Defective Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{27.1}$ has been prepared through a facile solid-state reaction in argon. X-ray diffractions combined with Rietveld refinements indicate that Ti$_2$Nb$_{10}$O$_{27.1}$ has the same crystal structure with stoichiometric Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{27.1}$ are at least six orders of magnitude and ~2.5 times larger than those of Ti$_2$Nb$_{10}$O$_{29}$, respectively. First-principles calculations reveal that the significantly enhanced electronic conductivity is attributed to the formation of impurity bands in Ti$_2$Nb$_{10}$O$_{29-x}$ and its conductor characteristic. As a result of the improvements in the electronic and ionic conductivities, Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$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 Li$_4$Ti$_5$O$_{12}$, alloying-type Si and Sn, and conversion-type Fe$_2$O$_3$ and Co$_3$O$_4$) have been developed. Among them, Li$_4$Ti$_5$O$_{12}$ has probably received the most attention\(^3\). Li$_4$Ti$_5$O$_{12}$ shows a spinel crystal structure with its cations located at both octahedral and tetrahedral sites\(^4\). It exhibits a high working potential (~1.57 V vs. Li/Li$^+$) and negligible volume change (<0.1%) during the lithiation and delithiation processes, respectively leading 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\(^5\). 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, Li$_4$Ti$_5$O$_{12}$ cannot fulfill the requirement of high energy density for EVs although it can fulfill 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$_2$O$_7$ and Ti$_2$Nb$_{10}$O$_{29}$, were firstly reported by Han et al. and Wu et al. in 2011 and 2012, respectively\(^7\). In these compounds,
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$_2$O$_7$ has a large theoretical capacity of 388 mAh g$^{-1}$ based on the five-electron transfer per formula unit, and that of Ti$_2$Nb$_{10}$O$_{29}$ is 396 mAh g$^{-1}$ based on its 22-electron transfer. These theoretical capacities are ~1.2 times larger than that of Li$_4$Ti$_5$O$_{12}$ and even surpass that of graphite. TiNb$_2$O$_7$ and Ti$_2$Nb$_{10}$O$_{29}$ exhibit Wadsley-Roth shear structures constructed by $m \times n \times \infty$ ($m = n = 3$ for TiNb$_2$O$_7$, Fig. 1a; $m = 4$ and $n = 3$ for Ti$_2$Nb$_{10}$O$_{29}$, Fig. 1b) ReO$_3$-type blocks, where $m$ and $n$ are respectively the length and width of the blocks in numbers of octahedral $^{10}$. All cations (Ti$^{4+}$ and Nb$^{5+}$ ions with molar ratios of 1 : 2 for TiNb$_2$O$_7$ and 1 : 5 for Ti$_2$Nb$_{10}$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$_2$O$_7$ and Ti$_2$Nb$_{10}$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$_2$O$_7$ and Ti$_2$Nb$_{10}$O$_{29}$. However, very limited studies have followed the reports from Han et al. and Wu et al. so far$^{11-17}$. Only TiNb$_2$O$_7$ 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$_2$O$_7$ 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 Ti$_2$Nb$_{10}$O$_{29}$. Using a facile solid-state reaction method, defective Ti$_2$Nb$_{10}$O$_{29-x}$ containing O$^{2−}$ vacancies has been successfully fabricated. Its crystal structure, material properties and electrochemical performances have been intensively studied and compared with the stoichiometric Ti$_2$Nb$_{10}$O$_{29}$. The results based on the experiments, Rietveld refinements and first-principle calculations reveal that Ti$_2$Nb$_{10}$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, Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{29}$. The peaks of the Ti–Nb–O sample calcined in argon (Fig. 2b) are very similar to those of Ti$_2$Nb$_{10}$O$_{29}$, suggesting the two samples share the same basic crystal structure. No diffractions from TiO$_2$, Nb$_2$O$_5$, TiNb$_2$O$_7$ or TiNb$_2$O$_{62}$ can be observed, indicating that the employment of the argon atmosphere
did not influence the formation of Ti$_2$Nb$_{10}$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 oxide$^{18}$. Hence, it can be deduced that Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{29}$ as the initial crystal data for Ti$_2$Nb$_{10}$O$_{29-x}$, the spectrum of Ti$_2$Nb$_{10}$O$_{29-x}$ was successfully refined by the Rietveld method. As a comparison, the refinement of Ti$_2$Nb$_{10}$O$_{29}$ was also carried on. Their Rietveld refinement results are summarized Table 1. As can be seen, Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{27.1}$. In addition, it has larger lattice parameters and a larger unit cell volume than those of the stoichiometric Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{29}$ and Ti$_2$Nb$_{10}$O$_{27.1}$ were further examined by the HRTEM tests (Fig. 3). As can be seen in Fig. 3a,b, the atomic layers in Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{27.1}$ and Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{29}$ and Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{27.1}$ is 1.30 m$^2$ g$^{-1}$, which is very similar to that of its stoichiometric counterpart (1.26 m$^2$ g$^{-1}$). This comparison suggests that the different calcination atmosphere negligibly affects the particle size.

Electronic conductivity. The electronic conductivities of Ti$_2$Nb$_{10}$O$_{29}$ and Ti$_2$Nb$_{10}$O$_{27.1}$ were determined based on a two-probe direct current method. Ti$_2$Nb$_{10}$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 $1 \times 10^{-9}$ 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 Ti$_2$Nb$_{10}$O$_{27.1}$ is increased by at least six orders of magnitude to a large value.
Table 1. Results of crystal analysis by Rietveld refinements in \( \text{Ti}_2\text{Nb}_{10}\text{O}_{29} \) and \( \text{Ti}_2\text{Nb}_{10}\text{O}_{27.1} \) (*Occupancy of \( \text{O}^{2-} \) in \( \text{O}_3 \) sites. †Occupancy of \( \text{O}^{2-} \) in \( \text{O}_4 \) sites. ‡Occupancy of \( \text{O}^{2-} \) in other \( \text{O} \) sites. §Weighted profile residual. ¶Profile residual. ‖Goodness of fit).

| Sample                  | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \alpha, \gamma \) (°) | \( \beta \) (°) | \( V \) (Å\(^3\)) | \( f^a_{1} \) | \( f^b_{1} \) | \( f^c_{1} \) | \( R_{wp} \) ‡ | \( R_p \) ¶ | \( \chi^2 \) ‖ |
|------------------------|-------------|-------------|-------------|--------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \( \text{Ti}_2\text{Nb}_{10}\text{O}_{29} \) | 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 |
| \( \text{Ti}_2\text{Nb}_{10}\text{O}_{27.1} \) | 15.53721 (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 |

Figure 3. HRTEM images of (a, b) \( \text{Ti}_2\text{Nb}_{10}\text{O}_{29} \) and (c, d) \( \text{Ti}_2\text{Nb}_{10}\text{O}_{27.1} \).
of 1.06 × 10⁻³ S cm⁻¹. Ti₂Nb₁₀O₂₇.₁ presents considerable amounts of Ti³⁺ and Nb⁴⁺ 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 S cm⁻¹⁵,⁶. For instance, the values of Li₃.₉Ni₀.₁₅Ti₄.₉₅O₁₂, Li₃.₈Cu₀.₃Ti₄.₉O₁₂ and Li₃.₉Cr₀.₃Ti₄.₈O₁₂ are 3.₁ × 10⁻⁸, 3.₆ × 10⁻⁸ and 4.₇ × 10⁻⁸ S cm⁻¹, respectively⁵,⁶. Therefore, compared with doping, the crystal structure modification based on the production of O²⁻ 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 Ti₂Nb₁₀O₂₉ 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 Ti₂Nb₁₀O₂₉, 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 ~1.₆ eV, which is large enough to confirm the insulator characteristic of Ti₂Nb₂O₂₉ since it is well known that the standard DFT calculation underestimates the band gap. Therefore, the electronic conductivity of the pristine Ti₂Nb₁₀O₂₉ is very low. In contrast, as shown in Fig. 5b, the Fermi level in Ti₂Nb₁₀O₂₇ is inside of some bands, suggesting that Ti₂Nb₁₀O₂₇ 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 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 ~1.₆ eV, which is large enough to confirm the insulator characteristic of Ti₂Nb₂O₂₉ since it is well known that the standard DFT calculation underestimates the band gap. Therefore, the electronic conductivity of the pristine Ti₂Nb₁₀O₂₉ is very low. In contrast, as shown in Fig. 5b, the Fermi level in Ti₂Nb₁₀O₂₇ is inside of some bands, suggesting that Ti₂Nb₁₀O₂₇ 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 orbitals (i.e., ionic Ti–O and Nb–O bonds are formed.).

**Li⁺ ion diffusion coefficient.** The Li⁺ diffusion coefficients of Ti₂Nb₁₀O₂₉ and Ti₂Nb₁₀O₂₇ were determined using the CV technique. The Ti₃Nb₁₉O₃₉/Li and Ti₃Nb₁₉O₃₇.₁/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 Ti₃Nb₁₉O₃₉/Ti₃Nb₁₉O₃₇.₁ 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 Li₈Ti₅O₁₂. Each cycle of the Ti₃Nb₁₉O₃₉/Li cell shows two cathodic peaks and three anodic peaks, and that of the Ti₃Nb₁₉O₃₇.₁/Li cell also exhibits five peaks at the similar positions but with larger intensities.

![Figure 4. FESEM images of (a) Ti₂Nb₁₀O₂₉ and (b) Ti₂Nb₁₀O₂₇.₁.](image-url)
These peaks can be ascribed to the Ti$^{3+}$/Ti$^{4+}$, Nb$^{4+}$/Nb$^{5+}$ and Nb$^{3+}$/Nb$^{4+}$ redox couples. A previous report reveals that the Ti$^{4+}$ and Nb$^{5+}$ ions in TiNb$_2$O$_7$ are simultaneously and continuously reduced during the discharge (lithiation) process$^{15}$. 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 Ti$^{3+}$/Ti$^{4+}$ and Nb$^{4+}$/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 TiNb$_2$O$_7$/Li cell (~1.64 V vs. Li/Li$^+$) and the Li$_4$Ti$_5$O$_12$/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 Ti$_2$Nb$_{10}$O$_{27.1}$ and Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{29}$/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 Ti$_2$Nb$_{10}$O$_{27.1}$/Li cell is lowered to 0.113 V. This smaller polarization of the Ti$_2$Nb$_{10}$O$_{27.1}$/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 equation$^{22}$:

$$I_p = 2.69 \times 10^5 S n^{1.5}D^{0.5}v^{0.5}$$  

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. Ti$_2$Nb$_{10}$O$_{29}$ has Li$^+$ ion diffusion coefficients of $5.43 \times 10^{-13}$ and $6.52 \times 10^{-13}$ cm$^2$ s$^{-1}$ during the lithiation and delithiation processes, respectively. In contrast, the corresponding values of Ti$_3$Nb$_{10}$O$_{27.1}$ are increased to $1.84 \times 10^{-14}$ and $2.37 \times 10^{-14}$ cm$^2$ s$^{-1}$. Since the Li$^+$ ion diffusion coefficients for Ti$_2$Nb$_{10}$O$_{27.1}$ and Ti$_2$Nb$_{10}$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 Ti$_2$Nb$_{10}$O$_{29}$, Ti$_3$Nb$_{10}$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 Ti$_2$Nb$_{10}$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 Ti$_3$Nb$_{10}$O$_{27.1}$ is two orders of magnitude larger than that of Li$_4$Ti$_5$O$_{12}$ ($1.81 \times 10^{-18}$ cm$^2$ s$^{-1}$), further confirming the advanced crystal structure of the defective Ti$_2$Nb$_{10}$O$_{27.1}$.
Discharge–charge performance. The discharge–charge behaviours of the Ti$_2$Nb$_{10}$O$_{29}$/Li and Ti$_2$Nb$_{10}$O$_{27.1}$/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 Ti$_2$Nb$_{10}$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 reaction. 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 Ti$_2$Nb$_{10}$O$_{29}$/Li cell delivers a discharge capacity of 354 mAh g$^{-1}$. At the same rate, the corresponding capacity for the Ti$_2$Nb$_{10}$O$_{27.1}$/Li cell is slightly decreased to 329 mAh g$^{-1}$. It is known that all the electrochemical energy in Ti$_2$Nb$_{10}$O$_{29}$ comes from the reversible redox reactions between Ti$^{3+}$ and Ti$^{4+}$ ions, between Nb$^{4+}$ and Nb$^{5+}$ ions,
and between Nb$^{3+}$ and Nb$^{4+}$ ions. Since there are considerable amounts of Ti$^{3+}$ and Nb$^{4+}$ ions in the defective Ti$_2$Nb$_{10}$O$_{29}$/Li and Ti$_2$Nb$_{10}$O$_{27.1}$/Li cells, its contents of Ti$^{4+}$ and Nb$^{5+}$ ions are smaller than those in its stoichiometric counterpart, leading to its lower initial discharge capacity. However, the Ti$_2$Nb$_{10}$O$_{29}$/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 $\Delta E$ vs. rate of both cells is plotted in Fig. 7b. The value of $\Delta E$ in this study is defined as the difference between the two potentials at the SOC of 50%
in each cycle. The Ti2Nb10O27.1/Li cell exhibits smaller ΔE values than those of the Ti2Nb10O29/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 Ti2Nb10O27.1 can significantly reduce its polarization and thus can favor its rate performance.

In spite of the slightly smaller capacities at 0.1 C, the Ti2Nb10O27.1/Li cell shows larger capacities at high rates than the Ti2Nb10O29/Li cell. For instance, while the Ti2Nb10O29/Li cell can offer a charge capacity of 185 mAh g−1 at 2 C, the Ti2Nb10O27.1/Li cell is able to deliver 209 mAh g−1. With further increase of the rate to 5 C (≈2 A g−1), the charge capacity of the Ti2Nb10O27.1/Li cell still reaches 180 mAh g−1, which is twice of that of the Ti2Nb10O29/Li cell (90 mAh g−1) and even exceeds the theoretical capacity of the popular Li4Ti5O12/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 Ti2Nb10O27.1 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 Ti2Nb10O29, respectively. These two improvements can facilitate the transport of electrons and Li+ ions in the Ti2Nb10O27.1 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 Ti2Nb10O27.1/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 Ti2Nb10O29/Li cell are only 67 mAh g−1 and 74.7%. Besides the good cyclability, the Ti2Nb10O27.1/Li cell also exhibits excellent Coulombic efficiency of ~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 Ti2Nb10O27.1 electrode. Its good cyclability is further supported by its ex situ XRD result. Figure 8 exhibits the XRD patterns of the Ti2Nb10O27.1 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 Ti2Nb10O27.1 was maintained during the repeated discharge and charge processes. Therefore, Ti2Nb10O27.1 is an intercalation-type anode material, similar to Ti2Nb10O29 (see Supplementary Fig. S1 online), TiNb3O7 and Li4Ti5O12. The desirable intercalation/deintercalation characteristic and good structural reversibility of Ti2Nb10O27.1 can also be ascribed to its good cyclability.

In summary, the defective Ti2Nb10O27.1 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 Ti2Nb10O29. In comparison with Ti2Nb10O29, Ti2Nb10O27.1 not only exhibits larger lattice parameters and a larger unit cell volume but also contains Ti4+ ions, Nb5+ ions and 6.6% O2− vacancies (vs. all O2− ions). As a result of this advanced crystal structure, Ti2Nb10O27.1 has improved electronic conductivity (1.06 × 10−3 S cm−1) and Li+ ion diffusion coefficients (averagely 2.11 × 10−14 cm2 s−1), which are respectively at least six orders of magnitude and ~2.5 times larger than those of Ti2Nb10O29. Consequently, Ti2Nb10O27.1 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 Ti₂Nb₁₀O₁₇.₁ possesses the same advantages of Li₄Ti₅O₁₂ but significantly larger capacities. Therefore, it is able to fulfill 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 Ti₂Nb₁₀O₂₉⁻ₓ samples were 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 Ti₂Nb₁₀O₂₉⁻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 Ti₂Nb₁₀O₂₉⁻ₓ) or air (for Ti₂Nb₁₀O₂₉). After polishing the two sides of the calcined pellets, gold films were evaporated onto both sides, forming Au/Ti₂Nb₁₀O₂₉⁻ₓ/Au and Au/Ti₂Nb₁₀O₂₉/Au symmetric ion blocking cells.

**Materials characterizations.** Detailed crystal structures of Ti₂Nb₁₀O₂₉⁻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 = 0.15418 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. 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 (Mbraun, 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 (DANVEC) as electrolyte. Their corresponding working electrodes were 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.

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 LIBs of EVs.

**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 (Uₗd = U – J = 1.5 eV) was employed, which has been proved to be a good approximation for Nb in electrode materials of Li₄Ti₅O₁₂. 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 scheme 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⁻¹.
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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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