Study of the lithium diffusion properties and high rate performance of TiNb$_6$O$_{17}$ as an anode in lithium secondary battery

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TiNb$_6$O$_{17}$ and TiNb$_2$O$_7$ were synthesized using a solid-state method. The techniques were used to assess the electrochemical performance and lithium diffusion kinetics of TiNb$_6$O$_{17}$ related to the unit cell volume with TiNb$_2$O$_7$. The charge-discharge curves and cyclic voltammetry revealed TiNb$_6$O$_{17}$ to have a similar redox potential to TiNb$_2$O$_7$ as well as a high discharge capacity. The rate performance of TiNb$_6$O$_{17}$ was measured using a rate capability test. SSCV and EIS showed that TiNb$_6$O$_{17}$ had higher lithium diffusion coefficients during the charging. From GITT, the lithium diffusion coefficients at the phase transition region showed the largest increase from TiNb$_2$O$_7$ to TiNb$_6$O$_{17}$.

Lithium secondary batteries have been studied for large scale energy devices, such as electric vehicles (EVs) and energy storage systems (ESSs), requiring high energy density and superior rate performance. The development of anode materials has been investigated due to importance of the charge rate and good reversibility for lithium secondary batteries. Commercial anode materials for batteries, such as graphite, have high capacities (370mAh/g). On the other hand, the active material has some problems, such as irreversible capacity loss, due to solid electrolyte interface (SEI) layer and lithium dendrite formation due to the low working voltage window at 0.8V. In particular, lithium dendrite formation leads to the safety hazard of lithium secondary batteries and the unsuitability of the active materials for batteries$^{1–3}$. The Si based materials such as SiO$_2$ showed also high capacity but could not be used to high volume expansion$^4$. In contrast, titanium-based anode materials allow lithium batteries to avoid SEI and lithium dendrite formation due to their safe working voltage area using the Ti$^{4+}$/Ti$^{3+}$ redox reaction (~1.5 V vs. Li/Li$^+$). Typically, Li$_{4}$Ti$_{5}$O$_{12}$ has been studied because of its working voltage area and zero strain properties, resulting in good rate performance due to its strong Ti-O covalent bond$^2$. Despite this, the material has a low theoretical capacity (175mAh/g) and is unsuitable for large-scale devices.

Recently, titanium niobium oxide (TNO) materials, such as TiNb$_2$O$_7$ and Ti$_2$Nb$_{10}$O$_{29}$, have been introduced as promising titanium-based anode materials owing to their nontoxic, good rate performance, low volume change, stable working voltage window (1–2.5 V), and high theoretical capacity (387–390mAh/g). The capacities of TNO materials are influenced by many redox reactions, such as one Ti (Ti$^{4+}$/Ti$^{3+}$) and two Nb reactions (Nb$^{3+}$/Nb$^{4+}$ and Nb$^{4+}$/Nb$^{5+}$)$^{5,6}$. On the other hand, they have lower capacity and reversibility than their theoretical capacities due to the low electronic conductivity and lithium diffusion properties into the structure called Wesley-Roth 2D structure$^{7–9}$. To solve these problems, many studies have been conducted to achieve TNO materials with high reversible capacity and improved rate performance, such as doping with other metals (Ru, Mo, etc.) to achieve high ionic conductivity and electrical conductivity and controlling the particle shape and size$^{1–3,6–12}$. Chunfu Lin et al. examined TiNb$_6$O$_{17}$, which is a new TNO material. The material is composed a large number of Nb ions and has a higher theoretical capacity (397 mAh/g) than TiNb$_2$O$_7$ and Ti$_2$Nb$_{10}$O$_{29}$. Moreover, the material has the same Wesley-Roth structure (monoclinic) but larger lattice parameters and unit cell volume than TiNb$_2$O$_7$ and Ti$_2$Nb$_{10}$O$_{29}$ (1122.541 Å vs. 803.21 Å, 1118.512 Å) due to the larger number of Nb$^{5+}$ ions with a larger size (0.64 Å) than that of Ti$^{4+}$ ions (0.605 Å)$^{13–15}$. This causes a more open lithium insertion/insertion site and improved rate performance; the schema of this theory is listed in Fig. 1. The material showed a higher discharge capacity and better lithium diffusion coefficients by charge-discharge, rate capability, and slow scan cyclic voltammetry (SSCV) than Ti$_2$Nb$_{10}$O$_{29}$ in Chunfu’s study$^{13}$.

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Therefore, this study examined the accurate lithium diffusion kinetics and electrochemical performance of TiNb₆O₁₇ compared to TiNb₂O₇ which has the smallest unit cell volume among the TNO materials and can clearly be compared with TiNb₆O₁₇. The materials were synthesized using a solid-state method. For electrochemical analysis, the charge-discharge curves and rate capability tests were conducted to determine their electrochemical performance. To examine the lithium diffusion kinetics, SSCV, electrochemical impedance spectroscopy (EIS), and a galvanostatic intermittent titration technique (GITT) were used. As a result, TiNb₆O₁₇ showed higher discharge capacity (284mAh/g vs. 264mAh/g) and better rate performance than TiNb₂O₇ (82mAh/g vs. 20mAh/g at 30°C). In addition, TiNb₆O₁₇ showed higher lithium diffusion coefficients than TiNb₂O₇ (mean value 10⁻¹² S²/m vs. 10⁻¹³ S²/m).

**Experimental**

**Synthesis of the active materials and characterization.** TiNb₂O₇ and TiNb₆O₁₇ were synthesized by a solid-state reaction method using TiO₂ (99.9%, Rare Metallic) and Nb₂O₅ (99.99%, Sigma-Aldrich) powders as the starting materials. TiO₂ and Nb₂O₅ were mixed by ball milling at a stoichiometric molar ratio for 4 h at 300 rpm. The mixed powder was pressed into pellets and calcined in air 1300°C for 12 h (5°C/min). The morphology and Ti and Nb content in the two TNO materials were observed by field-emission scanning electron microscopy (FE-SEM, Jeol JSM6500F) and energy dispersion spectroscopy (EDS) attached to FE-SEM. The crystalline structures of the materials were analyzed by X-ray powder diffraction (XRD, Rigaku, Ultima4) using Kα1 radiation at 45KV/40 mA in the range, 10–100° (2θ). Fourier-transform infrared spectroscopy (FT-IR, Shimadzu IR AFFinity-1S) and X-ray photoelectron spectroscopy (XPS, ThermoFisher K-alpha) were used to examine the chemical bonding and oxidation state of the TNO materials, respectively.

**Coin cell assembly and electrochemical analysis.** The composition of the TNO anodes was a mixture of active material (TiNb₂O₇ or TiNb₆O₁₇, 70 wt. %), conducting agent (Super-P, 20 wt. %), and polyvinylidene fluoride binder (PVdF 5130, 10 wt. %). The materials were mixed by ball-milling in 1-methyl-2-pyrrolidinone (NMP) until a viscous slurry formed and cast on Cu foil. The electrochemical properties were tested in CR2032-type coin cells. The cells were assembled with a TNO electrode as the working electrode and lithium metal as the counter electrode separated by a membrane with polypropylene in an Ar-filled glove box. The electrolyte was 1 M LiPF₄ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio 1:2. Cyclic voltammetry (CV) was conducted using a battery cycler (Won A tech, WBCS3000) at a scan rate of 0.1mVs⁻¹ and ranging from 0.05–0.3 mVs⁻¹ from 3.0 to 1.0 V (versus Li/Li⁺). Galvanostatic charge-discharge tests were performed using the battery cycles at 0.1 C (38.7mA/g of TiNb₂O₇ and 39.7mA/g of TiNb₆O₁₇) from 3.0 to 1.0 V. The rate capabilities were conducted over the voltage range of 3.0–1.0 V with a current density range 1.0 C to 30 C at room temperature. EIS was carried out by applying an AC signal of 5 mV amplitude over the frequency range from 100kHz to 10mHz using an electrochemical analyzer (NeoxScience, SP-300). GITT was tested at a current density of 0.1 C over the voltage range of 3.0–1.0 V using the electrochemical analyzer. The procedure of GITT consisted of galvanostatic charge pulses for each duration time (15 min), followed by a relaxation time (30 min).
Results and Discussion

Characterization. Figure 2(a),(b) shows SEM images (magnification ×20,000) of TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$. A comparison of the particle size and morphology was not accurate due to irregular particle formation by solid state synthesis. On the other hand, the morphologies of the two materials were similar in principle. The mean particle size of the two samples was approximately 1–3 μm. Figure 2(c)–(f) and (g)–(j) present SEM images of (c) TiNb$_2$O$_7$ (magnification ×5,000), and (g)–(j) EDS mapping images of oxygen, titanium, and niobium, and (k) the results of EDS analysis of TiNb$_2$O$_7$ and (l) TiNb$_6$O$_{17}$.

![Figure 2](image-url)
The specific surface area of TiNb\(_2\)O\(_7\) and TiNb\(_6\)O\(_17\) is 2.66 m\(^2\)/g and 2.36 m\(^2\)/g; the mean pore volume of the materials is 0.11 cm\(^3\)/g and 0.10 cm\(^3\)/g respectively. As the measurement was conducted by using standard multi point BET, the specific surface area of two materials is almost same. The results are corresponded to the SEM images showing similar particle size of two materials. Therefore, the surface area of the electrodes made by two TNO materials is also same and have not an effect on the electrochemical analysis such as lithium diffusion analysis.

XPS was used to analyze the chemical oxidation state of Ti and Nb in the samples, as shown in Fig. 5. Figure 5(a) TiNb\(_2\)O\(_7\), and (c) TiNb\(_6\)O\(_17\) showed Ti 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks at 464.18 eV & 458.38 eV (TiNb\(_2\)O\(_7\)), and 464.18 eV & 458.18 eV (TiNb\(_6\)O\(_17\)), respectively. These binding energies were similar and corresponded to the binding energies of Ti\(^{4+}\) in TiO\(_2\). The noise of the Ti spectra was attributed to the smaller content than Nb. In particular, the spectra of Ti in TiNb\(_2\)O\(_7\) showed more noise than that of TiNb\(_6\)O\(_17\). This may be because TiNb\(_6\)O\(_17\) has a similar crystal structure to Ti\(_2\)Nb\(_2\)O\(_29\), which is a Wadsley-Roth shear structure with a A2/m space group. Compared to the XRD patterns of calculated Ti\(_2\)Nb\(_2\)O\(_29\) and TiNb\(_6\)O\(_17\) synthesized in this study, most peak positions and intensities were in good agreement except for two main peak intensities, which coincides with the XRD patterns reported by Chunfu Lin. The powder XRD patterns of TiNb\(_6\)O\(_17\) was refined with the fullprof software and the rietveld parameters are a = 15.48089 Å, b = 3.81501 Å, c = 20.62921 Å, \(\alpha=90^\circ\), \(\beta=113.106^\circ\), and \(\gamma=1218.356^\circ\). The calculated rietveld refinement parameters of TiNb\(_6\)O\(_17\) is well matched the with the crystalline parameters of Ti\(_3\)Nb\(_9\)O\(_{26}\). FT-IR spectroscopy was conducted to characterize the Ti-O and Nb-O bond of TiNb\(_2\)O\(_7\) and TiNb\(_6\)O\(_17\). Figure 4(a) presents the FT-IR spectra of two samples. The peaks at 924 cm\(^{-1}\) and 520 cm\(^{-1}\) correspond to the stretching vibrations of the Nb-O bonds and Nb-O-Nb bridging bonds and the stretching vibration of 694 cm\(^{-1}\) and 839 cm\(^{-1}\) are Ti-O-Ti bonds. The BET specific surface area and volume of the TNO materials were studied by nitrogen adsorption techniques; Fig. 4(b) shows the corresponding isotherm. The specific surface area of TiNb\(_2\)O\(_7\) and TiNb\(_6\)O\(_17\) is 2.66 m\(^2\)/g and 2.36 m\(^2\)/g; the mean pore volume of the materials is 0.11 cm\(^3\)/g and 0.10 cm\(^3\)/g respectively. As the measurement was conducted by using standard multi point BET, the specific surface area of two materials is almost same. The results are corresponded to the SEM images showing similar particle size of two materials. Therefore, the surface area of the electrodes made by two TNO materials is also same and have not an effect on the electrochemical analysis such as lithium diffusion analysis.

Electrochemical analysis. Figure 6(a),(b) presents the charge and discharge curves of TiNb\(_2\)O\(_7\) and TiNb\(_6\)O\(_17\), at a current density of 0.1 C (38.7 mAg\(^{-1}\) and 39.7 mAg\(^{-1}\)) over the voltage range of 3.0–1.0 V. The curves of the two TNO anodes showed three plateau regions. The regions 1 and 3 are the solid-solution region. These regions mean the redox reaction of Ti\(^{4+}\) ↔ Ti\(^{3+}\) and Nb\(^{5+}\) ↔ Nb\(^{4+}\), respectively. Region 2 is a two-phase reaction.
reaction, which means the reaction of Nb$^{4+}$ ↔ Nb$^{5+}$. Compared to the initial discharge capacities, TiNb$_2$O$_7$ exhibited a larger discharge capacity (284 mAh g$^{-1}$) than that of TiNb$_6$O$_{17}$ (264 mAh g$^{-1}$). In addition, the irreversibility of TiNb$_6$O$_{17}$ was smaller than TiNb$_2$O$_7$ particularly from the 1st to 2nd cycles. CV of TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$ was conducted at a scan rate of 0.1 mVs$^{-1}$ from 3.0 V to 1.0 V and from 3.0 and 1.0 V for 10 cycles. As shown in Fig. 6 (c) TiNb$_2$O$_7$ and (d) TiNb$_6$O$_{17}$, both curves Fig. 6 (a) TiNb$_2$O$_7$ and curve (b) TiNb$_6$O$_{17}$ showed three current peaks at the oxidation and reduction state, respectively. Each peak is expressed in the curves (C$_p$ and A$_p$ mean the cathodic peaks and anodic peaks). Although the reduction peaks were C$_{p1}$ (Ti$^{4+}$ → Ti$^{3+}$), C$_{p2}$ (Nb$^{5+}$ → Nb$^{4+}$), and C$_{p3}$ (Nb$^{4+}$ → Nb$^{3+}$), A$_{p1}$, A$_{p2}$, and A$_{p3}$ mean the oxidation reaction of Nb$^{3+}$ → Nb$^{4+}$, Nb$^{4+}$ → Nb$^{5+}$, and Ti$^{3+}$ → Ti$^{4+}$. These potential regions of the current peaks were matched with the plateau regions in charge and discharge curves. These results show that the reaction mechanisms of the two TNO materials are the same. In addition, the reaction of Nb$^{4+}$ ↔ Nb$^{5+}$, which is corresponded to two-phase regions in the charge and discharge curves, showed the highest current peak area and is regarded as the main reaction. Compared to the CV curves of TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$, TiNb$_6$O$_{17}$ exhibits higher reactivity and reversibility from the peak area at all cycles. In addition, the decrease in the peak intensity during the cycle, particularly A$_{p2}$ and C$_{p1}$, suggests that the reversibility of TiNb$_6$O$_{17}$ is better than TiNb$_2$O$_7$. This is in agreement with the results of the charge and discharge tests.

To understand the electrochemical performance of the lithium diffusion properties of TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$, the rate capabilities were performed at various C-rates from 1 C to 30 C (discharge rate was fixed at 1 C). Figure 7 presents the rate performance of the two TNO materials. A comparison with the average capacities for the 5th cycle at each C-rate revealed TiNb$_6$O$_{17}$ to have charge capacities of 252, 230, 206, 187, 107, and 80 mAh g$^{-1}$ at 1 C, 2 C, 5 C, 10 C, 20 C, and 30 C, respectively. These values are larger than that of TiNb$_2$O$_7$ (234, 210, 174, 152, 52, and 19 mAh g$^{-1}$). In particular, the difference in the charge capacities at a high rate (20 C and 30 C) was distinct. When calculating the ratio of the average charge capacity, 30 C/1 C, the ratio was 8.12% for TiNb$_2$O$_7$ and 31.7% for TiNb$_6$O$_{17}$, which suggests that the reversibility of TiNb$_6$O$_{17}$ is better than TiNb$_2$O$_7$. This is in agreement with the results of the charge and discharge tests. In addition, a comparison of the cycling retention at 5 C to 30 C revealed TiNb$_6$O$_{17}$ to have better cycling properties, whereas TiNb$_2$O$_7$ exhibited a rapid decrease in capacity. This means the better electrochemical reversibility of the TiNb$_6$O$_{17}$. These studies including the results of the charge and discharge tests and CV indicated that lithium ion transport of TiNb$_6$O$_{17}$ is faster than the rate of TiNb$_2$O$_7$ due to the larger theoretical capacity and better lithium diffusion kinetics by larger lithium site.

Figure 8 presents the CV data of (a) TiNb$_2$O$_7$ and (b) TiNb$_6$O$_{17}$ at various scan rates in the range, 0.05–0.3 mVs$^{-1}$. CV at various scan rates is usually used to study the oxidation and reduction properties in electrochemical reactions and obtain the apparent chemical diffusion coefficient of Li-ions. With increasing scan rate, the anodic peaks move to a low potential and the cathodic peaks move to a high potential due to the increasing
polarization. In addition, the peak intensities of anodic and cathodic reaction increase with increasing scan rate. The peak current density ($I_p$) revealed a linear relationship with the square root of the scan rate ($\sqrt{v}$), which is expected for a diffusion-controlled process in Fig. 8(c) TiNb$_2$O$_7$ and (d) TiNb$_6$O$_{17}$.

Each color means the linearity of three anodic and cathodic peaks (Black: A$_{p1}$ and Cp$_{p1}$, Pink: A$_{p2}$ and Cp$_{p2}$, and Purple: A$_{p3}$ and Cp$_{p3}$). The relationship and chemical diffusion coefficient can be determined from the Randles-Sevcik equation (Eq. 1)\textsuperscript{16,17,23}:

$$I_p = 0.4463n^{3/2}F^{3/2}C_{Li}^{1/2} + SR^{-1}D_{Li}^{1/2}v^{1/2}$$

where $n$ is the charge transfer number; $F$ is Faraday’s constant; $C_{Li}$ is the Li-ion concentration in TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$; $S$ is the surface area per weight of active materials; $R$ is the gas constant; and $T$ is the absolute temperature (K). $D_{Li}$ is the Li-ion diffusion coefficient, and $v$ is the scan rate. In this study, $D_{Li}$ around three anodic and three cathodic peaks in Fig. 6(c) and (d) was calculated using the above equation. Table 1 lists the calculated $D_{Li}$.

As the results, TiNb$_2$O$_7$ showed the $D_{Li}$ value $10^{-14}$ cm$^2$/s which is similar to the diffusion coefficient in the previous study (for phase transition region)\textsuperscript{24}. Compared to $D_{Li}$ at the anodic peaks, $D_{Li}$ of TiNb$_6$O$_{17}$ was 20 times (A$_{p1}$), 12 times (A$_{p2}$), and 38 times (A$_{p3}$) higher than that of TiNb$_2$O$_7$. $D_{Li}$ of the peaks A$_{p1}$ (Nb$^{4+}$→Nb$^{5+}$) and A$_{p3}$ (Ti$^{3+}$→Ti$^{4+}$) of TiNb$_6$O$_{17}$ was particularly high. Although the gap of $D_{Li}$ at the A$_{p2}$ (Nb$^{4+}$→Nb$^{5+}$) between TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$ was smaller than those of A$_{p1}$ and A$_{p3}$, the difference was apparent. In the case of $D_{Li}$ at cathodic peaks, the values of TiNb$_6$O$_{17}$ were 5 times (C$_{p1}$, Nb$^{4+}$→Nb$^{3+}$), 15 times (C$_{p2}$, Nb$^{5+}$→Nb$^{4+}$), and 14 times (C$_{p3}$, Ti$^{4+}$→Ti$^{3+}$) higher than those of TiNb$_2$O$_7$. A comparison of the gap of D between TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$ at the anodic peaks revealed the difference in the $D_{Li}$ values at the cathodic peaks to be low except for C$_{p2}$. On the other hand, the $D_{Li}$ of TiNb$_2$O$_{17}$ at A$_{p2}$ and C$_{p2}$, meaning two phase transition in TNO materials were clearly higher than that of TiNb$_2$O$_7$. (12 and 15 times). In addition, the anodic and cathodic reaction of the TNO anodes means the de-lithiation and lithiation process during oxidation and reduction, respectively. Therefore, the lithium diffusion properties of TiNb$_6$O$_{17}$ were better than those of TiNb$_2$O$_7$. The reason is that TiNb$_2$O$_7$ has a larger unit cell volume and more open Li-ion sites than TiNb$_2$O$_7$. The advanced crystal structure of TiNb$_6$O$_{17}$ leads to a larger size and number of Li-ion transport paths in the crystal structure, facilitating Li-ion transport during the de-lithiation and lithiation processes\textsuperscript{16,12,18}.

Figure 5. XPS spectra of (a) Ti and (b) Nb element in TiNb$_2$O$_7$, (c) Ti and (d) Nb element in TiNb$_6$O$_{17}$.
Figure 9 presents the Nyquist plots of TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$ by EIS. EIS has been used to examine electrode materials because it can reveal the relationship between the crystal lattice with the electrochemical properties$^{24-29}$. This technique provides kinetic information that can be related to a specific state-of-charge or discharge (SOC, 

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**Figure 6.** (a) Charge/discharge curves of TiNb$_2$O$_7$ and (b) TiNb$_6$O$_{17}$ anodes at 0.1 C, (c) cyclic voltammetry of TiNb$_2$O$_7$ and (d) TiNb$_6$O$_{17}$ anodes in the potential window of 1.0–3.0 V at scan rate of 0.1 mVs$^{-1}$. 

**Figure 7.** Capacity retention of TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$ anodes at various scan rates (1 C, 2 C, 5 C, 10 C, 20 C, and 30 C); the discharge rate was fixed at 1 C.
SOD), because the measurement is run by applying a low amplitude signal around an equilibrium state. Figure 9(a) shows the Nyquist plot of TiNb₂O₇ and TiNb₆O₁₇ at the open circuit voltage (OCV) and an equivalent circuit (insert image). Each Nyquist plot was composed of a high-frequency semicircle and Warburg tail region followed by a steep sloping line in the low-frequency region. The R₁ and Cdl are the ohmic resistance between the electrolyte and surface of the electrode and double layer capacitance. The high-frequency semicircle means the charge-transfer resistance (Rct) relevant to the interfacial Li-ion transfer. The Zw is the Warburg impedance, which is related to Li-ion diffusion to the structure of the active materials and corresponds to the tail at a low frequency.

Compared to Rct, the TiNb₆O₁₇ anode shows a smaller Rct (58 Ω) than that of the TiNb₂O₇ cell (85 Ω). This means that the TiNb₆O₁₇ anode has a faster Li insertion process in the surface area than TiNb₂O₇. Figure 9(b) presents a plot of the real part resistance with the inverse square root of the angular speed in the low-frequency range of TiNb₂O₇ and TiNb₆O₁₇ anodes at the OCV state. The Warburg factor (σ) is determined from the slope, and is substituted using equation (Eq. 2 and 3):

Table 1. Calculated D Li⁺ values of (a) TiNb₂O₇ and (b) TiNb₆O₁₇ anodes from the CV results.

| TiNb₂O₇ | Anodic peak | Cathodic peak |
|---------|-------------|---------------|
| D Li⁺ (cm²s⁻¹) | A | B | C | A | B | C |
| TiNb₂O₇  | 5.69 × 10⁻¹⁵ | 3.01 × 10⁻¹⁴ | 1.60 × 10⁻¹⁵ | 1.16 × 10⁻¹⁴ | 2.33 × 10⁻¹⁴ | 1.08 × 10⁻¹⁵ |
| TiNb₆O₁₇ | Anodic peak | Cathodic peak |
| D Li⁺ (cm²s⁻¹) | A | B | C | A | B | C |
| TiNb₆O₁₇  | 1.12 × 10⁻¹⁴ | 3.72 × 10⁻¹⁴ | 6.13 × 10⁻¹⁴ | 5.35 × 10⁻¹⁴ | 3.43 × 10⁻¹⁴ | 1.56 × 10⁻¹⁴ |

Figure 8. Cyclic voltammetry with various scan rate of (a) TiNb₂O₇ and (b) TiNb₆O₁₇, linear relationship between the peak current of the cathodic/anodic reaction and the square root of the sweep rate (c) TiNb₂O₇ and (d) TiNb₆O₁₇ (●: anodic, ■: cathodic and linear: linear fitting).
$\sigma' = ++ Z'R (2)$

$\sigma = \frac{D}{RT}$ (3)

where $Z'$ is the real part resistance; $\omega$ is the angular frequency; $R$ is the gas constant; $T$ is the absolute temperature; $A$ is the surface area of the electrode; $F$ is the Faraday constant; and $C$ is the molar concentration of Li ion in an active material. Equations (2) and (3) were used to calculate the Warburg factor and lithium diffusion coefficient, respectively. Table 2 lists the calculated $D_{Li^+}$ values of (a) TiNb$_2$O$_7$ and (b) TiNb$_6$O$_{17}$ anodes from the EIS results.

|          | $D_{Li^+}$ (cm$^2$s$^{-1}$) (OCV) | $D_{Li^+}$ (cm$^2$s$^{-1}$) (1.36 V) | $D_{Li^+}$ (cm$^2$s$^{-1}$) (1.68 V) | $D_{Li^+}$ (cm$^2$s$^{-1}$) (1.98 V) |
|----------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| TiNb$_2$O$_7$ | $4.57 \times 10^{-14}$          | $6.64 \times 10^{-14}$          | $7.91 \times 10^{-13}$          | $1.85 \times 10^{-12}$          |
| TiNb$_6$O$_{17}$ | $1.27 \times 10^{-13}$          | $2.94 \times 10^{-13}$          | $1.12 \times 10^{-11}$          | $4.57 \times 10^{-11}$          |

Table 2. Calculated $D_{Li^+}$ values of (a) TiNb$_2$O$_7$ and (b) TiNb$_6$O$_{17}$ anodes from the EIS results.

$Z' = R_i + R_{ct} + \sigma \omega^{(-1/2)}$ (2)

$D_{Li^+} = \frac{R^2T^2}{2A^2 \pi^4 F^4 C^2 \sigma^2}$ (3)

Figure 9. (a) Nyquist plots of TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$ anodes at OCV state, (b) relationship between imaginary resistance ($Z'$) and inverse square root of angular speed ($\omega^{-0.5}$) low frequency region, (c) Nyquist plots of TiNb$_2$O$_7$, and (d) TiNb$_6$O$_{17}$. (Inert images: relationship between $Z'$ and $\omega^{-0.5}$).
\[ \text{Li}^{+} \text{chemical diffusion coefficient and analyze the phase transition of the two TNO materials. The techniques developed by Weppner and Huggins assumed one-dimensional diffusion in a solid solution electrode and a uniform current distribution throughout the electrode and estimated the electrochemically active area from the structure of the active material particles not for the diffusion reaction between the electrode surface and electrolyte. At the transitional GITT, a small constant current was applied to an electrode during a short time and the electrode was left to stand after reaching the OCV state. In this study, GITT was performed on the TNO materials to determine the diffusion coefficients at all redox potentials than TiNb_2O_7. In particular, the gap of TiNb_6O_{17} showed higher values than that of TiNb_2O_7 at all steps during the GITT measurements except for the 1st step and the end two steps of the end due to the large voltage variations. The two cells showed similar shapes and showed a similar three phases regions meaning the solid-solution regions (Ti^{4+} ↔ Ti^{3+} and Nb^{3+} ↔ Nb^{4+}) and two-phase reaction (Nb^{4+} ↔ Nb^{3+}) with the charge-discharge curves. These regions also showed the cyclic voltammetry peaks of C_{p1} (Ti^{4+} ↔ Ti^{3+}), C_{p2} (Nb^{3+} ↔ Nb^{4+}), and C_{p3} (Nb^{4+} ↔ Nb^{3+}); A_{p1}, A_{p2}, and A_{p3} mean the oxidation reaction of Nb^{3+} ↔ Nb^{4+}, Nb^{4+} ↔ Nb^{5+}, and Ti^{3+} ↔ Ti^{4+} in Fig. 6(c), (d), 10(c) TiNb_2O_7 and (d) TiNb_6O_{17} present the single steps of GITT. The steps are the results measured at the 3rd step during the charge state for the same duration and rest time. In Fig. 10(c) and (d), \Delta E, and \Delta E shows the change in the cell voltage during the duration time of 15 min from \( \tau \) to \( \tau - \tau_1 \), and the variation of the cell voltage during the rest time of 30 min. The voltage changes from the steps were recorded as a function of time and the lithium diffusion coefficient were calculated using the following equation based on Fick's second law:

\[
D_{Li} = \frac{4}{\pi} \left( \frac{m_g V_m}{M_g A} \right)^2 \left( \frac{\Delta E_s}{\tau dE/d\tau} \right)^2 \left( \frac{L}{D_{Li}^{1/2}} \right)
\]

(4)

where \( V_m \) is the molar volume of the active material; \( M_g \) is molecular weight of the materials; \( m_g \) is the mass of the active materials in an electrode; \( L \) is the lithium diffusion distance (thickness of the electrode); \( A \) is the electrode area; and \( \tau \) is the duration time. When the change in cell voltage with duration time exhibited a linear relationship on plotting against \( \tau^{1/2} \), equation (4) can be changed to the following simple equation:

\[
D_{Li} = \frac{4}{\pi} \left( \frac{m_g V_m}{M_g A} \right)^2 \left( \frac{\Delta E_s}{\Delta E/\tau} \right) \left( \frac{L}{D_{Li}^{1/2}} \right)
\]

(5)

This equation assumes that the molar volume (\( V_m \)) is stable with the change in Li content in an active material. In this study, the Li^{+} diffusion coefficient of the two TNO materials could be calculated, as shown in Fig. 10. (c)–(e). Figure 10(e) shows the linear relationship between the single steps in Fig. 10. (c), (d). The Li^{+} diffusion coefficients of the two TNO materials from the GITT results are presented as a function of SOC (%) vs. Log (\( D_{Li}^{1/2} \)) during the charge state in Fig. 10. (f). The coefficients were calculated at all steps during the GITT measurements except for the 1st step and the end two steps due to the large voltage variations. The two cells showed three minimum Li^{+} diffusion coefficient points in Fig. 10(f) and the voltages representing the points are shown. These minimum diffusion coefficients suggest a phase transition for strong attractive interactions between the intercalation species and the host matrix or some order-disorder transition during cycling. Compared to the SSCV and EIS results, the voltages are the three redox potentials of TNO materials, in which the cell voltages of TiNb_2O_7 and TiNb_6O_{17} are 1.42 V–1.38 V (Nb^{3+} → Nb^{4+}), 1.71–1.75 V (Nb^{4+} → Nb^{5+}), and 2.01–2.03 V (Ti^{3+} → Ti^{4+}) vs. 1.36 V, 1.68 V, and 1.98 V, respectively, from the SSCV and EIS measurements. This explains why the plot from GITT has an electrochemical reaction mechanism of two TNO materials with SSCV and EIS. The Li^{+} diffusion coefficients of TiNb_2O_7 and TiNb_6O_{17} from three points were calculated to be 1.11 \times 10^{-11} and 6.70 \times 10^{-11} cm^{3} s^{-1} (Nb^{3+} → Nb^{4+}), 2.74 \times 10^{-11} and 2.23 \times 10^{-11} cm^{3} s^{-1} (Nb^{4+} → Nb^{5+}), and 1.03 \times 10^{-10} and 7.47 \times 10^{-10} cm^{3} s^{-1} (Ti^{3+} → Ti^{4+}). The coefficients of TiNb_2O_7 showed higher values than that of TiNb_6O_{17} at all positions with the other Li^{+} diffusion measurements, which indicates that TiNb_2O_7 has superior Li^{+} diffusion kinetics than TiNb_6O_{17} owing to its larger unit cell volume. Compared to the diffusion coefficients of each transition region, the values increased from the (Nb^{3+} → Nb^{4+}) reaction to the (Ti^{3+} → Ti^{4+}) reaction, which correspond to the EIS results in Table 2. Among the three diffusion values, the diffusion coefficients of the (Nb^{4+} → Nb^{5+}) reaction showed the largest increase from TiNb_2O_7 to TiNb_6O_{17} and also corresponds to the EIS.
results. These trends suggest that the oxidation reaction is a two phase transition region of TNO materials with the charge-discharge curves and cyclic voltammetry results (the most reaction region). In the event of SSCV, the measurements showed a different tendency with EIS and GITT. The coefficients of the (Nb$^{4+} \rightarrow$ Nb$^{5+}$) reaction ($A_{p2}$) showed the largest values and the diffusion coefficients of the (Nb$^{3+} \rightarrow$ Nb$^{4+}$) reaction showed the largest increase from TiNb$_2$O$_7$ to TiNb$_6$O$_{17}$. This may be due to the inaccuracy of the SSCV measurements in this study. Compared to $A_{p2}$, both $A_{p1}$ and $A_{p3}$ showed a small peak current and a broad shape. Therefore, the diffusion coefficients of the two peaks may not be precise values.

Figure 10. Charge/discharge GITT curves of (a) TiNb$_2$O$_7$ and (b) TiNb$_6$O$_{17}$, single step of the relationship of single steps for (c) and (d) (V vs. $\tau^{1/2}$). (e) and (f) lithium diffusion coefficients calculated from GITT for TiNb$_2$O$_7$ and TiNb$_6$O$_{17}$ as a function of the SOC at the charge process.
Conclusions
Galvanostatic charge-discharge, cyclic voltammetry, and rate capability tests were conducted to analyze the electrochemical performance and properties of TiNbO$_x$ and TiO$_2$. From the results, two TNO materials showed three similar plateau regions and three redox peaks corresponding to two Nb redox and one Ti redox reaction. TiNbO$_x$ showed higher capacities of 284mAh/g than that of TiNbO$_2$, 264mAh/g. In the rate capability test, TiNbO$_x$ exhibited improved rate capacity of 80mAh/g at 30 C than 19mAh/g for TiO$_2$. SSCV, EIS, and GITT measurement were taken to investigate the performance and lithium diffusion properties related to the unit cell volume of the two TNO materials. The anodic and cathodic Li$^+$ diffusion coefficients from SSCV were in the range of 10$^{-14}$ to 10$^{-13}$ cm$^2$s$^{-1}$ for TiNbO$_2$ and 10$^{-13}$ to 10$^{-11}$ cm$^2$s$^{-1}$ for TiO$_2$. The anodic diffusion coefficients of TiNbO$_x$ were 5 times (Nb$^{4+}$ → Nb$^{5+}$), 15 times (Nb$^{4+}$ → Nb$^{5+}$), and 14 times (Ti$^{4+}$ → Ti$^{4+}$). From the EIS measurement, the coefficients were in the range of 10$^{-12}$ to 10$^{-13}$ cm$^2$s$^{-1}$ of TiNbO$_2$, and 10$^{-11}$ to 10$^{-13}$ cm$^2$s$^{-1}$ of TiO$_2$. At the OCV state and three oxidation potential region of the two TNO materials during the charging process. The three minimum diffusion coefficients points were determined from the GITT measurement. The diffusion coefficients of the two phase transition region (Nb$^{4+}$ → Nb$^{5+}$) were improved 10 fold compared to that of TiNbO$_2$. CV, EIS, and GITT indicated that TiNbO$_x$ has better lithium diffusion kinetics and electrochemical performance than TiO$_2$ because of its large unit cell volume and more open Li$^+$ insertion site.

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**Author Contributions**

Kwang-Sun Ryu decided the concept of the experiments, discussed the results and reviewed the manuscript. Yong-Seok Lee performed all experiments, analyzed the data and wrote the manuscript.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.

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