Orthorhombic Nb$_2$O$_{5-x}$ for Durable High-Rate Anode of Li-Ion Batteries

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HIGHLIGHTS
A novel micro-etching strategy is developed to prepare porous nano-crystal Nb$_2$O$_5$

The obtained Nb$_2$O$_5$ remains the morphology of the precursor but reconstructs unit cell

Oxygen vacancies and Nb$^{4+}$/Nb$^{5+}$ are introduced to porous Nb$_2$O$_{5-x}$ by anoxic annealing

Defect-rich and porous Nb$_2$O$_{5-x}$ works as durable, high-rate, and safe anode of LiBs
Orthorhombic Nb$_2$O$_5$ for Durable High-Rate Anode of Li-Ion Batteries

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SUMMARY

Li$_4$Ti$_5$O$_12$ anode can operate at extraordinarily high rates and for a very long time, but it suffers from a relatively low capacity. This has motivated much research on Nb$_2$O$_5$ as an alternative. In this work, we present a scalable chemical processing strategy that maintains the size and morphology of nano-crystalline precursor but systematically reconstitutes the unit cell composition, to build defect-rich porous orthorhombic Nb$_2$O$_5$, with a high-rate capacity many times those of commercial anodes. The procedure includes etching, proton ion exchange, calcination, and reduction, and the resulting Nb$_2$O$_5$ has a capacity of 253 mA h g$^{-1}$ at 0.5C, 187 mA h g$^{-1}$ at 25C, and 130 mA h g$^{-1}$ at 100C, with 93.3% of the 25C capacity remaining after cycling for 4,000 times. These values are much higher than those reported for Nb$_2$O$_5$ and Li$_4$Ti$_5$O$_12$, thanks to more available surface/sub-surface reaction sites and significantly improved fast ion and electron conductivity.

INTRODUCTION

Commercial lithium-ion Li$_4$Ti$_5$O$_12$ anodes currently in use in power lithium ion batteries (LIBs) on buses have an advantage over other commercial anodes because their capacity can sustain high rates. For example, graphite has a capacity of 62 mA h g$^{-1}$ at 10 C compared with 311 mA h g$^{-1}$ at 0.5 C and silicon-carbon composite (Si/C) has 54 mA h g$^{-1}$ at 10 C and 440 mA h g$^{-1}$ at 0.5 C, but Li$_4$Ti$_5$O$_12$‘s capacity of 145 mA h g$^{-1}$ at 10 C is rather close to that of 170 mA h g$^{-1}$ at 0.5 C (Wang et al., 2015). Nevertheless, the capacity of Li$_4$Ti$_5$O$_12$ is relatively low, so there is much impetus to find a higher-capacity replacement that can retain the advantage of rate insensitivity.

As Li$_4$Ti$_5$O$_12$, other early transition metal oxides comprised of similar mostly corner-sharing octahedra can also reversibly incorporate Li while retaining the structure without inordinate volume changes, thus providing better rate and cyclic performance. Among them, recent interest has been directed to Nb$_2$O$_5$ (Griffith et al., 2018) featuring outstanding anode properties, but being one of the simplest such oxides, Nb$_2$O$_5$ has already received much attention. Dunn et al. reported a mesoporous orthorhombic Nb$_2$O$_5$ nanocrystal, which, when combined with an equal mass of conducting carbon black, can make electrodes of 145 mA h g$^{-1}$ at 1 C and 105 mA h g$^{-1}$ at 100 C (Augustyn et al., 2013); however, at a more common ratio of active material (Nb$_2$O$_5$ to carbon black of ~8:1, its high-rate capacity is still limited. Other studies of orthorhombic Nb$_2$O$_5$ (also denoted as T- Nb$_2$O$_5$ in the literature) in the form of hollow nanosphere (Kong et al., 2014), nanobelt (Wei et al., 2008), nanosheet (Kong et al., 2015), and nanofiber (Viet et al., 2010) all reported broadly similar properties, with values such as 250 mA h g$^{-1}$ at 0.5 C in the first cycle that drops to 180 mA h g$^{-1}$ in the 50th cycle. Instead of using carbon black, various constructs to introduce current collectors, such as carbonaceous coating or inclusions, co-assemblies of Nb$_2$O$_5$ nanorods and carbon fiber (Deng et al., 2018a), and composites with holey graphene, have been explored, which achieved first-cycle values such as 190 mA h g$^{-1}$ at 200 mA g$^{-1}$ (1 C) and 90 mA h g$^{-1}$ at 20,000 mA g$^{-1}$ (100 C) (Sun et al., 2017). These devices already have properties approaching the theoretical capacity (200 mA h g$^{-1}$) of Nb$_2$O$_5$, but they also require complicated designs or synthesis, which is a potentially serious impediment toward practical applications.

Because orthorhombic Nb$_2$O$_5$ does have a higher theoretical capacity, we have sought to find a simple fabrication strategy to directly impart fast Li and electron conductivities into additive-free Nb$_2$O$_5$ to achieve high performance. Such a strategy is reported in this study, in which we fabricated well-crystallized and highly active defect-rich orthorhombic Nb$_2$O$_5$ by robust yet selective acid etching of a parent oxide followed by annealing. When the product is mixed with a modest, standard amount of carbon black and conducting binder, the resulting anode outperforms all the previously reported Nb$_2$O$_5$-based ones, having 253 mA h g$^{-1}$ at 100 mA g$^{-1}$ (0.5 C) and 130 mA h g$^{-1}$ at 20,000 mA g$^{-1}$ (100 C), taking less than 36 s to charge
or discharge). With a reasonable tap density of \(1.3 \text{ g cm}^{-3}\), its cyclic performance is especially outstanding, having a stable capacity, e.g., 176 mA h g\(^{-1}\) at 25 C (5,000 mA g\(^{-1}\)), over 4,000 cycles. Therefore, our Nb\(_2\)O\(_5\) could be a very attractive alternative to commercial high-rate Li\(_4\)Ti\(_5\)O\(_12\) anode (170 mA h g\(^{-1}\) at 0.5 C, 130 mA h g\(^{-1}\) at 20 C, 80 mA h g\(^{-1}\) at 80 C) (Wang et al., 2015) as a durable high-rate power source in practical applications.

**RESULTS**

**Synthesis and Physicochemical Property**

The precursor Sr(Ca\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) is an ABO\(_3\) perovskite that also comprises a network of corner-sharing BO\(_6\) octahedra. It was chosen because Sr and Ca, being more basic than Nb, can be easily etched away in acid to remove all the A-site Sr and B-site Ca, hopefully leaving behind an intact yet atomically loose/open framework (Figure 1). Acid etching, however, introduced H into the framework by ion exchange, forming HNbO\(_3\) (Figure 1), but H can be driven away later by calcination. The diffraction peaks (Figure 2A) of our Sr(Ca\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) match well with those of disordered Sr(Ca\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (JCPDS 17-0174), but they are slightly shifted toward higher angles indicating a 1.73% smaller unit cell (202.16 Å\(^3\) vs. 205.73 Å\(^3\)). The diffraction peaks of HNbO\(_3\) also find good correspondence with those of perovskite HNbO\(_3\) (JCPDS 36-0794), but the unit cell is 3.92% larger in our material (465.04 Å\(^3\) vs. 446.82 Å\(^3\)). Overall, the per-formula volume shrinks by 18.8% from 68.83 Å\(^3\) in Sr(Ca\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) to 55.85 Å\(^3\) in HNbO\(_3\), which suggests large internal strains left in HNbO\(_3\).

We believe one cause of such large internal strains is the reconstitutive nature of the acid-etch/ion-exchange process. Here, by reconstitution, we mean a compositional modification at the level of local atomic structure that is repeated throughout the entire crystal, yet this is accomplished without reconstructing the overall microstructure or the size/shape of the crystal. This is supported by the SEM images showing almost the same size distribution and morphology for Sr(Ca\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (Figure S1A) and HNbO\(_3\) (Figure S1B), indicating reconstitution at the unit cell level does not involve crystallite dissolution/reprecipitation that will most certainly result in a rather different morphology and size. Indeed, when a higher concentration of HCl and a longer reaction time were used, dissolution/reprecipitation did take place, producing larger, hexagonal platelets as shown in Figure S1E.

As HNbO\(_3\) is heated, it dehydrates at above 200°C, and such process is mostly complete by 400°C according to TGA (Figure S2A). Annealing at 700°C under Ar gave the final product Nb\(_2\)O\(_5\)-\(x\), which has the same structure as the Nb\(_2\)O\(_5\) phase identified by JCPDS 27-1003 (Figure 2A) with nearly the same lattice parameters. Still, its particle size and morphology remain largely similar to those of Sr(Ca\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) and HNbO\(_3\) as shown in Figure S1C. Therefore, the entire process is most likely reconstitutive at the unit cell level and
non-destructive at the single crystal level. Lastly, reheating Nb$_{2}$O$_{5-x}$ in air to 800°C in TGA causes full oxidation (Figure S2B), from which we determined $x = 0.61$ although the accuracy of this value is likely to be compromised somewhat because the decomposition of hydroxyl residues may still persist to high temperature.

The Ar-annealed Nb$_{2}$O$_{5-x}$ is black (Figures S4A–S4C), and it absorbs more light at longer wavelength outside the UV-absorption edge (Figure S4DUV). Because $x = 0.61$ indicates the presence of Nb$^{4+}$ or holes, one expects greatly improved conductivity over that of air-annealed Nb$_2$O$_5$, which is confirmed (1,000× higher) in Figures 2B and S5. In this respect, black niobia is analogous to black titania that also has greatly improved conductivity and enhanced light absorption compared with fully oxidized white titania (Chen et al., 2011, 2015; Cui et al., 2014; Wang et al., 2013a). Because of surface oxidation, XPS in Figure S6A reveals nearly the same Nb 3$d$ spectrum as in white Nb$_2$O$_5$ in Figure S6B, with $d_5/2$ and $d_{9/2}$ peaks at respective binding energies of 209.8 eV and 207 eV typical for Nb(V)-O bonds in Nb$_2$O$_5$. (Near the baseline, the two small peaks at 208.4 eV and 205.6 eV in Figure S6A could be assigned to Nb(IV)-O bonds.) A definitive differentiation between the two oxidation states comes from EPR in Figure 2C, which reveals prominently magnetic Nb in Nb$_{2}$O$_{5-x}$ but not in Nb$_2$O$_5$. Again, very similar findings were reported for black and white titania: they can be easily distinguished using bulk-sensitive EPR but not surface-limited XPS (Wang et al., 2011, 2013b).

Adsorption-desorption isotherms of N$_2$ identified distinct loops of type-IV isotherm (IUPAC classification) in all the samples (Figure 2D). A specific surface area of about 41.2 $m^2 g^{-1}$ was found for Nb$_{2}$O$_{5-x}$, twice that (20.8 $m^2 g^{-1}$) of Sr(Ca$_{1/3}$Nb$_{2/3}$)$_3$O$_7$ (precursor) and three times the value of Nb$_2$O$_5$ (14.3 $m^2 g^{-1}$, Figures S6C and S6D). Compared with Sr(Ca$_{1/3}$Nb$_{2/3}$)$_3$O$_7$, Nb$_{2}$O$_{5-x}$ has more pore volume (Figure 2E) especially in the <5 nm region, although it also has pores of 40–50 nm that are larger than the 20 nm pores of Sr(Ca$_{1/3}$Nb$_{2/3}$)$_3$O$_7$. This is not surprising in view of the defects and lattice vacancies created by acid etching. Further specific area and pore volume analysis found the etched product HNbO$_3$ had the largest specific

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**Figure 2. Physical Properties of Nb$_2$O$_{5-x}$**

(A and B) (A) XRD patterns of Sr(Ca$_{1/3}$Nb$_{2/3}$)$_3$O$_7$, HNbO$_3$, and Nb$_2$O$_5$. There is no indication of superlattice reflection in Sr(Ca$_{1/3}$Nb$_{2/3}$)$_3$O$_7$ due to B-site ordering, which if present occurs at about 19°. The lattice parameter of Nb$_2$O$_{5-x}$ (a = 6.171973 Å, b = 29.287891 Å, and c = 3.931551 Å) are nearly the same as that of JCPDS: 6.168 Å, 29.312 Å and 3.936 Å, see Rietveld refinement result in Figure S3; (B) conductivity of air-annealed Nb$_2$O$_5$ and Ar-annealed Nb$_{2}$O$_{5-x}$.

(C–E) (C) EPR spectra of Nb$_{2}$O$_{5-x}$ and Nb$_2$O$_5$; (D) nitrogen adsorption-desorption isotherms; and (E) BJH adsorption pore size distribution analysis of Sr(Ca$_{1/3}$Nb$_{2/3}$)$_3$O$_7$ and Nb$_{2}$O$_{5-x}$.

(F) Specific area and pore volume of Sr(Ca$_{1/3}$Nb$_{2/3}$)$_3$O$_7$ (noted as SCNO); HNbO$_3$; and 500°C-, 600°C-, 700°C-, and 800°C-annealed Nb$_2$O$_5$. 
surface area (242.5 m² g⁻¹) and pore volume (0.3979 cm³ g⁻¹), which represents a huge increase from those of the Sr(Ca₁/₃Nb₂/₃)O₃ precursor (20.8 m² g⁻¹ and 0.0978 cm³ g⁻¹, respectively.) These values progressively decrease during Ar annealing as shown in Figure 2F, although the pore volume did initially increase at 500°C likely because of dehydration of HNbO₃ that occurs below this temperature. Meanwhile, maximum conductivity is reached after ~600–700°C annealing (Figure S5), presumably due to increased hole concentration. So the optimal temperature for electrochemical performance that relies on specific surface area, porosity, and conductivity should lie around 600–700°C as will be seen later in electrochemical testing.

Defect-Rich Porous Crystal

A detailed examination of nanoscale structure and defects was carried out on Nb₂O₅₋ₓ using TEM. First, we verified that each particle is a single crystal. Next, we have chosen to orient the crystal to be perpendicular to 001 and 180 as shown in Figure 3 because it was reported that Li insertion occurs most easily along these planes (Brezesinski et al., 2010; Kim et al., 2012; Kumagai et al., 1999). (See inset in Figure 3A, which is a fast Fourier transform of the image.) In this single crystal, there is very prominent diffuse scattering around (000) but not at (000), which is a distinct feature of displacement or alloying randomness. In our material, alloying randomness may arise from the random placement of filled and vacant sites, namely atoms and vacancies, on both the Nb and O sublattices. Such diffuse scattering is especially prominent in Figure 3A as indicated by streaking, likely due to displacement waves to accommodate copious vacancies. At the direct, atomic level, although the overall structure is clearly crystalline, there are numerous disordered regions, some arranged into bands of various thickness (many around 2–3 nm), length (varying from 3–20 nm), and orientations, as encircled by white dotted lines in Figures 3A–3C (Xie et al., 2017). (Disorder and nanopores are also obvious in HNbO₃ in Figure S7, taken before high-temperature calcination.) This coexistence of order and disorder is especially evident in Figure 3B, and its extensive nature is highlighted in Figure 3C that is an enlarged view of one region in Figure 3A.

These disorders mostly likely originate from the interplay of (1) cation removal, from Sr, to Ca to H; (2) anion removal, from reduction; and (3) large changes in unit cell volume from Sr(Ca₁/₃Nb₂/₃)O₃ to HNbO₃ though not to Nb₂O₅₋ₓ, all while maintaining the same octahedral framework and the same crystal construct over a length scale of the order of 100 nm, which is the (single crystal) particle size in Figure S1. This implies the creation of a large vacancy population and internal strains, the latter activating the former to collapse (most likely by cooperative shear that is known to be more expedient than diffusion) into vacancy clusters and stacking faults; some of these final, extended, vacancy-derived defects may provide paths for rapid Li transport as speculated in the literature (Come et al., 2014; Griffith et al., 2016; Kim et al., 2012; Kodama...
et al., 2006; Lubimtsev et al., 2013). They may also afford a wider variety of electrochemically active sites to facilitate fast-rate charging/discharging. Lastly, they may more easily accommodate volume changes upon Li insertion/extraction, thus helping to maintain structural integrity during electrochemical cycling.

**Electrochemical Property and Performance**

With Nb$_2$O$_5$ as a reference, the improved performance of Nb$_2$O$_5$-$x$ is best illustrated using galvanostatic cyclic charge/discharge (CC) tests in Figure 4A for various charging rates. At 0.5 C, Nb$_2$O$_5$-$x$ has a capacity of 253 mA h g$^{-1}$, more than 50% higher than that of Nb$_2$O$_5$ (160 mA h g$^{-1}$). This advantage is maintained at other rates, e.g., at 25 C (5,000 mA g$^{-1}$), Nb$_2$O$_5$-$x$ has 187 mA h g$^{-1}$ vs. 105 mA h g$^{-1}$ for Nb$_2$O$_5$. Even at the extremely high rates of 100 C and 250 C, Nb$_2$O$_5$-$x$ still obtains 130 mA h g$^{-1}$ (vs. 75 mA h g$^{-1}$ for Nb$_2$O$_5$) and 70 mA h g$^{-1}$ (Nb$_2$O$_5$‘s was too small to measure), respectively. In addition, because of the high cut-off voltage (1–3 V), we also used Al foil as a cheaper substitute for Cu-foil current collector and again obtained a very similar high capacity at high rates as shown in Figure S8. Superior reversibility and stability was also demonstrated by the CC tests, e.g., when the rate returned to 0.5 C at the end of the test, Nb$_2$O$_5$-$x$ recovered 252 mA h g$^{-1}$—the same as the initial value—whereas Nb$_2$O$_5$‘s capacity had by now faded to 112 mA h g$^{-1}$ from the initial value of 160 mA h g$^{-1}$. Outstanding reversibility and durability were further confirmed by extended CC tests at 25 C (Figure 4B): throughout the 4,000-cycle test, 100% coulombic efficiency was achieved, and the final specific capacity was 93.3% of the original. This represents a change of only 0.00167%/cycle, which is remarkable for an extraordinarily large capacity and high rate for this class of electrodes after relatively long cycling. In contrast, when long-term durability was achieved for other electrodes, it was usually with a much more limited capacity or shorter cycles. Examples are carbon/Nb$_2$O$_5$ composite at 70–80 mA h g$^{-1}$ (charging/discharging rate not specified in this report) maintaining ~87% after 70,000 cycles (Song et al., 2017), Nb$_2$O$_5$@graphene at 70–80 mAh g$^{-1}$ at 50 C maintaining ~70% after 20,000 cycles (Deng et al., 2018b), and urchin-like Nb$_2$O$_5$ at 131 mA h g$^{-1}$ at 5 C maintaining 98% after 1,000 cycles (Liu et al., 2016a).

The CV profiles in Figure 5A confirm a larger current density for Nb$_2$O$_5$-$x$ throughout the entire test range (also see Figure S9 for performance after other Ar-annealing temperatures). Note that its cathodic peaks are broader than Nb$_2$O$_5$‘s, which has two distinct peaks around 1.48 V and 1.79 V. This supports our expectation that copious defect sites in Nb$_2$O$_5$-$x$ may offer a wider variety of electrochemically active sites for charging/discharging. To provide a more quantitative measure of this aspect, we used the CV test to measure the equivalent specific capacitance $C_L$ from $dQ/dt = C_L dV/dt$, which is expected to hold in the voltage range away from any peak, such as from 2.9 V to 3 V in Figure 5A. As shown in Figure S10B, the CV profiles in this range collected at 3 to 10 mV s$^{-1}$ give a current at 2.95 V that increases linearly with the voltage scan rate (Figure 5B), from which one obtains $C_L = 7.82$ mF g$^{-1}$ for Nb$_2$O$_5$-$x$ vs. 0.85 mF g$^{-1}$ for Nb$_2$O$_5$. Since the geometric surface areas of Nb$_2$O$_5$-$x$ (41.2 m$^2$ g$^{-1}$) and Nb$_2$O$_5$ (14.3 m$^2$ g$^{-1}$) differ only by a factor of 3, the almost 10X difference in $C_L$ is a testament of more—or more active—electrochemical sites available per unit surface area in Nb$_2$O$_5$-$x$. Electrochemical impedance spectroscopy (EIS) using the standard electrode configuration (Figure S11A) and the ion-blocking electrode configuration (Figure S11B) (Kanno and Murayama, 2001) also measured a (mostly electron) charge transfer resistance ($R_{ct}$) at high frequency, 54.6 Ω for Nb$_2$O$_5$-$x$ vs. 111 Ω for Nb$_2$O$_5$, and an ionic conductivity of 2.50×10$^{-5}$ S m$^{-1}$ for Nb$_2$O$_5$-$x$ vs. a value too small to measure for Nb$_2$O$_5$. Lastly, the EIS results obtained using the standard electrode configuration

![Figure 4. High-Rate Capacity and Stability](image-url)
allowed us to calculate a Li\(^+\) diffusion coefficient, which is \(4.836 \times 10^{-12}\) for Nb\(_2\)O\(_{5-x}\) and 7.547 \(\times 10^{-13}\) cm\(^2\) s\(^{-1}\) for Nb\(_2\)O\(_3\). (See Transparent Methods, which follows [Du et al., 2012] and data fitting, shown in Figure S12.) All these results are self-consistently supportive of Nb\(_2\)O\(_{5-x}\)’s outstanding high-rate performance in conjunction with facile electron and ion transport.

To further verify the above observations, we use a semi-empirical analysis to analyze the rate data from both the CV tests and the CC tests. In this analysis, we plot the data in Figure S13 against the scan rate \(v\) consistent with the following relation:

\[
I = a v^b
\]

Alternatively, we also plot the data against cycle time (Figure 5C) to be compared with the following relation (Lin et al., 2015):

\[
I = k_1 v + k_2 v^{1/2} \text{ or } I/v = k_1 + k_2 v^{-1/2}
\]

We obtain, for Nb\(_2\)O\(_{5-x}\), \(b \approx 0.9\) (Figures S13A and S13B) throughout the voltage range (1–2 V), and \(k_1 = 349\) F g\(^{-1}\) in Figure 5C in both the CV and CC tests. For diffusion-limited charge/discharge, \(b\) should be 0.5; for instantaneous, linear-capacitor-like charge/discharge, \(b\) should be 1.0, which is closer to the...
Correspondingly, for rate-independent charge/discharge, $k_1$ should account for the entire specific capacitance, overwhelming the diffusion-dependent contribution of the $k_2 v^{-1/2}$ term, which is again close to the case here. In comparison, for Nb$_2$O$_5$, while $b$ is still comparable or slightly smaller than that for Nb$_2$O$_5$-x (Figure S13), its $k_1 = 214 \text{ F g}^{-1}$ is considerably lower, indicating instantaneous linear-capacitor-like charge/discharge only makes a much smaller contribution. Specifically, we obtained the capacitor-like contribution of 58% for Nb$_2$O$_5$ compared with 87% for Nb$_2$O$_5$-x, which is extraordinarily high considering the fact that the well-celebrated pseudocapacitor, nanoparticle anatase TiO$_2$ (Wang et al., 2007), features only 55% according to our experience (see Figure S14.)

Therefore, a consistent picture emerges for Nb$_2$O$_5$-x as an excellent electrode with unusually fast charging/discharging kinetics, thanks to very fast ion and electron transport and very plentiful electrochemically active sites. To put these results into perspective, we compare the rate performance of Nb$_2$O$_5$-x with some Nb$_2$O$_5$-composite and two high-rate anode materials (Li$_4$Ti$_5$O$_12$ and TiO$_2$) in Figure S5D; outperformance of Nb$_2$O$_5$-x is apparent. Compared with other commercial common anode materials, our electrode has a higher capacity at high rates (213 and 204 mA h g$^{-1}$ at 5 C and 10 C, respectively) outperforming graphite, Si/C, and Li$_4$Ti$_5$O$_12$ in Figures S5E and S5F. Although rate properties may be improved with delicate structural designs, as illustrated in hierarchical graphite wrapped Si—500 mA h g$^{-1}$ at 5 C (Xu et al., 2017)—or by adding carbonaceous nano inclusions, e.g., in graphene-coated graphite—164 mA h g$^{-1}$ at 5 C (Liu et al., 2016b)—these materials will have higher costs and lower tap densities, which adversely affects their practicality. In contrast, our Nb$_2$O$_5$-x is carbon free, has a reasonable tap density of 1.3 g cm$^{-3}$, allows volumetric capacity of up to 328, 243, 169, and 91 mA h cm$^{-3}$ at 0.5 C, 25 C, 100 C, and 250 C, respectively, to be achieved and has been mass-produced (we achieved kg level production), which all bode well for making it a promising practical anode material.

**Mechanism Investigation**

Lastly, to confirm the excellent endurance of Nb$_2$O$_5$-x anodes, we examined the Li-charged and the Li-extracted states after 1,000 cycles and compared them with those of pristine Nb$_2$O$_5$-x before cycling.
Comparing their XRD (Figure 6A), we see despite peak broadening, crystallinity was maintained after cycling, indicating these sub-100 nm nanoparticles are structurally robust enough to withstand repeated Li-charging and extraction. Comparing their EIS (Figure 6B), although it has a lower slope closer to 45° at the low-to-intermediate frequency range after cycling, which is consistent with a more distributed resistive and capacitive character—perhaps caused by an increased frequency-dispersive conductivity (such as ion conductivity)—we see the charge transfer resistance is actually decreased by cycling. Comparing their Nb-3d XPS (Figure 6C vs. Figure S6A), we see cycling caused a significant increase of Nb (IV) compared with that in pristine Nb₂O₅₋ₓ (Figure S6A). Cycling, however, did cause a decrease in the equivalent specific capacitance Cₑ (Figure 6D, constructed from the CV data in Figures S10B and S10C), which is perhaps indicative of a decrease in the electrochemically active area because the charge transfer resistance did not suffer from cycling. On the other hand, these results could also be consistent with Li trapping at the active sites in Nb₂O₅₋ₓ after insertion, which leads to internal strains (thus broadening of XRD), loss of active sites (hence a smaller Cₑ), reduction of Nb (leaving Nb(IV)), and metal/ion conductivity (hence lower transfer resistance and battery-like charge storage EIS: in Figure 6B, pristine one from 26.1 Hz to 0.32 Hz; cycled one from 68.1 Hz to 0.12 Hz.). Of course, eventually, Li loss will deteriorate the Nb₂O₅₋ₓ electrode, which we did observe in past 4,000 cycles. Nevertheless, after 1,000 cycles, there was hardly any change in the microstructure according to TEM images (Figures 6E and 6F), attesting to the superior structural stability Nb₂O₅₋ₓ.

DISCUSSION

1. We have demonstrated that carbon-free defect-rich orthorhombic Nb₂O₅₋ₓ is an outstanding high-rate and durable LIBs’ negative electrode material, having an excellent capacity of 253 mAh g⁻¹ at 0.5 C, 187 mAh g⁻¹ at 25 C of which 93% is retained after 4,000 cycles, and 130 mAh g⁻¹ even at 100 C, much better than the commercial high-rate anode Li₄Ti₅O₁₂. Electrochemical kinetic analysis reveals that the energy storage is largely capacitive and non-solid-diffusion-limited in nature in this electrode.

2. A chemical processing strategy based on selective etching has been developed to maintain the crystal size and morphology of precursor powders but systematically reconstitute their unit cell composition into one appropriate for the final orthorhombic Nb₂O₅₋ₓ. The huge strain involved in reconstitution is instrumental to the preservation of the high defect density that is critical for the uncommon electrochemical activity.

3. The above finding and strategy may be applicable to other forms of Nb₂O₅₋ₓ and other oxides to enable high-performance new electrode materials. The simplicity and scalability of the fabrication method may allow large-scale industrial production.

Limitations of the Study

Although select etching as a synthesis method can be readily extended to many materials other than Nb₂O₅, it may be difficult to practice in doped materials if the dopant has a different chemistry from the main species. Etching is also likely to be sensitive to the surface structure, so the morphology of starting crystals could be critical. Future work is needed to define the universe of material composition and morphology suitable for this method.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.100767.

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AUTHOR CONTRIBUTIONS
Z.L. and W.D. performed the experiments and analyzed the data. J.W. contributed to optimizing synthesis condition of Nb2O5. C.D. and Y.L. carried out TEM imaging. Z.L. wrote the manuscript with contributions from all authors. I.W.C. and F.H. supervised the project and revised the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

Orthorhombic Nb$_2$O$_{5-x}$ for Durable High-Rate Anode of Li-Ion Batteries

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Fig. S1. SEM images. Related to Fig. 1. (A) Sr(Ca$_{1/3}$Nb$_{2/3}$)O$_3$, (B) HNbO$_3$, (C) 700 °C annealed Nb$_2$O$_{5-x}$, (D) 800 °C annealed Nb$_2$O$_{5-x}$, and (E) dissolved-and-recrystallized HNbO$_3$. (A-C) have similar characteristic length scale.
Fig. S2. Thermogravimetric analysis data. Related to Fig. 2. (A) HNbO$_3$ in N$_2$ atmosphere showing ~6% weight loss due to dehydration, and (B) Nb$_2$O$_{5-x}$ in air showing ~4% weight gain due to re-oxidation. From (B), we calculated x=0.61.
Fig. S3. Rietveld refinement of the powder XRD pattern of Nb$_2$O$_{5-x}$. Related to Fig. 2. Observed (circles) and calculated (continuous line) profiles of Nb$_2$O$_{5-x}$ using space group Pbma. Tick marks below indicate positions of allowed Bragg’s reflections. A difference curve ($I_{\text{obs.}} - I_{\text{calc.}}$) is shown at bottom. The structure refinement was stable and converged rapidly with Chi squared $\chi^2=2.89$, R-factor=14.8.
Fig. S4. Optical images and UV-vis diffuse reflectance spectra. Related to Fig. 2. Optical images of (A) complex oxide precursor Sr(Ca$_{1/3}$Nb$_{2/3}$)O$_3$, (B) 700 °C-Ar-annealed Nb$_2$O$_{5-x}$, (C) 800 °C-Ar-annealed Nb$_2$O$_{5-x}$. (D) UV-vis diffuse reflectance spectra of sample annealed in Ar from 400 °C to 800 °C and in air at 800 °C (black line).
Fig. S5. Conductivity of products in different annealing conditions. Related to Fig. 2. 500 °C-, 600 °C-, 700 °C-, 800 °C-Ar annealed Nb$_2$O$_{5-x}$, plus 800 °C-air annealed Nb$_2$O$_5$. 
Fig. S6. XPS data with specific surface area and pore size distribution analysis. Related to Fig. 2. XPS spectra of (A) black Nb$_2$O$_{5-x}$, and (B) white Nb$_2$O$_5$. (C) Nitrogen adsorption-desorption isotherms and (D) BJH adsorption pore size distribution analysis for Nb$_2$O$_{5-x}$. 
Fig. S7. TEM image of HNbO$_3$. Related to Fig. 3. Crystallites are about 5 nm in size, some apparently highly disordered.
Fig. S8. Related to Fig. 4. Rate performance of Nb$_2$O$_{5-x}$ with Al foil as current collector.
Fig. S9. CV curves of Nb$_2$O$_{5-x}$ annealed at different temperatures. Related to Fig. 5. The result identifies optimal annealing condition is 700 °C.
Fig. S10. CVs which equivalent specific capacitance is constructed from. Related to Fig. 5. CVs of (A) Nb₂O₅, (B) pristine and (C) 1,000-cycled Nb₂O₅ₓ at scan rates from 3 to 20 mV s⁻¹ over 2.9 - 3 V.
Fig. S11. Nyquist plots of Nb\textsubscript{2}O\textsubscript{5}, Nb\textsubscript{2}O\textsubscript{5-x} electrodes and Nb\textsubscript{2}O\textsubscript{5-x} pellet. Related to Fig. 5. Nyquist plots to evaluate (A) charge transfer resistance of Nb\textsubscript{2}O\textsubscript{5-x} and Nb\textsubscript{2}O\textsubscript{5} electrodes and (B) ionic conductivity at room temperature of pressed Nb\textsubscript{2}O\textsubscript{5-x} pellet. (Inset: schematic experimental setup for (B).)
Fig. S12. Linear fitting of $Z_{\text{real}}$ vs. $\omega^{-1/2}$. Related to Fig. 5. Warburg plot of real part of impedance vs. inverse square root of $\omega$ in the low-frequency region, from which the slope $\sigma$ can be obtained.
Fig. S13. *b*-values analysis. Related to Fig. 5. (A) *b*-values of Nb$_2$O$_{5-x}$ determined from (B) plot of current vs. potential; likewise, (C) *b*-values of Nb$_2$O$_5$ determined from (D) plot of current vs. potential.
Fig. S14. Contribution and percentage of capacitive contribution. Related to Fig. 5. (A) Capacitor-like contribution in the total capacity of Nb$_2$O$_{5-x}$. (B) Percentages of capacitive contributions in Nb$_2$O$_{5-x}$, Nb$_2$O$_5$ and TiO$_2$ (anatase).
Transparent Methods

Preparation of Sr(Ca$_{1/3}$Nb$_{2/3}$)O$_3$, Nb$_2$O$_5$, HNbO$_3$ and Nb$_2$O$_{5-x}$

The parent oxide to be used for selective acid etching was Sr(Ca$_{1/3}$Nb$_{2/3}$)O$_3$. It was synthesized by a sol-gel method starting with a solution of SrCl$_2$·6H$_2$O (0.74 g), CaCl$_2$ (0.1027 g) and citric acid monohydrate (3.5 g) in 7.5 mL deionized water, to which 7.5 mL ethylene glycol was added to stabilize the solution. A second solution of 0.5 g NbCl$_5$ in 15 mL ethyl alcohol was next added to the first, and the mixture was heated to 90 °C and held there until it gelled. The transparent yellow gel was calcined at 700 °C in air for 3 h to obtain Sr(Ca$_{1/3}$Nb$_{2/3}$)O$_3$ powders. Similarly, Nb$_2$O$_5$ was synthesized using the same procedure but without SrCl$_2$ and CaCl$_2$.

Powder of Sr(Ca$_{1/3}$Nb$_{2/3}$)O$_3$ was used to prepare HNbO$_3$ via acid etching, in which 13 mL 0.5 M HCl with 0.2 g Sr(Ca$_{1/3}$Nb$_{2/3}$)O$_3$ addition was left in a 25 mL Teflon-lined steel autoclave at 200 °C for 12 h. The etched powders were washed several times with deionized water and dried at 70 °C to obtain HNbO$_3$. Finally, Nb$_2$O$_{5-x}$ was obtained by annealing HNbO$_3$ at 700 °C for 4 h in an Ar atmosphere. A schematic summarizing the above is shown in Fig. 1.

Characterization of materials

The crystal structures of as-prepared materials were determined by X-ray diffraction (XRD, Bruker D2 phaser diffractometer, 4 kW) using Cu Kα radiation (λ = 0.15406 nm). Their morphology and microstructure were observed using a scanning electron microscope (SEM, Phenom Pro) and a transmission electron microscope (TEM, JEM2010-HR). Nitrogen adsorption/desorption isotherms at 77 K were collected by a Micrometrics ASAP 2010 analyzer, and analyzed by the Brunauer-Emmett-Teller (BET) method for the specific surface area and the Barrett-Joyner-Halenda (BJH) model for the pore size distribution. Thermal decomposition of HNbO$_3$ was studied using a thermal gravimetric analyzer (Thermal Analysis Q600SDT) at a heating rate of 10 °C min$^{-1}$ from room temperature to 900 °C. X-ray photoelectron spectroscopy (XPS) was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hν = 1253.6 eV), and electron paramagnetic resonance (EPR) spectra were collected using a Bruker EMX-8 spectrometer at 9.44 GHz at 300 K. Magnetic and electrical properties were also studied in a Physical Property Measurement System (PPMS, Quantum Design). UV-Vis diffuse reflectance spectra were performed at room temperature using a UV-4100 spectrophotometer operating from 1400 nm to 300nm. BaSO$_4$ was used as a 100 % reflectance standard. The powder sample was spread on a compacted base of BaSO$_4$ powder. The tap density was measured by mechanically tapping a 2-mL graduated cylinder, which contained the sample powder, until no more volume change was observed. The tap density was obtained by dividing powder mass by the final volume of the tapped powder.

Electrochemical characterizations

Electrochemical performance was evaluated using CR2016 coin cells with Nb$_2$O$_{5-x}$ and Nb$_2$O$_5$ anodes assembled in an Ar-filled glove box. The slurry for the electrode was made of
80 wt% active material (Nb₂O₅ or Nb₂O₅), 10 wt% conductive agent (acetylene black) and 10 wt% polyvinylidene fluoride (PVDF), the latter dissolved in N-methyl-2-pyrrolidone (NMP) before use. The slurry was cast onto a copper foil and dried at 70 °C for 7 h. The cell was then assembled using a pure Li foil as the counter electrode, a microporous polypropylene film (Whatman, GF/C) as the separator, and a mixture of ethylene carbonate, diethylene carbonate and dimethyl carbonate (1:1:1 in weight) with 1M LiPF₆ as electrolyte. For comparison (in Fig. 5E-F) commercial anode materials (Si/C and graphite purchased from BTR, P. R. China and MTI, P. R. China, respectively) were also assembled into coin cells using the same process. Galvanostatic charge-discharge (CC) tests and cyclic voltammetry (CV) were conducted between 1.0 and 3.0 V vs. Li/Li⁺ at room temperature in a LAND battery testing system. Lastly, electrochemical impedance spectroscopy (EIS) was measured using a CHI760E electrochemical workstation (Chenhua instrument, Shanghai, China).

The EIS data in the Nyquist plots have a semicircle in the high frequency range that indicates the charge transfer resistance, and an inclined line in the low frequency range that indicates Li⁺ diffusion into the bulk of the electrode; the latter commonly referred to as Warburg diffusion. The diffusion coefficient of Li⁺ can be calculated from the latter part using the following equation:

\[
D_{Li^+} = 0.5 \times \left[ \frac{V_m}{FS\sigma} \left( \frac{-dE}{dx} \right) \right]^2
\]

Here, \(V_m\) is the molecular volume (cm³ mol⁻¹), \(S\) is the electrode area (cm²), \(\frac{dE}{dx}\) is the slope of the Coulometric titration plot, \(F\) is the Faraday constant (96,486 C mol⁻¹), and \(\sigma\) is the Warburg factor which can be obtained from the EIS using the following relationship:

\[
Z_{real} = R_0 + R_{ct} + \sigma\omega^{-1/2}
\]

with \(R_0\) being the resistance between the electrolyte and electrode, \(R_{ct}\) the charge transfer resistance, and \(\omega\) the angle frequency. This leads to a linear dependence of \(Z_{real}\) vs. \(\omega^{-1/2}\), shown in Fig. S12 using our data, from which the slope \(\sigma\) can be obtained. An increased \(D_{Li^+}\) implied faster Li⁺ transport and electrochemical kinetics.