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Defective $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$: an advanced anode material for lithium-ion batteries

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To explore anode materials with large capacities and high rate performances for the lithium-ion batteries of electric vehicles, defective $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ has been prepared through a facile solid-state reaction in argon. X-ray diffractions combined with Rietveld refinements indicate that $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ has the same crystal structure with stoichiometric $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (Wadsley-Roth shear structure with $A2/m$ space group) but larger lattice parameters and 6.6% O^{2-} vacancies (vs. all O^{2-} ions). The electronic conductivity and Li^+ ion diffusion coefficient of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ are at least six orders of magnitude and ~ 2.5 times larger than those of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, respectively. First-principles calculations reveal that the significantly enhanced electronic conductivity is attributed to the formation of impurity bands in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ and its conductor characteristic. As a result of the improvements in the electronic and ionic conductivities, $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ exhibits not only a large initial discharge capacity of 329 mAh g^{-1} and charge capacity of 286 mAh g^{-1} at 0.1 C but also an outstanding rate performance and cyclability. At 5 C , its charge capacity remains 180 mAh g^{-1} with large capacity retention of 91.0% after 100 cycles, whereas those of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ are only 90 mAh g^{-1} and 74.7% .

The great success of lithium-ion batteries (LIBs) in portable electronic devices has triggered considerable efforts for their further applications in electric vehicles (EVs)¹. The two key requirements of the LIBs for EVs are high power density and high energy density, which respectively determine how fast and far the EVs can travel on a single charge. Unfortunately, the commonly used graphite anode material suffers from its poor rate performance and safety in spite of its large theoretical capacity (372 mAh g^{-1})². In this regard, many other anode materials (such as intercalation-type TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, alloying-type Si and Sn, and conversion-type Fe_2O_3 and Co_3O_4) have been developed. Among them, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ probably has received the most attention³. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows a spinel crystal structure with its cations located at both octahedral and tetrahedral sites⁴. It exhibits a high working potential ($\sim 1.57 \text{ V}$ vs. Li/Li^+) and negligible volume change ($< 0.1\%$) during the lithiation and delithiation processes, respectively lead to its high safety and good cyclability. Through the modifications by doping with foreign ions, compositing a second conductive phase and/or reducing the particle size, its intrinsically low electronic conductivity and Li^+ ion diffusion coefficient can be significantly improved, resulting in its high rate performance^{5,6}. However, it has a small theoretical capacity of only 175 mAh g^{-1} between 3.0 and 1.0 V vs. Li/Li^+ , which cannot be effectively increased. Thus, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cannot fulfil the requirement of high energy density for EVs although it can fulfil that of high power density.

As a new type of anode materials with large theoretical capacities, Ti–Nb–O compounds have attracted great research interest very recently. Two known Ti–Nb–O anode materials, TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, were firstly reported by Han *et al.* and Wu *et al.* in 2011 and 2012, respectively^{7–9}. In these compounds,

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Figure 1. Schematic representations of the unit cells for (a) TiNb_2O_7 and (b) $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$.

there is a one-electron transfer between Ti^{4+} and Ti^{3+} ions and two-electron transfer between Nb^{5+} and Nb^{3+} ions. As a result, TiNb_2O_7 has a large theoretical capacity of 388 mAh g^{-1} based on the five-electron transfer per formula unit, and that of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ is 396 mAh g^{-1} based on its 22-electron transfer. These theoretical capacities are ~ 1.2 times larger than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and even surpass that of graphite. TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ exhibit Wadsley-Roth shear structures constructed by $m \times n \times \infty$ ($m = n = 3$ for TiNb_2O_7 , Fig. 1a; $m = 4$ and $n = 3$ for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, Fig. 1b) ReO_3 -type blocks, where m and n are respectively the length and width of the blocks in numbers of octahedral¹⁰. All cations (Ti^{4+} and Nb^{5+} ions with molar ratios of 1 : 2 for TiNb_2O_7 and 1 : 5 for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$) randomly occupy the octahedral sites connected by edges and corners. Since no cations are resided at the tetrahedral sites, the Wadsley-Roth shear structure is more open than the spinel structure, inferring its larger Li^+ ion diffusion coefficient. In spite of the above advantages, TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ suffer from their intrinsically low electronic conductivities and Li^+ ion diffusion coefficients, which significantly limit their rate performances.

To fulfil the requirement of high power density, it is highly necessary to modify TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. However, very limited studies have followed the reports from Han *et al.* and Wu *et al.* so far^{11–17}. Only TiNb_2O_7 nanoparticles, nanofibers and nanoporous particles were prepared and exhibited good rate performances due to the short transport distance for electrons and Li^+ ions within the TiNb_2O_7 particles^{11–15}. Nevertheless, their fabrications are rather complex and their tap densities are rather small, limiting their practical applications. Crystal structure modification (including doping) has been demonstrated as an effective and facile strategy to improve the rate performance of intercalation-type electrode materials due to the resultant improvements of the electronic conductivity and/or Li^+ ion diffusion coefficient^{5,6}. In this study, for the first time, we have employed the strategy of crystal structure modification to improve the rate performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. Using a facile solid-state reaction method, defective $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ containing O^{2-} vacancies has been successfully fabricated. Its crystal structure, material properties and electrochemical performances has been intensively studied and compared with the stoichiometric $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. The results based on the experiments, Rietveld refinements and first-principle calculations reveal that $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ has a larger unit cell volume, enhanced electronic conductivity, improved Li^+ ion diffusion coefficient, large capacity, high rate performance and good cyclability. Therefore, $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ is able to fulfil the two key requirements of high power density and high energy density for EVs.

Results and Discussion

Crystal structure analysis. The observed, calculated, error XRD patterns for the two prepared Ti–Nb–O samples are plotted in Fig. 2. The sharp diffraction peaks are indicative of their good crystallinity rooted in the high-temperature calcination at 1200°C . The pattern of the Ti–Nb–O sample calcined in air (Fig. 2a) matches well with a Wadsley-Roth shear structure ($A2/m$ space group) and all peaks are in good agreement with those of JCPDS card No. 72-0159, which suggest the formation of pure $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. The peaks of the Ti–Nb–O sample calcined in argon (Fig. 2b) are very similar to those of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, suggesting the two samples share the same basic crystal structure. No diffractions from TiO_2 , Nb_2O_5 , TiNb_2O_7 or $\text{TiNb}_{24}\text{O}_{62}$ can be observed, indicating that the employment of the argon atmosphere

Figure 2. XRD patterns and Rietveld refinement results of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$.

did not influence the formation of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ -type crystals. A previous study confirmed that a similar reaction at non-oxidizing atmosphere resulted in the generation of O^{2-} vacancies and cations in lower valence state and thus the formation of nonstoichiometric transition oxide¹⁸. Hence, it can be deduced that $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ is a reasonable chemical formula to represent the Ti–Nb–O sample calcined in argon, in which Ti^{3+} and Nb^{4+} ions exist together with O^{2-} vacancies. Using the crystal data of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ as the initial crystal data for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$, the spectrum of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ was successfully refined by the Rietveld method. As a comparison, the refinement of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ was also carried on. Their Rietveld refinement results are summarized Table 1. As can be seen, $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ exhibits a considerably large amount of O^{2-} vacancies (6.6% vs. all O^{2-} ions) and thus a chemical formula of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$. In addition, it has larger lattice parameters and a larger unit cell volume than those of the stoichiometric $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. These increases can be due to the existence of the O^{2-} vacancies, Ti^{3+} ions with a larger size (0.67 Å) than that of Ti^{4+} ions (0.605 Å) and Nb^{4+} ions with a larger size (0.68 Å) than that of Nb^{5+} ions (0.64 Å)¹⁹.

The crystalline characteristics of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ were further examined by the HRTEM tests (Fig. 3). As can be seen in Fig. 3a,b, the atomic layers in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ are positioned in orderly and repeated patterns. When combining the three white stripes indicated by the arrows as a unit in Fig. 3a, the layers can be considered as an equidistant arrangement of the unit. The interval between the units is 1.03 nm, which is equal to a half of the lattice parameter c (Table 1). As shown in Fig. 1b, c is parallel to the width direction of the block (*i.e.*, n direction). Thus, the unit can reflect the width characteristic of the block. Similarly, in Fig. 3b, the interval between the units is 1.55 nm, corresponding to the lattice parameter a . This unit can reflect the length and width characteristics of the block since a is not parallel to or perpendicular to the length/width direction of the block (*i.e.*, m/n direction). When comparing Fig. 3a,c as well as Fig. 3b,d, it can be found that $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ have the same units, which indicates that the two samples have the same block structure and thus similar crystal structures. This finding is in good agreement with the XRD result.

Particle morphology and size. Figure 4a,b illustrate the particle morphologies and sizes of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$, respectively. Both samples exhibit similar morphologies with wide primary particle-size distributions ranging from less than 100 nm to more than 1 μm . Aggregates exist in both samples. Therefore, the morphologies show the common features of the powders from solid-state reaction. The BET specific surface area of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ is 1.30 $\text{m}^2 \text{g}^{-1}$, which is very similar to that of its stoichiometric counterpart (1.26 $\text{m}^2 \text{g}^{-1}$). This comparison suggests that the different calcination atmosphere negligibly affects the particle size.

Electronic conductivity. The electronic conductivities of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ were determined based on a two-probe direct current method. $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ has an electronic conductivity which is so low that it cannot be accurately measured using the electrochemical workstation. Since the electrochemical workstation has a current limit of 1 nA, it can be deduced that its electronic conductivity is below $1 \times 10^{-9} \text{ S cm}^{-1}$, inferring its insulator characteristic. This result can be due to the fact that there are no free electrons within its cations (Ti^{4+} and Nb^{5+} ions) in their highest valence states. In sharp contrast, the electronic conductivity of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ is increased by at least six orders of magnitude to a large value

Sample	a (Å)	b (Å)	c (Å)	α, γ (°)	β (°)	V (Å ³)	f_1^a	f_2^b	f_3^c	R_{wp}^d	R_p^e	χ^2^f
Ti ₂ Nb ₁₀ O ₂₉	15.52368 (58)	3.81104 (11)	20.54769 (67)	90 (–)	113.058 (3)	1118.512 (78)	1 (–)	1 (–)	1 (–)	0.0998	0.0789	6.593
Ti ₂ Nb ₁₀ O _{27.1}	15.53722 (67)	3.81393 (13)	20.55602 (78)	90 (–)	113.070 (3)	1120.694 (92)	0.339 (31)	0.710 (32)	1 (–)	0.0940	0.0733	5.638

Table 1. Results of crystal analysis by Rietveld refinements in Ti₂Nb₁₀O₂₉ and Ti₂Nb₁₀O_{27.1} (^aOccupancy of O²⁻ in O3 sites. ^bOccupancy of O²⁻ in O4 sites. ^cOccupancy of O²⁻ in other O sites. ^dWeighted profile residual. ^eProfile residual. ^fGoodness of fit).

Figure 3. HRTEM images of (a,b) Ti₂Nb₁₀O₂₉ and (c, d) Ti₂Nb₁₀O_{27.1}.

Figure 4. FESEM images of (a) $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and (b) $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$.

of $1.06 \times 10^{-3} \text{ S cm}^{-1}$. $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ presents considerable amounts of Ti^{3+} and Nb^{4+} ions with unpaired electrons, which can greatly contribute to the significant improvement of the electronic conductivity²⁰. It is known that the electronic conductivities of doped metal oxides are generally in the range of only 10^{-9} – $10^{-7} \text{ S cm}^{-1}$ ^{5,6}. For instance, the values of $\text{Li}_{3.9}\text{Ni}_{0.15}\text{Ti}_{4.95}\text{O}_{12}$, $\text{Li}_{3.8}\text{Cu}_{0.3}\text{Ti}_{4.9}\text{O}_{12}$ and $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ are 3.1×10^{-8} , 3.6×10^{-8} and $4.7 \times 10^{-8} \text{ S cm}^{-1}$, respectively^{5,6}. Therefore, compared with doping, the crystal structure modification based on the production of O^{2-} vacancies in this work is a much more effective strategy to enhance the electronic conductivity of metal oxides.

In order to understand more about the physical essence of the pristine $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and its defective material, DFT calculations were carried out, and their calculated total density of states (TDOS) and partial density of states (PDOS) are illustrated in Fig. 5. As can be seen in Fig. 5a, for the valence band of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, O 2p, Ti 3d and Nb 4d states fill up the relative lower electronic states from -5.4 eV to 0.3 eV . The clear overlaps of these states indicate significant hybridization between Ti 3d and O 2p orbitals and between Nb 4d and O 2p orbitals (*i.e.*, ionic Ti–O and Nb–O bonds are formed.). The conduction band mainly comprises unoccupied Ti and Nb states, located from 1.9 eV to 6 eV . The resultant band gap is $\sim 1.6 \text{ eV}$, which is large enough to confirm the insulator characteristic of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ since it is well known that the standard DFT calculation underestimates the band gap. Therefore, the electronic conductivity of the pristine $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ is very low. In contrast, as shown in Fig. 5b, the Fermi level in $\text{Ti}_2\text{Nb}_{10}\text{O}_{27}$ is inside of some bands, suggesting that $\text{Ti}_2\text{Nb}_{10}\text{O}_{27}$ is no longer an insulator but changed to be a conductor. In addition, impurity bands appear close to but below the Fermi level. These impurity bands are composed of the Ti 3d and Nb 4d states with slightly hybridization with the O 2p states. After the calcination in argon, the production of O^{2-} vacancies in the defective material alters the electron configurations of Ti and Nb ions, leading to the formation of the impurity bands, the conductor characteristic and thus the huge improvement of the electronic conductivity.

Li^+ ion diffusion coefficient. The Li^+ diffusion coefficients of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ were determined using the CV technique. The $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cells were tested at a scanning rate of 0.1 mV s^{-1} for four cycles and then successively at 0.3, 0.5 and 0.7 mV s^{-1} for one cycle each between 3.0 and 0.8 V vs. Li/Li^+ at room temperature, as displayed in Fig. 6a,b. For each cell at 0.1 mV s^{-1} , the intensive cathodic peak shifts to a larger potential after the first cycle. This shift may be attributed to the variation of the electronic structure of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ rooted in the irreversible lithiation process in the first cycle (note that the initial Coulombic efficiency for each cell is not 100% as presented below)^{12,17}. In fact, such shift can also be observed in other intercalation-type anode materials, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ²¹. Each cycle of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ cell shows two cathodic peaks and three anodic peaks, and that of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell also exhibits five peaks at the similar positions but with larger intensities.

Figure 5. Calculated TDOS and PDOS of (a) $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ ($\text{Ti}_4\text{Nb}_{20}\text{O}_{58}$) and (b) $\text{Ti}_2\text{Nb}_{10}\text{O}_{27}$ ($\text{Ti}_4\text{Nb}_{20}\text{O}_{54}$). Fermi levels are shown by dot lines.

These peaks can be ascribed to the $\text{Ti}^{3+}/\text{Ti}^{4+}$, $\text{Nb}^{4+}/\text{Nb}^{5+}$ and $\text{Nb}^{3+}/\text{Nb}^{4+}$ redox couples. A previous report reveals that the Ti^{4+} and Nb^{5+} ions in TiNb_2O_7 are simultaneously and continuously reduced during the discharge (lithiation) process¹⁵. Thus, each of the five peaks may be assigned to two or more redox couples. For instance, the cathodic peaks centered at ~ 1.88 V vs. Li/Li^+ (at 0.1 mV s^{-1}) may correspond to $\text{Ti}^{3+}/\text{Ti}^{4+}$ and $\text{Nb}^{4+}/\text{Nb}^{5+}$ redox couples. Among all the peaks at 0.1 mV s^{-1} , the cathodic one centered at ~ 1.61 V vs. Li/Li^+ and the anodic one centered at ~ 1.73 V vs. Li/Li^+ are relatively intensive. Taking the middle points between these two peaks, The average working potentials of both cells were determined to be ~ 1.71 V vs. Li/Li^+ , which is similar to those of the $\text{TiNb}_2\text{O}_7/\text{Li}$ cell (~ 1.64 V vs. Li/Li^+)¹⁷ and the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ cell (~ 1.57 V vs. Li/Li^+). Such reasonably high working potentials are able to suppress the reduction of electrolyte and avoid the formation of thick solid-electrolyte interphase (SEI) layers and lithium dendrites on $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ particle surfaces, resulting in their high safety for EVs. The potential differences between the cathodic and anodic peaks reflect the polarization degree of the cells. The $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ cell shows a polarization of 0.123 V based on the intensive cathodic and anodic peaks at 0.1 mV s^{-1} , while that of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell is lowered to 0.113 V. This smaller polarization of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell together with its sharper cathodic and anodic peaks is indicative of its better electrochemical kinetics.

In addition, there is a linear relationship between the peak current of the intensive cathodic/anodic reaction I_p and the square root of the sweep rate $v^{0.5}$, as illustrated in Fig. 6c. As a result, the Li^+ ion diffusion coefficient D can be calculated based on the Randles-Sevcik equation²²:

$$I_p = 2.69 \times 10^5 S n^{1.5} C D^{0.5} v^{0.5} \quad (1)$$

where S , n , and C are respectively the electrode surface area of contact between the active materials and electrolyte, the charge transfer number and the molar concentration of Li^+ ions in solid. $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ has Li^+ ion diffusion coefficients of 5.43×10^{-15} and $6.52 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ during the lithiation and delithiation processes, respectively. In contrast, the corresponding values of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ are increased to 1.84×10^{-14} and $2.37 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. Since the Li^+ ion diffusion coefficients for $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ during the lithiation process are smaller than those during the delithiation process, it can be confirmed that the lithiation process is the rate-limiting step for both samples. Obviously, compared with $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ delivers a ~ 2.5 times larger Li^+ ion diffusion coefficient during the lithiation process. The increases in the Li^+ ion diffusion coefficient may be attributed to the crystalline characteristics of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$. Its larger unit cell volume may lead to wider Li^+ ion transport paths in its crystal structure, and its 6.6% O^{2-} vacancies may imply more Li^+ ion transport paths. Both improvements can facilitate the transport of Li^+ ion in the active particles during the electrochemical reaction, resulting in its larger Li^+ ion diffusion coefficients. Moreover, it is worth noting that the average Li^+ ion diffusion coefficient of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ is two orders of magnitude larger than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($1.81 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$), further confirming the advanced crystal structure of the defective $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$.

Figure 6. CV curves of (a) $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ and (b) $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cells, and (c) relationship between peak current of cathodic/anodic reaction I_p and square root of sweep rate $v^{0.5}$.

Discharge–charge performance. The discharge–charge behaviours of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cells were examined under galvanostatic conditions by performing several discharge–charge cycles. Figure 7a compares their discharge–charge curves at different rates (0.1, 0.5, 1, 2 and 5 C) between 3.0 and 0.8 V vs. Li/Li^+ . Despite of the differences in the reversible capacities, the curve-shapes for the two cells are similar, demonstrating the defects (O^{2-} vacancies, Ti^{3+} ions and Nb^{4+} ions) in $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ do not affect the fundamental electrochemical reaction mechanism. At 0.1 C, each sample shows a short discharge plateau at ~ 1.65 V vs. Li/Li^+ and a short charge plateau at ~ 1.68 V vs. Li/Li^+ , which match well with the two intensive peaks in the CV curves (Fig. 6). These two plateaus can correspond to a two-phase reaction⁹. The sloping curves before and after the plateau region are indicative of two different solid-solution reactions. During the first cycle at 0.1 C, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ cell delivers a discharge capacity of 354 mAh g^{-1} . At the same rate, the corresponding capacity for the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell is slightly decreased to 329 mAh g^{-1} . It is known that all the electrochemical energy in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ comes from the reversible redox reactions between Ti^{3+} and Ti^{4+} ions, between Nb^{4+} and Nb^{5+} ions,

Figure 7. (a) (i) Initial discharge–charge curves at 0.1 C, second discharge–charge curves at (ii) 0.1 C, (iii) 0.5 C, (iv) 1 C, (v) 2 C and (vi) 5 C of Ti₂Nb₁₀O₂₉/Li and Ti₂Nb₁₀O_{27.1}/Li cells; (b) polarization ΔE of Ti₂Nb₁₀O₂₉/Li and Ti₂Nb₁₀O_{27.1}/Li cells at 0.1, 0.5, 1, 2 and 5 C; and (c) cyclability of Ti₂Nb₁₀O₂₉/Li and Ti₂Nb₁₀O_{27.1}/Li cells at 5 C along with Coulombic efficiency of Ti₂Nb₁₀O_{27.1}/Li cell. Identical discharge–charge rates were used.

and between Nb³⁺ and Nb⁴⁺ ions. Since there are considerable amounts of Ti³⁺ and Nb⁴⁺ ions in the defective Ti₂Nb₁₀O_{27.1}, its contents of Ti⁴⁺ and Nb⁵⁺ ions are smaller than those in its stoichiometric counterpart, leading to its lower initial discharge capacity. However, the Ti₂Nb₁₀O_{27.1}/Li cell exhibits a larger initial Coulombic efficiency (86.9%) than that of its stoichiometric counterpart (82.8%) probably due to its better electrochemical kinetics. Thus, its initial charge capacity (286 mAh g⁻¹) can approach that of its stoichiometric counterpart (294 mAh g⁻¹).

Rate performance and power density. With increasing the rate, the plateaus become inconspicuous; the discharge curves monotonically drop and the corresponding charge curves monotonically rise, indicating the increasing polarization. The polarization ΔE vs. rate of both cells is plotted in Fig. 7b. The value of ΔE in this study is defined as the difference between the two potentials at the SOC of 50%

Figure 8. *Ex situ* XRD patterns of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ electrodes after (i) as-fabricated, (ii) first-discharged to 0.8 V vs. Li/Li^+ , (iii) first-charged to 3 V vs. Li/Li^+ , and (iv) charged to 3 V vs. Li/Li^+ in the 10th cycle. Identical discharge–charge rates were used.

in each cycle. The $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell exhibits smaller ΔE values than those of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ cell at all rates. Especially, the difference between the ΔE values in the two cells becomes larger when the rate increases. These results suggest that the defects in $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ can significantly reduce its polarization and thus can favor its rate performance.

In spite of the slightly smaller capacities at 0.1 C, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell shows larger capacities at high rates than the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ cell. For instance, while the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ cell can offer a charge capacity of 185 mAh g^{-1} at 2 C, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell is able to deliver 209 mAh g^{-1} . With further increase of the rate to 5 C ($\sim 2 \text{ A g}^{-1}$), the charge capacity of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell still reaches 180 mAh g^{-1} , which is twice of that of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ cell (90 mAh g^{-1}) and even exceeds the theoretical capacity of the popular $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ cell (175 mAh g^{-1}). During the electrochemical reaction of an LIB, electrons and Li^+ ions simultaneously transport in active material particles. Since both samples in this work have similar particle sizes, their rate performances are determined by their electronic conductivities and Li^+ ion diffusion coefficients. As demonstrated previously, the defective $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ exhibits improved electronic conductivity and Li^+ ion diffusion coefficient, which are at least six orders of magnitude and ~ 2.5 times larger than those of the stoichiometric $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, respectively. These two improvements can facilitate the transport of electrons and Li^+ ions in the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ particles, resulting in the better rate performance and thus higher power density. All these discharge–charge results are well consistent with the previous CV analysis.

Cyclability. The two cells were further subjected to cyclability evaluation at 5 C, as displayed in Fig. 7c. The $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell remains a large charge capacity of 164 mAh g^{-1} after 100 cycles, which keeps 91.0% of its initial charge capacity. In sharp contrast, the corresponding values for the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ cell are only 67 mAh g^{-1} and 74.7%. Besides the good cyclability, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}/\text{Li}$ cell also exhibits excellent Coulombic efficiency of $\sim 100\%$ throughout the cycling (Fig. 7c). These results demonstrate the highly reversible characteristic, outstanding structural stability as well as fast electronic and ionic transport in the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ electrode. Its good cyclability is further supported by its *ex situ* XRD result. Figure 8 exhibits the XRD patterns of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ electrodes after as-fabricated, first-discharged to 0.8 V vs. Li/Li^+ , first-charged to 3 V vs. Li/Li^+ , and charged to 3 V vs. Li/Li^+ in the 10th cycle. As can be seen, the four patterns are very similar. There are little diffraction peak shift and no new peaks at different SOC in spite of some variations in peak intensity, which confirms that basic monoclinic crystal structure of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ was maintained during the repeated discharge and charge processes. Therefore, $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ is an intercalation-type anode material, similar to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (see Supplementary Fig. S1 online), TiNb_2O_7 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The desirable intercalation/deintercalation characteristic and good structural reversibility of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ can also be ascribed to its good cyclability.

In summary, the defective $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ has been fabricated through a facile solid-state reaction in argon. It shows a Wadsley–Roth shear structure with $A2/m$ space group, the same as that of the stoichiometric $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. In comparison with $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ not only exhibits larger lattice parameters and a larger unit cell volume but also contains Ti^{3+} ions, Nb^{4+} ions and 6.6% O^{2-} vacancies (vs. all O^{2-} ions). As a result of this advanced crystal structure, $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ has improved electronic conductivity ($1.06 \times 10^{-3} \text{ S cm}^{-1}$) and Li^+ ion diffusion coefficients (averagely $2.11 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$), which are respectively at least six orders of magnitude and ~ 2.5 times larger than those of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. Consequently, $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ presents outstanding electrochemical performances in terms of the capacity, rate performance and cyclability. At 0.1 C, it delivers a large initial discharge capacity of 329 mAh g^{-1} and charge capacity of 286 mAh g^{-1} . At 5 C, it still remains a large charge capacity of 180 mAh g^{-1} with large capacity retention of 91.0% over 100 cycles, in sharp contrast to the corresponding values of only

90 mAh g⁻¹ and 74.7% from Ti₂Nb₁₀O₂₉. Clearly, this intercalation-type Ti₂Nb₁₀O_{27.1} possesses the same advantages of Li₄Ti₅O₁₂ but significantly larger capacities. Therefore, it is able to fulfil the two requirements of high power density and high energy density and thus may be a superior and practical anode material for the LIBs of EVs.

Method

Material preparations. The defective Ti₂Nb₁₀O_{29-x} was fabricated through a one-step solid-state reaction using TiO₂ (Sigma–Aldrich, 99.9%) and Nb₂O₅ (Sigma–Aldrich, 99.9%) with a predetermined molar ratio of TiO₂ : Nb₂O₅ = 2 : 5. These precursors were mixed and milled by a ball-milling machine (SPEX 8000M) for 4 h, and finally calcined at 1200 °C for 4 h in a tube furnace in an argon atmosphere. As a comparison, the stoichiometric Ti₂Nb₁₀O₂₉ was also synthesized by the same process except for the calcination in an air atmosphere.

To prepare the Ti₂Nb₁₀O_{29-x} and Ti₂Nb₁₀O₂₉ samples for electronic conductivity measurements, the above precursors were uni-axially pressed into pellets with a diameter of 10.25 mm at a pressure of 1000 kg cm⁻². The pressed pellets were calcined at 850 °C for 5 h and then at 1200 °C for 48 h in argon (for Ti₂Nb₁₀O_{29-x}) or air (for Ti₂Nb₁₀O₂₉). After polishing the two sides of the calcined pellets, gold films were evaporated onto both sides, forming Au/Ti₂Nb₁₀O_{29-x}/Au and Au/Ti₂Nb₁₀O₂₉/Au symmetric ion blocking cells.

Materials characterizations. Detailed crystal structures of Ti₂Nb₁₀O_{29-x} and Ti₂Nb₁₀O₂₉ were identified using X-ray diffractions (XRD) combined with Rietveld refinements. XRD patterns for the refinements were recorded in an angle interval of 5–130° (2θ) with a step width of 0.03° and a counting time of 8 s per step using an X-ray diffractometer (Bruker D8, Germany) with a monochromatic Cu Kα radiation (λ = 0.1506 nm). *Ex situ* XRD patterns were collected between 15° to 70° (2θ) at a scanning speed of 1° min⁻¹. The refinements were carried out using the GSAS program with the EXPGUI interface^{23,24}. During these refinements, the following instrumental and structural parameters were refined: background parameters, zero-shift, unit cell parameters, profile parameters, atomic fractional coordinates, atomic isotropic displacement parameters and atomic occupancies. The site occupancies were constrained to the designed chemical formulas. Morphologies, particle sizes and microstructures were examined using a field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) and a high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100, Japan). Nitrogen adsorption–desorption isotherms at 77 K were obtained in a surface area analyser (Quantachrome NOVA 2200e, USA). Specific surface areas were derived based on the Brunauer–Emmett–Teller (BET) model. Electronic conductivity tests were performed on the ion blocking cells using an electrochemical workstation (Zahner zennium, Kronach, Germany) under a small voltage of 50 mV until the corresponding currents stabilized.

Electrochemical tests. Electrochemical performances were examined by the tests of CR2016 coin cells assembled in an argon-filled glove box (Mbraum, Unilab, Germany). In these cells, pure Li foils were used as counter and reference electrodes, microporous polypropylene films (Celgard 2400, Celgard LLC., USA) as separators, and a mixture of ethylene carbonate, dimethyl carbonate and diethylene carbonate (1 : 1 : 1 by weight) containing 1 M LiPF₆ (DAN VEC) as electrolyte. Their corresponding working electrodes were fabricated by a slurry-coating procedure. The slurries contained 65 wt% active materials (Ti₂Nb₁₀O_{29-x} or Ti₂Nb₁₀O₂₉), 25 wt% super P[®] conductive carbon (TIMCAL Ltd.) and 10 wt% polyvinylidene fluoride (PVDF, Sigma–Aldrich) in N-methylpyrrolidone (NMP, Sigma–Aldrich). After homogeneously blended, these slurries were uniformly coated on Cu plates. The coated plates were then dried in a vacuum oven at 120 °C for 10 h and finally roller-pressed by a rolling machine to form the working electrodes.

Galvanostatic discharge–charge tests were conducted using a multi-channel battery testing system (LANHE CT2001A, China) with a cut-off potential of 3.0–0.8 V vs. Li/Li⁺. All discharge/charge rates were denoted using C-rate where 396 mA g⁻¹ was assigned to the current density of 1 C based on the theoretical capacity of Ti₂Nb₁₀O₂₉ (396 mAh g⁻¹). To prepare the electrodes for the *ex situ* XRD experiments, the coin cells at different states of charge (SOC) were disassembled, and then the working electrodes were washed by dimethyl carbonate for three times and dried at 80 °C. Cyclic voltammetry (CV) measurements were performed using the above electrochemical workstation.

Calculation methodology. All calculations were performed using the projector-augmented wave (PAW) method within the density functional theory (DFT), as implemented in the Vienna *ab initio* simulation package (VASP)^{25–27}. Electronic exchange–correlation functional was treated within the spin-polarized generalized gradient approximation (GGA) parameterized by Perdew–Burke–Ernzerhof (PBE)²⁸. To address the on-site Coulombic interactions in the localized *d* electrons of Nb ions, the GGA + *U* method with an additional Hubbard-type *U* term (*U*_{eff} = *U* – *J* = 1.5 eV) was employed, which has been proved to be a good approximation for Nb in electrode materials of LIBs^{29,30}. Wave functions are expanded in plane waves up to a kinetic energy cut-off of 500 eV. Brillouin-zone integrations were approximated using special k-point sampling of Monkhorst–Pack scheme³¹ with a k-point mesh resolution of 2π × 0.05 Å⁻¹. Lattice vectors (both unit cell shape and size) are fully relaxed together with atomic coordinates until the Hellmann–Feynman force on each atom is less than 0.01 eV/Å.

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Author Contributions

C.L. conceived the project. C.L. designed and conducted most experiments with help from H.Z. G.W., L.Y. and Y.L. provided assistance in imaging and data analysis. C.L., S.Y. and S.W. conducted the first-principles calculations. S.L., J.L. and Z.Z.Z. provided scientific guidance. C.L. and S.Y. wrote the manuscript with help from S.L. and S.W. All author reviewed the manuscript.

Additional Information

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