

A comprehensive review study on pure titanium niobium oxide as the anode material for Li-ion batteries

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Abstract

Li-ion batteries (LIBs) are in increasing demand due to their application in a large variety of fields such as portable electronic devices and electric vehicles. However, the development of high-performance electrode materials with a long lifetime, excellent rate capability, and high safety is considered as a significant challenge in the advancement of LIBs. Recently, titanium niobium oxide (TNO) compounds have been considered as one of the most promising intercalation-type anode materials and highly potential alternatives to commercial graphite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes. This family of materials possess high theoretical capacities (377–402 mAh/g) resulting from their multiple redox couples ($\text{Ti}^{4+}/\text{Ti}^{3+}$, $\text{Nb}^{5+}/\text{Nb}^{4+}$, $\text{Nb}^{4+}/\text{Nb}^{3+}$), high safety, low volume changes during cycling, high working potential, and excellent cyclic stability. However, their low electronic/ionic conductivities would result in their poor rate performance. Various strategies such as ion doping, composite preparation with conductive materials, dimensional/morphological controlling, and defective structure engineering design have been proposed to improve the rate performance of TNO materials. In this review study, dimensional/morphological controlling, and defective structure engineering approaches are reviewed for enhancing the electrochemical properties of pure TNO anodes. In this context, the detailed findings of the most important recent literature on TNO anode materials are reviewed, from their optimal synthesis parameters, and the obtained morphological/structural features to their electrochemical properties. Furthermore, the challenges to the practical use of TNO

This is the accepted manuscript (postprint) of the following article:

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<https://doi.org/10.1016/j.jallcom.2022.165117>

anodes in full-cell LIBs are presented. Finally, the research gaps and the future perspective are proposed.

Keywords: Titanium niobium oxide (TNO), Anode materials, Li-ion batteries, Morphology, Defective structure, Structure-performance correlation

Contents

1. Introduction	
2. Li-ion storage mechanism in TNO materials	
3. Morphological controlling of TNO materials	
3.1. Particulate TNO materials	
3.2. 1D TNO materials	
3.3. Three dimensional TNO materials	
3.3.1. Spherical structures	
3.3.2. Porous structures	
3.4. Comparison between the best reports of different morphologies	
4. TNO thin-films	
5. Defective crystal structure design	
6. Full cell considerations	
7. Summary and perspectives.	
Declaration of Competing Interest	
References	

1. Introduction

Low-carbon and renewable energy storage technologies are highly needed worldwide due to environmental issues such as climate change, global warming, and limited fossil fuel reserves. Li-ion batteries (LIBs) are among the industrially most widely used energy storage systems in the consumer electronics and electrified transport sectors. It is known that the

capabilities of the electrode materials are the most important influencing factors in the performance of LIBs [1–13].

There are three known mechanisms for the electrochemical Li-ion storage in LIBs, including intercalation-deintercalation [14–18], alloying-dealloying [12,19–25], and conversion reactions [26–28]. The first mechanism is based on a Li intercalation-deintercalation process, which is particularly shown by metal oxides and other compounds with a two-dimensional (2D) layered structure or a three-dimensional (3D) network structure, allowing the reversible Li intercalation into their lattices without destroying the crystal structure. Titanium oxides and ternary oxides of titanium and niobium including TNO are intensively explored in this family. The second mechanism is alloying and dealloying, in which appropriate elements (A) or metals (M) are alloyed with Li to form intermetallic compounds of Li_xA or Li_xM which have different distinct crystal structures with physical properties different from those of Li, A, and M. Elements such as Si and Sb, and metals such as Sn, Zn, In, Bi, and Cd can form alloys with Li metal and have been extensively studied. The third mechanism is the conversion or redox reactions with Li, involving Li_2O and a transition metal, especially Co and Fe. A decomposition of Li_2O to metal and oxygen is not generally possible. Although in the presence of nanosized transition metal particles, the mentioned decomposition process is possible and Li cycling can occur, as exemplified by the following reaction:

$$\text{nano CoO} + 2\text{Li} \leftrightarrow \text{nano CO} + \text{Li}_2\text{O}, \text{ resulting in large reversible capacities [29–34].}$$

Although alloying-dealloying and conversion type anodes have much higher capacities compared to intercalation-deintercalation anodes, their large volume changes during cycling result in their inferior cyclic stability. Therefore, intercalation-deintercalation anodes such as carbon-based and Ti-based materials can be introduced as preferred materials for industrial LIBs. Although graphite anodes are commercially used in LIBs, they suffer from safety issues

due to the growth of Li dendrites on their surface at the low operating potentials (~ 0.2 V vs. Li/Li⁺) [35–38].

To address the mentioned challenges of graphite anodes, low-strain Ti-based oxides have attracted tremendous attention as novel alternative anode materials for LIBs. Compared to carbonaceous anodes, these materials have higher safety due to their higher working potential (1.2–1.8 V vs. Li/Li⁺), which prevents the formation of Li dendrites and solid electrolyte interphase (SEI). However, it should be mentioned that the high working potential of an anodic material would lead to the lowering of the battery voltage and consequently, reduces its energy density. The reason is that the battery energy density is the product of the battery voltage and its specific capacity, and the battery voltage is on account of the potential difference between the anode and the cathode. Therefore, further investigations on discharging Ti-based anodes at lower cut-off potentials, using suitable high-potential cathodes and suitable full-cell designs should be carried out [1,39–43].

Because volume changes of Ti-based anodes during cycling are negligible (about 0.2–9.3%), they are referred to as low-strain anode materials with high cyclic stability. The most common types of Ti-based low-strain oxides are lithium titanium oxide (LTO) [44–51] and titanium niobium oxide (TNO). The general formula for TNO materials is $\text{TiNb}_x\text{O}_{2+2.5x}$ and up to now, TiNb_2O_7 , $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, $\text{TiNb}_6\text{O}_{17}$, and $\text{TiNb}_{24}\text{O}_{62}$ have been studied as anode materials for LIBs [52–57]. The high theoretical capacity of TNO compounds is related to their multiple redox couples, including $\text{Ti}^{4+}/\text{Ti}^{3+}$ (~ 2.0 V), $\text{Nb}^{5+}/\text{Nb}^{4+}$ (1.5–1.8 V), and $\text{Nb}^{4+}/\text{Nb}^{3+}$ (1.3–1.5 V). According to the x value in the general formula of $\text{TiNb}_x\text{O}_{2+2.5x}$, the theoretical capacity of TNO materials can be calculated as follows [29]:

$$C = 403 - 5441 / (133x + 80) \text{ (mAh/g)} \quad (1)$$

By reviewing the literature on the family of TNO anodes, it can be concluded that TiNb_2O_7 ($x = 2$) and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ ($x = 5$) with respective theoretical capacities of 388 mAh/g and 397 mAh/g are the most studied anodes for LIBs. Both TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ compounds have a monoclinic ReO_3 -type crystal structure with different structural units. Moreover, the operation potential of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (1.7 V) is higher than that of TiNb_2O_7 (1.64 V) [30–33].

Despite the advantages of TNO anode materials, they have poor intrinsic electronic conductivity and low Li-ion diffusion coefficient, restricting their rate capability. Till now, some efforts such as ions doping [58–65], preparing composites with conductive materials such as graphene [1,66–77], and dimensional/morphological controlling [78,79] have been performed to improve the Li-ion storage capability of TNO anode materials, especially at high charge/discharge rates.

In the authors' previous review article [80], recent advances in the development of TNO-based composites with various reinforcements such as carbon, graphene, and carbon nanotubes (CNTs) were studied. Although there are some general review articles on TNO anode materials for LIBs [1,52,81], to the best of the authors' knowledge, there is no comprehensive study on specifically pure TNO materials to highlight the efficient strategies to improve the electrochemical performance of pure TNO anodes. Accordingly, the focus of the current study is to review the recent advances in pure TNO anode materials from various aspects including synthesis methods and the influencing parameters, morphological/structural findings, and the main electrochemical features.

As mentioned above, TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ are the most studied materials in the TNO family and consequently, these materials are studied in the current research. Moreover, it can be understood from the literature that morphological/dimensional controlling and also preparing defective crystal structures of TNO are the main performed structural engineering

processes on TNO materials. Accordingly, the current review paper is divided into two main sections of morphological/dimensional control and defective crystal structure design, and the processing/structure/properties/performance relationships for TNO materials are reviewed in each section. Finally, in the last section, full-cell considerations and major challenges in using TNO anodes in practical LIBs are presented. It is worth noting that understanding the relationships between the processing, structure, and performance of pure TNO materials also provides a research direction for those investigating other structural engineering processes such as doping and composite fabrication, to identify the TNO material with the most effective morphological/ dimensional/defective features.

2. Li-ion storage mechanism in TNO materials

LIBs exhibit a working principle based on the “rocking chair” mechanism, which relies on the shuttle of Li-ions between cathode and anode [9]. Various studies on the Li-ion storage mechanism via X-ray diffraction (XRD) analysis revealed that the Li-ion intercalation pathway could be proposed as follows: (1) insertion of Li-ions from the electrolyte into TiNb_2O_7 to form $\text{Li}_{0.88}\text{TiNb}_2\text{O}_7$ (first solid solution); (2) transformation of $\text{Li}_{0.88}\text{TiNb}_2\text{O}_7$ to $\text{Li}_{2.67}\text{TiNb}_2\text{O}_7$ (two-phase coexistence), and (3) evolution from $\text{Li}_{2.67}\text{TiNb}_2\text{O}_7$ to the final fully lithiated $\text{Li}_4\text{TiNb}_2\text{O}_7$ (final solid-solution) [82]. Although various investigations have been performed in this field, it is required to apply advanced in-situ/ex-situ characterization techniques combined with theoretical calculations to conduct in-depth fundamental studies on the lithium storage mechanism of TNO materials.

3. Morphological controlling of TNO materials

Morphological controlling approaches such as nanosizing, can mainly increase the efficient contact between the electrode material and electrolyte and also shorten the diffusion distance

of Li-ions, leading to an improvement in the battery rate capability. As shown in Fig. 1, the literature review has shown that the main morphologies reported for the pure TiNb_2O_7 / $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ anode materials are rod-like morphologies (nanorods, nanotubes, and nanowires) [83–85], spherical shapes (nanospheres and microspheres) [86–88], and porous structures (mesoporous, nanoporous, and macroporous) [89,90]. In the following sections, the main results of the prepared TiNb_2O_7 / $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ anodes with the mentioned morphologies are reviewed and compared. Moreover, the electrochemical properties of the reviewed studies on TNO materials with different morphologies, are summarized in Table 1.

Table 1. The electrochemical performance of TNO anode materials with different morphologies, reviewed in this study.

Material	Preparation method	Morphology	Cyclic performance	Rate performance	Charge transfer resistance (Ω) after cycling	Li-ion diffusion coefficient (cm^2/s)	Reference
TiNb_2O_7	Hydrothermal	Nanoparticles	271 mAh/g at 0.775 C after 100 cycles (capacity retention of 90.9%)	-	-	-	Ise et al. [91]
TiNb_2O_7	solid-state	Microparticles	248 mAh/g at 0.775 C after 100 cycles (capacity retention of 86.8%)	-	-	-	Ise et al. [91]
TiNb_2O_7	Solution mixing	Nanoparticles	154 mAh/g at 0.5 C after 500 cycles (capacity retention of 82.8%)	64 mAh/g at 5 C	50.64	-	Paulraj et al. [92]
TiNb_2O_7	Sol-gel	Sub-microparticles	195 mAh/g at 5 C after 100 cycles	205 mAh/g at 5 C	31	-	Lu et al. [93]
TiNb_2O_7	Solid-state	Microparticles	130 mAh/g at 5 C after 100 cycles	131 mAh/g at 5 C	42	-	Lu et al. [93]
$\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$	Solid-state	Microparticles	27 mAh/g after 200 cycles at 12.62 C	58 mAh/g at 12.62 C	-	1.5×10^{-13}	Pham-Cong et al. [94]

TiNb ₂ O ₇	Solution mixing	Nanoparticles	160 mAh/g after 500 cycles at 1.03 C	152.1 mAh/g at 7.75 C	-	-	Li et al. [85]
TiNb ₂ O ₇	Solid-state	Microparticles	-	98 mAh/g at 5 C	-	-	Li et al. [85]
Ti ₂ Nb ₁₀ O ₂₉	Solid-state	Nanoparticles	114.9 mAh/g at 10 C after 500 cycles	184 mAh/g at 5 C	148.6	-	Liu et al. [35]
TiNb ₂ O ₇	Sol-gel	Nanorods	140 mAh/g at 10 C after 100 cycles (capacity retention of 91%)	182 mAh/g at 5 C	-	3.39×10 ⁻¹⁴	Hu et al. [83]
TiNb ₂ O ₇	Sol-gel	Nanorods	123.2 mAh/g at 10 C after 500 cycles	183.3 mAh/g at 5 C	-	-	Lou et al. [95]
Ti ₂ Nb ₁₀ O ₂₉	Electrospinning	Nanofibers	109 mAh/g after 2000 cycles at 12.62 C	193 mAh/g at 12.62 C	-	8 × 10 ⁻¹³	Pham-Cong et al. [94]
TiNb ₂ O ₇	Sol-gel	Nanowires	209 mAh/g after 500 cycles at 1.03 C	181.7 mAh/g at 7.75 C	-	-	Li et al. [85]
Ti ₂ Nb ₁₀ O ₂₉	Electrospinning	Hollow-nanofibers	128 mAh/g at 10 C after 500 cycles	206 mAh/g at 5 C	-	-	Fu et al. [96]
TiNb ₂ O ₇	Electrospinning	Hollow-nanofibers	235 mAh/g at 1 C after 700 cycles	238 mAh/g at 5 C	-	-	Park et al. [97]
TiNb ₂ O ₇	Electrospinning	Hollow-nanofibers	160 mAh/g at 10 C after 900 cycles –	-	28.98	-	Yu et al. [98]
TiNb ₂ O ₇	Electrospinning	Nanofibers	60 mAh/g at 10 C after 900 cycles	-	85.16	-	Yu et al. [98]
TiNb ₂ O ₇	Solvothermal	Microspheres	115 mAh/g at 10 C after 500 cycles	175 mAh/g at 5 C	-	-	Li et al. [86]
Ti ₂ Nb ₁₀ O ₂₉	Solvothermal	Microspheres	173.5 mAh/g at 10 C after 500 cycles	223.5 mAh/g at 5 C	119.3	-	Liu et al. [35]
Ti ₂ Nb ₁₀ O ₂₉	Solvothermal	Microspheres	185 mAh/g at 10 C after 200 cycles	227 mAh/g at 5 C	-	-	Liu et al. [99]
Ti ₂ Nb ₁₀ O ₂₉	Solvothermal	Nanospheres	215 mAh/g after 500 cycles at 10 C	241 mAh/g at 5 C	-	-	Xia et al. [100]
Ti ₂ Nb ₁₀ O ₂₉	Solvothermal	Nanospheres	141.5 mAh/g at 10 C after 1000 cycles	196 mAh/g at 5 C	-	-	Lou et al. [101]
TiNb ₂ O ₇	Solvothermal	Nanospheres	212 mAh/g at 5 C after 1000 cycles	238 mAh/g at 5 C	-	-	Cheng et al. [78]
TiNb ₂ O ₇	Solvothermal	Microspheres	78 mAh/g at 5 C after 1000 cycles	155 mAh/g at 5 C	-	-	Cheng et al. [78]
TiNb ₂ O ₇	Solvothermal	Microspheres	182 mAh/g at 5 C after 1000 cycles	250 mAh/g at 5 C	-	1.4 × 10 ⁻¹²	Park et al. [79]

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Ti ₂ Nb ₁₀ O ₂₉	Solvothermal	Hollow microspheres	158 mAh/g at 7.57 C after 1000 cycles	258.6 mAh/g at 5 C	-	-	Zeng et al. [88]
Ti ₂ Nb ₁₀ O ₂₉	Solvothermal	Microspheres	130 mAh/g at 7.57 C after 1000 cycles	208 mAh/g at 5 C	-	-	Zeng et al. [88]
TiNb ₂ O ₇	Sol-gel	Macro-porous	87 mAh/g at 10 C after 1000 cycles	124 mAh/g at 5 C	-	-	Lou et al. [89]
TiNb ₂ O ₇	Sol-gel	Mesoporous	175 mAh/g at 1 C after 300 cycles	130 mAh/g at 5 C	-	-	Fei et al. [102]
TiNb ₂ O ₇	Sol-gel	Mesoporous	100 mAh/g at 10 C after 2000 cycles	217 mAh/g at 5 C	-	-	Jo et al. [90]
TiNb ₂ O ₇	Sol-gel	Mesoporous	200 mAh/g at 5 C after 1000 cycles	236 mAh/g at 5 C	-	-	Guo et al. [103]

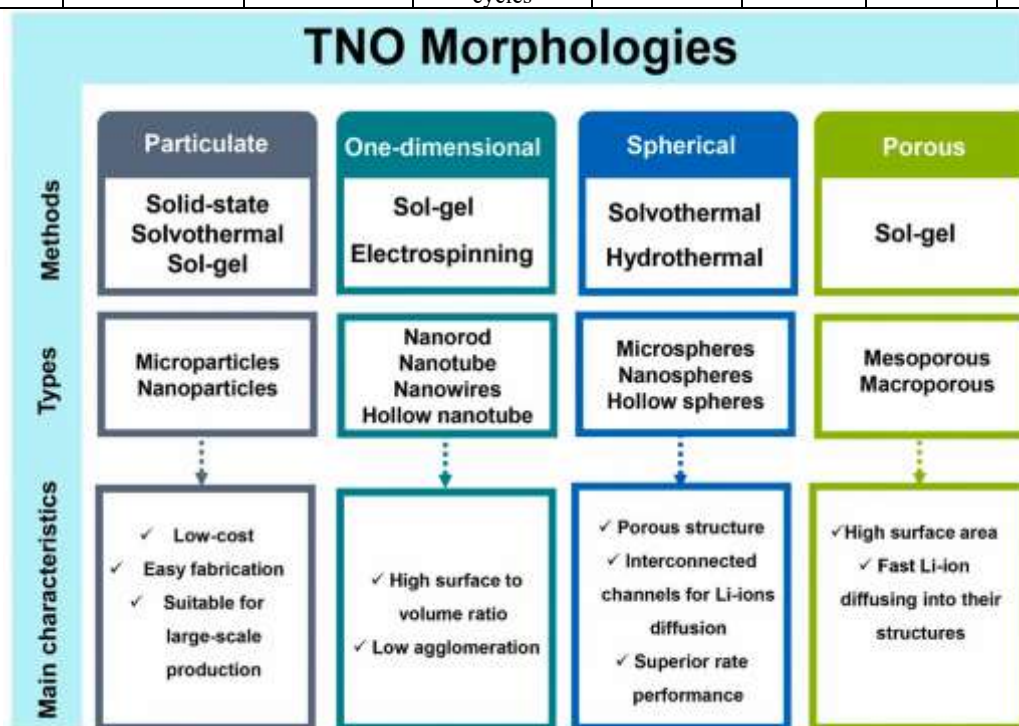


Fig. 1. The main reported morphologies for TNO anode materials in LIBs.

3.1. Particulate TNO materials

Materials with particulate morphologies are typically prepared by simple and inexpensive methods which are amenable for scale-up. Solid-state methods are commonly adopted for the fabrication of particulate TNO materials; however, some studies have reported the use of hydro/solvothermal and sol-gel methods for this purpose. To improve the Li-ion storage

capability of the active electrode materials, the production of nano-sized particles is desirable [91,93,104,105]. For example, Ise et al. [91] synthesized TiNb_2O_7 nanoparticles with high crystallinity using the hydrothermal method. For comparison, TiNb_2O_7 particles were also prepared using a solid-state route. The results showed that the synthesized TiNb_2O_7 had particle sizes ranging from 50 to 300 nm, while the solid-state prepared TiNb_2O_7 had particle sizes ranging from 0.5 to 1 μm . The Brunauer–Emmett–Teller (BET) results proved that the specific surface area (SSA) of the hydrothermal synthesized TiNb_2O_7 was about 2.35 times higher than that of the solid-state prepared sample.

Paulraj et al. [92] synthesized TiNb_2O_7 nanoparticles by simply mixing niobium chloride and titanium (IV) isopropoxide in ethanol and glacial acetic acid for 2 h followed by calcination at 750 °C for 2 h. The transmission electron microscopy (TEM) images demonstrated the formation of TiNb_2O_7 nanoparticles with sizes ranging from 50 to 100 nm. The electrochemical results showed that at 0.1 C, the first discharge capacity of 200 mAh/g for TiNb_2O_7 nanoparticles was achieved. Increasing the discharge rate from 0.1 to 1, 3, and 5 C, resulted in the decrease of the capacity from 200 to 143, 90, and 64 mAh/g, respectively. The cyclic stability evaluations demonstrated that the TiNb_2O_7 nanoparticles maintained 84% of their initial capacity after 500 cycles at 0.5 C. Interestingly, the electrochemical impedance spectroscopy (EIS) results indicated the formation of an unexpected SEI layer on the electrode after cyclic tests. However, there was no discussion about the reason for the formation of the SEI layer.

In another work, Lu et al. [93] used a novel sol-gel method to synthesize sub-micron TiNb_2O_7 particles. For this purpose, after mixing the titanium isopropoxide and niobium chloride in a stoichiometric ratio and adding 5 wt% agar powders to the solution, the calcination treatment was done at 800 °C in the air for 8 h, and the prepared sample was denoted as A-

TNO. For comparison, TiNb_2O_7 was prepared by the solid-state method and this sample was denoted as N-TNO. The scanning electron microscopy (SEM) images of the N-TNO and A-TNO samples revealed that the use of the solid-state method resulted in the formation of cuboidal particles with sizes of 0.3–0.5 μm . However, the A-TNO sample possessed a larger particle size of about 2.5 μm with a severe agglomeration of submicron particles caused by Agar. The BET results showed the SSA value of 6.78 m^2/g for the A-TNO sample was about 5.55 times higher than that of the N-TNO one (1.22 m^2/g). The higher SSA of A-TNO could be ascribed to the microporous nature of particles prepared by the appropriate method.

At 0.1 C, the first discharge capacity for the A-TNO sample was 284 mAh/g while for the N-TNO sample, it was 265 mAh/g. The electrochemical tests at all C-rates from 0.5 to 10 C revealed the higher capacities of the A-TNO compared to the N-TNO sample. For example, at a high rate of 10 C, the capacity of 174 mAh/g was achieved for the A-TNO sample, which was about two times higher than that of the N-TNO one. The EIS results demonstrated that the charge transfer resistance of the A-TNO sample was about 26% lower than that of the N-TNO sample, and the Li-ion pathways in the A-TNO material were shorter. In addition, the cyclic stability tests at 5 C and after 100 cycles showed that the capacity of A-TNO was more than 200 mAh/g, and about 33% higher than that of the N-TNO sample (about 150 mAh/g).

Based on the data reported in the literature, the capacities of pure TNO materials with particulate morphologies, at different C-rates were collected and plotted as a curve in Fig. 2. As shown in this figure, the TNO nanoparticles show a better rate performance in comparison with the micron-sized particles.

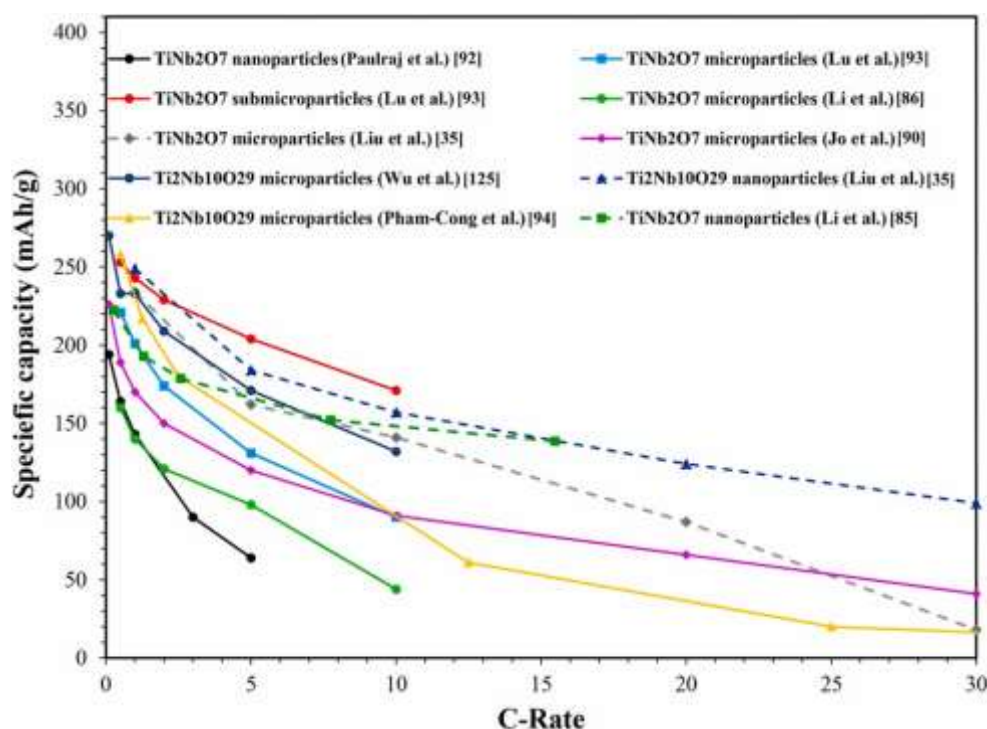


Fig. 2. The rate capability comparison of reviewed TNO anode materials with particulate morphology in this study.

As can be observed in Fig. 2, the TNO anode materials with particulate morphologies have poor electrochemical performance at high charge/discharge rates. On the other hand, since the solid-state method is one of the most appropriate methods for the industrialization of TNO materials, more investigations on the affecting parameters of the solid-state method are suggested to improve the electrochemical performance of TNO anode materials.

3.2. 1D TNO materials

Nanosizing is an effective structural engineering strategy to improve the Li-ion storage capability of the anodic materials, especially at high charge/discharge rates. 1D nanomaterials such as nanorods, nanowires, nanofibers, and nanotubes, are mostly considered to be high-capacity and stable electrode materials, due to their effective contact with the electrolyte, uniform structure, and strong tolerance to stress changes, because of their large surface-to-

volume ratio and low affinity to self-aggregation [83]. Hence, the synthesis of 1D TNO nanomaterials is beneficial for achieving high-rate LIBs with high cyclic stability. There are limited studies in the literature on the Li-ion storage capability of 1D TNO nanomaterials. Nanorods, nanofibers, and hollow nanofibers are the only 1D morphologies reported in the literature.

The literature review indicated that the sol-gel method is the most widely used approach to fabricate TNO nanorods [83,95]. Hu et al. [83] synthesized TiNb_2O_7 nanorods by the sol-gel method. For this purpose, a solution was prepared to contain sodium dodecyl sulfate (SDS) surfactant, glacial acetic acid, hydrochloric acid, ethyl alcohol, niobium chloride, and titanium (IV) isopropoxide. It is worth noting to mention that glacial acetic acid and hydrochloric acid were used for their pH modulation and catalytic functions. After mixing the solution at 80 °C for 12 h, calcination treatment was performed at 700 °C for 2 h. The findings proved the formation of high-purity TiNb_2O_7 nanorods with an average length and diameter of 300 nm and 100 nm, respectively. The presence of SDS was the main reason for the formation of the TiNb_2O_7 nanorods. Generally, the adsorption of SDS on the crystal surfaces leads to the growth of TiNb_2O_7 in a preferred direction. The electrochemical investigations showed that the TiNb_2O_7 nanorods delivered high Li-ion storage capability, especially at higher charge/discharge rates. For example, the capacities of 233, 182, and 122 mAh/g were, respectively, achieved at 1, 10, and 20 C. Furthermore, the Li-ion diffusion length could be shortened by using the TiNb_2O_7 nanorods. Diffusion time has a linear relationship with diffusion length. Therefore, due to the short diffusion length in TiNb_2O_7 nanorods, the diffusion time would be shorter, leading to improved rate capability. Also, the cyclic stability studies showed that the specific capacity of 140 mAh/g at 10 C after 100 cycles was maintained for

TiNb₂O₇ nanorods. The high cyclic stability is owing to the strain-relaxing characteristics of the nanorod morphology.

In another work, Lou et al. [95] prepared TiNb₂O₇ nanorods using a facile sol-gel method. For this purpose, Nb₂O₅ particles were dissolved in hydrofluoric acid (HF) followed by the addition of NH₃OH for Nb(OH)₅ precipitation. After filtering and drying, the solid Nb (OH)₅ particles were added to oxalic acid. Finally, the solution of tetrabutyl titanate in ethanol was added to the prepared solution and after mixing and calcination, crystalline TiNb₂O₇ was obtained. The morphological analyses revealed the formation of 1D TiNb₂O₇ nanorods with lengths of 300–600 nm and diameters of 100–300 nm. The electrochemical results proved that TiNb₂O₇ nanorods delivered the capacities of 226, 140.4, and 83.9 mAh/g at the respective rates of 1, 20, and 50 C, indicating their good rate performance. Moreover, the long-term cyclic stability tests at a high rate of 10 C revealed that a capacity of 123.2 mAh/g could be achieved for TiNb₂O₇ nanorods after 500 cycles.

Finally, further investigations on the sol-gel preparation of TNO anode materials with cheaper precursors are proposed. From another point of view, the synthesis time of the sol-gel method is shorter than the solid-state and hydro/solvothermal methods, and it should therefore be considered for future studies on the TNO anode materials.

In addition to the nanorod morphology, the synthesis of TNO nanofibers and nanotubes (hollow nanofibers) using the electrospinning method has also been developed. Pham-Cong et al. [94] reported the fabrication of Ti₂Nb₁₀O₂₉ nanofibers (NFs) by a simple electrospinning process followed by annealing at different temperatures (700, 800, and 900 °C). Furthermore, Ti₂Nb₁₀O₂₉ powders were prepared through a solid-state reaction. Fig. 3 depicts the preparation method and electrochemical performance of the synthesized samples. Cyclic voltammetry (CV) measurements were performed to investigate the redox kinetics of Ti₂Nb₁₀O₂₉ materials,

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as shown in Figs. 3b and c. Three oxidation peaks are visible during anodic sweeping. The cathodic peaks are contributed to the Li-ion insertion in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. The sharp anodic and cathodic peaks at ~ 1.69 and ~ 1.63 V could be related to the $\text{Nb}^{5+}/\text{Nb}^{4+}$ valence variations. The formation of the SEI layer and Li dendrites on the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ surfaces is prevented at these high potentials. Although, the electrolyte polarization effect resulted in a positive shift of the cathodic peaks to higher voltages during the first cycle.

Furthermore, the intensity of the cathodic and anodic peaks in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs is higher than that of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder. Li-ion diffusion coefficient is directly proportional to the current intensity [94,106,107] and according to the Arrhenius equation, the Li-ion diffusion coefficient is inversely proportional to the activation energy. Consequently, the higher intensity of CV peaks could be attributed to the higher Li-ion diffusion coefficient and lower activation energy for Li-ion diffusion. Therefore, it can be concluded that the activation energy for Li-ion intercalation in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs is lower than $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder. The improved electronic conductivity and smaller particle size in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs are the other reasons for this observation.

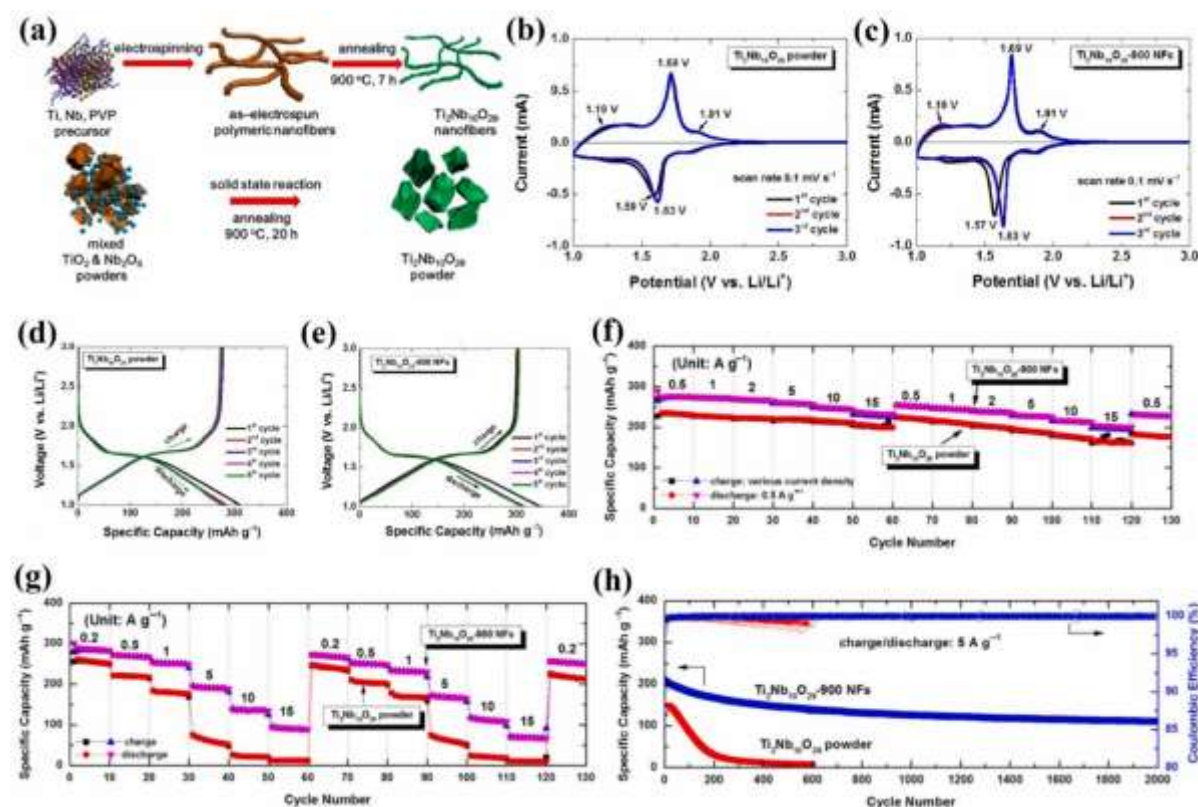


Fig. 3. Formation procedure and electrochemical performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder; (a) schematic illustration of the preparation of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder, (b, c) CV curves for various cycles at a scan rate of 0.1 mV/s , (d, e) charge-discharge curves under a current density of 50 mA/g (0.13C), (f) charge rate performance with discharge fixed at 0.5 A/g , (g) rate performance at various charge-discharge current densities in the range of $0.2\text{--}15 \text{ A/g}$, and (h) long-term cycling at a current density of 5 A/g [94].

The discharge/charge curves at 0.13 C using $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder/Li and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29} - 900$ NFs/Li cells are shown in Figs. 3d and e. Consistent with the CV outcomes, three regions were detectable in each curve: region 1 (open circuit voltage) from 3.0 to 1.9 V , region 2 from 1.9 to 1.6 V , and region 3 from 1.6 to 1.0 V . In region 2, the discharge and charge plateaus at ~ 1.69 and $\sim 1.63 \text{ V}$ are consistent with the two sharp peaks in CV curves. The first charge and discharge capacities for the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder anode are 278 and 309 mAh/g , corresponding

to 15.1 and 17.1 mol Li-ion extraction/insertion, respectively. While for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs these values are 304 (16.7 mol Li) and 344 (19.1 mol Li), respectively. The increased specific capacity in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs could be attributed to the larger electrode/electrolyte contact area and shortened Li-ion diffusion paths compared to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder.

To examine the cyclic stability of the samples, the charge rate performances were examined in which the discharge rate was fixed at 0.5 A/g and the charge rates were gradually increased. As can be seen in Fig. 3f, a small loss in the capacity as a function of the charging rate was observed in both samples. In contrast, by increasing both charge and discharge rates, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs showed much better rate capabilities than the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders, as observed in Fig. 3g. Moreover, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs annealed at 700 and 800 °C displayed strong capacity loss upon cycling due to their lower crystallinity and the best performance was observed for the one annealed at 900 °C. Long-term cycling measurements are shown in Fig. 3h. The specific capacity of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs was 212 mAh/g at 5 A/g, and it was maintained at 109 mAh/g (49.6% capacity retention) after 2000 cycles. In contrast, a sharp capacity loss for the other electrode to 27 mAh/g was observed after 200 cycles. The structural changes in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ anodes were studied by reassembling the cells. The SEM and XRD results revealed that even after 2000 cycles, no significant cracks were visible on the NF anodes due to the stress release through the radial direction of NFs during the lithiation/delithiation processes. Also, a thin SEI layer is likely to be formed on the surface of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder anode, causing its poor performance.

The outstanding cyclic and rate performances of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs compared to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders could be attributed to some reasons. At first, the specific surface area of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs (6.95 m²/g) was about 4 times higher than that of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders (1.66 m²/g), resulting in a shortened Li-ion diffusion distance and a more available electrolyte

/electrode interface. Moreover, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ NFs consisted of highly crystalline interconnected channels which resulted in strain relaxing caused by volume expansion of electrode during cycling. However, since strain relaxing did not occur in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders, crack generation was possible. Thereby, the defective sites of electrodes fabricated from $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders served as the preferential sites for SEI formation and, consequently, Li-ion consumption. In other words, the capacity fading of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders could be related to the SEI formation.

Li et al. [85] developed a new technique to fabricate TiNb_2O_7 nanowires by the sol-gel method using sulfonated polymer nanotubes (SPNTs) as a template. After the synthesis of SPNTs, the solution of SPNTs, tertbutyl titanate, and NbCl_5 in ethanol was prepared. After mixing, the calcination treatment at 800 °C for 5 h was carried out (this sample is denoted as TNS). For comparison, TiNb_2O_7 nanoparticles (TN sample) were also prepared. The morphological and electrochemical analyses of the TNS and TN samples are shown in Fig. 4. The SEM images showed the successful formation of TNS without agglomerations (Fig. 4a), while obvious agglomeration can be seen in Fig. 4b for the TN sample. The electrochemical results showed that at 1.03 C, the first discharge and charge capacities of 232.3 and 207.1 mAh/g were achieved for the TNS sample, while those values for TN samples were 208.5 and 196.2 mAh/g, respectively. Outstanding cyclic stability with 90% capacity retention after 500 cycles was observed for the TNS samples, while the capacity retention was only 77% for the TN sample, as can be seen in Fig. 4c. Similar to the cyclic stability, the capacities of the TNS samples were higher than those of TN samples in all charge/discharge rates (Fig. 4d). For example, at a high rate of 15 C, the capacity of the TNS sample was 168.1 mAh/g which was about 21% higher than that of the TN sample (138.6 mAh/g).

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<https://doi.org/10.1016/j.jallcom.2022.165117>

Furthermore, the long-term stability of the TNS samples at a high rate of 12.62 C and after 2000 cycles was investigated. As can be seen in Fig. 4e, the anode showed a high first discharge capacity of 212.9 mAh/g which was decreased to 97.7 mAh/g after 2000 cycles (55% reduction). The findings are very interesting and show that the proposed novel method is simpler and cheaper than the electrospinning method and can be considered for further investigations. The better electrochemical performance of the TNS sample over the TN one can be related to the SPNTs template. Assembling the nanoparticles into a nanowire morphology using SPNTs templates, would significantly prevent their aggregation and improve the electrochemical performance.

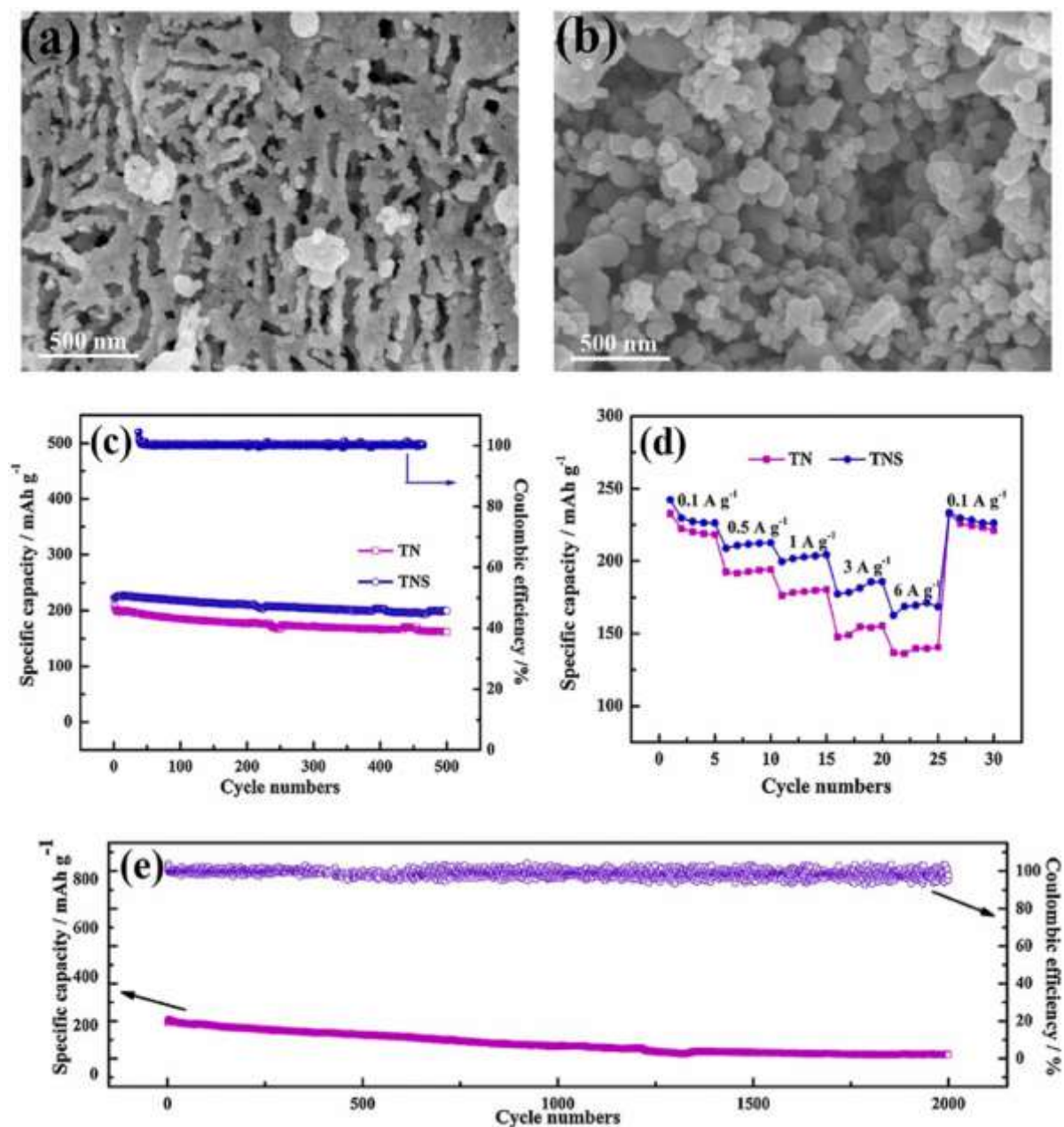


Fig. 4. Morphology and electrochemical properties of TNO nanowires; SEM images of (a) the TNS sample, and (b) the TN sample, (c) cyclic stability of the TNS and TN samples at 1.03C, (d) rate performance of TNS and TN samples, and (e) long-term stability of the TNS sample at 12.62C [85].

The synthesis of TNO anode materials with hollow nanofiber or nanotube structures has also been reported in the literature [96–98]. Fu et al. [96] reported the synthesis of porous Ti₂Nb₁₀O₂₉ hollow nanofibers via the co-electrospinning method followed by annealing in air.

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The prepared material revealed an average fiber diameter of ~500 nm, shell thickness of ~90 nm, and a large specific surface area of 40.6 m²/g, which could facilitate the electron/ion transport, provide a large electrode/electrolyte contact area, and enhance the pseudocapacitive behavior. Accordingly, the Ti₂Nb₁₀O₂₉ hollow nanofibers displayed considerably good electrochemical performance, including a high reversible capacity (307 mAh/g at 0.1 C), high initial columbic efficiency (ICE) value (90.8%), excellent rate performance (136 mAh/g at 20 C), and outstanding cyclic life (0.06% capacity loss per cycle at 10 C, over 500 cycles). The outstanding cyclic stability of Ti₂Nb₁₀O₂₉ hollow nanofibers could be attributed to their hollow-nanofiber structures, which effectively accommodate the volume changes of the electrode during cycling.

In another work, Park et al. [97] used a novel template-free method to synthesize TiNb₂O₇ nanotubes as the anode material for LIBs. For the synthesis of TiNb₂O₇ nanotubes, two separate solutions as the core solution and shell solution were used. A solution including heavy mineral oil and n-octane was prepared as the core solution. For shell solution, different amounts of acetic acid and ethanol were mixed, and then, the niobium (V) ethoxide and titanium (IV) tetraisopropoxide were added as the niobium and titanium sources, respectively. To achieve the desired viscosity of the electrospinning solution, the polyvinylpyrrolidone (PVP) was added to the shell solution. After placing the core and shell solutions in a syringe, the electrospinning process was carried out on an aluminum foil. Finally, the prepared samples were calcined in air at different temperatures between 700 and 1300 °C for 15 h.

The formation of TiNb₂O₇ nanotubes using the electrospinning method generally involves three steps including forming the Nb/Ti hydroxides through a hydrolysis reaction, decomposition of organic compounds at low temperatures, and finally, the calcination of TiNb₂O₇. The results showed that the hydrolysis and calcination temperature play major roles

in the final structure and morphology of TiNb_2O_7 . The optimum calcination temperature in the performed work was 700 °C and increasing the temperature resulted in the aggregation of tubes and the subsequent loss of tubular morphology. They also investigated the effect of the ratio between acetic acid and metal precursors on the obtained morphology. The results showed that reducing the amount of acetic acid would facilitate the formation of porous nanotubes. The BET results demonstrated that decreasing the ratio of acetic acid to metal precursors from 1 to 0.5 would increase the SSA from 51 to 151 m^2/g . The findings revealed the outstanding cyclic stability and rate performance of all three prepared samples. All the samples maintained their capacities above 200 mAh/g after 700 cycles at 1 C. Also, the capacity was more than 100 mAh/g at a high rate of 100 C.

The performed works showed that the TiNb_2O_7 hollow nanofibers would show better electrochemical properties compared to nanofibers. The findings in the study of Yu et al. [98] demonstrated the positive effects of hollowing out the nanofibers on the Li-ion storage capability of the TiNb_2O_7 anodes. They performed an experimental study comparing the Li-ion storage capability of TiNb_2O_7 hollow nanofibers (denoted as HTNO in Fig. 5), and TiNb_2O_7 nanofibers (denoted as TNO in Fig. 5), prepared by electrospinning method. The preparation method, morphological features, and the electrochemical performance of TiNb_2O_7 hollow nanofibers and TNO nanofibers are shown in Fig. 5. For the preparation of HTNO, two-sol solutions as the outer sol and inner sol were used. The outer sol was composed of poly(vinylpyrrolidone) and Ti and Nb precursors, and the inner sol was composed of a polymeric solution. For the synthesis of the TNO sample, the inner and outer solutions were the same. The heat treatment step at 800 °C in the air was done for calcination of the HTNO/TNO samples and removal of the polymeric carriers. The SEM images showed the

successful formation of HTNO and TNO nanofibers with a diameter of 220 nm (Figs. 5b and 5c).

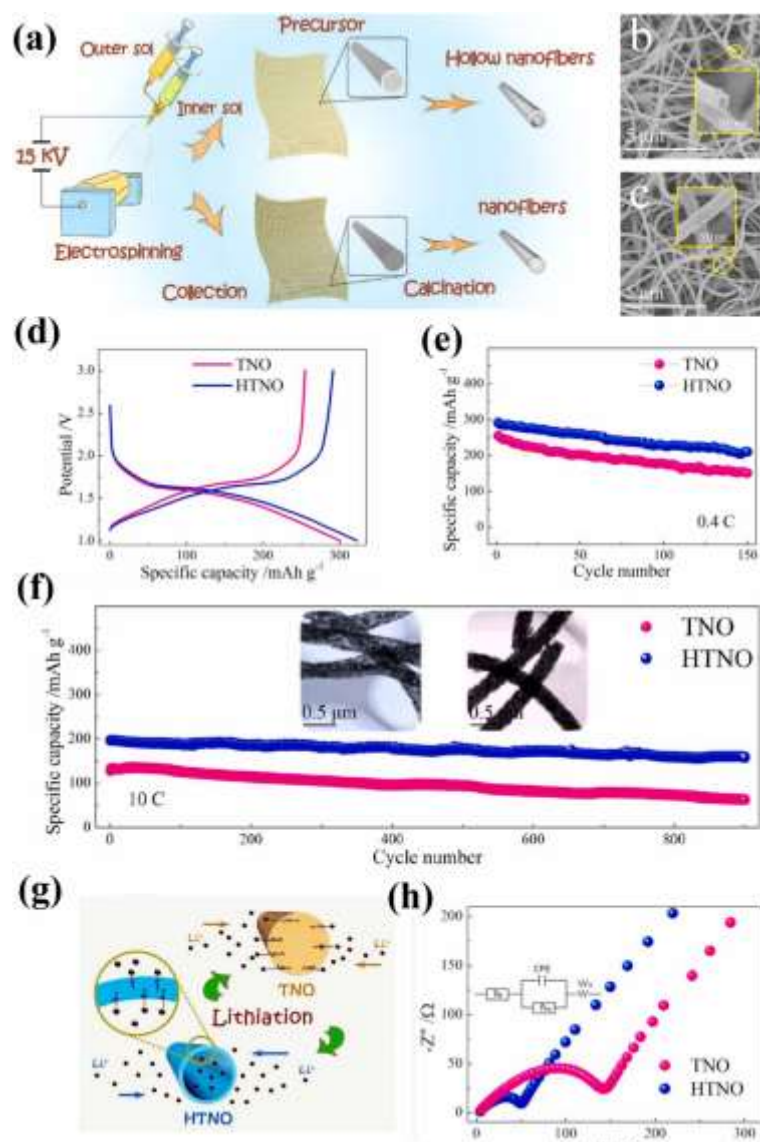


Fig. 5. Preparation method, morphologies, and electrochemical analyses of the TiNb₂O₇ hollow nanofibers; (a) schematic illustration of the electrospinning method for the synthesis of both TiNb₂O₇ hollow nanofibers and TiNb₂O₇ nanofibers, SEM images of (b) TiNb₂O₇ hollow nanofibers, and (c) TiNb₂O₇ nanofibers, (d) first charge/discharge curves of samples at 0.4C, (e) cyclic stability of samples at 0.4C, (f) long-term cyclic stability at 10C, (h) mechanism of Li-ion diffusion into the TiNb₂O₇ hollow nanofibers structure vs TiNb₂O₇ nanofibers and (i) Nyquist plots of the samples [98].

As shown in Fig. 5d, the electrochemical results demonstrated that at 0.4 C, the initial discharge/charge capacities of 322.8/291.7 mAh/g were achieved for HTNO samples which were higher than those of the TNO sample (300.8/255.1 mAh/g). The higher ICE value of the HTNO sample in comparison with the TNO could be related to the hollow structure of the HTNO, which provides more reversible Li-ion storage sites. Moreover, the cyclic stability tests revealed that the reversible capacity of 210.2 mAh/g with the capacity retention of 72% for HTNO samples was maintained after 150 cycles at 0.4 C. On the other hand, as shown in Fig. 5e, the reversible capacity of TNO samples decreased to 150.5 mAh/g after 150 cycles at 0.4 C (58.9% capacity retention). The hollow structure of HTNO provides more pathways for the diffusion of Li-ions (Fig. 5g). The EIS results also demonstrated the beneficial effects of hollow structures in reducing the charge transfer resistance and increasing the electrical conductivity of HTNO anodes (Fig. 5h).

To compare the rate performance of 1D TNO materials, their reported capacities at different rates were collected from literature and plotted, as shown in Fig. 6. The best rate capability is related to the TiNb_2O_7 anodes with nanotubular morphology, reported in the study by Park et al. [97]. Accordingly, it can be concluded that the hollow nanofibers are the best choices as 1D TNO materials in LIBs. From another viewpoint, it can be revealed that the TiNb_2O_7 nanowires show intermediate electrochemical performance between nanorod and hollow nanofibers. Owing to the preference of the sol- gel method with SPNTs compared to the electrospinning route in terms of time and cost, the former method can be considered a practical method for the synthesis of TNO.

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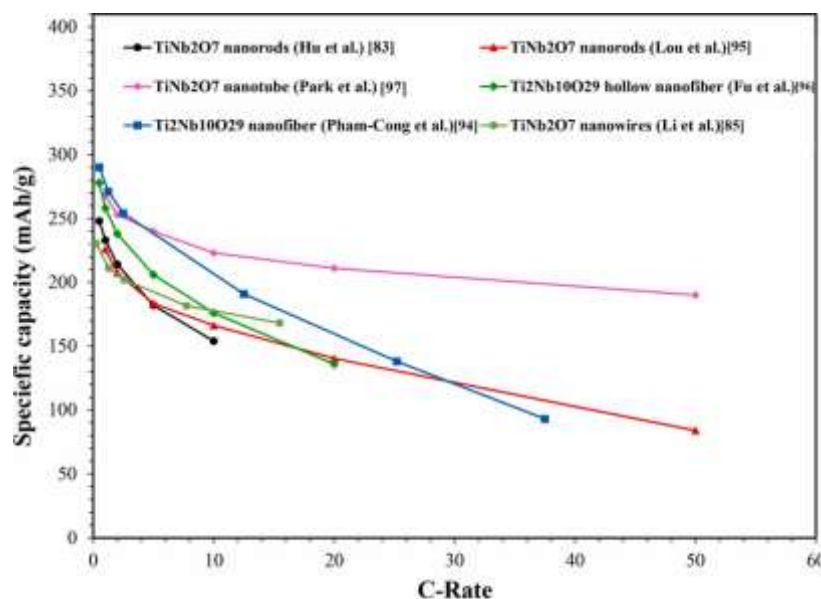


Fig. 6. The comparison of the rate capabilities of reviewed pure 1D TNO anode materials in this study.

3.3. Three dimensional TNO materials

The three-dimensional (3D) TNO materials, reviewed in this study, can be divided into two main groups of spherical and porous structures. It is worth noting that while spherical structures have porosities, their pores are not as high as 3D porous structures.

3.3.1. Spherical structures

The solvothermal method has been extensively adopted to prepare TiNb_2O_7 / $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ with spherical morphologies as the anode materials for LIBs [79,86,88,108]. For example, Li et al. [86] prepared TiNb_2O_7 microspheres by the solvothermal method and calcination treatment at 700 °C for 2 h. Moreover, they prepared TiNb_2O_7 using the solid-state method followed by the calcination step at 900 °C for 10 h. The schematic illustration of these methods and the electrochemical performance of the prepared samples are shown in Fig. 7. The morphological characterizations revealed that TiNb_2O_7 microspheres with a diameter of 2–3 μm were formed after the solvothermal method. The formation mechanism of the TiNb_2O_7

microspheres is based on the nucleation and self-assembly of the initially formed TiNb_2O_7 nanoparticles, as demonstrated by SEM images at different solvothermal times in their work. The BET results showed that the SSA value of the TiNb_2O_7 microspheres synthesized by the solvothermal method ($25.26 \text{ m}^2/\text{g}$) was approximately 3.84 times higher than that of the bulk TiNb_2O_7 synthesized by the solid- state route.

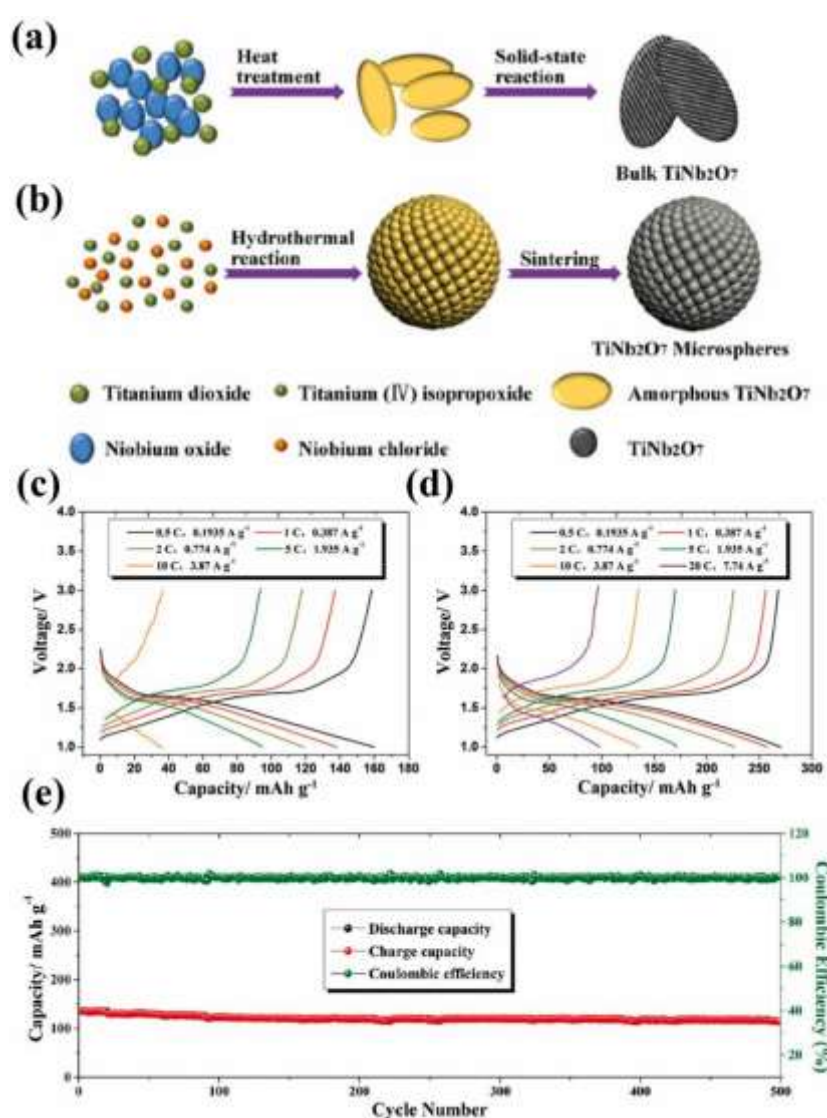


Fig. 7. The synthesis approaches and electrochemical properties of TiNb_2O_7 microspheres and microparticles, (a) solid-state synthesis of TiNb_2O_7 microparticles, (b) solvothermal synthesis of TiNb_2O_7 microspheres, rate performance of (c) TiNb_2O_7 microparticles, and (d) TiNb_2O_7 microspheres, (e) cyclic stability of the TiNb_2O_7 microspheres at 10C [86].

The electrochemical studies indicated that at 1 C, the discharge capacity of TiNb_2O_7 microspheres was 258 mAh/g, which was about 87% higher than that of bulk TiNb_2O_7 (138.1 mAh/g). The difference between the electrochemical performance of the two samples was more pronounced at higher rates. As shown in Figs. 7c and 7d, the discharge capacity of the TiNb_2O_7 microspheres (100 mAh/g) at a high rate of 10 C was about 1.73 times higher than that of bulk TiNb_2O_7 (36.6 mAh/g). The better electrochemical performance of TiNb_2O_7 microspheres compared to bulk TiNb_2O_7 could be attributed to the well-distributed TiNb_2O_7 nanoparticles in the hierarchical structure, which could provide more sites for Li-ion accommodation and shorten the Li-ion pathways. Also, the porous hierarchical structure consisted of many interconnected porous channels, which could be beneficial for electron/ ion transport.

Besides the TiNb_2O_7 microspheres, the synthesis of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres has also been reported. Liu et al. [35] presented the preparation of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ mesoporous microspheres and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles by solvothermal route, where the solvents were isopropanol-glycerol and isopropanol for the former and latter samples, respectively. Both procedures were followed by calcination at 900 °C for 10 h. The schematic illustration of the formation mechanisms, morphological analyses, and electrochemical properties of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles is shown in Fig. 8. The SEM images shown in Figs. 8b and 8c revealed the formation of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres with hierarchical and mesoporous structures composed of nanoparticles. This particular structure could reduce the diffusion distance of Li-ions and provide a large contact area between electrode and electrolyte. Therefore, the electrochemical performance of LIBs with $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres is improved compared to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles, as revealed by the rate capability and cyclic performance tests in Figs. 8d and 8e. By increasing the C-rate, the discharge capacity loss of TNO microspheres occurred more slowly, compared to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles. The

discharge capacities of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles were 173.5 and 114.9 mAh/g after 500 cycles at 10 C, with a capacity retention of 86.8% and 71.1%, respectively.

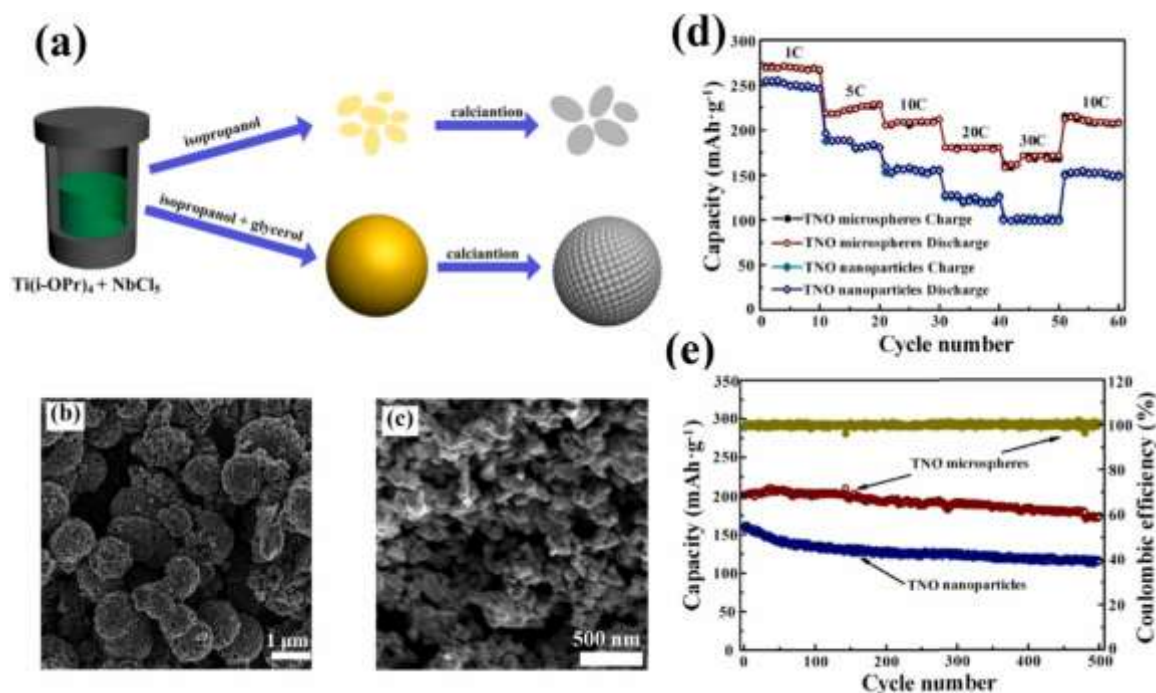


Fig. 8. The synthesis approach and the electrochemical performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles; (a) schematic representation of the preparation processes of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles, FESEM images of (b) $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres and (c) $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles, (d) rate capability and (e) cyclic performance at 10C for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles. Reproduced from [35].

In another study, the fabrication of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres via a solvothermal method followed by subsequent annealing was presented by Liu et al. [99]. $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres were assembled from aggregated $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles with an average particle size of 50 nm. Electrochemical measurements revealed the excellent and stable performance of these materials as the LIBs anode. For example, a discharge capacity of 185 mAh/g after 200 cycles

was obtained at 10 C (with a capacity retention of 94%) by the prepared anode. The advanced electrochemical performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres could be attributed to the produced small particle sizes and the presence of porosities in their special structure. This distinctive morphological feature resulted in the facilitation of Li-ion diffusion and penetration of the electrolyte into the electrode surface, great tolerance to the volume changes upon cycling, and also prolongation of the cell lifetime.

Previous studies have shown that the size reduction of the $\text{TiNb}_2\text{O}_7/\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ spheres can have a significant impact on their electrochemical performance [78,100,101]. As it is well known, some unique chemical and physical characteristics can be obtained through dimensional and morphological control. For example, decreasing the particle size of materials, especially to the nanometer range would result in shortening the electrons and Li-ions transmission within the active material and improve the contact area between electrode material and electrolyte. These features would increase the rate of electrochemical reactions and improve the performance of LIBs at higher charge/ discharge rates. Besides, reducing the particle size would result in increasing the SSA and providing more active sites for chemical reactions, and therefore improve the specific capacity and the performance of LIBs. In summary, reduction of the particles' dimensions would notably improve the electrical conductivity, ion/electron transfer rates, and pseudocapacitive property of TNO materials. It is worth noting that the pseudocapacitive behavior is an intrinsic property of TNO, leading to the accelerated redox reactions at faradic surfaces and consequently an improved rate performance [31,109].

By reviewing the literature, it can be deduced that the use of a capping agent is necessary to control the size of the $\text{TiNb}_2\text{O}_7/\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ spheres. P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$), and F127 ($\text{EO}_{102}\text{PO}_{70}\text{EO}_{102}$) are two common block copolymers for size controlling purposes in the

hydro/solvothermal method [78,100]. For the first time, Xia et al. [100] reported the synthesis of hierarchical porous $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres composed of interconnected nanoparticles via a simple solvothermal route combined with calcination. For this purpose, they used P123 copolymer in the solvothermal synthesis of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. For comparison, $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ micro-rods were fabricated by a facile solid-state reaction process followed by thermal treatment. The morphological characterizations revealed that without using P123, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microspheres with a diameter of 1–3 μm could be obtained, while the application of P123 resulted in the formation of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres with a diameter of 100–500 nm. The adsorption of P123 on the surface of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ particles can reduce the nucleation sites, and suppress the growth phenomenon. Results indicated that in comparison with bulk $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ micro-rods, the SSA of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres was larger, and therefore the transport pathways for ions/electrons were shorter. These features resulted in improving the electrochemical performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres as the LIBs anode. This electrode revealed a high-rate capability of 208 mAh/g at 20 C and long cyclic life of 215 mAh/g after 500 cycles at 10 C.

In another study, Lou et al. [101] synthesized porous hierarchical $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres using the F127 block copolymer by solvothermal method. The prepared $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres with diameters in the range of 300–500 nm consisted of primary nanoparticles. For comparison, $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microparticles were prepared by a solid-state approach. The schematic illustration of the preparation method, the structural characterizations, and the electrochemical performance of the prepared materials are depicted in Fig. 9. The XRD pattern of the synthesized $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres was in agreement with the standard diffraction pattern of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, as shown in Fig. 9a. Furthermore, the Raman spectrum of the samples also confirmed the formation of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ material, as shown in Fig. 9b. The capacity and

retention capability of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres at various rates are presented in Fig. 9c. The $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ microparticles provided much lower charge capacities than the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres, especially at the rate of 50 C.

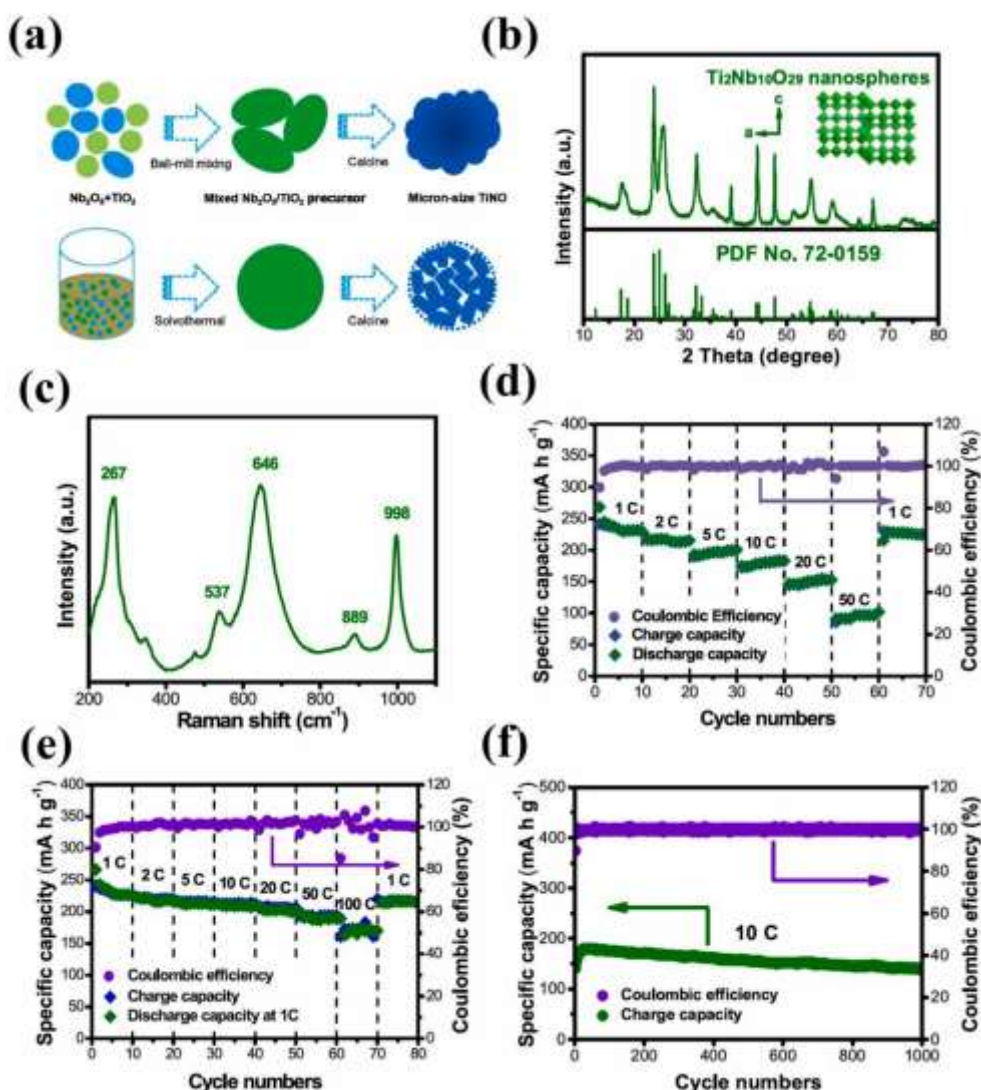


Fig. 9. Preparation method and properties of micron-size bulk $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and porous $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres; (a) schematic illustration of the preparation steps of the samples, (b) XRD pattern and standard diffraction pattern, (c) Raman spectrum of the synthesized $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres, (d) rate performance of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres, (e) charge rate performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ electrodes with a fixed discharge rate at 1 C, and (f) long-term cyclic performance and Coulombic efficiency of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres anode at 10 C after three cycles at 0.1 C [101].

It should be noted that the charging process of the full-cells depends on the discharging process. Therefore, in the research done by Lou et al., the discharge rate of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ /Li half cells was fixed at 1 C while the charge rates were varied. This test is especially relevant and applicable to the batteries in electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to the preference to charge these vehicles at night to avoid the peak load of electric output. Consequently, because of the adequate time, the charge rate can be reduced to increase the charge capacity. Findings revealed that by increasing the C-rate, the specific capacities decreased slightly (Fig. 9e), although even at high charge rates of 50 and 100 C, high capacities of 193.5 and 172.1 mAh/g were achieved which demonstrated the outstanding high-rate performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres. Fig. 9f shows the long-term cyclic performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanospheres at 10 C after 3 activation cycles at 0.1 C. During the first 50 cycles, the capacity increased gradually, followed by a slight decrease in the subsequent cycles. After 1000 cycles, a high capacity of 141.5 mAh/g was achieved. This better rate capability could be attributed to the shorter pathways for Li-ion diffusion in primary nanoparticles due to the porous hierarchical morphology. Besides, the pseudocapacitive effects play an important role in the excellent rate behavior and long-term cycle stability.

So far, the electrochemical performance of microspheres and nanospheres has been compared. For example, Cheng et al. [78] prepared the TiNb_2O_7 nanospheres and microspheres by solvothermal method and compared their electrochemical performance. To prepare the TiNb_2O_7 nanospheres, the P123 block copolymer was added in ethanol, and then NbCl_5 and tetrabutyl titanate were added to the solution as, respectively, the Nb and Ti sources. After transferring the prepared mixture into the Teflon-lined autoclave, the solvothermal treatment was done at 220 °C for 16 h, followed by a calcination step at 800 °C for 5 h to crystallize the particles. TiNb_2O_7 microspheres were prepared by a similar approach without using the P123

block copolymer. The morphological studies showed that the presence of P123 block copolymer would lead to the successful formation of TiNb_2O_7 nanospheres with an average diameter of 500 nm composed of 30–50 nm nanoparticles, while the TiNb_2O_7 microspheres had an average diameter of 2 μm . The BET results showed that the SSA value of the TiNb_2O_7 nanospheres ($23.4 \text{ m}^2/\text{g}$) was about 25% higher than that of TiNb_2O_7 microspheres ($18.6 \text{ m}^2/\text{g}$).

Rate performance tests revealed that TiNb_2O_7 nanospheres delivered a specific capacity of 212 mAh/g at a high rate of 5 C after 1000 cycles, while TiNb_2O_7 microspheres rapidly lost their capacity after 1000 cycles and the capacity was only 80 mAh/g after 1000 cycles. The TiNb_2O_7 nanospheres with uniform nanoporous structures, effectively buffer the strain caused by the charge/ discharge processes. Furthermore, TiNb_2O_7 nanospheres delivered higher specific capacities in all C-rates, compared to TiNb_2O_7 microspheres. For example, the capacities of TiNb_2O_7 nanospheres at the high rates of 10, 20, and 50 C were, respectively, 219, 208, and 167 mAh/g. The better electrochemical performance of the TiNb_2O_7 nanospheres compared to TiNb_2O_7 microspheres, especially at high C-rates could be ascribed to the nanoporous structure which facilitates and fasten the Li-ion diffusion into the structure, as confirmed by EIS results. The smaller size of TiNb_2O_7 would not only reduce the Li-ion diffusion length but also would increase the efficient contact between the electrolyte and the electrode.

In addition to the size of TNO spheres, their porosity has a significant impact on their electrochemical properties. Park et al. [79] used different amounts of diethylenetriamine (DETA) as a porosity controller in the formation of TiNb_2O_7 . The samples were prepared by a solvothermal method via the addition of various amounts of DETA to the solution containing Ti and Nb precursors. The samples prepared with 0.025, 0.05, and 0.1 ml DETA were named PTNO MS-1, PTNO MS-2, and PTNO MS-3, respectively. The results showed that the

synthesized materials had no specific morphology without using DETA. The SEM images showed a similar size distribution for all samples, but their pore sizes were different. By increasing the concentration of DETA, the pore sizes increased and the largest pore size of 30 nm was obtained for the PTNO MS-3 sample.

Moreover, the BET results showed that SSA values of 25.2 and 19.8 m²/g were achieved for the PTNO MS-2 and PTNO MS-3 samples, respectively. Pore size values of 15.9 and 35.4 nm were also obtained for the PTNO MS-2 and PTNO MS-3 samples, respectively. The electrochemical results showed that at 0.1 C, the first discharge capacity was 286 mAh/g for PTNO MS-2 which was about 17.6% higher than that of the PTNO MS-1 sample. The long-term cyclic stability of samples at 5 C and after 1000 cycles showed that the PTNO MS-2 sample maintained the capacity of 182 mAh/g, which was higher than that of PTNO MS-1 (142 mAh/g). The PTNO MS-2 also presented superior rate capability compared to PTNO MS-1, at all C-rates. For example, a capacity of 143 mAh/g was obtained at a high rate of 100 C for PTNO MS-2 sample.

The recent work by Zeng et al. [88] showed that the hollow Ti₂Nb₁₀O₂₉ microspheres show better electrochemical performance compared to the Ti₂Nb₁₀O₂₉ block microspheres. The mesoscopic Ti₂Nb₁₀O₂₉ cages were constructed from nanorods. The schematic illustration of the synthesis steps obtained morphologies, and the electrochemical performance of TNO hollow microspheres are given in Fig. 10. They prepared carbon spheres as the template, and then mesoscopic cages were prepared through the hydrothermal process followed by annealing, as schematically presented in Fig. 10a. For comparison, the mesoscopic block sample was synthesized via the same procedure but without using the template. The morphological and electrochemical features of the prepared samples are shown in Fig. 10. SEM images (Figs. 10b

and c) showed that $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cages were assembled from nanorods with a length of 100 nm. The shell of the cage and the big hollow in the center can be seen in the TEM image (Fig. 10d).

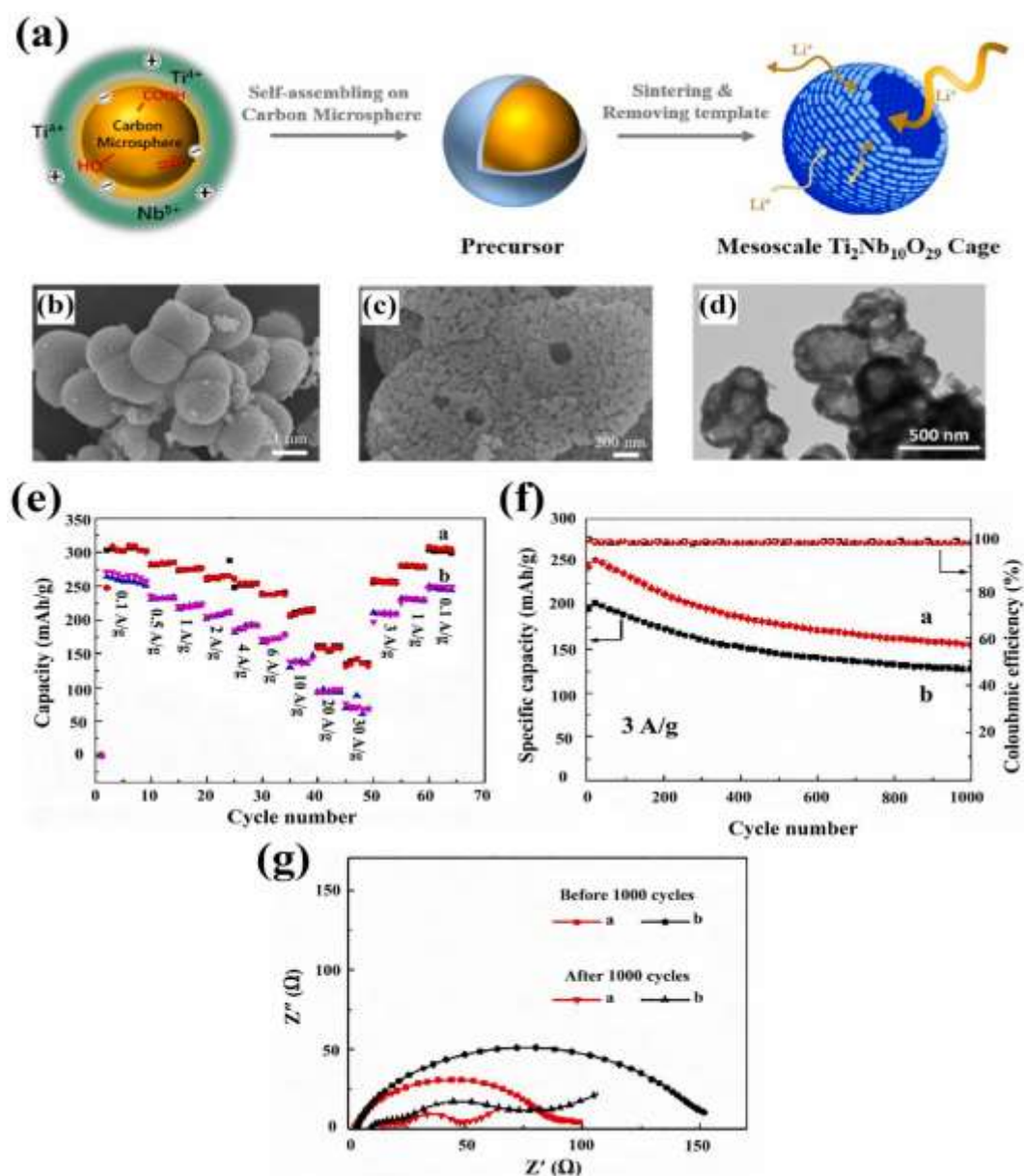


Fig. 10. Preparation method, morphology, and electrochemical performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cages and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ blocks; (a) schematics of the synthesis procedure of mesoscopic $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cage, (b, c) SEM images, and (d) TEM image of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cages, (e) rate performance, (f) cyclic capability at 3 A/g and (g) Nyquist plots of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cages and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ blocks. In the figure: a is $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cages, b is $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ blocks [88].

The rate capability of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ with the cage structure is superior to block one, as revealed by Fig. 10e. The long-term cycling performance of the mesoscopic cages was greater than $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ blocks and the coulombic efficiency of the former was about 100%, as demonstrated in Fig. 10f. The Nyquist plots of both samples before and after 1000 cycles are shown in Fig. 10e. Before 1000 cycles, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cage electrode showed a smaller diameter semicircle than the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ block, confirming the shorter diffusion path of the charge carriers in the cage structure. After 1000 cycles, two semicircles were observed in the Nyquist plots of both samples, demonstrating the formation of SEI film even at high working voltages. At high frequencies, the semicircle diameter of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cage anode is smaller which confirms the small volume change of this material upon cycling. After 1000 cycles, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cage electrode exhibited a more massive slope and smaller semicircle diameter, confirming the smaller ohmic and charge transfer resistance of this electrode compared to block one. The enhanced electrochemical performance of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ cage electrode could be attributed to the porous structure of the cage which increases the contact area between the electrode and electrolyte and consequently, accelerates the diffusion of Li-ions.

Finally, for better comparison, we collected the rate performance data of spherical TNO materials. As can be seen in Fig. 11, the TiNb_2O_7 nanospheres [78] and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ hollow microspheres [88] show the best electrochemical performance compared to the other samples reported in the literature. So far, extensive works have been done on the electrochemical performance of TNO microspheres. However, there are very limited works on TNO nanospheres and TNO hollow spheres. For further improvements in TNO materials with spherical morphologies, it is suggested to study the effect of adding different amounts of capping agents on the size of TNO spheres. Moreover, it seems that the TNO hollow nanospheres would exhibit outstanding electrochemical properties. Therefore, it is proposed to

study the simultaneous effects of capping agents and templates for the synthesis of hollow TNO nanospheres.

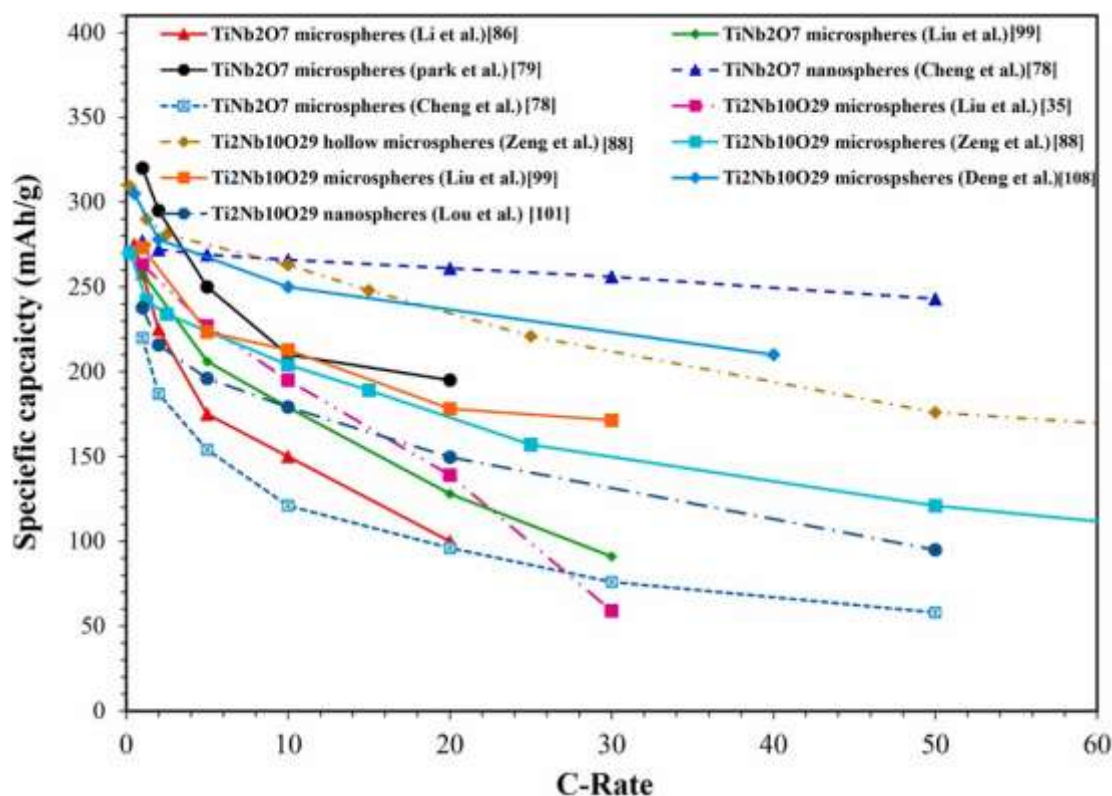


Fig. 11. The rate capability comparison of the reviewed pure TNO anode materials with spherical morphologies in this study.

3.3.2. Porous structures

One of the most effective methods to promote electrolyte penetration into the electrode surface and accelerate the diffusion of Li-ions into the TiNb₂O₇/ Ti₂Nb₁₀O₂₉ structures is the synthesis of porous structures. Although the volume changes of the TNO anodes are very low during cycling (4–7%), the void spaces of porous structures can mitigate the mechanical stresses caused by volume changes, and improve their cyclic stability. Hard templating and soft templating methods are commonly used for the synthesis of porous structures. According to the pore sizes, materials with pore sizes between 2 and 50 nm are called mesoporous, and the materials with pore sizes larger than 50 nm are called macroporous [89,90,102,103]. The

synthesis routes of both types of mesoporous and macroporous TiNb_2O_7 anodes have been reported in the literature and will be reviewed and discussed subsequently.

As an example, Lou et al. [89] prepared the macroporous TiNb_2O_7 anodes for LIBs. For this purpose, colloidal polystyrene (PS) crystals in a packed system were used as hard templates and they were immersed in a mixed solution of Ti and Nb precursors. After calcination at 900 °C in air, the PS template was removed, and then macroporous TiNb_2O_7 was achieved. The schematic illustration of the formation mechanism of macroporous TiNb_2O_7 is shown in Fig. 12a. The three-dimensional (3D) porous structure of the TiNb_2O_7 is shown in Figs. 12b and 12c, in which the honeycomb structure has a wall thickness of 50 nm with an average pore diameter of 100 nm. The BET results proved that the SSA value of synthesized macroporous TiNb_2O_7 was about 27 m^2/g . The electrochemical evaluation revealed that at 1 C, the initial discharge/charge capacities of 251/ 212 mAh/g were achieved for the macroporous TiNb_2O_7 , and upon continuing the cycles to 50, the capacity decreased to 139 mAh/g (65% capacity retention). In contrast to the cyclic performance, the rate performance of the prepared samples was appropriate, and the capacities of 124, 105, and 84 mAh/g were, respectively, achieved at 5, 10, and 20 C (Fig. 12d). Fig. 12e shows the cyclic stability of macroporous TiNb_2O_7 at 1 C and the capacity of 139 mAh/g with a capacity retention of 65% was achieved after 50 cycles. The long-term cyclic stability tests revealed that after 1000 cycles at 10 C, the capacity of macroporous TiNb_2O_7 decreased from 104 to 87 mAh/g (Fig. 12f).

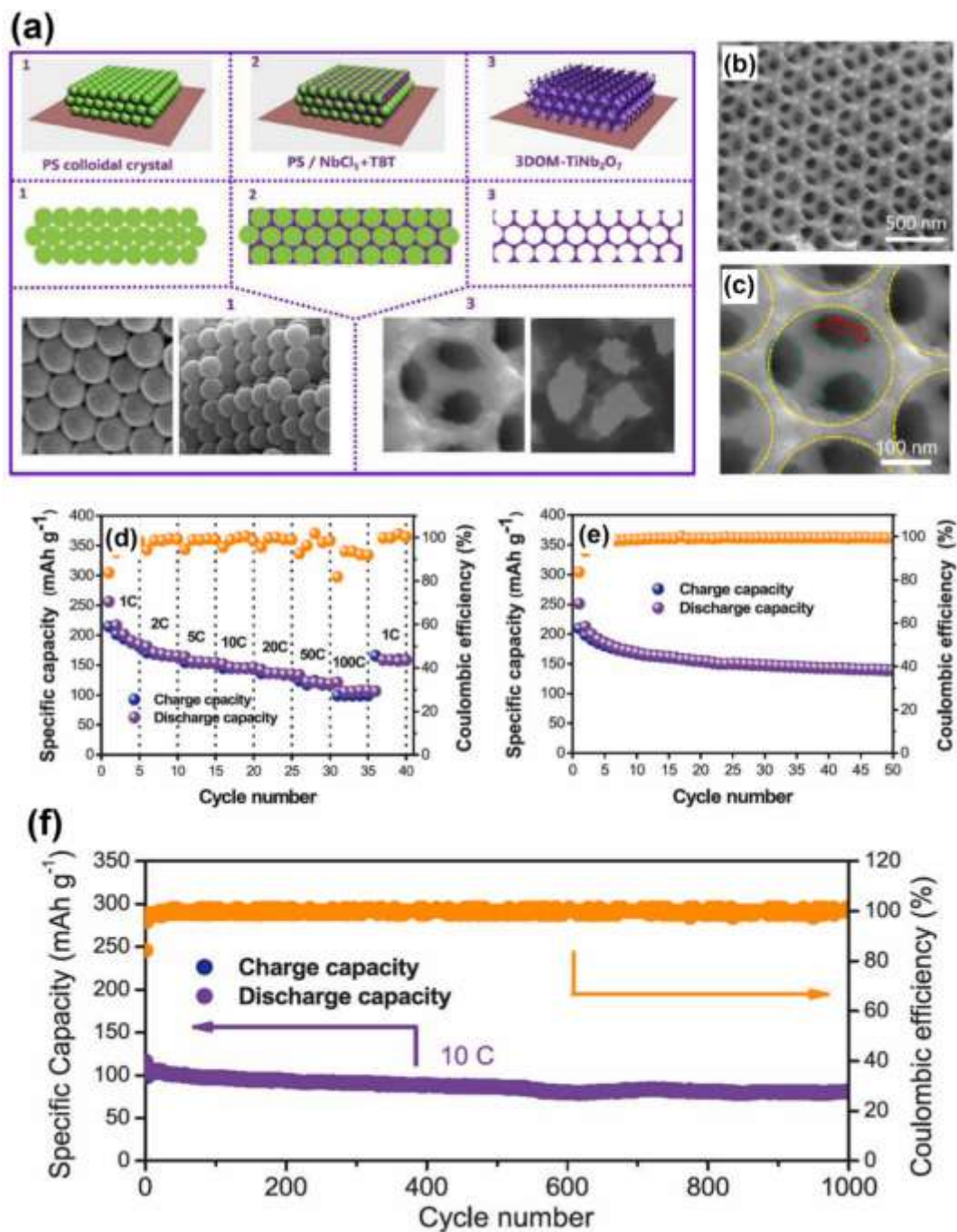


Fig. 12. Preparation method and electrochemical performance of macroporous TiNb_2O_7 ; (a) schematic illustration of the synthesis approach of macroporous TiNb_2O_7 , (b and c) SEM images of macroporous TiNb_2O_7 at different magnifications, (d) rate performance, and (e) cyclic stability at 1C, and (f) long-term cyclic stability of the macroporous TiNb_2O_7 at 10C [89].

This is the accepted manuscript (postprint) of the following article:

Aghamohammadi, H., Hassanzadeh, N., & Eslami-Farsani, R. (2022). A comprehensive review study on pure titanium niobium oxide as the anode material for Li-ion batteries. *Journal of Alloys and Compounds*, 911, 165117.

<https://doi.org/10.1016/j.jallcom.2022.165117>

SiO₂ templates are commonly used for the synthesis of mesoporous TiNb₂O₇. For example, Fei et al. [102] used Santa Barbara Amorphous-15 (SBA-15) mesoporous SiO₂ as the template for the synthesis of TiNb₂O₇ mesoporous material. After preparing the SBA 15 template, it was added to the solution of NbCl₅ and titanium (IV) isopropoxide. After mixing for 12 h and drying, calcination was done at 1000 °C for 5 h in the air (denoted as S-TNO). A similar approach was conducted without using SBA-15 (the sample was denoted as L-TNO). The XRD results revealed that the average crystallite size of the S-TNO was about 10.2 nm, while it was 24 nm for the L-TNO. The BET results demonstrated that the SSA value for S-TNO and L-TNO samples were, respectively, 79.5 and 4.3 m²/g. The much higher SSA for the S-TNO is due to its mesoporous structure.

The electrochemical results showed that at 1 C, the first discharge capacity of S-TNO was 213 mAh/g, which was about 1.17 times higher than that of L-TNO (98 mAh/g). The cyclic tests indicated the presence of a stable condition for the S-TNO sample upon cycling, while the large capacity fading was observed for the L-TNO sample. The capacity fading of the L-TNO sample was related to the larger particle size of the L-TNO sample which would increase the diffusion length. Also, the results showed that the capacity fading of the L-TNO at a low rate of 0.1 C was more than its degradation at a higher rate of 1 C. At lower rates (0.1 C), more activation of the anodic material would occur and consequently, more volume expansion would be observed compared to the samples cycled at higher rates. However, the porous nature of S-TNO samples can tolerate and reduce the volume expansion.

In another work, tetraethyl orthosilicate (TEOS) was used for the in-situ formation of SiO₂ templates, to produce ordered mesoporous TiNb₂O₇ anodes for LIBs [90]. For this purpose, after mixing titanium isopropoxide and niobium ethoxide stoichiometrically, the prepared solution was added to the solution containing TEOS and poly (ethylene oxide)-*b*-poly(styrene)

copolymer. After calcination at 900 °C and removing SiO₂ by washing, the mesoporous TiNb₂O₇ was obtained. The formation mechanism of ordered mesoporous TiNb₂O₇ is based on the controlled sol-gel method and the incorporation of inorganic species into the block copolymer. After mixing the Ti and Nb sources, the hydrolysis and condensation of metal alkoxides occurred and the prepared (Ti, Nb) sol was susceptible to being mixed with block co-polymer solution due to their hydrophilicity, leading to the formation of mesoporous TiNb₂O₇. The TEM analyses of mesoporous TiNb₂O₇ before and after the SiO₂ etching step indicated the successful formation of a mesoporous structure with an average pore size of 10 nm. The BET analysis showed a high SSA value for mesoporous TiNb₂O₇ (74 m²/g).

To compare the electrochemical results, bulk TiNb₂O₇ was also prepared using the solid-state method. The results showed that the first discharge/ charge capacities of 366/ 289 mAh/g were achieved for the mesoporous TiNb₂O₇ at 0.1 C, which was higher than that of bulk TiNb₂O₇ (246/228 mAh/g). The rate performance of the mesoporous TiNb₂O₇ anode was remarkably higher than that of the bulk TiNb₂O₇ anode in all charge/discharge rates. For example, at a high rate of 20 C, the mesoporous TiNb₂O₇ delivered the reversible capacity of 162 mAh/g which was about 3 times higher than that of the bulk TiNb₂O₇ sample. The long-term cyclic stability tests at a high rate of 10 C revealed that the capacity of 100 mAh/g was obtained after 2000 cycles. It was also shown that the carbon coating would improve the long-term cyclic stability of the mesoporous TiNb₂O₇ by about 100%.

Polymeric materials can also be used as soft templates in the synthesis of porous TiNb₂O₇ materials. Guo et al. [103] used F127 copolymer as a soft template for the formation of mesoporous TiNb₂O₇ anodes via a simple route. Fig. 13 shows the preparation method and electrochemical performance of different mesoporous TiNb₂O₇ anodes. After mixing the Ti and Nb sources, the solution was added to the solution of F127, ethanol, HCl, and acetic acid. After

mixing, the obtained powders were calcined at different temperatures between 600 and 1000 °C in air, as schematically illustrated in Fig. 13a. BET and crystallinity evaluations revealed that 700 °C was the optimum calcination temperature. Electrochemical measurements showed that at 0.1 C, the reversible capacity of 280 mAh/g was achieved for the calcined sample at 700 °C, and by increasing the charge/discharge rates, no considerable capacity fading was observed. For example, the reversible capacity values of 219 mAh/g, 195 mAh/g, and 128 mAh/g were obtained for the calcined sample at 700 °C at the rates of 10, 20, and 50 C, respectively (Fig. 13b). Furthermore, the Li-ion storage capabilities of the calcined samples at 850 and 1000 °C were investigated. The rate performance of the calcined sample at 850 °C was relatively similar to the calcined sample at 700 °C but their long-term cyclic performance was poor. Both rate performance and cyclic stability of the calcined sample at 1000 °C were unfavorable (Figs. 13d and 13e). Therefore, the superior electrochemical performance of the sample calcined at 700 °C, could be ascribed to the interconnected mesoporous framework that would lead to the facilitation of Li-ion diffusion into the structure by shortening diffusion lengths and the strain/stress relaxation of the anode during charge/discharge processes. Moreover, the full-cell assembly of the prepared TiNb_2O_7 with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode resulted in the reversible capacity of 220 mAh/g at 1 C with the capacity retention of 82% after 1000 cycles.

Although there are very limited studies on the porous TNO anode materials for LIBs, the rate performance of mesoporous TiNb_2O_7 reported by Guo et al. [103], was superior to the other counterparts, as shown in Fig. 14. Writing a conclusion from only a few reports on porous TNO anode materials is not valid. Further investigations for comparing the electrochemical performance of porous TNO anodes prepared by soft and hard templates are proposed to be done in the future.

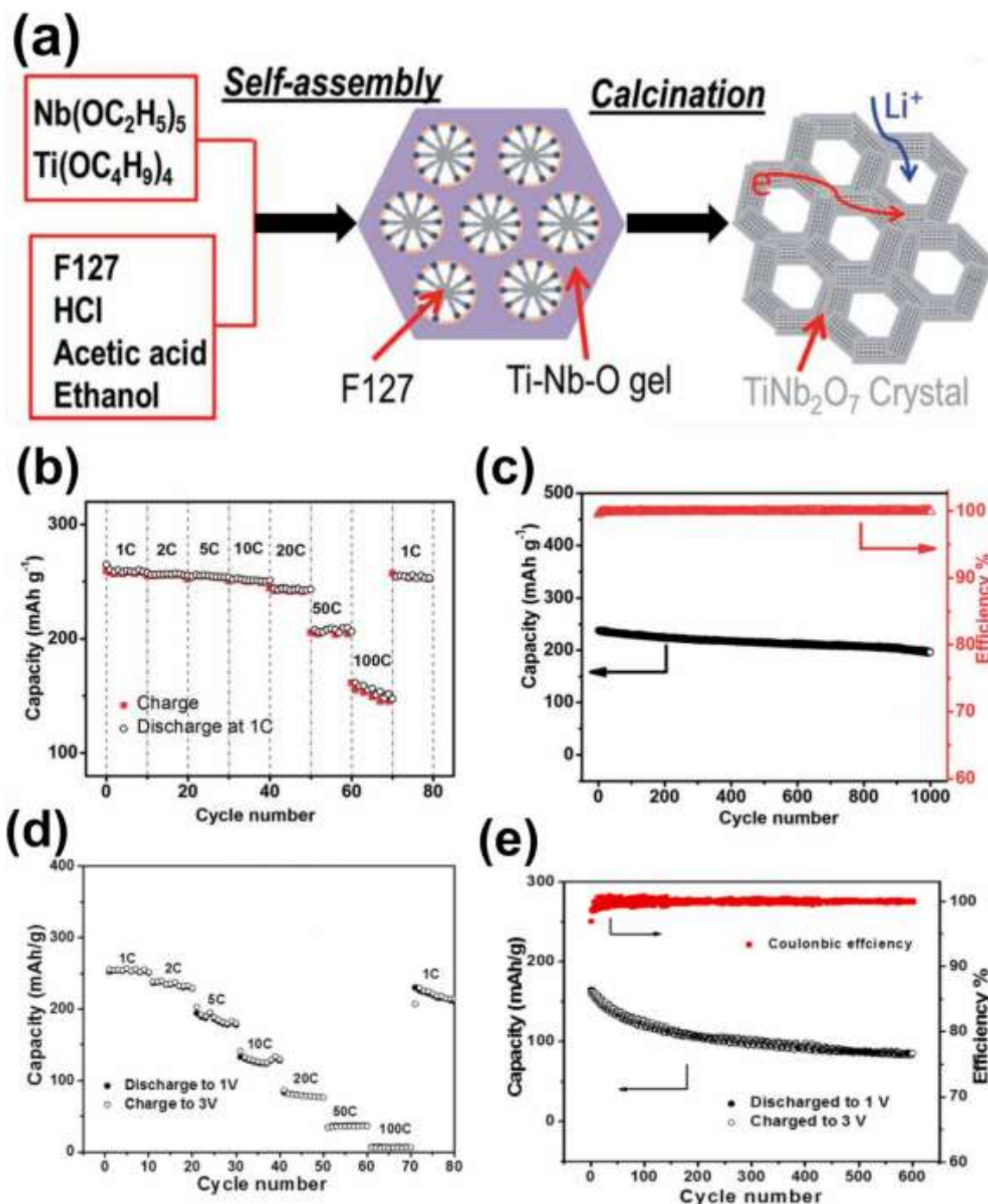


Fig. 13. Preparation method and electrochemical performance of the mesoporous TiNb_2O_7 ; (a) schematic illustration of the synthesis procedure of mesoporous TiNb_2O_7 by using copolymer F127 templates, (b) rate performance, and (c) cyclic performance (at 5C) of the sample calcined at 700 °C, (d) rate performance, and (e) cyclic performance (at 5C) of the sample calcined at 1000 °C [103].

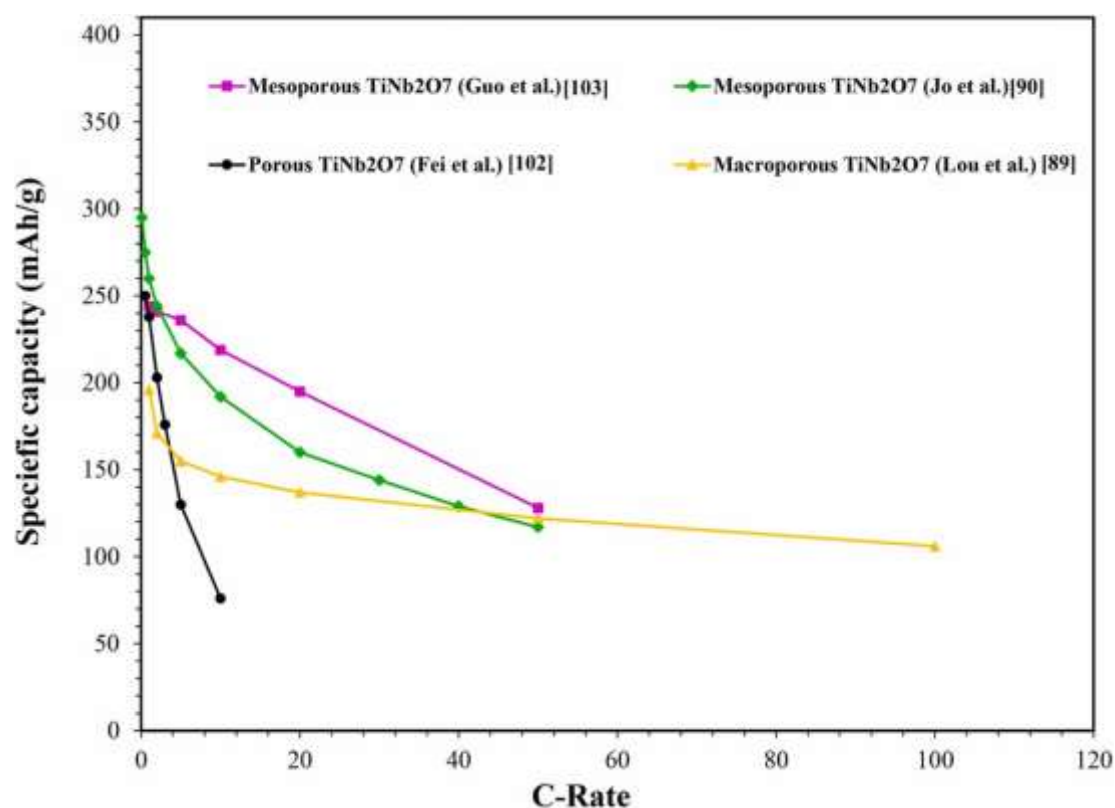


Fig. 14. The comparison of the rate capabilities of the reviewed porous TNO anodes in this study.

3.4. Comparison between the best reports of different morphologies

According to the reviewed papers in this work, we have compared the best electrochemical performance of each morphology for identifying the best morphology for TNO materials. As can be observed in Fig. 15, the TiNb₂O₇ nanospheres have the best electrochemical performance in comparison to the other morphologies. For example, at a high rate of 20 C, the capacities of TiNb₂O₇ nanospheres are about 23.7%, 33.8%, and 110.48% higher than those of TiNb₂O₇ nanotubes, TiNb₂O₇ mesopores, and Ti₂Nb₁₀O₂₉ nanoparticles, respectively. Therefore, based on these results, it can be deduced that the TiNb₂O₇ nanospheres are the best choice for the construction of LIBs.

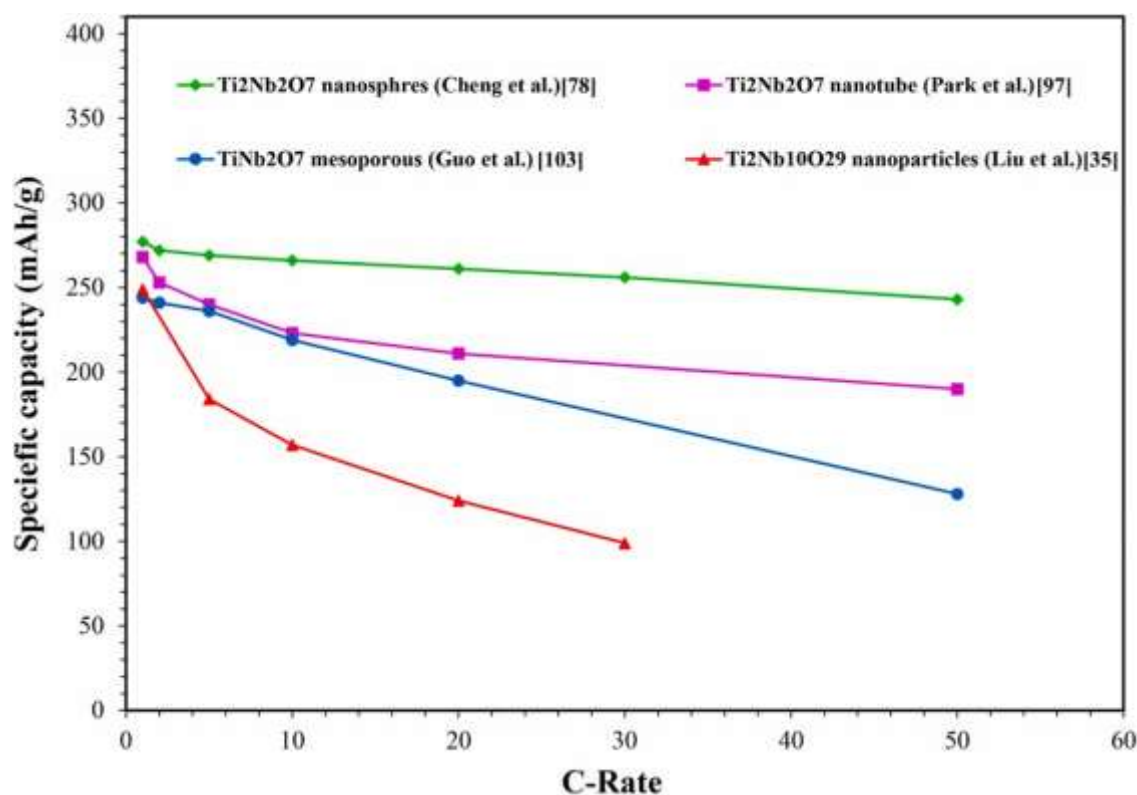


Fig. 15. The rate capability comparison of the best TNO anode materials with different morphologies.

4. TNO thin-films

Pulsed laser deposition (PLD) is a recognized method for producing thin films [110–113]. However, as far as the authors know, there are very limited studies on the Li-ion storage capability of the TNO thin films. There are several factors influencing the electrochemical performance of thin-film anodes prepared by the PLD method such as the deposition time and temperature and the applied pressure.

Daramalla et al. [114] investigated the electrochemical performance of LIBs constructed from TiNb_2O_7 thin films as the anode. They first synthesized TiNb_2O_7 powders using the solid-state method. The obtained powders were deposited on the $\text{Pt}(200)/\text{TiO}_2/\text{SiO}_2/\text{Si}(100)$

substrates using the PLD method at 750 °C for 40 min at two pressures of 50 and 100 mTorr, and the respective samples were denoted as TNO50 and TNO100. The morphological and electrochemical properties of both TNO50 and TNO100 samples are depicted in Fig. 16. Atomic force microscopy (AFM) was used to analyze the surface morphology and roughness of the samples. As can be seen in Figs. 16a and 16b, the surface roughness of the TNO100 samples (18 nm) was higher than that of the TNO50 (10 nm). The higher surface roughness of the TNO100 sample could be related to the presence of higher oxygen content in this sample. Also, the TNO100 sample consisted of spherical particles, while the TNO50 sample consisted of particles with different morphologies. The first charge/discharge curves of the TNO50 and TNO100 samples at a current density of 30 $\mu\text{A}/\text{cm}^2$ are respectively shown in Figs. 16c and 16d. The first discharge capacity of 175 $\mu\text{A}/\mu\text{m cm}^2$ was achieved, which was about two times higher than that of the TNO50 sample (88 $\mu\text{A}/\mu\text{m cm}^2$). As can be seen in Figs. 16e and 16f, the capacity of the TNO100 sample is almost twice that of the TNO50 sample in almost all cycles. The higher capacity of the TNO100 sample compared to the TNO50 sample could be attributed to its higher roughness and specific surface area.

In another study, Daramalla et al. [115] investigated the effect of the crystallinity of the TiNb_2O_7 thin films on their electrochemical properties. The PLD process was done at a constant pressure of 100 mTorr for 40 min at different temperatures of 400–750 °C. The structural, morphological, and electrochemical characteristics of the samples prepared at different temperatures are depicted in Fig. 17. The XRD results showed that the crystallinity of the thin film was enhanced by increasing the temperature from 400–750 °C, as can be seen in Fig. 17a. AFM and SEM images revealed that the amorphous TNO prepared at the temperature of 400 °C showed no specific morphology with the roughness of 8 nm, while the well-crystalline samples (prepared at the temperature of 750 °C) showed orientated morphologies with the

roughness of 15 nm. The electrochemical results demonstrated a significant difference between the capacities of the samples prepared at different temperatures.

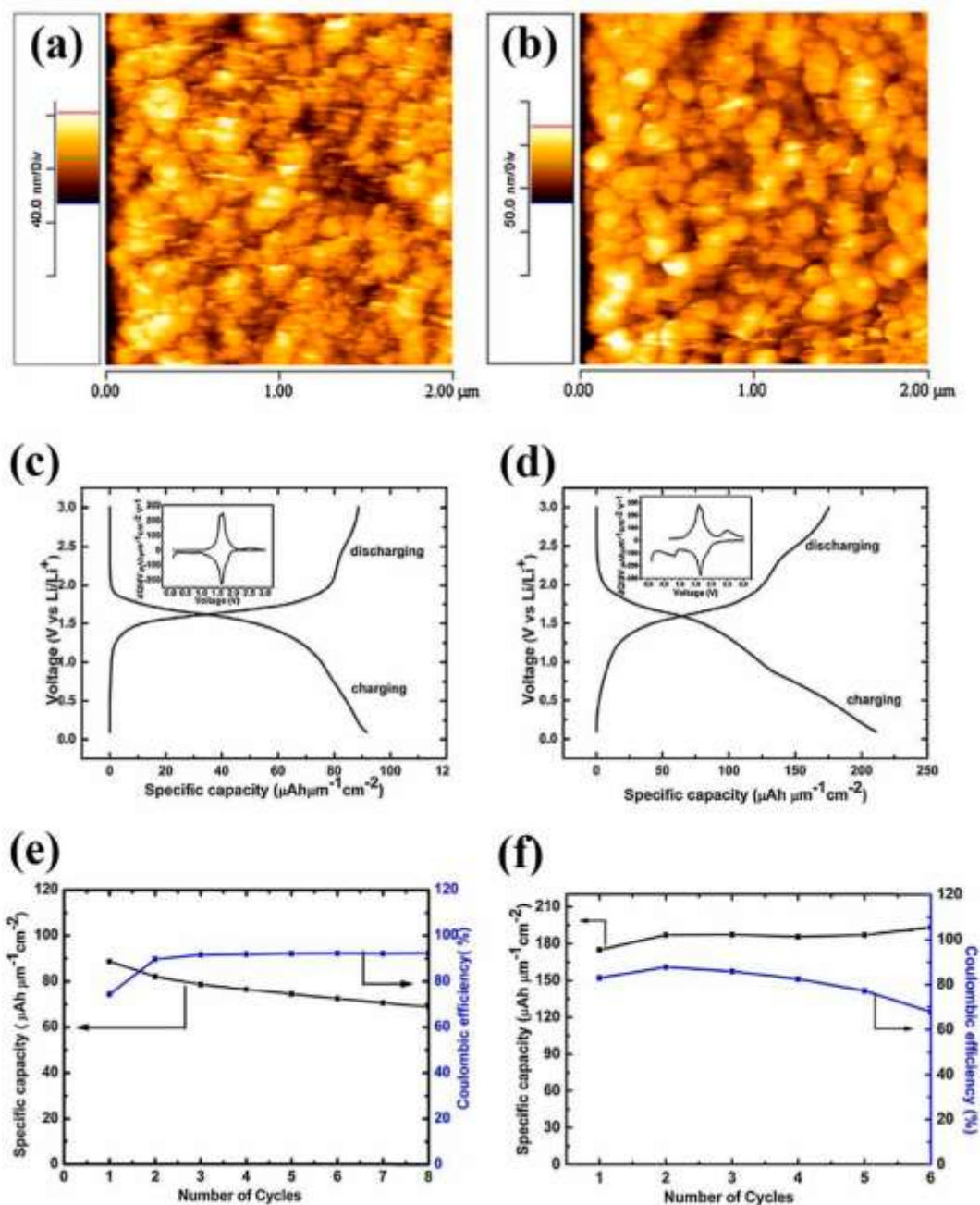


Fig. 16. Surface morphology and electrochemical performance of the TiNb₂O₇ thin-films; AFM images of (a) TNO50, and (b) TNO100, charge/discharge curves at 30 μA/cm² for (c) TNO50, and (d) TNO100, cyclic stability at 30 μA/cm² for (e) TNO50, and (f) TNO100 [114].

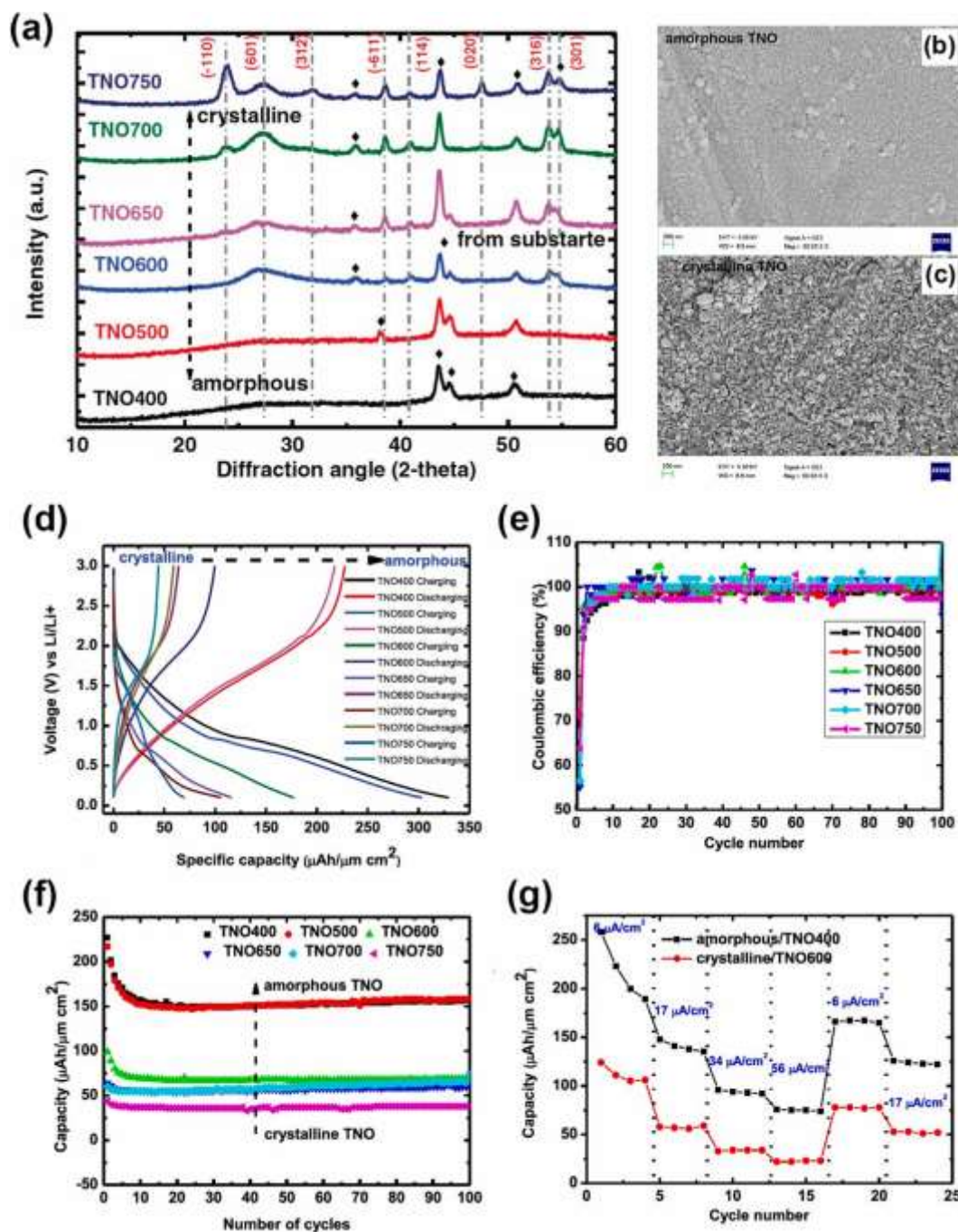


Fig. 17. Structural analyses and electrochemical properties of PLD deposited TiNb_2O_7 samples at different temperatures; (a) XRD patterns of the samples, (b) SEM image of TNO400, (c) SEM image of TNO 750, (d) charge/discharge curves of the samples at a current density of 17 $\mu\text{A}/\text{cm}^2$, (e) columbic efficiency of samples, (f) cyclic stability at a current density of 17 $\mu\text{A}/\text{cm}^2$, and (g) comparison between the rate performance of TNO400 and TNO600 samples [115].

As can be seen in Fig. 17d, the electrochemical results revealed a decreasing trend for the Li-ion storage capability of the TNO thin- film as a function of the degree of crystallization. For example, at a current density of $17 \mu\text{A}/\text{cm}^2$, the discharge capacities of TNO400, TNO500, TNO600, TNO700, and TNO750 samples (the number after TNO refers to the PLD temperature) were, respectively, 227, 217, 99, 64, 60, and $44 \mu\text{A}/\mu\text{m cm}^2$. This trend was also observed in the cyclic stability and rate performance behavior of the samples (Figs. 17f and g). The EIS results also confirmed the lower charge transfer resistance of the amorphous TNO sample in comparison with the crystalline TNO. The surface analyses after cycling showed a significant evolution in the morphology/roughness of the amorphous TNO.

5. Defective crystal structure design

The findings of works carried out on the $\text{TiNb}_2\text{O}_7/\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ anode materials have shown that their rate capability can be significantly improved by creating defects in their structures. For example, the presence of oxygen vacancies in the TNO structures can significantly improve their electrical/ ionic conductivity. Two general approaches of applying controlled heat treatment and solvent impregnation to create oxygen vacancy defects in TNO structures have been proposed in the literature [116–118].

So far, different calcination atmospheres to generate defective TNO structures have been investigated. Vacuum, argon, and nitrogen are the well-known mediums for generating defective TNO. For example, Lin et al. [119] prepared $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders through the solid-state method. For the creation of defects in the structure of the synthesized powders, the calcination step was done in an argon atmosphere at 1200°C for 4 h. For comparison, another sample was calcined in air. The XRD analyses proved the presence of the Ti^{3+} and Nb^{4+} along

with oxygen vacancies in the argon-calcined sample. The results demonstrated the presence of 6.6% oxygen vacancies in the argon-calcined powders and the exact chemical formula for the prepared powder was $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$. Moreover, the lattice parameter of the argon-calcined powders ($\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$) was larger than the air-calcined ones ($\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$). The increase in the lattice parameters could be related to the presence of the Ti^{3+} and Nb^{4+} ions, which have larger sizes compared to the Ti^{4+} and Nb^{5+} ions, respectively. Furthermore, the electrical conductivities of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders were investigated. The results showed that the electrical conductivity of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powder was only $1 \times 10^{-9} \text{ S.cm}^{-1}$, while it was $1.06 \times 10^{-3} \text{ S.cm}^{-1}$ for $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$. The low electrical conductivity of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ could be ascribed to the absence of free electrons in Ti^{4+} and Nb^{5+} cations, while the presence of Ti^{3+} and Nb^{4+} with unpaired electrons in $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ would improve the electrical conductivity. They also conducted the density-functional theory (DFT) for $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$. Fig. 18a shows the total density of states (TDOS) and partial density of states (PDOS) of both samples. As can be seen, the valance band of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ is located at -5.4 – 0.3 eV , while the conduction band is located at 1.9 – 6 eV with a bandgap of 1.6 eV . The high bandgap of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ shows its insulating feature. However, as can be seen in Fig. 18a, the fermi level of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ is inside of some bands, suggesting its conducting characteristics.

In addition, the rate performance and cyclic stability of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ samples were far superior to those of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. For example, as shown in Fig. 18b, increasing the C-rate from 0.1 to 5 C would lead to a decrease in the discharge capacity of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ slightly from 329 to 209 mAh/g (36.47% reduction). However, the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ loosed 75% of its discharge capacity (354 mAh/g) at 0.1 C by increasing the current density to 5 C. The lower polarization of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ compared to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ is shown in Fig. 18c, which would result in a better rate capability of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$. It is worth noting that both samples showed

good cyclic stability, but the capacity of $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ was about twice that of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ in all cycles (Fig. 18d).

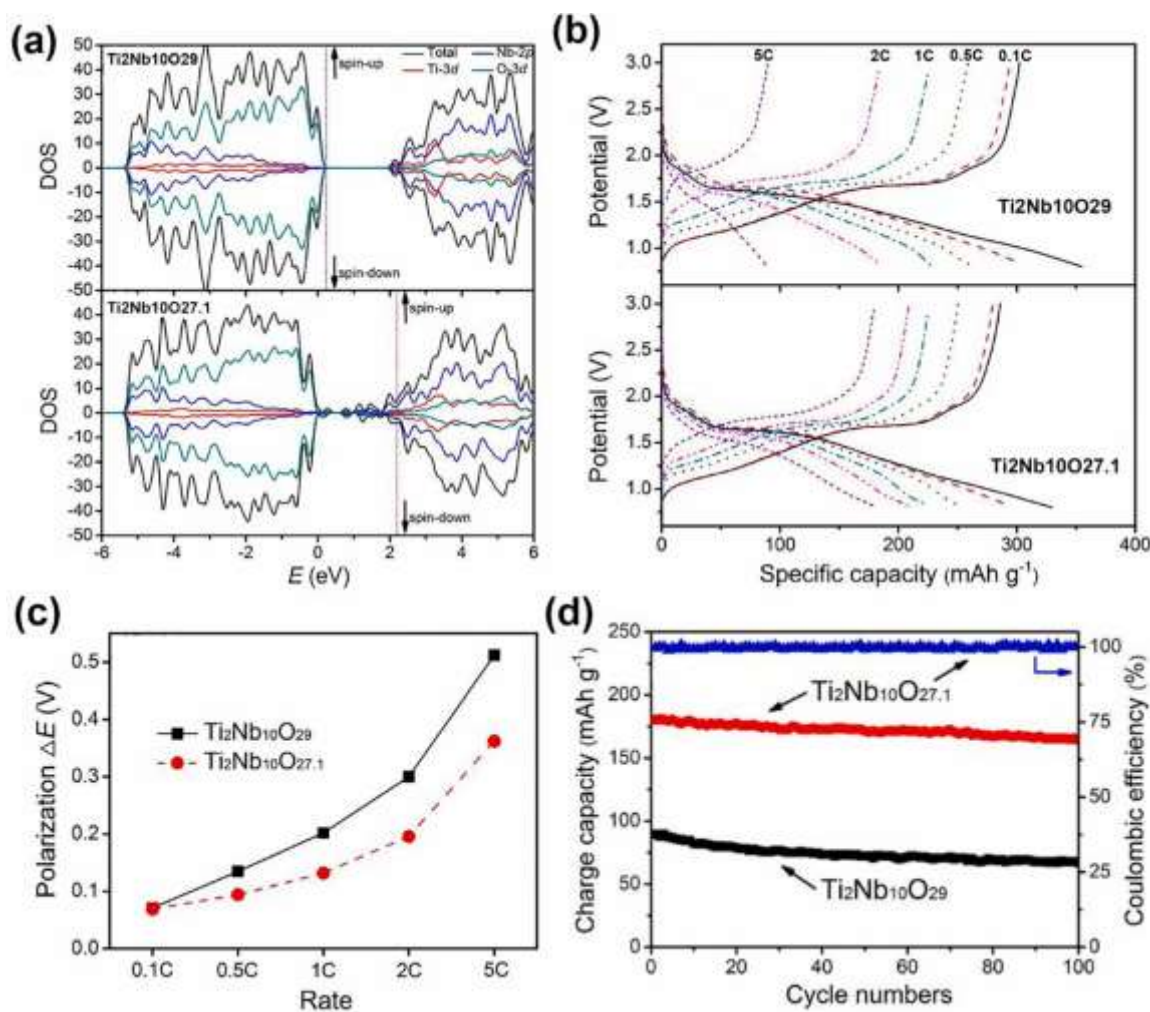


Fig. 18. Electrochemical performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$; (a) calculated TDOS and PDOS, (b) rate performance, (c) polarization value and (d) cyclic stability at 5C for half-cell LIBs with $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{27.1}$ electrodes [119].

Inada et al. [120] investigated the effects of calcination atmosphere on the electrochemical performance of TiNb_2O_7 anodes prepared by the solid-state route. In their work, the calcination step at 1050 °C for 2 h was conducted in vacuum and air conditions. Although the XRD patterns and morphological features of both samples were relatively similar, the color of air-calcined

powders was white, while vacuum-calcined powders had a blue color. The color- changing of TiNb_2O_7 can be related to the occurrence of the partial reduction phenomenon. Applying the thermogravimetric (TG) analysis under air resulted in the color-changing of the vacuum-calcined TiNb_2O_7 from blue to white. These results proved that the presence of oxygen vacancies in the vacuum-calcined TiNb_2O_7 was the main reason for its blue color. Electrochemical measurements revealed that the advantage of the vacuum-calcined TiNb_2O_7 compared to the air-calcined sample is more evident at higher charge/discharge rates and higher cycle numbers. For example, the results exhibited that by increasing the current density from 1 to 5 mA/cm^2 , the discharge capacity of the air-calcined TiNb_2O_7 decreased from 250 to 80 mAh/g (68% reduction). On the other hand, the vacuum-calcined TiNb_2O_7 only lost 44% of its capacity at 1 mA/cm^2 . Compared with the air- calcined TiNb_2O_7 , the improved electrochemical performance of the vacuum-calcined sample could be attributed to the electrical conductivity enhancement caused by the presence of oxygen vacancies.

In another research reported by Tojo et al. [121], $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ with oxygen defects were prepared via a solid-state reaction process followed by an annealing treatment. The effect of the annealing atmosphere on the crystal structure, morphology, electronic conductivity, and electrochemical performance of the produced TNO material was investigated. $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ samples annealed in the air (A-TNO) and vacuum (V-TNO) revealed nearly the same crystal structure, size, and morphology but the color of V-TNO was dark blue while it was white for the A-TNO. Due to thermogravimetric tests, oxygen defects were introduced to the V-TNO sample which led to the partial reduction of Ti^{4+} in V-TNO into Ti^{3+} . Consequently, much higher electronic conductivity was observed for the V-TNO material which enhanced its rate performance as the LIB anode. Both A-TNO and V-TNO anodes delivered the discharge capacity of $\sim 250 \text{ mAh}/\text{g}$ at the current density of 0.5 mA/cm^2 , while at the higher current

density of 10 mA/cm², V-TNO and A-TNO revealed the capacities of 150 and 50 mAh/g, respectively.

To improve the electronic conductivity and Li-ion diffusion coefficient, Deng et al. [108] employed a strategy including nanosizing and crystal structure modification. For this purpose, the solvothermal process followed by calcination in N₂ was adopted to produce Ti₂Nb₁₀O_{29-x} mesoporous microspheres with lower-valence Reproduced from [121]. cations (i.e., Nb⁴⁺ ions) and O²⁻ vacancies. Ti₂Nb₁₀O₂₉ was prepared by the same procedure but calcined in air. Fig. 19 shows the schematic illustration of the preparation method, structural analyses, and electrochemical evaluations of the obtained samples. The chemical valences of the produced samples were analyzed by XPS, as shown in Figs. 19b and 19c. The XPS peaks of Ti₂Nb₁₀O₂₉ demonstrated that the chemical states of Ti and Nb elements in this material are, respectively, Ti⁴⁺ and Nb⁵⁺. The Ti-2p_{3/2} and Ti-2p_{1/2} peaks in Ti₂Nb₁₀O_{29-x} did not shift (in comparison with Ti₂Nb₁₀O₂₉), but the Nb-3d_{5/2} and Nb-3d_{3/2} peaks shifted by 0.1 eV indicating the reduction of a small fraction of Nb⁵⁺ ions to Nb⁴⁺ ions in Ti₂Nb₁₀O_{29-x}.

CV curves revealed that crystal-structure modification did not affect the fundamental mechanism of the electrochemical reaction but decreased the polarization and improved the reaction kinetics. Additionally, the strong cathodic/anodic peak in CV curves was in good agreement with the discharge/charge plateau. The Nyquist plots of the samples are shown in Fig. 19d, and each plot is composed of two depressed semicircles and one slope. The depressed semicircles in the high and medium frequency ranges could be attributed to the interface parameters of the electrode and the charge-transfer resistance at the electrode-electrolyte interface, respectively. The slope in the low-frequency range could be related to the Warburg resistance, demonstrating the Li-ion diffusion coefficient. The results revealed that the presence

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<https://doi.org/10.1016/j.jallcom.2022.165117>

of O²⁻ vacancies and lower-valence cations in Ti₂Nb₁₀O_{29-x} could improve the electrochemical kinetics, significantly.

This is evident from the cyclic performance results in Fig. 19e. that the capacity retention of 90.2% and 92.1% is achieved after 100 cycles at 10 C, for the Ti₂Nb₁₀O₂₉/Li and Ti₂Nb₁₀O_{29-x}/Li cells, respectively, which could be ascribed to the outstanding structural stability of the mesoporous microspheres. The exceptional rate performance and large specific capacity of the Ti₂Nb₁₀O_{29-x} mesoporous microspheres can be attributed to their unique characteristics, including the presence of nanosized primary particles and the hierarchical structure of microspheres, increase in the Li-ion diffusion coefficient owing to the modification of crystal-structure, providing unpaired 4d electrons by the Nb⁴⁺ ions and therefore increasing the electronic conductivity of Ti₂Nb₁₀O_{29-x}, and the pseudocapacitive effect of the defective material.

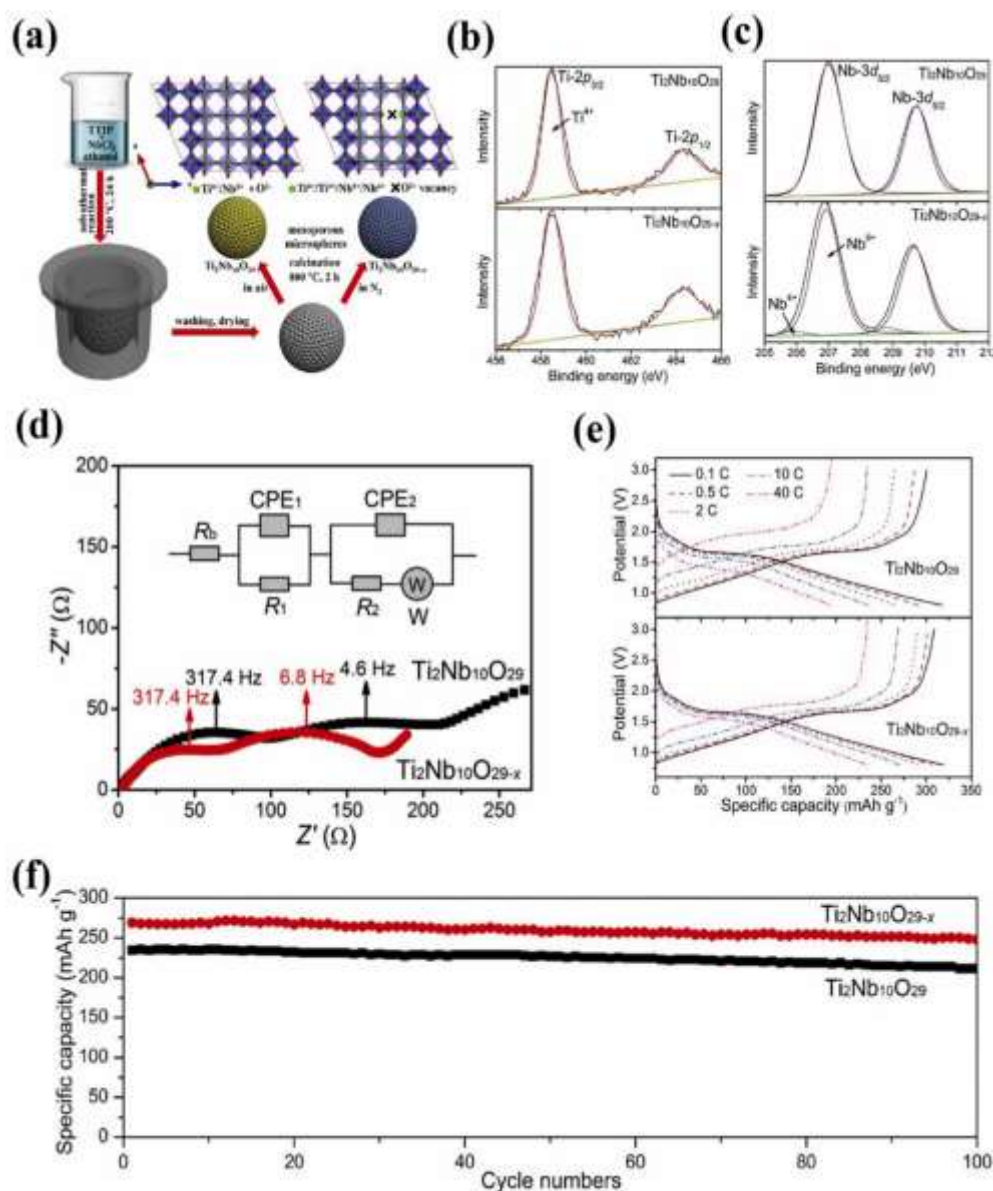


Fig. 19. Preparation method and properties of the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ mesoporous microspheres; (a) Synthesis processes and crystal structures of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ mesoporous microspheres, XPS spectra of (b) Ti and (c) Nb elements in $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}$ mesoporous microspheres, (d) Nyquist plots with selected equivalent circuit (inset) and (e) cyclic performance at 10 C for the $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}/\text{Li}$ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29-x}/\text{Li}$ cells.

Although most reports on the electrochemical performance of the defective TNO indicated the positive role of defects on the Li-ion storage capability of TNO, there is a conflicting report in this field. Adhami et al. [122] investigated the effect of calcination atmosphere on the

electrochemical properties of TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders synthesized by the solid-state method. They conducted the calcination step at 900 °C for 2 h in two atmospheres of air and argon. The findings revealed that for both TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders, the calcination treatment in an argon atmosphere would result in the preparation of powders with smaller crystal sizes. Electrochemical results indicated that for both TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ powders, the cyclic stability and rate performance of argon-calcined powders were lower than those of air-calcined powders. The EIS results demonstrated the faster Li-ion diffusion for air-calcined powders compared to argon-calcined samples.

In a recent study, Choi et al. [123] investigated the effects of oxygen vacancies and crystallinity of TiNb_2O_7 on its electrochemical performance by changing the calcination temperature and medium. They applied two calcination temperatures of 800 and 1000 °C in two atmospheres of air and vacuum. The samples were denoted as TNO-800-A, TNO-800-V, TNO-1000-A, and TNO-1000-V, in which A and V were used for air and vacuum. The results showed that increasing the calcination temperature would result in an increase in particles sizes due to the crystal growth phenomena. However, the calcination medium did not have a significant effect on the morphology of the produced samples. The findings indicated the presence of oxygen vacancies and also about 3% volume expansion in the vacuum-calcined samples. TEM images showed that the D-spacing of the (−303) plane increased from 0.34 to 0.36 nm by calcination under vacuum atmosphere at 1000 °C, compared to the calcination in air. Furthermore, the electrochemical tests showed that the first discharge capacities of 208, 215, 266, and 284 mAh/g were achieved at 0.05 C for TNO-1000-A, TNO-1000-V, TNO-800-A, and TNO-800-V, respectively. The cyclic stability tests at 2 C indicated that the presence of oxygen vacancies can increase the capacity retention from 92.9% to 100%.

Another method to create oxygen vacancies in the TNO structure is ethanol impregnation, but there is only one reported study in this field of research. Zhang et al. [116] studied the effect of oxygen vacancies on the electrochemical performance of TiNb_2O_7 anode materials for LIBs. After synthesizing TiNb_2O_7 powders by the solvothermal method, the calcination process was conducted in two different atmospheres of argon (denoted as Ar-TNO) and air (referred to as TNO) at 750 °C for 3 h. The air-calcined samples were then mixed with ethanol and placed in an autoclave for heating at 250 °C for 1 h (referred to as S-TNO). The morphological studies indicated the production of more uniform nanoparticles in terms of size and morphology for S-TNO samples compared to the other two samples. The structural and electrochemical properties of the samples are given in Fig. 20. The SSA of the S-TNO (39.77 m^2/g) was respectively about 19% and 30% higher than those of Ar-TNO and TNO samples (Fig. 20a). The XPS analyses revealed the occurrence of peak shifting for oxygen, titanium, and niobium to lower binding energies, indicating the presence of atoms with lower valance states (Figs. 20b to 20d). The results showed that the oxygen vacancies of the S-TNO and Ar-TNO were, respectively, about 9 and 5 times higher than those of the TNO sample. The reason for the higher oxygen vacancy in the S-TNO sample can be explained as the oxygen captured from TNO by ethanol through reflux and subsequent heat treatment process, resulting in the production of vacancies in TNO.

The results proved that although there was no considerable difference between the initial capacities of the samples at a current density of 100 mA/g, the capacity retentions of the S-TNO (72.97%) and Ar-TNO (71.77%) samples were much higher than that of the TNO sample (47.07%) after 300 cycles. Moreover, the rate performance of the S-TNO sample was better than the other samples at all charge/discharge rates (Fig. 20e). The EIS results demonstrated the positive effects of oxygen vacancies in reducing the charge transfer resistance of samples (Fig. 20f). In other words, the charge transfer resistance of the S-TNO and Ar-TNO samples

were, respectively, about 22.36 and 37.76 Ω which were much lower than that of the TNO sample (81.2 Ω). As can be seen in Fig. 20g, similar behavior is also observed for the cyclic performance of the samples.

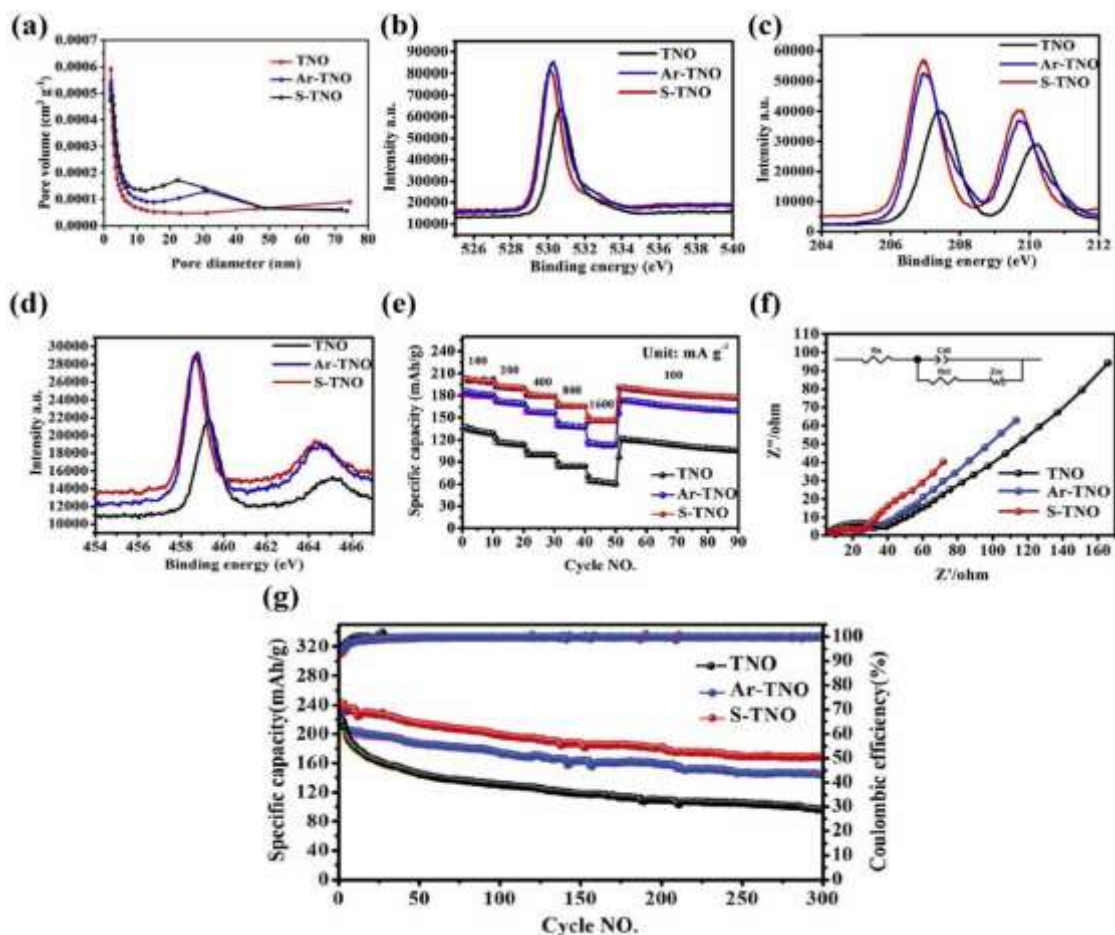


Fig. 20. Structural analyses and electrochemical performance of the samples treated by the ethanol impregnation method, (a) pore size distribution of the samples, XPS survey spectra of (b) O 1s, (c) Nb 3d, and (d) Ti 2p of the samples, (e) rate performance, (f) Nyquist plots and (g) cyclic stability of the samples at 100 mA/g [116].

6. Full cell considerations

To investigate the usability of the TNO anode materials for practical LIBs, the electrochemical performance of full-cell LIBs should be studied. So far, only few experiments on the use of TNO materials in full-cell LIBs have been performed. LiFePO₄ (LFP),

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<https://doi.org/10.1016/j.jallcom.2022.165117>

LiNiMnCoO₂ (NMC), and LiNi_{0.5}Mn_{1.5}O₄ (LMNO) are the investigated cathode materials for the construction of full-cell LIBs with TNO anode materials [103,124–126]. Cheng et al. [124] reported the fabrication of bulk Ti₂Nb₁₀O₂₉ by solid-state reaction (ball-milling) of TiO₂ and Nb₂O₅ precursors. In the half-cell configuration, the prepared Ti₂Nb₁₀O₂₉ anode delivered a capacity of 144 mAh/g after 800 cycles at 10 C. To further understand the structural changes of Ti₂Nb₁₀O₂₉ during cycling, the XRD patterns of Ti₂Nb₁₀O₂₉ were recorded after 1st, 100th, and 800th charging cycles. The results showed that no new peak and no peak shifting appeared even after 800 cycles, which confirmed the high cycling stability of the prepared material. The construction of a full-cell by coupling the anode with an LFP cathode led to a specific capacity value of 100 mAh/g after 1000 cycles at 1 C.

As mentioned earlier, Guo et al. [103] synthesized mesoporous TiNb₂O₇ using polymeric templates and investigated the applicability of the optimum sample for LIBs by constructing a full-cell with LNMO cathode. The reversible capacity of 220 mAh/g at 1 C with a capacity retention of 82% after 1000 cycles was delivered. In another study, Jayaraman et al. [127], synthesized all parts of full-cell LIBs in the form of nanotubes using electrospinning. They constructed the LIBs using TiNb₂O₇, Polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) nanofibers, and LiMn₂O₄ nanofibers as the anode, separator, and cathode, respectively. The electrochemical measurements at 1 C (based on the theoretical capacity of the cathode material), showed that the first discharge and charge capacities of 116 and 138 mAh/g were respectively achieved for the full-cell assembly. The fuel-cell retained 79% of its capacity after 200 cycles.

Energy density is one of the most important considerations for the usability of anode materials in full-cell LIBs. However, there are very limited studies to calculate the energy density of full-cell LIBs with TNO anodes. Lyu et al. [128] prepared a series of TNO@C/NMC

full-cells with different TNO loadings, from 4.3 to 13.4 mg/cm². The results revealed that the full-cell with TNO mass loading of 9.5 mg/cm² exhibited the highest energy density of 114.7 Wh/kg and a volumetric energy density of 287 Wh/L. Additionally, the specific capacities and the energy densities of full-cells increased with increasing cut-off voltages. However, the calculated energy density of the TNO@C/NMC full cell was about 110 Wh/kg even with an upper cut-off voltage of 3.0 V. After the optimization of active material loading and upper cut-off voltage, the TNO@C/NMC full-cell delivered a high energy density of 142.8 Wh/kg (357 Wh/L) and a good energy density retention over 80% after 500 cycles. In another study, Takami et al. [129] fabricated large-size LIBs using NMC cathode and TNO anode. These batteries showed high energy densities of 350 Wh/L and 138 Wh/kg.

Although the mentioned reports are promising for the commercialization of the TNO anodes in practical LIBs, some reports have reported significant issues. As mentioned in the introduction section, Ti-based anode materials are called safe anode materials because of their high working voltage which inhibits the SEI formation on their surface. However, there are some reports in the literature about the formation of the SEI layer on the TNO surface, which acts as a barrier to using TNO anode materials in LIBs. As far as the authors know, there are some signs of SEI formation on the TNO surface in some reports, but mainly without discussion of its formation mechanism.

Wu et al. [125] attempted for the first time to explain the formation mechanism of the SEI layer on the TNO surface and its impact on the usability of the TiNb₂O₇ anode in full-cell LIBs. They prepared TiNb₂O₇ particles by ball-milling of TiO₂ and Nb₂O₅ precursors and then calcining them at 1000 °C for 24 h in air. The electrochemical results of half-cell and full-cell LIBs prepared by TiNb₂O₇ are given in Fig. 21. The results showed that the reversible capacity of 256 mAh/g was achieved at 0.1 C. Also, the capacity retention of the TiNb₂O₇ at 0.1 C and

after 200 cycles was 64.8% (173.4 mAh/g). The XPS and EIS results demonstrated the SEI formation on the anode during cycling. The findings indicated the SEI formation on TiNb_2O_7 during the lithiation process and its partial dissolution during the de-lithiation process, demonstrating the low stability of the SEI layer of the TiNb_2O_7 . However, an increase in the thickness of the SEI layer by progressing the cycle numbers was approved by their results. These results were also proved by SEM analyses, as shown in Figs. 21a to f. The SEI formation after 200 cycles can also be demonstrated by Nyquist plots of the samples before and after cycling (Fig. 21h and i).

Furthermore, the useability of the TiNb_2O_7 was investigated by the construction of full-cell LIBs using TiNb_2O_7 and LiFPO_4 as the anode and cathode materials, respectively. As can be seen, the full-cell lost about 25% of its initial capacity only after ten cycles, indicating the poor cyclic stability of the battery. The battery images at different temperatures revealed the occurrence of a swelling phenomenon due to the gas formation during cycling (Figs. 21k to m). In literature, there are two hypotheses for gas generation on LTO and TNO anode materials. The first hypothesis is based on the electrolysis of present water in electrolytes, resulting in the generation of H_2 . The other idea is based on the reaction between $\text{Ti}^{4+}/\text{Nb}^{5+}$ and carbonates that leads to the formation of the CO_2 , CO gases, and the formation of the SEI layer on the TNO. To address the gas formation and swelling phenomena, they proposed that the addition of ascorbic acid in the electrolyte can prevent the SEI formation and the following gas formation problems (Fig. 21n to q).

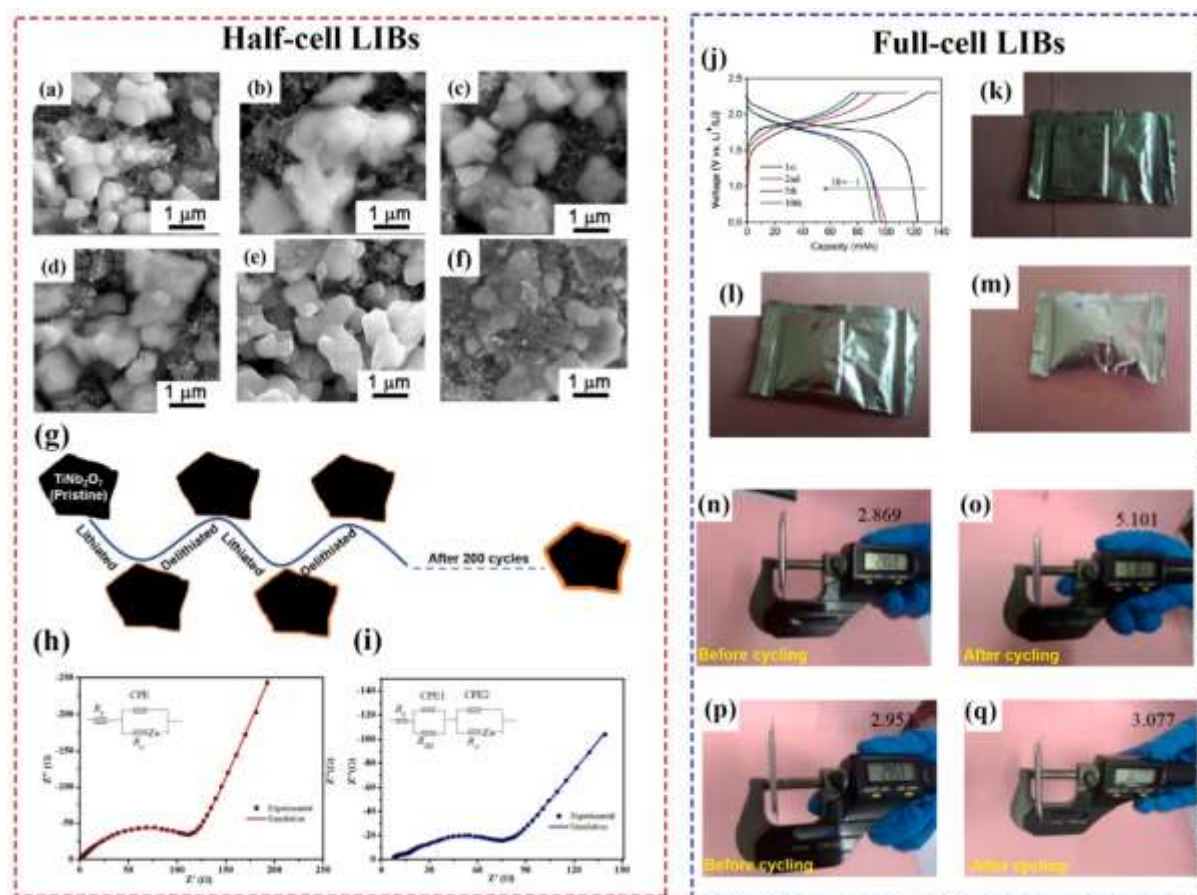


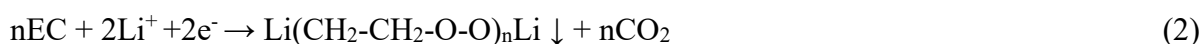
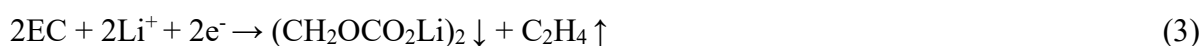
Fig. 21. Electrochemical performance of the TNO/Li half-cell and TNO-LFP full-cell batteries; SEM images of the TNO/Li half-cell at different conditions for the first cycle f charge/ discharge (a) before cycling, (b) 50% full discharge, (c) 100% full discharge, (d) 50% full-charge, (e) 100% full-charge, (f) SEM image of sample after 200 cycles, (g) schematic illustration of the SEI formation on the TNO anode after cycling, (h) Nyquist plots of TNO before cycling, (i) Nyquist plots of TNO after cycling, (j) charge/discharge curves of TNO/LFP full cell for different cycle numbers, (k) image of TNO/LFP full cell before tests, and swelling phenomenon for TNO/LFP full cell at (l) 25 C and (m) 40 C, thickness measurement of the TNO/LFP full cell in different conditions of (n) before cycling without addition of VC to electrolyte, (o) after 250 cycling without addition of VC to electrolyte, (p) before cycling with addition of VC to electrolyte, (q) after 250 cycling with addition of VC to electrolyte [125].

In another experimental study, Buannic et al. [130] reported the gas generation and poor cyclic stability of the TNO anode materials in full-cell LIBs. They used the solvothermal method followed by the solid-state route to improve the electrochemical properties of the TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ anode materials. For comparison, they also prepared samples by solvothermal and solid-state methods. They also investigated the effects of calcination temperatures of 750 and 950 °C for preparing the samples. The results showed that the application of lower calcination temperature resulted in the lower crystallinity of the product in addition to the presence of some Nb_2O_5 impurities. However, the higher calcination temperature led to the formation of high-purity samples with a high degree of crystallinity. The BET results showed the higher SSA of the solvothermal synthesized samples than those prepared by the solid-state route. The electrochemical results of half-cell and full-cell LIBs are shown in Fig. 22. The half-cell measurements revealed the highest capacity and the lowest capacity fading for both TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ samples prepared by a combination of solvothermal and solid-state methods (Figs. 22a and 22b). They examined the application of the TiNb_2O_7 anodes prepared by combining the solvothermal and solid-state methods, in the full-cell assembly. For this purpose, two different cathode materials of LMNO and NMC were used. Two TiNb_2O_7 powders with SSA values of 32 m^2/g (marked as TNO7–32) and 6 m^2/g (marked as TNO7–6) prepared, respectively, at calcination temperatures of 750 and 950 °C, were used as the anodes. They also investigated the electrochemical performance of LTO anodes in full-cell LIBs, for comparison.

The results showed that the LTO sample maintained its initial capacity value after 150 cycles. However, the TNO7–32 sample lost its initial capacity quickly as a function of the cycle numbers and its capacity was lower than the LTO sample. The Li-ion consumption by the thick SEI layer can be the reason for this large capacity fading, which can be attributed to the high

SSA of this sample. Although the initial capacity of the TNO7–6 sample was lower than that of the TNO7–32 sample, its capacity fading was so lower than that of the TNO7–32 one. The lower SSA of the TNO7–6 sample compared with the TNO7–32 can be introduced as the main reason for its higher capacity retention. The lower SSA of the TNO7–6 electrode implies the homogenous coverage of the carbon black. Moreover, they examined the gas generation of the mentioned electrodes during cycling. The results showed the lower gas generation values over time for the TNO7–6 sample compared with the TNO7–32 sample (Figs. 22c to f). Therefore, the higher capacity fading of the TNO7–32 sample can be attributed to its higher gas generation. A similar trend is also observed for the full-cells with NMC cathode, while in this condition, the gas generation of the full-cell with LTO is lower than both investigated TNO samples (Fig. 22g). These results revealed the occurrence of side reactions between the electrolyte and Nb cations in TNO samples. Consequently, the use of electrolyte additives can be efficient for the reduction of gas generation in full-cell LIBs.

As mentioned above, gas generation is a significant issue for the TNO anode materials. In a recent study reported by Parikh et al. [126], mass spectrometry (MS) was done to evaluate the gas generation of LIBs with TNO/Li half-cells, NMC/Li half-cells, and TNO/ NMC full cells. The TNO particles were prepared using the sol-gel method. The results revealed that the C₂H₄, CO₂, and O₂ gases were detected by MS. However, they stated that the H₂ gas is also present but it cannot be detected by the MS method. The formation of the mentioned gases can be related to the reduction of the ethylene carbonate (EC) component of electrolyte at the surface of TNO to form the SEI layer, according to the following equations:



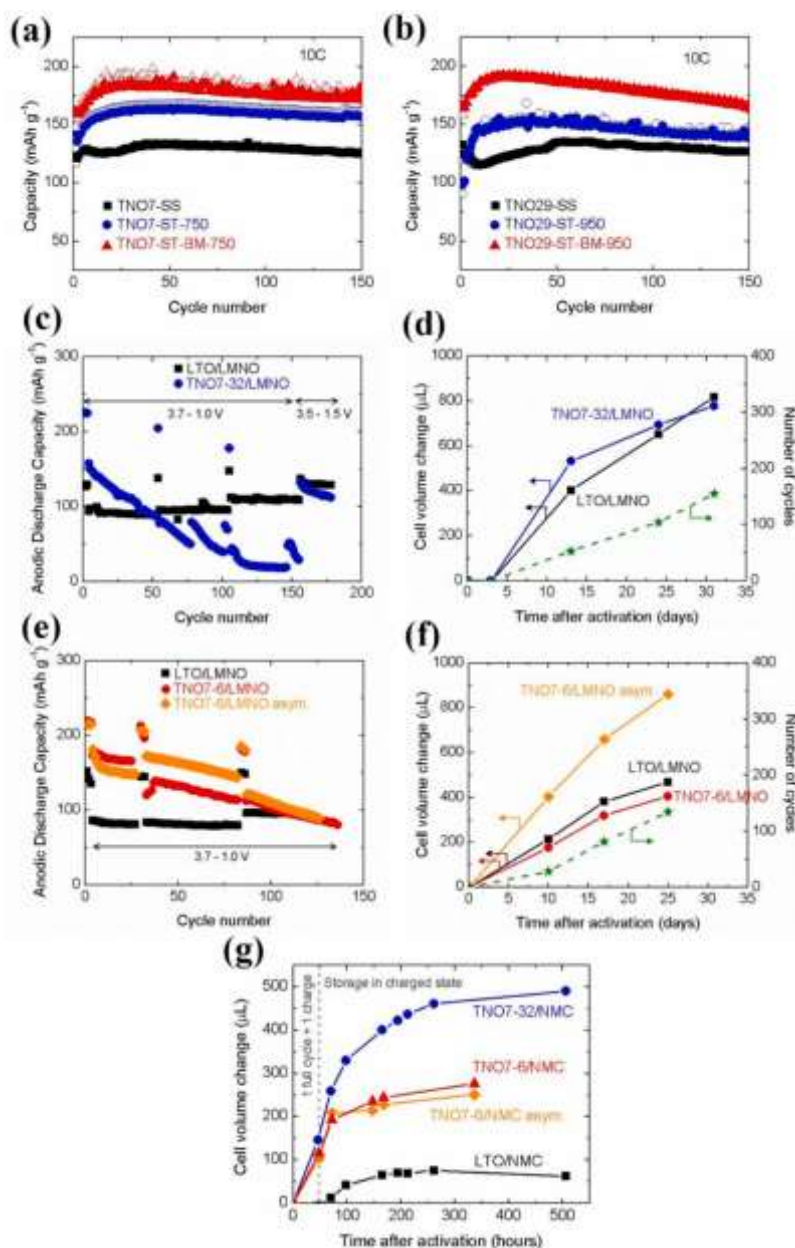


Fig. 22. The electrochemical performance of the TNO in both half-cell and full-cell assemblies; (a) cyclic performance of TiNb_2O_7 half-cell sample prepared by different approaches of solvothermal, solid-state, and combination of the solvothermal and solid-state methods, (b) cyclic performance of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ half-cell sample prepared by different approaches of solvothermal, solid-state and combination of the solvothermal and solid-state methods, (c) comparison of the cyclic performance of TNO7/LMNO and LTO/LMNO full-cells at 1C, (d) comparison of the cell-volume changes of TNO7/LMNO and LTO/LMNO full-cells, (e) comparison of the cyclic performance of TNO32/LMNO and LTO/LMNO full-cells at 1C, (f) comparison of the cell-volume changes of TNO32/LMNO and LTO/LMNO

full-cells and (g) comparison of the cell-volume changes of TNO7/NMC TNO32/NMC and LTO/NMC full-cells [130].

The gas evolution and TEM images of the SEI formation on the TNO surface are shown in Fig. 23. As can be observed in Fig. 23a, the lithiation (discharge) process for TNO/Li half-cell releases the highest amount of C₂H₄ gas. On the other hand, the amount of the released gas species decreased with the progress of the delithiation (charge) process. These observations could be related to the dynamic formation and dissolution of the SEI layer. The TEM images (Figs. 23b and 23c) indicated the formation of the SEI layer. The electrochemical investigation of the NMC/Li half-cells at 3–4.4 V indicated an increment in the amount of CO₂ gas at the end of the delithiation process (charge). According to Eqs. (4)–(6), the formation of HF and oxidation of EC resulted in the decomposition of LiCO₃ and the formation of CO₂, as follows:



The results showed that CO₂ gas generation is more severe in full-cells compared to the TNO/Li and NMC/Li half-cells. In full-cell configurations, the CO₂ gas is released by breaking the SEI layer through the discharge process. However, the amount of the released C₂H₄ gas in full-cell configurations is less than half-cell LIBs. They also investigated the rate effects on the gas evolution of the half-cell and full-cell LIBs (Figs. 23d to f). In the case of the TNO/Li half-cells, the amount of all gas species increased as a function of the C-rate. For example, by increasing the C-rate from 0.1 to 3, the amount of the released C₂H₄ increased from 1.8 to 42.8 nmol.min⁻¹.g⁻¹. The increase in the gas generation of the TNO/Li half-cells can be related to the polarization of the TNO to the lower electrochemical potentials and the facilitation of electrolyte decomposition.

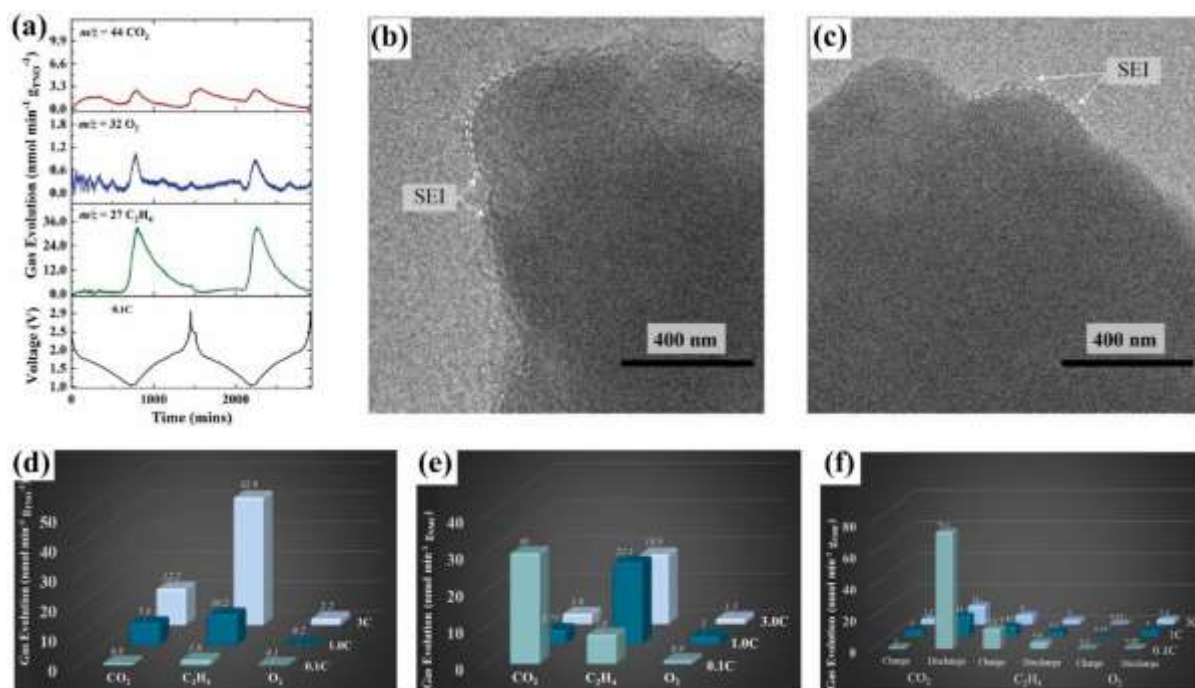


Fig. 23. (a) Voltage and gas evolution of the TNO/Li half-cell as a function of time, (b) TEM image of TNO electrode after complete Li insertion during the first cycle, (c) TEM image of TNO electrode after complete Li insertion after two cycles, (d) gas evolution of TNO/Li as a function of C-rate, (e) gas evolution of NMC/Li as a function of C-rate, and (f) gas evolution of TNO/NMC as a function of C-rate [126].

7. Summary and perspectives

In this study, the publications on the electrochemical performance of pure titanium niobium oxide (TNO) compounds as anode materials for LIBs were reviewed. The literature review showed that morphological controlling and defect engineering are the two main approaches for improving the electrochemical performance of pure TNO anode materials. Moreover, the application of TNO compounds in full-cell LIBs was studied in this work. The main points of reviewed studies and our suggestions for future works are summarized as follows:

1. The solid-state method is a well-known route for the synthesis of TNO materials with particulate morphologies. However, the application of other methods such as sol-gel and

solvothermal can lead to the production of TNO materials with smaller particle sizes and consequently, better electrochemical properties. The particulate TNO materials are proper for large-scale production and industrialization, but their properties are weaker than other morphologies. Therefore, more investigations should be carried out to improve the electrochemical performance of TNO anode materials synthesized by the solid-state method. It is proposed to study the effect of different solid-state parameters on the particle size of the obtained TNO material in the future, to achieve materials with smaller particle sizes.

2. One-dimensional TNO structures are mostly synthesized using the sol-gel and electrospinning methods. Findings showed that by increasing the porosity and also fabricating hollow one-dimensional structures, the electrochemical properties, especially the rate capability, can be improved due to the decreased Li-ion diffusion pathways. The electrospinning method is not applicable for large-scale production, while the template-assisted sol-gel method can be developed for the industrialization of one-dimensional TNO anodes.
3. Three-dimensional spherical and porous TNO structures have been introduced as superior materials for high-rate Li-ion batteries. The porous microsphere and nanosphere morphologies can be achieved using solvothermal methods. By using size- controlling agents, the electrochemical performance of spherical TNO structures can be significantly improved. Moreover, it has been reported that the formation of hollow microspheres can improve the rate capability of TNO materials by decreasing the Li- ion pathways. Three-dimensional porous structures can be also synthesized using the template-assisted sol-gel approach (polymeric and ceramic templates). Compared to the other TNO morphologies,

few studies have focused on three-dimensional porous structures, consequently, further studies in this field are needed.

4. According to the reviewed papers in this study, we have compared the best electrochemical performance obtained from each specific morphology to identify the greatest morphology for TNO materials. Our comparison findings revealed that the TiNb_2O_7 nanospheres show the best electrochemical performance, compared with other morphologies. For example, at a high rate of 20 C, the capacities of the TiNb_2O_7 nanospheres are about 23.7%, 33.8%, and 110.48% higher than those of TiNb_2O_7 nanotubes, TiNb_2O_7 mesoporous material, and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ nanoparticles, respectively. Also, the synthesis of TNO hollow nanospheres can be introduced as the next interesting topic in this field.
5. Apart from morphological engineering, the literature review showed that the rate performance of the TNO anodes can be significantly improved by creating structural defects through various mechanisms. Performing controlled calcination treatment under different atmospheres (such as vacuum, argon, and nitrogen instead of air), and ethanol impregnation are the two main reported approaches to partially reduce Ti^{4+} to Ti^{3+} and Nb^{5+} to Nb^{4+} to generate oxygen vacancies. The published papers regarding defect engineering processes are mainly focused on TNO materials with particulate morphologies and therefore, further investigations on other morphologies of TNO such as one- dimensional and spherical ones should be performed.
6. Few studies have been performed on the application of TNO compounds in full-cell LIBs. There are some reports in the literature on the gassing problem and subsequent, swelling and high capacity fading of LIBs. Therefore, more studies should be focused on solving the gassing problem of the TNO anodes for fuel-cell applications.

7. Despite the numerous advantages of TNO anodes, there are still several challenges in their commercialization that need to be addressed. For example, despite the advantages of their relatively high redox potential, it leads to a reduction in the energy density of the TNO full-cells. Therefore, further research are required on discharging TNO anodes at lower cut-off potentials, using proper high-potential cathodes, and designing suitable full-cells should be carried out.
8. Although TNO anodes have high theoretical capacities, further explorations should be carried out to increase the lithiation/delithiation ability of TNO anodes at high C-rates and to meet the commercial requirements to achieve high energy and high-power LIBs. In this regard, it is beneficial to employ some strategies that include morphological control, introducing vacancies or dopants into TNO, making TNO-based composites, and increasing the ionic and electronic conductivities of TNO materials. Another important issue for the commercialization of TNO full batteries is the possibility of gas generation. The absence of an SEI layer on the surface of TNO anodes can result in the evolution of harmful gases due to the degradation of the electrolyte at the TNO/electrolyte interface. Another obstacle to the industrialization of the TNO anode materials is the cost of their elements which suggests the application of TNO-based LIBs in special cases.

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