Dual Phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 Nanowire Arrays as Integrated Anodes for High-rate Lithium-ion Batteries

Jin-Yun Liao,^a Victor Chabot,^a Meng Gu,^b Chongmin Wang,^b Xingcheng Xiao,^{c,*} Zhongwei Chen^{a,*}

^aDepartment of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1;

^bEnvironmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, USA

^cGeneral Motors Global Research & Development Centre, 30500 Mound Road, Warren, Michigan 48090, United States.

Corresponding Author

Dr. Xingcheng Xiao

E-mail: xingcheng.xiao@gm.com

Dr. Zhongwei Chen

E-mail: zhwchen@uwaterloo.ca

Phone: 519-888-4567 ext. 38664

Fax: 519-746-4979

Abstract

Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is well known as a zero strain material inherently, which provides excellent long cycle stability as negative electrode for lithium ion batteries. However, the low specific capacity (175 mA h g^{-1}) limits it to power batteries although the low electrical conductivity is another intrinsic issue need to be solved. In this work, we developed a facile hydrothermal and ion-exchange route to synthesize the self-supported dual-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire arrays to further improve its capacity as well as rate capability. The ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to TiO_2 in the dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire is around 2:1. The introduction of TiO_2 into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ increases the specific capacity. More importantly, by interface design, it creates a dual-phase nanostructure with high grain boundary density that facilitates both electron and Li ion transport. Compared with phase-pure nanowire $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 nanowire arrays, the dual-phase nanowire electrode yielded superior rate capability (135.5 at 5 C , 129.4 at 10 C , 120.2 at 20 C and $115.5 \text{ mA h g}^{-1}$ at 30 C). *In-situ* transmission electron microscope clearly shows the near zero deformation of the dual phase structure, which explains its excellent cycle stability.

Keywords

Li-ion batteries; $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 ; Dual phase; Nanowire arrays;

1. Introduction

As the alternative power source of choice for most portable electronic devices and a promising energy-storage candidate in electric vehicle and renewable energy systems, rechargeable lithium ion batteries attract great attention and have actively changed our lifestyles.[1-6] As well known, the commercial market for anode materials is dominated by graphite-based materials. However, there are still some safety concerns, particularly when used for high power batteries.[7-10] One of the key safety issues is the dendritic lithium growth on the surface of graphite-based anodes at high current density when the potential approaches almost 0V (vs. Li/Li^+) at the end of Li insertion. Being inherently safe and chemically compatible with the electrolyte, titanium oxide based materials (e.g. TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$) have been considered to be alternatives to graphite-based anodes in Li-ion batteries.[10-14] Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with a theoretical capacity of 175 mA h g^{-1} has a very flat Li ion insertion potential at around 1.55 V (vs. Li/Li^+), which will not form a solid electrolyte interphase (SEI) layer due to the higher reduction potential of electrolyte solvents. As a “zero-strain” material, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has excellent structural stability with an almost negligible volume change during the Li^+ insertion and extraction processes, indicating virtually unlimited cycle life.[15-18] On the other hand, low cost and environmentally friendly anatase TiO_2 is generally considered to be one of the best lithium ion hosts among the TiO_2 polymorphs, due to its fast Li ion insertion/extraction, high insertion potential (2.0 V), low volume expansion (3-4%) during lithium insertion, and high theoretical capacity of 336 mA h g^{-1} . [19-22] Despite these advantages, both materials still suffer from extremely low electronic conductivity and ion conductivity, which seriously limit rate performance. Recently, we reported TiO_2 -C/ MnO_2 core-

double shell nanowire arrays as anode electrode to improve both electronic conductivity (carbon) and capacity (MnO_2).^[11] The novel $\text{TiO}_2\text{-C/MnO}_2$ core-double shell nanowire arrays show significantly improved capacity and rate capability but at the expense of safety issues, discharge to as a low potential as 0.01 V. It is well known that interfacial design is another way to enhance the electronic transport properties of electrodes. By reducing interfacial spacing down to the nanoscale regime, the grain boundaries would apparently act as channels to transport electrons in the particles.^[4,5,7,16,23,24] Therefore, we believe a wise strategy to increase grain boundary density is to develop binary or multiphase compounds rather than single phase compounds. Several dual-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ materials have been reported recently to show improved electrochemical performance compared with pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials.^[25-28] However, most of them have spherical morphology or nanoparticles, which could potentially limit both electron and ion transportation.^[6,29]

In this work, we developed a facile hydrothermal and ion-exchange route to prepare self-supported dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ nanowire arrays. The as-prepared well-ordered arrays grown directly on current collecting substrates were particularly interesting owing to their vectorial ion and electron transport properties. It simplified the cell fabrication process, since it could be directly used as the electrode without polymer binder and conductive additives. As a result, more surface area can be in contact with electrolyte to facilitate the charge transfer. Additionally, the high density of grain boundaries in the dual phase structure improved the electrical conductivity. The unique structure provides a synergetic effect which attributed to the significantly improved electrochemical performance.

2. Experimental

2.1 Preparation of electrode

A piece of titanium foil ultrasonically cleaned in water, acetone and ethanol for 15 min each, was **firstly** placed against the wall of a 40 ml Teflon-lined stainless steel autoclave filled with 30 mL of 1 M NaOH aqueous solution. **Secondly**, the sealed autoclave was put in an electric oven at 220 °C for 18h.[11,18,29] After completion of the hydrothermal reaction, the titanium foil covered with $\text{Na}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ nanowires was immersed in 0.5 M HCl solution for 3 h to replace Na^+ with H^+ , rendering $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ nanowire arrays on Ti foil. **Thirdly**, the Ti foil was removed from HCl solution and rinsed with water, ethanol and dried at 60 °C. **Last but not the least**, the $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ nanowire arrays grown on Ti foil were immersed in 2 M LiOH solution and kept at 60 °C for 0 h, 2 h and 10 h, respectively. After rinsing with copious amounts of deionized water and ethanol, the titanium foils covered with nanowires were calcined at 600 °C for 3 h in air.

2.2 Materials Characterization

The phase purity and crystal structure of the obtained materials were studied using an X-ray diffraction (XRD, Bruker AXS D8 Advance) system with $\text{Cu K}\alpha$ radiation from **10-80°**. A field emission scanning electron microscope (FE-SEM, LEO FESEM 1530), transmission electron microscope (TEM, Philips CM300) and high-resolution transmission electron microscope (HRTEM) were used to examine the morphologies and crystalline structures of the samples. The *in-situ* TEM was carried out by constructing a nano-battery inside a TEM. Its setup included a Nano factory Scanning Tunneling Microscopy holder. The working electrode was the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -

TiO₂ nanostructure, while the counter electrode was Li/Li₂O. The Li₂O surface layer can be used as a solid electrolyte. All electron microscopy work **was** performed in a FEI Titan at 300 kV. The Raman spectra were collected on a BrukerSenterra spectrometer equipped with a 20mW diode laser, using an excitation wavelength of 532 nm and the spectrum range was from 45 cm⁻¹ to 4000 cm⁻¹.

2.3 Evaluation of Electrochemical Behavior

The electrochemical characterization was performed using 2032-type coin cells with two-electrodes, assembled in an Ar-filled dry glove box using Ti-based nanowire arrays/Ti-foil and Li metal as the working electrode and counter electrode, respectively. 1M LiPF₆ in ethyl carbonate (EC)/dimethyl carbonate (DMC) (3/7 by volume) was used as an electrolyte and two pieces of porous 25 μm thick polypropylene were used as separators. The discharge-charge cycling was performed between 1.0-3 V (vs. Li/Li⁺) at room temperature, using different C-rates on a battery tester (Neware) (1 C=175 mA g⁻¹). Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 100 KHz to 100 mHz on an electrochemical workstation (Versa STAT MC, Princeton Applied Research), and the amplitude of the alternating voltage was 10 mV. The impedance parameters were determined by fitting of the impedance spectra using Z-view software. Cyclic voltammetry (CV) testing was performed between 1 and 3 V (vs. Li/Li⁺) with a scan rate of 0.1 mV s⁻¹.

3. Results and discussion

The morphology of the nanowire arrays was examined with scanning electron microscopy (SEM). As shown in Fig. 1, after annealing at 600 °C for 3 h, the bulk materials show no

remarkable changes to their external morphology despite undergoing different LiOH treatment time (0 h, 2 h and 10 h). The mean diameter of nanowire samples determined from SEM imaging is around 80 nm (Fig. 1A-C). The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire array film shown in Fig. 1D has a highly oriented one dimensional (1D) structure with a typical length of 12 μm . However, unlike smooth TiO_2 nanowires, the surface of the LiOH treated nanowires becomes rougher, which may increase the effective surface area, providing more active sites for electrochemical reactions. Furthermore, the large open space between neighboring nanowires allows facile electrolyte diffusion throughout the whole electrode.

X-ray diffraction (XRD) was used to identify the crystallographic structure; the results are shown in Fig. 2A. With the exception of the reflections owing to metallic titanium (38.2° , 40.1° , 52.8° , 70.4° and 77.5°), all Bragg peaks in TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ patterns are consistent with those of pure anatase TiO_2 (JCPDS No. 65-2900) [12,13] and pure cubic spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase (JCPDS No. 49-0207), [15,17] respectively. In addition, with a short ion exchange time between $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{H}_2\text{O}$ and LiOH, H^+ in hydrogen titanate was not completely replaced by Li^+ . This is evidenced by the both anatase TiO_2 and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ peaks observed in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 diffraction pattern following the calcination process, as desired this should result in a greater degree of grain boundary. According to the XRD refinement data of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowires (data not shown), the ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to TiO_2 in the dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire is around 2:1. The dual phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire can also be proved by its Raman spectrum shown in Fig. 2B. The observed peaks at 143, 397, 514, and 641cm^{-1} for TiO_2 nanowire sample are characteristic of the anatase TiO_2 phase, [11] and the main peaks at 235, 465 and 669cm^{-1} are consistent with the spectra that were reported for the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials. [23] Raman spectra of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 design reveals, both anatase TiO_2

and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ vibration peaks, which demonstrates the formation of a dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 composite.

Further morphology and composition of as prepared nanowire samples were performed using transmission electron microscopy (TEM), and related TEM images including selected area diffraction (SAED) patterns and high resolution TEM (HRTEM) prepared at different steps are shown in Fig.3. With increasing ion exchange time in LiOH solution, rougher nanowires could be obtained. However, according to the SAED patterns (inset of Fig. 3A, C and E), after the ion-exchange process in LiOH solution (10 h) the crystal phase has changed from single crystalline anatase TiO_2 (Fig. 3A) to spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowires (Fig. 3E). The co-existing SAED pattern of 2 h ion exchange sample also confirmed the formation of dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire arrays. Furthermore, a well-crystallized structure with lattice fringes of about 0.36 nm and 0.48 nm can be clearly seen in Fig.3D, which corresponds to the (101) and (111) interplanar spacing of anatase TiO_2 and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, respectively, and is consistent with the presence of a dual phase.

The electrochemical performance of the as-prepared TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes was evaluated in half-cells, utilizing metallic lithium film as both the counter and reference electrode. Fig.4 shows the cyclic voltammogram (CV) curves for as-prepared nanowire electrodes between 1 and 3 V (vs. Li/Li^+) with a scan rate of 0.1 mVs^{-1} . The main pair of redox peaks at 1.70 V/2.08 V in the TiO_2 nanowire sample was ascribed to anatase TiO_2 . Additional redox peaks can be observed with a relatively small intensity at approximately 1.53 V/1.62 V and were attributed to the lithium ion insertion/extraction of TiO_2 -B phase,[19] Only one oxidation/reduction peak is observed for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, which was undetected in anatase TiO_2 sample and provides further indication that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be obtained in pure form

with sufficient time for the ion exchange process. Two pairs of oxidation and reduction peaks at 2.08 V/1.70 V and 1.64 V/1.49 V, which are ascribed to anatase TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, respectively,[11,15,17] indicated a dual phase composite materials when a shorter ion exchange time in LiOH solution was utilized.

The initial three charge-discharge cycle profiles for the prepared titanium oxide based nanowire electrodes with a current rate of 0.1 C (1 C=175 mA g^{-1}) are shown in Fig.5. The flat discharge plateau at about 1.55 V was observed in both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes due to Li ions being extracted from the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material, which is in agreement with the results of the anodic peak potential observed in the CV curve. The voltage plateau at around 2.0 and 1.7 V are verified the lithium ion insertion/extraction of anatase TiO_2 . The initial discharge capacities were 282 mA h g^{-1} for TiO_2 , 206 mA h g^{-1} for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 to 175 mA h g^{-1} for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes. The higher specific capacity of TiO_2 -based electrodes should be ascribed to the superior theoretical capacity of anatase TiO_2 comparing to $\text{Li}_4\text{Ti}_5\text{O}_{12}$. After the first cycle, the discharge capacities decreased due to the reduced number of electron transferred per formula unit; however the stability was gradually enhanced with increasing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ purity.

Rate capability is another very important consideration for practical Li-ion batteries in electric vehicles. To examine the effect of the different composite electrode on rate capability, these three Ti-based nanowire electrodes (pure TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 and pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$) were studied by charging/discharging at different current rates ranging from 0.1 to 30 C and then back to 0.1 C (1C=175 mA/g). As shown in Fig.6A, TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire electrodes exhibit higher specific capacity compared with the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ due to the superior theoretical capacity of anatase TiO_2 materials (Fig.6A). The figure also provides closer comparison between these TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes at various charge-discharge rates from 0.1 C to 30 C. The

dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowire arrays show lower capacities at low current rates from 0.1 C to 2 C, but superior rate capability to TiO_2 at higher rates from 5 C to 30 C. Specifically, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 electrode has a superior rate performance with discharge capacities of 135.5, 129.4, 120.2 and 115.5 mA h g^{-1} at 5 C, 10 C, 20 C and 30 C, respectively, while the TiO_2 electrode has discharge capacities of only 102.6, 75.2, 66.8, and 46.8 mA h g^{-1} at 5 C, 10 C, 20 C and 30 C, respectively. After measuring high rate capacity, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite anode is still able to provide capacity of 199.5 mA h g^{-1} when the current rate was set back to 0.1 C, corresponding to initial capacity retention of 98.8%. This exclusively demonstrates the improved rate stability of these materials over the pure TiO_2 nanowire (94.5% capacity retention) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowire anode (98.4% capacity retention).

In order to understand the enhanced rate capability of dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 composite electrode, electrochemical impedance spectroscopy (EIS) measurements were carried out in order to compare the conductivity of the prepared three nanowire electrodes. Nyquist plots of the three Ti-based nanowire electrodes are shown in Fig.6B. In the equivalent circuit (Fig.6B inset), R_s in the equivalent circuit represents the electrolyte resistance, which corresponds to the intercept of high frequency semicircle at Z' axis. The R_{SEI} and R_{ct} corresponds to the high frequency semicircle, represent the solid electrolyte interface (SEI) layer resistance and charge transfer resistance at the electrolyte/electrode interface, which are usually overlapped. W represents the Warburg impedance of Li ion diffusion into the active materials. CPE (CPE1 and CPE2) is the constant phase-angle element, involving double layer capacitance. The system resistance of R_s is similar for all three electrodes at around 6 ohm. This could be ascribed to the fact that those nanowires are grown directly on the Ti substrates that are used as the current collectors, which ensures good electrical conductivity in the electrodes. The transfer resistances

($R_{SEI}+R_{ct}$) of TiO_2 , $Li_4Ti_5O_{12}-TiO_2$, and $Li_4Ti_5O_{12}$ nanowire electrodes are 114.6, 52.1 and 83.4 ohm, respectively. This suggests that the dual phase $Li_4Ti_5O_{12}-TiO_2$ nanowire arrays have the lowest activation energy for the Li^+ diffusion and undergo a fast faradic reaction due to the increased grain boundary density. This supports the increased high-rate capability of the composite nanowire anode in comparison to the other two pure compound electrodes. The grain boundaries, which had a lower energy barrier for Li diffusion, in fact facilitated the lithium ion diffusion. Similar work has demonstrated that the grain boundaries in $LiCoO_2$ have low energy barrier for lithium ion diffusion.[32]

Moreover, the cyclability of $Li_4Ti_5O_{12}-TiO_2$ composite nanowire electrode was also investigated shown in Fig. 7. After operating the $Li_4Ti_5O_{12}-TiO_2$ nanowire electrode at 10 C for 100 cycles, the charge capacity was $129.3mAh\ g^{-1}$, 97.5% of 1st charge capacity, with a high coulombic efficiency of around 99.8%. Based on the minimal charge capacity fading even after 100 cycles for the $Li_4Ti_5O_{12}-TiO_2$ nanowire electrode, corresponding to only a 2.5% loss, it could be expected that no significant morphological changes or crystallite degradation occurred during charge/discharge for $Li_4Ti_5O_{12}-TiO_2$ nanowire electrode.

The morphology evolution of $Li_4Ti_5O_{12}-TiO_2$ nanowire by lithium insertion is shown in Fig. 8. Fig. 8A is a TEM image of the pristine $Li_4Ti_5O_{12}-TiO_2$ nanowire anode before reacting with the Li_2O solid electrolyte; and Fig. 8B shows the TEM image of the $Li_4Ti_5O_{12}-TiO_2$ after a certain time amount of lithiation. Comparing the $Li_4Ti_5O_{12}-TiO_2$ dual phase structure before and after lithiation, only some strain contrast could be seen, no volume expansion was observed. This no-volume expansion characteristic is very important for its stable cycling. On the other hand, the appearance of the strain contrast

indicated a small amount of structural defects that may have resulted due to the lithium diffusion.

We also compared this work with other dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 based electrodes reported in recent literature. These reports include: TiO_2 - $\text{Li}_4\text{Ti}_5\text{O}_{12}$ mesoporous spheres, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanocrystalline, petal-like $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanosheets, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 sub-microspheres, TiO_2 nanotube- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite, carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanocomposite, nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 , and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 hierarchical sphere morphologies. By comparison, well-aligned dual $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 composite nanowire arrays growing directly on Ti foil without any additive exhibited superior electrochemical performance to other reported dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 composite electrodes, especially at high current rates (Table 1). This superior rate capability should be attributed mainly to the large space that facilitate the fast lithium ion transfer, direct 1D ion/electron transport path way, no-volume expansion characteristic, and small diameter of nanowires (80 nm) that can provide short diffusion length.

4. Conclusion

In summary, we have rationally designed and fabricated self-supported dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire array architectures by a facile and convenient solution chemical approach, and its electrochemical characteristics were investigated in this work. For comparison, pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 nanowire arrays were also investigated. According to the XRD refinement data of composite materials, the ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 is around 2:1 in the dual phase composite $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 materials, which is very close to the value calculated from CV discharge profile. The HRTEM results indicate that a large number of grain boundaries have been formed in these composite nanowire materials during the ion-exchange and annealing process, and the *in-situ*

TEM results show the dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire anode has no-volume expansion characteristics during charge/discharge. The electrochemical results clearly demonstrated that the electrochemical properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire array composite electrode were much better than those of other two pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 nanowire arrays considered. The excellent rate capability of the dual phase nanowire composite could be related to the train boundary interface areas embedded in the composite nanowires, which would enhance structural stability and improve lithium storage kinetics by reducing the diffusion time of both lithium ions and electrons. These important findings could open up new opportunities for dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 composite anode materials in constructing high rate-capability binder free energy storage devices.

Acknowledgment

This work was financially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), the University of Waterloo and the Waterloo Institute for Nanotechnology. The authors thank Mr. Hey Woong Park, Mr. Drew Higgins, and Mr. Gregory Lui at the University of Waterloo for their help in editing the manuscript.

Corresponding Author

xingcheng.xiao@gm.com (Xingcheng Xiao)

zhwchen@uwaterloo.ca (Zhongwei Chen)

References

- [1] J. M. Tarascon, Armand, M. Armand, Nature, 414 (2001), 359-367.

- [2] Y. K. Sun, S. T. Myung, B. C. Park, J. Prakash, I. Belharouak, K. Amine, *Nat. Mater.*, 8 (2009), 320-324.
- [3] P. G. Bruce, B. Scrosati, J. M. Tarascon, *Angew. Chem. Int. Ed.*, 47 (2008), 2930-2946.
- [4] H. Wu, G. Y. Zheng, N. A. Liu, T. J. Carney, Y. Yang, Y. Cui, *Nano Lett.*, 12 (2012), 904-909.
- [5] L. W. Ji, Z. Lin, M. Alcoutlabi, X. W. Zhang, *Energy Environ. Sci.*, 4 (2011), 2682-2699.
- [6] J. Y. Liao, X. Xiao, D. Higgins, D. Lee, F. Hassan, Z. Chen, *Electrochim. Acta*, 108 (2013), 104-111.
- [7] A. P. Yu, H. W. Park, A. Davies, D. C. Higgins, Z. W. Chen, X. C. Xiao, *J. Phys. Chem. Lett.*, 2 (2011), 1855-1860.
- [8] G. N. Zhu, Y. G. Wang, Y. Y. Xia, *Energy Environ. Sci.*, 5 (2012), 6652-6667.
- [9] Y. Q. Wang, L. Gu, Y. G. Guo, H. Li, X. Q. He, S. Tsukimoto, Y. Ikuhara, L. J. Wan, *J. Am. Chem. Soc.*, 134 (2012), 7874-7879.
- [10] F. Wang, R. Robert, N. A. Chernova, N. Pereira, F. Omenya, F. Badway, X. Hua, M. Ruotolo, R. G. Zhang, L. J. Wu, V. Volkov, D. Su, B. Key, *J. Am. Chem. Soc.*, 133 (2011), 18828-18836.
- [11] J. Y. Liao, D. Higgins, G. Lui, V. Chabot, X. Xiao, Z. Chen, *Nano Lett.*, 13 (2013), 5467-5473.
- [12] M. Armand, J. M. Tarascon, *Nature*, 451 (2008), 652-657.
- [13] Y. C. Qiu, K. Y. Yan, S. H. Yang, L. M. Jin, H. Deng, W. S. Li, *Acs Nano*, 4(2010) 6515-6526.
- [14] L. F. Cui, L. B. Hu, J. W. Choi, Y. Cui, *Acs Nano*, 4(2010) 3671-3678.
- [15] G. N. Zhu, H. J. Liu, J. H. Zhuang, C. X. Wang, Y. G. Wang, Y. Y. Xia, *Energy Environ. Sci.*, 4 (2011) 4016-4022.

- [16] L. Zhao, Y. S. Hu, H. Li, Z. X. Wang, L. Q. Chen, *Adv. Mater.*, 23 (2011) 1385-1388.
- [17] H. S. Li, L. F. Shen, K. B. Yin, J. Ji, J. Wang, X. Y. Wang, X. G. Zhang, *J. Mater. Chem. A*, 1(2013) 7270-7276.
- [18] L. F. Shen, E. Uchaker, X. G. Zhang, G. Z. Cao, *Adv. Mater.*, 24(2012) 6502-6506.
- [19] S. H. Liu, Z. Y. Wang, C. Yu, H. B. Wu, G. Wang, Q. Dong, J. S. Qiu, A. Eychmuller, X. W. Lou, *Adv. Mater.*, 25 (2013) 3462-3467.
- [20] Y. S. Luo, J. S. Luo, J. Jiang, W. W. Zhou, H. P. Yang, X. Y. Qi, H. Zhang, H. J. Fan, D. Y. W. Yu, C. M. Li, T. Yu, *Energy Environ. Sci.*, 5(2012) 6559-6566.
- [21] W. X. Guo, X. Y. Xue, S. H. Wang, C. J. Lin, Z. L. Wang, *Nano Lett.*, 12 (2012) 2520-2523.
- [22] J. H. Jeun, K. Y. Park, D. H. Kim, W. S. Kim, H. C. Kim, B. S. Lee, H. Kim, W. R. Yu, K. Kang, S. H. Hong, *Nanoscale*, 5(2013) 8480-8483.
- [23] Y. F. Tang, F. Q. Huang, W. Zhao, Z. Q. Liu, D. Y. Wan, *J. Mater. Chem.*, 22 (2012) 11257-11260.
- [24] N. A. Liu, L. B. Hu, M. T. McDowell, A. Jackson, Y. Cui, *Acs Nano*, 5(2011) 6487-6493.
- [25] M. M. Rahman, J. Z. Wang, M. F. Hassan, D. Wexler, H. K. Liu, *Adv. Energy Mater.* 2011, 1, 212-220.
- [26] X. Li, C. Lai, C. W. Xiao, X. P. Gao, *Electrochim. Acta*, 56(2011) 9152-9158.
- [27] J. Wang, H. L. Zhao, Q. Yang, C. M. Wang, P. P. Lv, Q. Xia, *J. Power Sources*, 222 (2013) 196-201.
- [28] F. X. Wu, X. H. Li, Z. X. Wang, H. J. Guo, *Nanoscale*, 5(2013) 6936-6943.
- [29] J. Y. Liao, B. X. Lei, H. Y. Chen, D. B. Kuang, C. Y. Su, *Energy Environ. Sci.*, 5 (2012) 5750-5757.
- [30] K. M. Kim, K. Y. Kang, S. Kim, Y. G. Lee, *Current Appl. Physic.*, 12(2012) 1199-1206.

- [31] X. J. Zhu, C. S. Ong, X. X. Xu, B. L. Hu, J. Shang, H. L. Yang, S., Liu, Y. W. Katlakunta. X. X. Chen, L. Pan, J. Ding, R. W. Li, Scientific Report 2014, doi:10.1038/srep01084.
- [32] M. M. Rahman, J. Z. Wang, M. F. Hassan, S. L. Chou, D. Wexler, H. K. Liu, J. Power Sources, 195(2010) 4297-4303.

Figures

Fig. 1 Cross-sectional SEM images of TiO₂ (A, 0 h), Li₄Ti₅O₁₂-TiO₂ (B and D, 2 h), and Li₄Ti₅O₁₂ (C, 10 h) samples with different ion-exchange time in LiOH solution.

Fig. 2 XRD patterns (A) and Raman spectra (B) of TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowires.

Fig.3 TEM images, HRTEM and SAED patterns (inset) of TiO_2 nanowire (A,B), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 composite nanowire (C,D), and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowire (E,F).

Fig.4 CV curves of TiO_2 nanowire, $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ composite nanowire, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowire electrodes.

Fig.5 The first three charge-discharge curves at 0.1 C of TiO_2 nanowire (A), $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ composite nanowire (B), and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowire electrodes (C).

Fig. 6(A) The rate performance at various current rates from 0.1 C to 30 C and then back to 0.1 C (1C = 175 mA/g) of TiO_2 nanowire, $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ composite nanowire, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowire electrodes. (B) Electrochemical impedance spectra (Nyquist plots) of electrodes at full charge states.

Fig. 7 Cyclic performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ nanowire electrode beyond 100 cycles at a rate of 10 C.

Fig. 8 *In-situ* TEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ nanowire anode. (A) Pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ nanowire before lithation; (B) Lithiated $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-TiO}_2$ nanowire.

Table

Table 1. Comparison of rate performance (mA h g^{-1}) of self-supported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 (LTO- TiO_2) with other dual phase LTO- TiO_2 based anode nano-materials reported recently. $1\text{C}=175 \text{ mA/g}$.

	0.1 C	0.2 C	0.5 C	1 C	2 C	5C	10 C	20 C	30 C
<i>Our LTO/TiO_2 nanowire arrays</i>	<i>210</i>	—	<i>175</i>	<i>150</i>	<i>142</i>	<i>135.5</i>	<i>129.4</i>	<i>120.2</i>	<i>115.5</i>
High grain boundary LTO/ TiO_2 ²⁸	—	—	167	145	137	121	105	—	—
Petal-like LTO/ TiO_2 nanosheets ²³	185.5	—	177.2	163.3	145.8	137.7	127.5	112.5	—
High rate dual-phase LTO/ TiO_2 ⁸	—	—	—	150	143	130	125	—	—
LTO/ TiO_2 composite ¹⁹	—	175	—	137	134	—	—	—	—
Hierarchical C- TiO_2 /LTO spheres ¹²	—	230	—	180	172	141	120	93	77
TiO_2 nanotube/LTO (2:8) ⁶	—	175	—	165	—	150	135	75	—
Nanocrystalline LTO/ TiO_2 ³⁰	—	193	170	145	130	120	—	—	—

Graphical abstract

Self-supported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanowire array 3D anodes exhibiting superior electrochemical performance have been developed through a facile hydrothermal process, followed by an ion exchange process. With this unique dual phase nanowire array structure, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ leads to high physical stability resulting in long cycling stability while the TiO_2 improves the capacity of the electrode, and the dual phase structure contributes to high-rate cyclability.