodic and anodic peaks (ΔE_p). By the 4th cycle, the redox peaks near 0.78 V and 2.3 V almost disappeared. Concurrently, a distinct redox peak pair started to evolve around 1.67 V, which suggests a new phase was formed. The ΔE_p reduced from 140 mV on the 5th cycle to 74 mV on the 100th cycle, indicating continued improvement of the newly formed phase (Supplementary Fig. 3). This observation also implies that the new Nb₂O₅ structure formed upon a-to-c transformation electrochemically offers improved charge storage and transport kinetics.

Structural Characterization of a-to-c Nb₂O₅ Electrode

TEM, grazing incidence sXRD, and *ex situ* extended X-ray absorption fine structure (EXAFS) were conducted to elucidate the new rock-salt phase of Nb₂O₅ (Fig. 3). The phase transformation upon electrochemical cycling between 3 – 0.5 V was first evaluated via SAED and HR-TEM (Fig. 3a-f). The pristine sample exhibited diffuse rings in SAED (Fig. 3a), consistent with the amorphous feature observed in HR-TEM (Fig. 3b). The SAED pattern began to sharpen after the 1st cycle (Fig. 3c), suggesting the formation of nanocrystallites within the amorphous matrix (Fig. 3d). After the 20th cycle, both SAED and HR-TEM showed that the oxide had become fully crystalline (Figs. 3e-f). In addition, focused ion beam (FIB)/TEM and *ex situ* TEM were performed at different locations on an electrode after 100 cycles (Supplementary Fig. 4-5) as well as on electrodes at different states of charge (Supplementary Fig. 6). It was shown that the electrode remained crystalline, with no evidence of large amorphous regions or intermediates. Furthermore, grazing incidence sXRD of the delithiated sample (Supplementary Fig. 7) showed no significant change in peak shape or peak position at different incidence angles, i.e., probing depth. Thus, the sample remains nanocrystalline throughout, indicating the uniformity of the film and insignificant surface disorders. This further suggests the new crystalline structure obtained through electrochemical cycling accounts for the performance improvement compared to its initial amorphous counterpart, which will be discussed later.

We determined the structure of the crystalline phase after the 20th cycle with *ex situ* grazing-incidence sXRD (Fig. 3g). We indexed all major peaks to a previously unreported Nb₂O₅ cubic rock-salt phase with the space group of Fm $\bar{3}$ m. The lattice parameter *a* of the cubic structure is 4.146(7) Å. Based on the Scherrer equation and the width of the diffraction peaks,²⁹ the new phase has a crystallite size of ~10 nm. To exclude the possibility that the charged (delithiated) electrode could be the rock-salt lithium niobate (Li₃NbO₄), additional results were obtained from secondary ion mass spectrometry depth profile (Supplementary Fig. 8) and inductively coupled plasma mass spectrometry. The results confirm that the new phase is RS-Nb₂O₅ not RS-Li₃NbO₄ (Supplementary Information). Notably, the a-to-c phase transformation was not observed when the NCNO electrode was cycled above 1.1 V even with extended cycling and the electrode remained amorphous (Supplementary Fig. 2a, Supplementary Fig. 9).

Ex situ EXAFS analysis was utilized to examine the local structural evolution of Nb during the first discharge (lithiation) (Fig. 3h). Standard EXAFS spectra for Nb, NbO₂, and Nb₂O₅ are provided in Supplementary Fig. 10. In the pristine sample, two broad peaks near 1.6 Å and 2.5 Å were assigned to Nb–O and Nb–Nb bond,¹⁰ respectively. The amorphous material contains distorted NbO₆, NbO₇, and NbO₈, causing large variation in the Nb–O and Nb–Nb distances.⁴ Discharging to lower voltages led to narrowing of the Nb–O peak, accompanied by intensity increase in the Nb–Nb peak (Supplementary Table 1). This implies the a-to-c transformation. The a-to-c transformation would require ordering of the distorted polyhedra, leading to converging radial distances, and higher intensity from the coordinated Nb–O and Nb–Nb shell.

Multielectron Redox of the *RS*-Nb₂O₅ Electrode

Ex situ Nb K-edge X-ray absorption near edge structure (XANES) and XPS were carried out to evaluate the valence state of Nb in the sample at various states of discharge (Fig. 4a-b). The XANES spectrum from the pristine sample most closely matched the H-Nb₂O₅ standard, indicating a Nb oxidation state in the bulk of around +5. Upon discharging to 1 V, the edge position of the sample nearly matched the NbO₂ standard, suggesting the Nb oxidation state decreased to +4. A further discharge to 0.5 V shifted the edge of the spectrum to even lower energy, indicating a Nb oxidation state below +4 in the bulk of the electrode.

Ex situ Nb 3d core level XPS spectra (Fig. 4b) were obtained from electrodes at open-circuit voltage, discharged to 1.0 V and 0.5 V, and charged back to 3.0 V. At open circuit, the sample exhibited Nb_{3/2} and Nb_{5/2} peaks at 209.5 and 206.7 eV, indicating Nb⁵⁺.^{30,31} Upon discharging to 1 V, the primary peaks were shifted 1.0 eV lower, consistent with the reduction from Nb⁵⁺ to Nb⁴⁺ seen in the XANES spectra.³² In addition, two new sets of doublets appeared at lower binding energies of 206.5/203.6 eV and 205.4/202.6 eV, corresponding to Nb²⁺ and Nb¹⁺, respectively.^{33,34} Further discharging to 0.5 V resulted in increased intensity of the Nb¹⁺ peak relative to the Nb²⁺ and Nb⁴⁺ peaks, suggesting significant reduction of Nb. As XPS is a surface technique (probing the top 10 nm of a surface),³⁵ the results suggest that the surface of the *RS*-Nb₂O₅ may experience larger reduction, forming suboxides not present in the bulk.³⁶ Upon charging back to 3.0 V, the electrode returned to Nb⁵⁺, with only minimal residual Nb⁴⁺ and Nb²⁺. The XPS results demonstrate that the Nb in *RS*-Nb₂O₅ undergoes multielectron redox in Nb (> 1:1 Li/Nb) upon lithiation/delithiation and that the process is reversible. In comparison, a DRX Li₃NbO₄ has been reported as high-capacity positive electrode, but it was claimed that the Nb ion stayed pentavalent throughout the charging/discharging processes and the charge compensation was achieved through solid-state redox of oxygen ions.³⁷

The voltage profile for lithium intercalation into *RS*-Nb₂O₅ was simulated using density functional theory (DFT). The pseudo-binary *RS*-Nb₂O₅-Li₃Nb₂O₅ phase diagram constructed from these calculations is shown in Fig. 4c and the calculated and experimental voltage profiles are plotted in Fig. 4d. Overall, the average Perdew-Burke-Ernzerhof (PBE) voltage is 1.76 V, which is in excellent agreement with the experimental average voltage of 1.67 V.

High Rate Performance and Cycling Stability

The rate capability of *RS*- and *a*-Nb₂O₅ electrodes at different current rates of 20, 50, 100, 200, and 1000 mA g⁻¹ is shown in Fig. 5a. The *RS*-Nb₂O₅ electrode exhibited a high reversible capacity of 269 mAh g⁻¹ at a current density of 20 mA g⁻¹, corresponding to ~1.42 electron redox per Nb. The high capacity of *RS*-Nb₂O₅ is among the best of reported Nb₂O₅ and niobate electrodes (Supplementary Fig. 11).^{6,16,38,39} Additionally, we observed a <10% drop in capacity at an increased current rate of 200 mA g⁻¹ (243 mAh g⁻¹), while at a current rate of 1000 mA g⁻¹ the electrode capacity was slightly lower at 191 mAh g⁻¹. In comparison, *a*-Nb₂O₅ electrode at the rate of 1000 mA g⁻¹ showed a considerably lower capacity (73 mAh g⁻¹). The *a*-Nb₂O₅ electrode retained only 43% of its low-rate capacity, while the *RS*-Nb₂O₅ was able to retain over 70% of its low-rate capacity when discharging/charging within 12 min. When the current rate was subsequently returned to 20 mA g⁻¹, the capacity of the *RS*-Nb₂O₅ electrode returned to 267 mAh g⁻¹, suggesting its great reversibility and rate capability. These results are further elaborated in Supplementary Fig. 12, which highlights the dramatic difference of the two electrodes through cyclic voltammetry, dQ/dV, and rate capability.

The cycle life of the *RS*-Nb₂O₅ and *a*-Nb₂O₅ electrodes at a current rate of 200 mA g⁻¹ is shown in Fig. 5b. The *RS*-Nb₂O₅ electrode exhibited a high reversible capacity of 224 mAh g⁻¹ at the 400th cycle with a 0.02% capacity loss. During the first four formation cycles of *RS*-Nb₂O₅ (at 20 mA g⁻¹), the initial Coulombic efficiency (CE) was 75%. After 10 cycles, the CE of the electrode exceeded 99%. By the 400th cycle, the electrode demonstrated a CE of more than 99.93%. In comparison, the *a*-Nb₂O₅ electrode exhibited a CE of 98.78% and experienced a capacity loss of more than 15% by the 400th cycle. The improved stability of the *RS*-Nb₂O₅ electrode can be attributed to the retention of its cubic framework and its nanostructure throughout the lithiation/delithiation processes (Supplementary Fig. 13).

Charge Storage and Transport Kinetics of *RS*-Nb₂O₅

To elucidate the lithium migration mechanisms in Li₃Nb₂O₅, we calculated the kinetically resolved activation barriers⁴⁰ for 38 Li hopping paths sampled from 6 representative low energy configurations to account for the possible effect of the local environments. In contrast to the DRX lithium transition metal oxide cathodes,^{21,41} we find that a direct octahedral-octahedral (o-o) hop is preferred compared to an octahedral-tetrahedral-octahedral (o-t-o) hop (Supplementary Fig. 14). The local environment along the o-o hop can be characterized by x-Li, where 0 ≤ x ≤ 4 is

the number of Li ions occupying the neighboring edge-sharing octahedral sites of a migration path (Supplementary Fig. 15). The number of Nb occupying the neighboring sites is $4 - x$. As shown in Fig. 5c, an increase in x -Li significantly decreases the migration barriers due to lower electrostatic repulsion from Li^+ compared to $\text{Nb}^{3+/4+}$.

While the migration barriers for 2 or fewer Li in neighboring octahedra are > 750 meV, the 4-Li and 3-Li pathways have barriers below 350 meV, which are significantly lower than the 420-520 meV observed for lithium migration in graphite.⁴² This observation is similar to what has been reported for DRX cathodes, where a larger number of transition metals adjacent to intermediate tetrahedral site also leads to higher barriers.⁴³ Assuming a completely random arrangement of Li and Nb, we expect that 4-Li and 3-Li hops would form $\sim 47\%$ ($0.6^4 + {}^4C_3 0.6^3 0.4$) of migration pathways in $\text{Li}_3\text{Nb}_2\text{O}_5$, creating a percolating network of low-barrier pathways for fast Li diffusion.

To comprehensively investigate the charge storage and transport kinetics of *RS-Nb₂O₅*, we conducted kinetic analyses through GITT and CV with varying scan rates,^{44,45} respectively (Extended Data Fig. 1, Supplementary Fig. 16). The studies provide further evidence of the enhanced kinetics of the new cubic phase compared to its amorphous counterpart through improved ion mobility. These exceptional properties of *RS-Nb₂O₅* facilitate high power performance.

Electrical Properties of *RS-Nb₂O₅*

Intercalation electrode materials are mixed ionic and electronic conductors. The electrical conductivity of the materials has a significant impact on their power performance.⁴⁶ Therefore, the electrical conductivity of *RS-Nb₂O₅* was evaluated through Mott-Schottky (M-S) analysis, 2-point probe conductivity measurement as well as PF-TUNA for comparison to *a-Nb₂O₅* (Fig. 6 and Supplementary Table 2). Mott-Schottky analysis (Supplementary Fig. 17) was carried out for pristine, *a-* and *RS-Nb₂O₅* samples (Fig. 6a). The positive slope in Fig. 6c for each sample is indicative of an n-type semiconductor response where electrons are the major charge carriers, as expected for Nb_2O_5 .^{5,6,47} The more depressed the slope in the M-S curves, the higher the concentration of carriers accordingly. As shown in Supplementary Table 2, *RS-Nb₂O₅* exhibited the highest charge carrier concentration.

Besides the M-S measurements, a two-point probe measurement (Supplementary Fig. 18, Table 2)^{46,48} was carried out to determine the overall electrical conductivity of the samples. The electrical conductivity of *RS-Nb₂O₅* is 33x higher than that of a cycled *a-Nb₂O₅*, and over 4 orders of magnitude higher than the pristine amorphous Nb_2O_5 . Together with the M-S results, the increased electrical conductivity of *RS-Nb₂O₅* indicates that both charge carrier concentration and electron mobility have increased in the new *RS* structure.

PF-TUNA imaging was conducted on cycled *a-Nb₂O₅* and *RS-Nb₂O₅* samples (Fig 6b-d) to simultaneously map the electrical conductivity and topography of each sample. PF-TUNA imaging of the pristine sample suggests negligible conductivity (Supplementary Fig. 19a), indicating its insulating nature. While conductance in the cycled *a-Nb₂O₅* sample (Fig. 6b) increased compared to the pristine sample, the observed average current of *RS-Nb₂O₅* (Fig. 6c) was two orders of magnitude higher than that of *a-Nb₂O₅*. The 3D image in Fig. 6d features electrical current mapping overlaid on topography to provide direct visualization of the current distribution across the surface of *RS-Nb₂O₅*. The higher TUNA current in *RS-Nb₂O₅* suggests that the *a-to-c* transformation has led to higher electrical conductivity, consistent with the results from the two-point probe measurements. The PF-TUNA imaging indicates that despite the greatly increased electrical conductivity of the *RS-Nb₂O₅* electrode relative to the *a-Nb₂O₅*, the surface was still heterogeneous at the nanoscale. Within the $5 \times 5 \mu\text{m}^2$ region shown in Fig. 6d, uneven current distribution was observed over the surface. We postulate that the observed heterogeneity is associated with the phase transformation process, which self-adapts to promote the lowest migration barriers for both ion and electron transport.

Rock Salt Formation of Various Ceramic Materials

Previously, Xiong *et al.* have discovered an *a-to-c* transformation in TiO_2 nanotube electrode during electrochemical lithiation.¹⁸ We resolved the structure of the crystalline TiO_2 through Rietveld refinement as a rock-salt phase ($\text{Fm}\bar{3}\text{m}$) instead of the initial assignment of a spinel phase ($\text{Fd}\bar{3}\text{m}$) (Supplementary Fig. 19a-b and Table 3). The *RS-TiO₂* exhibited superior rate performance (Supplementary Fig. 19c). M-S analysis of *RS-TiO₂* showed that the electrode has three orders of magnitude higher charge carrier concentration ($8.76 \times 10^{21} \text{ N/cm}^3$) than that ($2.01 \times 10^{19} \text{ N/cm}^3$) of a typical anatase TiO_2 .⁴⁶ Based on our studies in both Nb_2O_5 and TiO_2 systems along with recent works in other metal oxide systems,^{18,21} we postulate that electrochemically-driven crystallization in metal oxide electrodes may provide a generalizable concept in materials synthesis for electrode materials with high capacity, power and cycling stability.

We underscore the importance to overcome the nucleation barriers for new rock-salt phase by manipulating the overpotential for the transformation during electrochemical cycling (e.g., lithiation below 1.1 V for the a-to-c transformation in Nb_2O_5).

We evaluated the energy difference between the rock-salt structure and the ground state structure for other transition metal oxides (Supplementary Fig. 21) as a metric for the likelihood for rock-salt formation. It should be noted that TiO_2 ,¹⁸ V_2O_5 ,²¹ and Nb_2O_5 , which have all been demonstrated to form DRXs during electrochemical cycling, have low calculated energy differences. In general, the group VIB and VIIB transition metal oxides are less stable (larger energy differences) than group IVB and group VB transition metal oxides, with the exception of Mn. In particular, Ta_2O_5 is predicted to be another potential candidate for DRX formation.

In summary, we report a new rock-salt Nb_2O_5 electrode material produced through an electrochemically-driven crystallization of an amorphous nanochanneled Nb_2O_5 . The *RS*- Nb_2O_5 exhibits multi-electron redox per Nb for Li-ion storage. DFT calculations reveal significant low-energy lithium migration paths that lead to the exceptional electrochemical performance of the *RS*- Nb_2O_5 . The cubic structure affords a material with high rate performance due to increased Li-ion diffusivity and electrical conductivity. In parallel, the new crystal displays high stability owing to the structural integrity upon lithiation/delithiation. The self-organization of atoms into the optimal crystalline structure during electrochemical cycling suggests a new synthetic avenue to access rare metal oxide structures with unique properties. The utilization of electrochemical cycling to form novel crystalline structures can be advantageous in designing other enhanced electrode materials.

Acknowledgement

This work was supported by the National Science Foundation [Grant No. DMR-1454984]. Use of the environmental AFM was supported by NSF MRI [Grant No. 1727026]. The authors acknowledge Prof. Bruce Dunn from the University of California, Los Angeles for insightful discussion. The authors also thank Dr. Wenqian Xu from Argonne National Laboratory for support of synchrotron XRD measurements. Philip Boysen from the Boise State University machine shop for his knowledge and expertise in the production of equipment used in this study. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE of Science by Argonne National Laboratory under Contract NO. DE-AC02-06CH11357. XPS, ToF-SIMS, and data analysis were supported by the U.S. DOE Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award no. 10122 and performed using EMSL (grid.436923.9), a DOE Office of Science User Facility sponsored by the Biological and Environmental Research program. This research also used recourses at the Surface Science Laboratory and Boise State Center for Materials Characterization at Boise State University. We also thank Heather Rapoza for her contribution to the graphical abstract. Y. Z, J. Q., Z. Z, C. C. and S. P. O. acknowledge funding from the National Science Foundation Materials Research Science and Engineering Center program through the UC Irvine Center for Complex and Active Materials (DMR-2011967) for the computational portions of this work; the use of data and software resources from the Materials Project, funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under contract No. DE-AC02-05-CH11231: Materials Project program KC23MP; and computing resources provided by the Extreme Science and Engineering Discovery Environment (XSEDE) under grant ACI-1548562.

Author Contributions Statement

H. Xiong and P. Barnes conceived and designed all experiments. S. P. Ong, Y. Zuo, J. Qi, Z. Zhu and C. Chen designed all computational modeling work. P. Barnes and K. Dixon synthesized the materials. P. Barnes conducted all electrochemical measurements. S. Lee, P. Barnes, and C. Deng conducted structural characterization by XAS. H. Zhou, Z. Ma, P. Barnes, C. Deng, E. Gabriel conducted structural characterization by sXRD. J. Connell and Y. Du collected XPS. D. Hou, Y. Liu, K. Smith, P. Barnes collected FIB/TEM, HR-TEM, and SAED. P. Barnes, H. Zhu, O. Maryon, and P. Davis designed and performed PF-TUNA experiments. P. Barnes, A. Weltner, and P. Simmonds designed and collected two-point probe measurements. Z. Zhu, Y. Zhou, and Y. Du conducted ToF-SIMS measurements. D. Schwartz and P. Barnes conducted and analyzed ICPMS measurements. P. Barnes, H. Xiong, S. Lee, J. Connell, D. Hou, H. Zhou, Z. Ma, P. Davis, Z. Zhu, Y. Du and P. Simmonds analyzed the collected data. P. Barnes, Y. Zuo, H. Xiong, and S. P. Ong wrote the manuscript. All authors were involved in editing of the manuscript.

Competing Interests Statement

The authors declare no competing interest

Figure Captions

Fig. 1 | Characterization of the as-prepared nanochanneled Nb₂O₅ (NCNO). a, Top view and b, side view SEM images of the as-prepared samples. The NCNO has uniform pores with $\sim 56.3 \pm 2.3$ nm average pore diameter and $\sim 28 \pm 8$ nm wall thickness. c, low magnification TEM image and d, SAED of the as-prepared NCNO, where the diffuse ring indicates its amorphous nature.

Fig. 2 | Voltage profiles and differential capacity plots of the nanochanneled Nb₂O₅ subjected to electrochemical cycling. a, Voltage profiles of the NCNO electrode for the first 20 cycles. b, Differential capacity (dQ/dV) plots between 3 and 0.5 V vs Li/Li⁺. The peak below 1.1 V during discharge (lithiation) is evidence of the a-to-c transformation (blue dashed box). The disappearance of the cathodic peak below 1.1 V beyond the 3rd cycle is the evidence that the phase transformation had nearly completed.

Fig. 3 | SAED and HR-TEM images of the NCNO samples at different stages of electrochemical cycling, grazing incidence XRD of a cycled NCNO sample, and Nb K-edge EXAFS of samples at different states of discharge. a-c, SAED images of samples at the pristine state, after the 1st cycle, and after the 20th cycle, respectively. d-f, Corresponding HR-TEM images of the samples in a-c. For the pristine state, diffuse rings in SAED and an absence of periodic structures in HR-TEM demonstrate its amorphous nature. After the 1st cycle, faint and broadened diffraction rings appeared in SAED. Defined grains were visible in HR-TEM, and a ~ 7 nm crystallite with a lattice spacing of 2.14 Å was shown, indicative of the corresponding (200) planes in the cubic rock-salt phase. After the 20th cycle, the phase became fully crystalline, displaying well-defined SAED rings and crystalline domains in HR-TEM. g, Grazing-incidence sXRD of the NCNO electrode at charged state (delithiated) after 20 cycles. The structure is in good agreement with the simulated rock-salt Nb₂O₅ phase (black, space group Fm $\bar{3}$ m) with a lattice spacing of 4.146(7) Å. A unit cell of RS-Nb₂O₅ is presented in the inset. h, Fourier-transformed EXAFS spectra (not phase shift corrected) at Nb K-edge of the NCNO electrodes during the first discharge at different voltages. The narrowing of Nb-O peak and increasing intensity of Nb-Nb peak upon discharging below 1 V reveal the process of a-to-c transformation.

Fig. 4 | Characterization of the oxidation state of Nb in RS-Nb₂O₅, compound phase diagram computed by PBE, and voltage profiles of Li_xNb₂O₅. a, Nb K-edge XANES of Nb₂O₅ electrodes at various states of discharge. The lower edge position of electrode discharged at 0.5 V compared to the standard NbO₂ indicates the lower oxidation state of Nb than +4. b, XPS spectra of the RS-Nb₂O₅ electrodes upon lithiation/delithiation processes in the range 3 – 0.5 V. c, The compound phase diagram was computed using the PBE functional. The two end members are Nb₂O₅ and Li₃Nb₂O₅. The compositional resolution of $x=0.5$ increments in Li_xNb₂O₅ was used across the whole region of the phase diagram. An intermediate stable phase was observed at the composition LiNb₂O₅. d, Comparison between experimental and computational voltage profiles of Li_xNb₂O₅ ($0 \leq x \leq 3$) upon electrochemical cycling. The average PBE voltage of 1.76 V agrees with the measured voltage of 1.67 V.

Fig. 5 | Electrochemical performance of RS-Nb₂O₅ and a-Nb₂O₅ sample with calculated migration barrier for RS-Li₃Nb₂O₅. a, Rate capability of RS- and a-Nb₂O₅ electrodes. While the a-Nb₂O₅ electrode retained 43% of its low-rate capacity at a 1000 mA g⁻¹ rate, the RS-Nb₂O₅ electrode was able to retain over 70% of its low-rate capacity under the same condition. b, Comparison of the cycling stability of RS- and a-Nb₂O₅ electrodes. By the 400th cycle, the RS-Nb₂O₅ electrode reached a Coulombic efficiency (CE) of 99.93%, as compared to the 98.78% CE of the a-Nb₂O₅ electrode. c, Distributions of Li migration barriers at the end of discharge in RS-Li₃Nb₂O₅. The different local environments are categorized by the number of neighboring sites occupied with Li ions, and thus termed neighbors x-Li ($0 \leq x \leq 4$). There are 2, 12, 12, 10, 2 hopping paths for 0, 1, 2, 3, 4 Li local environments, respectively. For each local environment, a distribution of calculated NEB barriers with standard deviation represented by an error bar is shown.

Fig. 6 | Characterization of the electrical conductivity of RS-Nb₂O₅ and a-Nb₂O₅ samples. a, Mott-Schottky analysis for pristine, a-, and RS-Nb₂O₅ samples. The RS-Nb₂O₅ had the highest concentration of charge carriers. In addition, it showed the lowest flat-band potential, suggesting that it requires the lowest potential to reach an equivalent electron density in the bulk and interface, and thus is more conductive than its counterparts. b and c, PF-TUNA images of the

peak current map for the cycled *a*- and *RS*-Nb₂O₅ samples, respectively. The observed average current of *RS*-Nb₂O₅ sample was two orders of magnitude higher than that of *a*-Nb₂O₅ sample. **d**, The overlay of a PF-TUNA current map on topography of the *RS*-Nb₂O₅ electrode.

References

- 1 Melot, B. C. & Tarascon, J. M. Design and Preparation of Materials for Advanced Electrochemical Storage. *Accounts of Chemical Research* 46, 1226-1238, doi:10.1021/ar300088q (2013).
- 2 Ohzuku, T., Sawai, K. & Hirai, T. Electrochemistry of L-Niobium Pentoxide in a Lithium Nonaqueous Cell. *J Power Sources* 19, 287-299, doi:10.1016/0378-7753(87)87005-2 (1987).
- 3 Reichman, B. & Bard, A. J. The Application of Nb₂O₅ as a Cathode in Non-Aqueous Lithium Cells. *Journal of the Electrochemical Society* 128, 344-346, doi:10.1149/1.2127416 (1981).
- 4 Nowak, I. & Ziolek, M. Niobium compounds: Preparation, characterization, and application in heterogeneous catalysis. *Chemical Reviews* 99, 3603-3624, doi:10.1021/Cr9800208 (1999).
- 5 Aegerter, M. A. Sol-gel niobium pentoxide: A promising material for electrochromic coatings, batteries, nanocrystalline solar cells and catalysis. *Solar Energy Materials and Solar Cells* 68, 401-422, doi:10.1016/S0927-0248(00)00372-X (2001).
- 6 Le Viet, A., Reddy, M. V., Jose, R., Chowdari, B. V. R. & Ramakrishna, S. Nanostructured Nb₂O₅ Polymorphs by Electrospinning for Rechargeable Lithium Batteries. *J Phys Chem C* 114, 664-671, doi:10.1021/jp9088589 (2010).
- 7 Kim, J. W., Augustyn, V. & Dunn, B. The Effect of Crystallinity on the Rapid Pseudocapacitive Response of Nb₂O₅. *Adv Energy Mater* 2, 141-148, doi:10.1002/aenm.201100494 (2012).
- 8 Yan, L. T. et al. Recent advances in nanostructured Nb-based oxides for electrochemical energy storage. *Nanoscale* 8, 8443-8465, doi:10.1039/c6nr01340f (2016).
- 9 Brezesinski, K. et al. Pseudocapacitive Contributions to Charge Storage in Highly Ordered Mesoporous Group V Transition Metal Oxides with Iso-Oriented Layered Nanocrystalline Domains. *J Am Chem Soc* 132, 6982-6990, doi:10.1021/ja9106385 (2010).
- 10 Augustyn, V. et al. High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance. *Nat Mater* 12, 518-522, doi:10.1038/NMAT3601 (2013).
- 11 Wang, X. L. et al. High-Performance Supercapacitors Based on Nanocomposites of Nb₂O₅ Nanocrystals and Carbon Nanotubes. *Adv Energy Mater* 1, 1089-1093, doi:10.1002/aenm.201100332 (2011).
- 12 Mukherjee, R., Krishnan, R., Lu, T. M. & Koratkar, N. Nanostructured electrodes for high-power lithium ion batteries. *Nano Energy* 1, 518-533, doi:10.1016/j.nanoen.2012.04.001 (2012).
- 13 Wei, M. D., Qi, Z. M., Ichihara, M. & Zhou, H. S. Synthesis of single-crystal niobium pentoxide nanobelts. *Acta Materialia* 56, 2488-2494, doi:10.1016/j.actamat.2008.01.049 (2008).
- 14 Brauer, G. Die Oxide des Niobs. *Zeitschrift für anorganische und allgemeine Chemie* 248, 1-31, doi:10.1002/zaac.19412480101 (1941).
- 15 Schäfer, H., Gruehn, R. & Schulte, F. The Modifications of Niobium Pentoxide. *Angewandte Chemie International Edition in English* 5, 40-52, doi:10.1002/anie.196600401 (1966).
- 16 Griffith, K. J., Forse, A. C., Griffin, J. M. & Grey, C. P. High-Rate Intercalation without Nanostructuring in Metastable Nb₂O₅ Bronze Phases. *J Am Chem Soc* 138, 8888-8899, doi:10.1021/jacs.6b04345 (2016).
- 17 Pralong, V. Lithium intercalation into transition metal oxides: A route to generate new ordered rock salt type structure. *Progress in Solid State Chemistry* 37, 262-277, doi:10.1016/j.progsolidstchem.2010.08.002 (2009).
- 18 Xiong, H. et al. Self-Improving Anode for Lithium-Ion Batteries Based on Amorphous to Cubic Phase Transition in TiO₂ Nanotubes. *J Phys Chem C* 116, 3181-3187, doi:10.1021/jp210793u (2012).
- 19 Yildirim, H., Greeley, J. P. & Sankaranarayanan, S. K. R. S. Concentration-Dependent Ordering of Lithiated Amorphous TiO₂. *J Phys Chem C* 117, 3834-3845, doi:10.1021/jp312079r (2013).
- 20 Jung, H. et al. Redox Cycling Driven Transformation of Layered Manganese Oxides to Tunnel Structures. *J Am Chem Soc* 142, 2506-2513, doi:10.1021/jacs.9b12266 (2020).
- 21 Liu, H. D. et al. A disordered rock salt anode for fast-charging lithium-ion batteries. *Nature* 585, 63-67, doi:10.1038/s41586-020-2637-6 (2020).
- 22 Schmuki, P. & Virtanen, S. in *Electrochemistry at the Nanoscale Vol. 1* (ed Nanostructure Science and Technology) (Springer, 2009).
- 23 Liu, C. F., Neale, Z. G. & Cao, G. Z. Understanding electrochemical potentials of cathode materials in rechargeable batteries. *Materials Today* 19, 109-123, doi:10.1016/j.mattod.2015.10.009 (2016).

- 24 Sasaki, T., Ukyo, Y. & Novak, P. Memory effect in a lithium-ion battery. *Nat Mater* 12, 569-575, doi:10.1038/Nmat3623 (2013).
- 25 Madej, E., La Mantia, F., Schuhmann, W. & Ventosa, E. Impact of the Specific Surface Area on the Memory Effect in Li-Ion Batteries: The Case of Anatase TiO₂. *Adv Energy Mater* 4, doi:10.1002/aenm.201400829 (2014).
- 26 Ventosa, E., Löffler, T., La Mantia, F. & Schuhmann, W. Understanding memory effects in Li-ion batteries: evidence of a kinetic origin in TiO₂ upon hydrogen annealing. *Chem Commun* 52, 11524-11526, doi:10.1039/c6cc06070f (2016).
- 27 Ovejas, V. J. & Cuadras, A. Effects of cycling on lithium-ion battery hysteresis and overvoltage. *Scientific Reports* 9, doi:doi.org/10.1038/s41598-019-51474-5 (2019).
- 28 Dahlman, C. J. et al. Dynamics of Lithium Insertion in Electrochromic Titanium Dioxide Nanocrystal Ensembles. *J Am Chem Soc* 143, 8278-8294, doi:10.1021/jacs.0c10628 (2021).
- 29 Scherrer, P. The space grid of aluminium. *Physikalische Zeitschrift* 19, 23-27 (1918).
- 30 Garbassi, F., Bart, J. C. J. & Petrini, G. Xps Study of Tellurium-Niobium and Tellurium-Tantalum Oxide Systems. *Journal of Electron Spectroscopy and Related Phenomena* 22, 95-107, doi:Doi 10.1016/0368-2048(81)80019-9 (1981).
- 31 Ozer, N., Rubin, M. D. & Lampert, C. M. Optical and electrochemical characteristics of niobium oxide films prepared by sol-gel process and magnetron sputtering - A comparison. *Solar Energy Materials and Solar Cells* 40, 285-296, doi:Doi 10.1016/0927-0248(95)00147-6 (1996).
- 32 Bahl, M. K. Esca Studies of Some Niobium Compounds. *Journal of Physics and Chemistry of Solids* 36, 485-491, doi:Doi 10.1016/0022-3697(75)90132-8 (1975).
- 33 Simon, D., Perrin, C. & Baillif, P. Electron spectrometry study (ESCA) of niobium and its oxides Application to the oxidation at high temperature and low oxygen pressure. *C R Hebd Acad Sci, Ser C* 283, 241-244 (1976).
- 34 Jouve, J., Belkacem, Y. & Severac, C. X-Ray Photoelectron-Spectroscopy Study of Phosphorus Incorporation in Anodic Oxide-Films on Niobium. *Thin Solid Films* 139, 67-75, doi:Doi 10.1016/0040-6090(86)90049-0 (1986).
- 35 Verma, P., Maire, P. & Novak, P. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. *Electrochimica Acta* 55, 6332-6341, doi:10.1016/j.electacta.2010.05.072 (2010).
- 36 Monfort, Y., Maisseu, A., Allais, G., Deschanv.A & Delavign.P. Structure and Morphology of Niobium Suboxides. *Physica Status Solidi a-Applied Research* 15, 129-142, doi:DOI 10.1002/pssa.2210150115 (1973).
- 37 Yabuuchi, N. et al. High-capacity electrode materials for rechargeable lithium batteries: Li₃NbO₄-based system with cation-disordered rocksalt structure. *Proceedings of the National Academy of Sciences of the United States of America* 112, 7650-7655, doi:10.1073/pnas.1504901112 (2015).
- 38 Preefer, M. B. et al. Multielectron Redox and Insulator-to-Metal Transition upon Lithium Insertion in the Fast-Charging, Wadsley-Roth Phase PNB₉O₂₅. *Chemistry of Materials* 32, 4553-4563, doi:10.1021/acs.chemmater.0c00560 (2020).
- 39 Griffith, K. J., Wiaderek, K. M., Cibir, G., Marbella, L. E. & Grey, C. P. Niobium tungsten oxides for high-rate lithium-ion energy storage. *Nature* 559, 556-563, doi:10.1038/s41586-018-0347-0 (2018).
- 40 Van der Ven, A., Ceder, G., Asta, M. & Tapesch, P. D. First-principles theory of ionic diffusion with nondilute carriers. *Physical Review B* 64, doi:DOI:10.1103/PhysRevB.64.184307 (2001).
- 41 Lee, J. et al. Unlocking the Potential of Cation-Disordered Oxides for Rechargeable Lithium Batteries. *Science* 343, 519-522, doi:10.1126/science.1246432 (2014).
- 42 Thinius, S., Islam, M. M., Heitjans, P. & Bredow, T. Theoretical Study of Li Migration in Lithium-Graphite Intercalation Compounds with Dispersion-Corrected DFT Methods. *J Phys Chem C* 118, 2273-2280, doi:10.1021/jp408945j (2014).
- 43 Acevedo-Pena, P. & Gonzalez, I. EIS Characterization of the Barrier Layer Formed over Ti during its Potentiostatic Anodization in 0.1 M HClO₄/x mM HF (1 mM ≤ x ≤ 500 mM). *Journal of the Electrochemical Society* 159, C101-C108, doi:10.1149/2.035203jes (2012).
- 44 Conway, B. E., Birss, V. & Wojtowicz, J. The role and utilization of pseudocapacitance for energy storage by supercapacitors. *J Power Sources* 66, 1-14, doi:Doi 10.1016/S0378-7753(96)02474-3 (1997).
- 45 Wang, J., Polleux, J., Lim, J. & Dunn, B. Pseudocapacitive contributions to electrochemical energy storage in TiO₂ (anatase) nanoparticles. *J Phys Chem C* 111, 14925-14931, doi:10.1021/jp074464w (2007).

- 46 Savva, A. I. et al. Defect generation in TiO₂ nanotube anodes via heat treatment in various atmospheres for lithium-ion batteries. *Physical Chemistry Chemical Physics* 20, 22537-22546, doi:10.1039/c8cp04368j (2018).
- 47 Rani, R. A., Zoolfakar, A. S., O'Mullane, A. P., Austin, M. W. & Kalantar-Zadeh, K. Thin films and nanostructures of niobium pentoxide: fundamental properties, synthesis methods and applications. *Journal of Materials Chemistry A* 2, 15683-15703, doi:10.1039/c4ta02561j (2014).
- 48 Islam, S. Z., Reed, A., Wanninayake, N., Kim, D. Y. & Rankin, S. E. Remarkable Enhancement of Photocatalytic Water Oxidation in N₂/Ar Plasma Treated, Mesoporous TiO₂ Films. *J Phys Chem C* 120, 14069-14081, doi:10.1021/acs.jpcc.6b02622 (2016).

Methods

Electropolishing of Nb Metal

The nanochanneled niobium oxide (NCNO) samples were prepared based on the method reported previously.⁴⁹ In short, Nb foil of 127 μm thickness (35 x 40 mm², Alfa Aesar, 99.8% annealed) was cut, sonicated sequentially in acetone, isopropanol, and deionized water for 5 min each, and electropolished in 2M sulfuric acid (Fisher Scientific, 95-98%) in methanol (Fisher Scientific, 99.9%) solution. Electropolishing was conducted at 15 V with a Pt mesh counter electrode at -70 °C for 2 hours.

Nanochannel Nb₂O₅ Synthesis

NCNOs were prepared by electrochemical anodization of Nb metal, using a method adopted from the work by Schmuki et al.⁵⁰ Using a 10 wt% K₂HPO₄ in glycerol solution at 180°C, the Nb film was anodized at 25 V from 5 min up to 15 min. The as-anodized samples were then ultrasonically cleaned in DI water for 2 min. NCNO samples were then placed under vacuum and dried overnight at 110°C. The NCNO electrode contains a high density of channels (4 x 10¹⁴ pores m⁻²), resulting in a surface area of 60-80 m² g⁻¹ (via SEM image analysis). This agrees with results from anodized aluminum oxides with similar pore structures.⁵¹

TiO₂ Nanotube Synthesis

Ti foil (Alfa Aesar, 32 μm thick) was cut into 4 x 4.5 cm pieces and sonicated in acetone, isopropanol, and DI water for 5 minutes each. The prepared foil was then anodized in a solution of 0.27 M NH₄F in formamide (Fisher Scientific), with Pt mesh as the counter electrode, for 30 minutes at 15 V. The as-anodized samples were then ultrasonically cleaned in nanopure water. Samples were dried overnight in a vacuum oven at 110°C.

Structural Characterizations

Grazing incidence synchrotron X-ray diffraction (sXRD) measurements were conducted at Sector 12-ID-D, Advanced Photon Source (APS) at Argonne National Laboratory. The X-ray wavelengths of both $\lambda = 0.684994 \text{ \AA}$ and 0.61990 \AA were used in this study. For varying the structural probing depths, a series of incidence angles (α) from 0° up to 1° were adopted in the grazing incidence sXRD measurements. In order to minimize the scattering contribution from the bulk Nb foil substrate, we placed the sample on top of a convex shaped Teflon support for the measurements where the tail of the incident X-ray beam sweeps through the surface layer of the electrode samples. Additional in-house XRD measurements were taken with a Rigaku Miniflex diffractometer with Cu K α irradiation at $\lambda = 1.5406 \text{ \AA}$. XPS samples were loaded without air exposure through an Ar glove box connected directly to the UHV system. XPS measurements were performed using a Specs PHOIBOS 150 hemispherical energy analyzer with a monochromated Al K α X-ray source. Survey and core level spectra were collected using a pass energy of 40 and 20 eV, respectively, and all spectra were referenced to the binding energy of sp³-hybridized carbon at 284.8 eV. X-ray absorption spectroscopy (XAS) at beamline 12-BM-B in Argonne National Laboratory was used to determine the chemical environment of the materials. Samples for XAS were prepared with free-standing NCNO films peeled off from an Nb substrate. The films were placed onto a copper current collector and cycled in a Li half-cell. Scanning electron microscopy (SEM) images were taken with a FEI Teneo field emission SEM. SEM images were analyzed using the National Institutes of Health ImageJ V1.8 to determine pore size, size distribution, and surface area of the oxides. TEM, HRTEM, and SAED characterization of the samples were completed on a JEOL JEM-2100 at an acceleration voltage of 200 kV. TEM characterization were also completed on a JEOL JEM2100F microscope with a working

voltage of 200 kV. A Zeiss NVision 40 was employed to prepared a TEM specimen ($RS-Nb_2O_5$ electrode after 100 cycles). By following the standard FIB lift-out procedure, the lamella was transferred to a TEM grid. A 30kV Ga beam was employed for general milling. The final lamella was showered by a 5kV Ga beam to reduce the ion beam damage from the 30kV Ga beam.

Inductively coupled plasma mass spectrometry was conducted on a Thermo Fisher iCAP RQ ICP-MS coupled to a Teledyne Analyte Excite+ 193 nm laser ablation (LA) system. Each sample measurement is an average of three replicate analyses, consisting of a gas blank subtracted ablation peak, both of which are the average of 100 sweeps over 5 secs. Elemental concentrations are standardized against standard glasses (GSD and GSE*), except P, Ge and Se, which were standardized against sequential dilutions of single element ICPMS standards. Concentrations are reported in the form of grams of analyte per gram sample X 100 (wt%) assuming a sample volume for samples and standards. No detection (ND) indicates samples which had reading below the limit of detection, which is defined as 3X the background measured before each ablation pass. GSE measured at the largest possible spot size to compare accuracy at count rates comparable to that of the unknowns. Accepted values are from GeoREM preferred values (mean of new analyses).

ToF-SIMS measurement was performed at Environmental Molecular Sciences Laboratory (EMSL), which is located at Pacific Northwest National Laboratory. A TOF.SIMS5 instrument (IONTOF GmbH, Münster, Germany) was used. Dual beam depth profiling was used. A 2.0 keV Cs^+ beam was used as the sputtering beam and a 25 keV Bi^+ beam used as the analysis beam for signal collection. The Cs^+ sputtering beam (~65 nA) was scanned over a $200 \times 200 \mu m^2$ area, and the equivalent sputter rate (SiO_2 as a reference) was about 0.75 nm/s. The Bi^+ beam was focused to be about 5 μm diameter with a beam current was about 0.70 pA with a 10 kHz frequency. The Bi^+ beam was scanned over an area of $70 \times 70 \mu m^2$ at the Cs^+ sputter crater center. A low energy (10 eV) electron flood gun was used for charge compensation in all measurement.

Electrochemical Characterizations

Working electrodes were cut into 15 mm diameter disks using a disk cutter EQ-T06-Disc (MTI, Co). All batteries were prepared in an argon-filled glove box (MBraun) where oxygen levels were maintained below 0.5 ppm. Electrodes removed from cells for analysis were thoroughly washed with dry dimethyl carbonate (Aldrich) and allowed to dry under the inert atmosphere. Li half-cells were assembled in coin-type cells (Hohsen 2032) with Li metal foil (FMC) as the counter electrode, microporous polyolefin separators (Celgard 2325), and 1.2 M $LiPF_6$ in ethylene carbonate/ethyl methyl carbonate (3:7 weight ratio) electrolyte (Gen II, Tomiyama). Half-cells were cycled galvanostatically between 3 and 0.5 V vs Li/Li^+ using an automated Maccor battery tester at 25°C. Four cells were electrochemically tested to confirm reproducibility (Supplementary Fig. 22). A three-electrode cell ECC-ref (EL-Cell®) was used for the galvanostatic intermittent titration technique (GITT) measurements. The cell was made with Li metals as both the reference electrode and the counter electrode, glassy fiber separators (Whatman 2325), and Gen II electrolyte. The current was applied at 60 μA for 30 min, which was followed by a 12 hr relaxation to approach the steady state where the voltage variation is $< 2 \text{ mV hr}^{-1}$.

Mass of the Nb_2O_5 films was determined by dissolution of the oxide film in 1% HF in concentrated HCl solution and measuring the weight difference of the samples before and after etching. This solution allows selective etching of Nb_2O_5 over Nb. The remaining substrate was examined by SEM and energy-dispersive X-ray spectroscopy (EDS) at 5kV using an FEI Teneo FE-SEM to ensure that no residual Nb_2O_5 was left on the substrate. The mass loading of the electrodes was determined to be $\sim 1.06 \pm 0.25 \text{ mg cm}^{-2}$.

Two-Point Probe Measurements, Mott-Schottky Analysis, and PF-TUNA Measurements

Two-point electrical conductivity measurements and PeakForce tunneling atomic force microscopy (PF-TUNA) were used to determine the out-of-plane (i.e., through sample) conductivity of NCNO. For the two-point probe measurements, a silver paint contact was placed on the surface of the oxide film with another point of contact to the Nb foil. The contacts were then connected to the measurement device setup with Au wires. A current ranging from 0.2 - 20 μA was applied by a Keithley 237 High Voltage Source Measurement Unit and the resulting voltage was recorded by a Keithley 2000 Multimeter.

Mott-Schottky analysis was performed using the SPEIS program on a Bio-Logic VMP-240 in a three-electrode cell (EL-Cell®). Kapton tape was utilized as a mask leaving a disk electrode of 12.7 mm diameter for niobium oxide sample. A Pt mesh counter electrode and an Ag/AgCl reference electrode were used in an aqueous 1 M NaOH solution for Nb₂O₅ samples or 1 M KOH for TiO₂ samples. The charge carrier concentration of the samples was determined by the space charge capacitance (C_{sc})⁵² obtained from the imaginary part of the impedance Z'' :

$$C_{sc} = -\frac{1}{2\pi f Z''} \quad \text{Equation 1}$$

where f is the frequency. Bode plots in the frequency range of 100 mHz - 100 kHz with a voltage amplitude of 10 mV from 0.1 to -1 V vs. Ag/AgCl in 0.05 V increments were collected to determine the frequency at which $|Z|$ is constant for all samples and is suitable for Mott-Schottky analysis as seen in Supplementary Fig. 17.

The $|Z|$ plateaus at a frequency of about 1 kHz; therefore, the curves at 1.486 kHz were used to calculate the charge carrier density for each sample. The flat-band potential can also be obtained from the Mott-Schottky plots by finding the x-intercept of the tangent line to the linear region of each curve. The following equation relates the charge carrier density to the capacitance of the sample, where q is the charge of an electron, ϵ is the dielectric constant (assumed to be a constant value of 42), ϵ_0 is the vacuum permittivity constant, N_D is the charge carrier density, A is the geometric surface area, V_{fb} is the flat-band potential, V is the applied potential, k is Boltzmann's constant, and T is the absolute temperature in Kelvin.⁵²

$$C_{sc}^{-2} = \left(\frac{2}{q\epsilon\epsilon_0 N_D A^2} \right) \left(V - V_{fb} - \frac{kT}{q} \right) \quad \text{Equation 2}$$

Eqn 2 is then differentiated with respect to the voltage to obtain the charge carrier density as shown below.

$$N_D = \frac{2}{q\epsilon\epsilon_0 A^2} \left(\frac{dC^{-2}}{dV} \right)^{-1} \quad \text{Equation 3}$$

Ex situ PF-TUNA was performed using a Bruker Dimension Icon atomic force microscope (AFM) in an Ar-filled MBraun glovebox with <0.1 ppm water and oxygen. PF-TUNA provides spatially resolved nanoscale through-sample conductivity maps of resistive materials in response to an applied bias. A Bruker DDESP conductive diamond tip probe (100 nm nominal radius of curvature tip composed of 0.01-0.025 Ω-cm antimony (n)-doped Si) with a setpoint force of 70 nN was used to simultaneously image the electrode topography and conductivity. The electrodes were placed directly onto the metallic vacuum chuck, and a bias voltage of -10 V was applied to the chuck (i.e., bottom surface of the electrode). 20 x 20 μm² images with 1024 x 1024 pixels were obtained to yield 20 nm lateral resolution maps at a TUNA gain sensitivity of 20 pA/V (±10 V full scale, corresponding to ±200 pA sensitivity). Images were processed and analyzed in Nanoscope Analysis version 1.90. A first order plane fit was applied to the raw topographical data to account for sample tip and tilt, with an additional first-order flatten applied to correct for small line-to-line offsets in the Z piezo. A conductivity skin was then overlaid on the 3D topography image to visualize variations in current density via color contrast.

DFT Calculations

All DFT calculations were carried out using the Vienna *ab initio* simulation package (VASP)⁵³ within the projector augmented wave approach.⁵⁴ The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)⁵⁵ was adopted for the exchange-correlation functional. The kinetic energy cutoff was set to 520 eV and a k -point density of at least 1000 per reciprocal atom was used for structural relaxations of Nb₂O₅. The electronic energy and atomic forces were converged to within 10⁻⁵ eV and 0.02 eV/Å, respectively, in line with the settings in the Materials Project database.⁵⁶

Structure Enumeration

First, we enumerated and calculated the energies of all orderings in a $\sqrt{5} \times \sqrt{5} \times 2$ supercell of cubic rock-salt $\text{Li}_3\text{Nb}_2\text{O}_5$. The Li and Nb occupancy of the octahedral sites (Wyckoff symbol: $4b$) was set at x Li: 0.4 Nb, where x ranges from 0 to 0.6 at the interval of 0.1. 0.6 and 0.4, respectively, at the octahedral interstitial sites in a fcc oxygen lattice. Lithium was then removed in 0.5 increments from $\text{Li}_3\text{Nb}_2\text{O}_5$ and the symmetrically distinct orderings were then calculated for each composition. All symmetrically distinct orderings were generated with an enumeration algorithm interfaced with the Python Materials Geomics (pymatgen) library.^{57,58} These orderings were then fully relaxed using DFT calculations and the lowest energy configurations were used for subsequent analysis.

Intercalation Voltage Profile

The pseudo-binary stability diagrams for $\text{Li}_x\text{Nb}_2\text{O}_5$ ($0 \leq x \leq 3$) were constructed from previous structure enumeration and DFT relaxations. The stable intermediate phases in the stability diagram were used for static calculations with a denser Γ -centered k -mesh of $9 \times 8 \times 7$ to obtain more accurate energies. The voltage profile was then obtained by computing the average voltage between any two stable intermediate phases: where E is the total DFT energy and e is the electronic charge.⁵⁹

$$V = - \frac{E(\text{Li}_{x_1}\text{Nb}_2\text{O}_5) - E(\text{Li}_{x_2}\text{Nb}_2\text{O}_5) - (x_1 - x_2)E(\text{Li})}{(x_1 - x_2)e} \quad \text{Equation 4}$$

Nudged Elastic Band Calculations

The migration barriers were calculated using climbing image nudged elastic band (CI-NEB) methods. The calculations were performed on $2\sqrt{5} \times 2\sqrt{5} \times 4$ supercells of the rock-salt primitive cell. These configurations were directly obtained by doubling each lattice vector of the low energy structures from previous voltage profile calculations. The number of images used for all CI-NEB calculations was 5. The energies and forces were converged to 5×10^{-5} eV per supercell and 0.05 eV/Å, respectively. It is expected that the neighboring atoms around the migration paths would have substantial effects on the barriers. In particular, there are 4 octahedral neighboring atoms sharing edges with the two octahedral migrating Li atoms and these neighboring atoms can be occupied by either Nb or Li. Herein, six representative low energy configurations were used as starting structures to construct the Li migration paths with x Li and $(4-x)$ Nb occupying the edge-sharing neighboring atoms (see Fig. 5c). The barriers variation for each x are marginal, justifying the use of these representative configurations.

Data Availability

The data that support the findings of this study are available from the corresponding authors on reasonable request.

- 49 Barnes, P. et al. Electropolishing valve metals with a sulfuric acid-methanol electrolyte at low temperature. *Surface & Coatings Technology* 347, 150-156, doi:10.1016/j.surfcoat.2018.04.082 (2018).
- 50 Lee, K., Yang, Y., Yang, M. & Schmuki, P. Formation of Highly Ordered Nanochannel Nb Oxide by Self-Organizing Anodization. *Chemistry-a European Journal* 18, 9521-9524, doi:10.1002/chem.201201426 (2012).
- 51 Roslyakov, I. V. et al. Annealing induced structural and phase transitions in anodic aluminum oxide prepared in oxalic acid electrolyte. *Surface & Coatings Technology* 381, doi:DOI:10.1016/j.surfcoat.2019.125159 (2020).
- 52 Baram, N. & Ein-Eli, Y. Electrochemical Impedance Spectroscopy of Porous TiO₂ for Photocatalytic Applications. *J Phys Chem C* 114, 9781-9790, doi:10.1021/jp911687w (2010).
- 53 Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* 54, 11169-11186, doi:DOI 10.1103/PhysRevB.54.11169 (1996).
- 54 Blochl, P. E. Projector Augmented-Wave Method. *Physical Review B* 50, 17953-17979, doi:DOI 10.1103/PhysRevB.50.17953 (1994).
- 55 Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Physical Review Letters* 77, 3865-3868, doi:DOI 10.1103/PhysRevLett.77.3865 (1996).
- 56 Jain, A. et al. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *Apl Materials* 1, doi:DOI:10.1063/1.4812323 (2013).

- 57 Hart, G. L. W. & Forcade, R. W. Algorithm for generating derivative structures. *Physical Review B* 77, doi:DOI:10.1103/Physrevb.77.224115 (2008).
- 58 Ong, S. P. et al. Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis. *Computational Materials Science* 68, 314-319, doi:10.1016/j.commatsci.2012.10.028 (2013).
- 59 Aydinol, M. K., Kohan, A. F., Ceder, G., Cho, K. & Joannopoulos, J. Ab initio study of lithium intercalation in metal oxides and metal dichalcogenides. *Physical Review B* 56, 1354-1365, doi:DOI 10.1103/PhysRevB.56.1354 (1997).