Electrospun $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers as anode material for high-rate and low-temperature lithium-ion batteries

H.L. Zou^a, H.F. Xiang^{a,*}, X. Liang^a, X.Y. Feng^a, S. Cheng^a, Y. Jin^c, C.H. Chen^b

^a School of Materials Science and Engineering, Hefei University of Technology, Anhui Hefei 230009, P. R. China

^b CAS Key Laboratory of Materials for Energy Conversions, Department of Materials Science and Engineering, University of Science and Technology of China, Anhui Hefei 230026, China

^c Electrical Engineering and New Materials, China Electric Power Research Institute, Beijing 100192, P. R. China

Abstract

$\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers with one-dimensional (1D) morphology and excellent electrical conductivity are prepared via a facile electrospinning technique. The as-prepared $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers exhibit excellent lithium storage performance with superior rate capability and low-temperature performance: 140 mAh g⁻¹ at 10 C and 91 mAh g⁻¹ at 50 C rates at room temperature, 100 mAh g⁻¹ at 1 C rate at -20 °C. The superior electrochemical performance of $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers is attributed to the 1D nano-architectures composed of nanocrystals and the reduced grain size in $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$, both of which facilitate the Li⁺ ion transport. The $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers also have a high Ti³⁺ concentration and an in-situ surface coating layer of Li₂CrO₄, which could

* Corresponding author. Tel.: +86-551-62901457; fax: +86-551-62901362
E-mail address: hfxiang@hfut.edu.cn (H.F. Xiang)

enhance intraparticle and interparticle electronic conductivities of $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ grains, respectively.

Keywords: $\text{Li}_4\text{Ti}_5\text{O}_{12}$, nanofibers, electrospinning, low-temperature, lithium-ion batteries

1. Introduction

Spinel lithium titanate, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (denoted as LTO), is one of the most concerned anode materials for long-life and safe lithium (Li) ion batteries (LIBs) [1-3]. Compared to the commonly used graphite anode materials, LTO possesses zero-strain structural durability during the lithium insertion/extraction process and excellent safety characteristics with no Li dendrite formation [4-7]. Nevertheless, its near-insulating electronic conductivity ($10^{-13} \text{ S cm}^{-1}$) severely limited its electrochemical kinetics, especially at high current densities and low temperature [8-10]. So far, various strategies including size reducing [11-13], bulk doping [14,15] and surface modification [16,17] have been presented to improve the kinetic performance of LTO. Recently, one-dimensional (1D) LTO nanofibers prepared by electrospinning techniques presented high rate capability [18-20], because of the enhanced Li^+ ion transport from short Li^+ diffusion paths and high electrode-electrolyte contact areas [21,22]. Nevertheless, the electron transport in the inner of nanofibers composed of nanocrystals and between the LTO nanofibers is still a bottleneck for the development of high-performance LTO nanofibers.

Surface coating and heteroatoms doping are two most common strategies to improve the electronic conductivity of LTO anode materials. Carbon coating has been widely reported to enhance the conductivity of LTO nanofibers by direct carbonization of the as-spun precursor [23-26]. Huang and Hu fabricated conformal carbon-coated LTO nanofibers with excellent electrochemical performance [27,28]. The conductive TiN/TiO_xN_y layer has also been reported to improve the conductivity of the electrospun LTO nanofibers using nitridation process [29]. Nevertheless, both the preparation of those carbon-coated LTO nanofibers and the nitridation process need be performed in a protective or reactive atmosphere, which made the material preparation complicated and thus costly. Moreover, surface coating can only improve interparticle electronic conductivity, cannot alter the intraparticle conductivity of LTO. In comparison, doping heteroatoms is a facile and effective way to enhance the material intrinsic conductivity by changing the Ti⁴⁺ and Li⁺ surrounding states [2]. Moreover, the enrichment of the heteroatoms on the surface in the sintering process can produce a conductive phase on the surface of LTO, which can further increase the interparticle electron transfer speed [30]. Kim et al. reported that the Ag-modified LTO nanofibers showed the enhanced electrochemical performance compared to the bare LTO nanofibers, due to the Ag doping in the bulk and simultaneity incorporation of Ag nanoparticles (<5 nm) at the interface between LTO primary particles [30]. Chromium (Cr) doping/coating has been proved to effectively enhance the electrochemical performance of

LTO [31,32]. Wang prepared high-rate LiCrTiO_4 anode material by an electrospinning technique, while LiCrTiO_4 has a lower theoretical capacity than LTO [33]. Most recently, we fabricated Cr-modified LTO via a facile sol–gel process, and the optimal composition of $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ showed a synergistic effect of Cr modification on bulk doping, surface coating, and size reducing [34].

In this work, we prepare $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers using a facile electrospinning method, in order to combine the synergistic strategy of Cr modification with 1D nano-architectures composed of LTO nanocrystals. The as-prepared $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers have a high Ti^{3+} concentration and an in-situ surface coating layer of Li_2CrO_4 , which could enhance intraparticle and interparticle electronic conductivities of $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ grains, respectively. Moreover, the 1D nano-architectures of $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers as well as the reduced grain size contribute to the good Li^+ ion transport. Therefore, the $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers exhibit high capacity, superior rate capability and excellent low-temperature performance as an anode material for LIBs.

2. Experimental

2.1 Material preparation and characterization

The $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers denoted as “LCTONF” were synthesized by an electrospinning technique. The precursor solution for electrospinning was prepared by dissolving 6.808 g tetrabutyl titanate (TBT), 0.507 g chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 1.742 g lithium acetate (LiAc) and 2.500 g polyvinyl pyrrolidone

(PVP, MW=1,300,000) in a mixed solution with 30 mL ethanol and 10 mL acetic acid, and then was vigorously stirred overnight. Subsequently, the precursor solution was injected into a plastic syringe with four 23-gauge stainless steel needles. The DC voltage of 20 kV is loaded on the needles, and the distance between the needle and a collector was 15 cm. The spinning speed is controlled at 2.0 mL h⁻¹ using an auto-syringe pump. After the electrospinning, the as-spun nanofibers were dried at 80 °C in an electric oven and then heat-treated at 700 °C for 3 h in air. For comparison, pristine Li₄Ti₅O₁₂ nanofibers without adding chromium nitrate were also prepared with the same method and named “LTONF”. All chemicals used in this work were purchased from Sinopharm Chemical Reagent Co., Ltd. The samples were identified by X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS), and then the EXPGUI interface for the GSAS was used for the Rietveld refinement. The morphologies and structures of the nanofibers were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6390LA) and transmission electron microscopy (TEM, FEI Titan 80–300) with energy dispersive X-ray spectroscopy (EDX).

2.2 Electrochemical measurements

The electrochemical properties of LCTONF and LTONF were measured in coin half cells (CR2032-type). The electrode laminates were fabricated as below: 80% active material, 8% multi-wall carbon nanotubes (MWCNT) and 7% carbon black as conductive additives, and 5% polyvinylidene fluoride (PVDF) binder were mixed with N-methyl-2-pyrrolidinone (NMP) to form a homogenous slurry, which was

subsequently coated onto a copper foil. After drying at 70 °C, the laminates were punched into discs (14 mm in diameter with 1.5 mg active material). Li metal foil was used as the counter and reference electrode. The coin half cells were assembled in an argon-filled glove box (MBraun) with a polypropylene microporous membrane (Celgard 2400) as the separator and 1 M LiPF₆ / ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1, w/w) as the electrolyte.

Discharge (Li insertion)-charge (Li extraction) tests were performed in the range of 1.0 to 2.5 V (vs. Li/Li⁺) on a multi-channel battery cycler (Arbin BT2000) and the 1 C rate corresponds to 175 mA g⁻¹. Electrochemical impedance spectroscopy (EIS) measurements of the coin half cells those were charged to 2.5 V were performed using a CHI 604 electrochemical workstation (Chenhua Corp.) in the frequency range from 10⁵ Hz to 0.1 Hz.

3. Results and discussion

Morphologies of the electrospun LTONF and LCTONF were confirmed through SEM and shown in Fig. 1. Both the as-spun fibrous precursors of LTONF (Fig. 1a) and LCTONF (Fig. 1b) are interconnected with long fibers with smooth surfaces. The as-spun LTONF precursor fibers are continuous curved with an average diameter of ~250 nm, while the as-spun LCTONF precursor fibers are fairly straight with the average diameter of ~180 nm. Since the morphology formation of the as-spun fibers is tightly related to the conductivity of the precursor solution, the finer LCTONF precursor fibers are probably due to the enhanced conductivity by adding Cr³⁺ into the precursor solution. According to the thermogravimetry results (Fig. S1), those two

kinds of precursor fibers can be decomposed completely at 700 °C to form LTONF (Fig. 1c) and LCTONF (Fig. 1d). Due to the slow decomposition of PVP, the fiber morphology is well-defined after heat treatment except for a little shrinkage on the diameter of the fibers. Dislike the smooth appearance of the precursor fibers, LTONF and LCTONF are both composed of nanoparticles so that they have coarse outlines. Additionally, the nanoparticles in LCTONF have the much smaller size than those in LTONF (clearly shown in insets of Fig. 1c and 1d).

The morphologies of LTONF and LCTONF were further characterized by TEM and high-resolution TEM (HRTEM), as shown in Fig. 2. As clearly shown in Fig. 2a, LTONF is composed of highly crystalline and inter-connected grains with the size of 80~130 nm, and the grain boundaries can be observed (Fig. 2a), similar as previous other electrospun nanofibers [29,35]. However, the grains in LCTONF are fairly small, in average size of 40~60 nm (Fig. 2b), which results in much more grain boundary than LTONF. It is recently proposed that the abundant presence of grain boundaries is very favorable for fast Li^+ and electron transport in LTO anode materials [36]. The smaller grains in LCTONF are attributed to the retarded long-range order of the lattice by Cr^{3+} [32,34]. The lattice fringe of ca. 0.4802 nm in Fig. 2c is corresponding to the inter-planar distance of (111) planes of spinel LTO. The presences of Ti, O, and Cr elements in the LCTONF are substantiated by EDX spectrum (Fig. S2), and the distribution of these elements is uniform from the EDX elemental mapping in Fig. 2d. The distribution of Cr in line with those of Ti and O indicates that Cr has been uniformly doped in LCTONF.

Structural features of electrospun LTONF and LCTONF were analyzed by XRD and Raman and presented in Fig. 3. As shown in Fig. 3a, both the samples have sharp diffraction peaks, which suggests that they are well crystallized. All the peaks can be assigned to the face-centered cubic spinel structure with the Fd3m space group of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (JCPDS no. 49-0207), while some impurity of rutile TiO_2 and Li_2TiO_3 are observed in LTONF. To confirm the impact of Cr doping in the LTO, the XRD data were refined by Rietveld refinement using GSAS software. Fig. 3c, Fig. 3d and Table 1 show the refinement graphs and results of LTONF and LCTONF with a perfect fitting condition. Those results confirm that $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ exists as the main component in LCTONF and doping a small amount of Cr in LTO does not significantly change the lattice parameter of LTO. Fig. 3b shows the Raman spectra of LTONF and LCTONF. The Raman spectra at 751, 672, 510, 427, 400, 346, 264, and 231 cm^{-1} can be identified as the characteristic peaks of the pristine LTO, which is consistent with previous literature [37]. The peaks at 672, 427 and 231 cm^{-1} are ascribed to the symmetric stretching vibration (ν_{sym}) of Ti-O bonds, asymmetric stretching vibration (ν_{asym}) of Li-O bonds and bending vibration (δ) of O-Ti-O bonds, respectively [38]. In addition to the eight Raman spectra mentioned above, another weak peak appears at 585 cm^{-1} in the Raman spectrum of LCTONF, which is corresponding to stretching in CrO_6 octahedron where doped Cr^{3+} ions occupy octahedral 16d sites in the LTO lattice [39]. Moreover, introduction of Cr leads to shifting of the strongest peak from 231 to 672 cm^{-1} , and the peaks at 427 and 672 cm^{-1} shift to the lower wavenumber in LCTONF. This suggests that the local

surroundings around the TiO_6 octahedron and LiO_4 tetrahedra change drastically with Cr^{3+} doping.

To further evaluate the surface state of LCTONF, XPS was carried out to measure the Ti2p spectra for LTONF and LCTONF (Fig. 4). The Ti 2p_{3/2} main peaks for LTONF consist of a sharp peak at 458.9 eV assigned to Ti^{4+} ions and a shoulder peak at 457.4 eV assigned to Ti^{3+} ions (Fig. 4a), in good agreement with Chen's results [12]. However, LCTONF clearly exhibits the different Ti 2p spectrum in Fig. 4b. The sharp peak at 457.3 eV indicates that some Ti^{4+} may be reduced to Ti^{3+} , and the Cr^{3+} ions ($R=0.062$ nm) dopes into the octahedral 16d Li/Ti sites of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [40]. Herein, it is proposed that despite the style of $3\text{Cr}^{3+} \rightarrow \text{Li}^+ + 2\text{Ti}^{4+}$ [32], partially Cr doping is following by $3\text{Cr}^{3+} \rightarrow (1+x) \text{Li}^+ + (2-x) \text{Ti}^{4+} + x \text{Ti}^{3+}$. Because the Cr^{3+} ions radius is smaller than that of Li^+ ions, the Cr^{3+} is easier to occupy the 16d Li sites, and promotes the reduction of Ti^{4+} to Ti^{3+} to balance the charge. As reported previously [9], the higher proportion of Ti^{3+} ions in LCTONF can sufficiently enhance the intrinsic electronic conductivity.

Electrochemical properties of LTONF and LCTONF as anode materials were investigated in half cells. As shown in Fig. 5a, the reversible capacities of LTONF and LCTONF at 0.2C reach 157 and 167 mAh g^{-1} , respectively. The higher capacity of LCTONF is mainly ascribed to the enhanced conductivity and the reduced impurities of rutile TiO_2 and Li_2TiO_3 impurities. Additionally, the first discharge curve of LCTONF contains two plateaus at about 2.1 V and 1.55 V. The corresponding differential capacities (dQ/dE) curves in Fig. 5b

clearly show that the corresponding cathodic peak at 2.1 V only appears for LCTONF rather than for LTONF. In our recent report [34], the irreversible peak at 2.1 V vs. Li/Li⁺ is assigned to the Li insertion into Li₂CrO₄ existing on the surface of Li_{3.9}Cr_{0.3}Ti_{4.8}O₁₂ particles. Herein, we propose that Li₂CrO₄ also exists on the surface of LCTONF. As reported [41], Li₂CrO₄ electrode can deliver a specific capacity of 230 mAh g⁻¹ when it is discharged to 1.9 V. Here the capacities of the LTONF and LCTONF above 1.9 V are 4.66 and 5.86 mAh g⁻¹, respectively, so the capacity from the contribution of the Li₂CrO₄ component in LCTONF is 1.20 mAh g⁻¹. Thus it can be roughly calculated that the content of Li₂CrO₄ is 0.52% in LCTONF. After initially discharging, the Li-rich phase of Li_{3+x}CrO₄ is formed and its high conductivity can enhance the Li insertion/extraction kinetics into/from LCTONF, even though its content is very low [31,41].

The rate capabilities of LTONF and LCTONF are shown in Fig. 6. In Fig. 6a, LTONF delivers reversible capacities of 146 mAh g⁻¹ at 1C, 139 mAh g⁻¹ at 2C, 127 mAh g⁻¹ at 5C, 112mAh g⁻¹ at 10C, 100 mAh g⁻¹ at 20C and 60 mAh g⁻¹ at 50C. These results are much higher than those of our previous LTO materials [6,34,42], even the LTO/graphene composites [43,44]. Similar as other electrospun LTO nanofibers [28,29], our nanofiber anode material also show superior rate capability mainly because of the advantages of 1D nano-architectures on shortening the electron and Li⁺ transport paths [20]. Furthermore, LCTONF in Fig. 6b exhibits much higher rate capabilities than

LTONF, e.g., 165 mAh g⁻¹ at 1C, 161 mAh g⁻¹ at 2C, 154 mAh g⁻¹ at 5C, 141mAh g⁻¹ at 10C, 126 mAh g⁻¹ at 20C and 91 mAh g⁻¹ at 50C. The flat plateau of LCTONF is well maintained even at 50C (Fig. 6b), which is because LCTONF has much smaller voltage polarization (Fig. S3a) and lower impedance (Fig. S4a). Fig. 6c clearly shows that both LTONF and LCTONF exhibit stable cycling performance under various current rates. When the current density returns to low value (1C) from high rate tests, the capacity of LCTONF electrode also restores to 163mAh g⁻¹ as same as the initial value, which indicates a good reversibility of LCTONF. The results of CV evaluation at room temperature with different scan rates further confirmed that LCTONF has good electrochemical reaction kinetics (Fig. S3b). The redox peaks are still sharp even the rates are increased to 1.0 mV s⁻¹, which indicates the electrode has low polarization and fast electrochemical reaction rate, resulting in an excellent rate performance of LCTONF. Furthermore, according to Yang's report [45], the Li⁺ diffusion coefficient in LCTONF is calculated to be 1.17×10⁻¹⁰ cm² s⁻¹, which is higher than those of other LTO electrodes reported previously [46-48]. Additionally, there is a small cathodic peak at a low potential of 1.3~1.4 V (Fig. S3b), which is corresponding to the pseudocapacitive effect [49]. The pseudocapacitive effect is derived from the distinct surface Li storage in LCTONF because of their small particle sizes and large specific surface area. The cycling stabilities of LTONF and LCTONF were evaluated at 5 C, as shown in Fig. 6d. The initial capacity (152 mAh g⁻¹) of LCTONF can remain 76%, i.e., 116 mAh g⁻¹ after

800 cycles. This fading trend is similar as that of LTONF, which suggests that t LCTONF has the same zero-strain characteristics as spinel LTO anode material. Moreover, the impedances of LTONF and LCTONF before and after cycling at room temperature are shown in Fig. S3c, Fig. S3d and Fig. S4a. Before cycling, the charge transfer impedances of the pristine LTONF and LCTONF electrodes are similar, being about 200 ohm (Fig. S3c). The impedances of both samples are significantly reduced after the first 3 cycles, especially for LCTONF, only 50 ohm (Fig. S4a). This result can be explained from two aspects: (a) LCTONF has the higher concentration of Ti^{3+} in the bulk phase, which increases the intraparticle conductivity; (b) $\text{Li}_{3+x}\text{CrO}_4$ on the particle surface can increases the interparticle conductivity. And after 800 cycles, the small impedance of LCTONF is maintained.

It is vital to improve the low-temperature performance for the practical application of LTO based batteries, because of the huge capacity fading of LTO materials at low temperature [2,50,51]. The capacities of LTONF and LCTONF at low temperatures have been investigated (Fig. 7). As shown in Fig. 7a, the reversible capacities of LTONF at 1.0 C charge-discharge rate are 146 mAh g^{-1} at $25\text{ }^{\circ}\text{C}$, 126 mAh g^{-1} at $0\text{ }^{\circ}\text{C}$, 80 mAh g^{-1} at $-10\text{ }^{\circ}\text{C}$ and only 29 mAh g^{-1} at $-20\text{ }^{\circ}\text{C}$. The rapid capacity fading especially at $-10\text{ }^{\circ}\text{C}$ and $-20\text{ }^{\circ}\text{C}$ is mainly due to both the surface electrochemical reaction rate and the interparticle charge transfer slow down as the temperature decreasing. However, LCTONF delivers higher reversible capacities of about 166, 153, 129 and 100 mAh g^{-1} at 25, 0,

-10, and -20 °C, respectively (Fig. 7b). Moreover, the ac impedances of LTONF and LCTONF (charge to 2.5 V) at different temperatures were measured and shown in Fig. S4. With the decrease of operating temperature, the charge transfer impedances increase rapidly. There is a weak charge transfer reaction at the interface between the electrolyte and the electrode, which is very consistent with Tao's results [52]. LTONF shows a larger electrode polarization than LCTONF, and the gap between the charge and discharge plateaus is bigger and bigger along with decreasing the temperature. That means LCTONF has excellent reaction kinetics with respect to LTONF at low temperature. In addition, the excellent dynamic performance of LTONF is very stable at low temperature even during long cycling (Fig. 7c).

The outstanding electrochemical performance of LCTONF is ascribed to the following aspects (as illustrated in Fig. 8). First of all, adding a small amount of $\text{Cr}(\text{NO}_3)_3$ into the precursor solution can effectively improve the conductivity and decrease the diameter of the as-spun fibers. During the subsequent sintering process, in-situ formation of the Li_2CrO_4 surface layer and the suppression from Cr atoms on the long-range order in the LTO lattice cooperatively suppress the growth of LTO grains and build up the LCTONF with smaller grains. The 1D nano-architectures can shorten the Li^+ ion and electron transfer paths. At the same time, Cr^{3+} prefers to enter the 16d Li sites, which could effectively promote the reduction of Ti^{4+} into Ti^{3+} in the body region, and improve the intraparticle electronic conductivity of LCTONF. Additionally the Li_2CrO_4 surface layer can improve the interparticle conductivity.

Finally, the Cr doping in LCTONF significantly inhibits the formations of electrochemical inertia rutile TiO_2 and Li_2TiO_3 , and thus enhances the electrochemical performance of LCTONF, especially at high rates and low temperature.

4. Conclusions

In summary, $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers with a typical 1D nano-architectures were successfully fabricated via a facile electrospinning method. The as-prepared $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers have a high Ti^{3+} concentration and an in-situ surface coating layer of Li_2CrO_4 , which could enhance intraparticle and interparticle electronic conductivities of $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ grains, respectively. Moreover, the 1D nanofibers structure and the reduced grain size in $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ facilitate the Li^+ ion transport. As anode materials for lithium-ion batteries (LIBs), the electrospun $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$ nanofibers exhibit the high reversible capacities of 167, 140, and 91 mAh g^{-1} at 0.2, 10, and 50 C rates, respectively. When the discharge-charge test is carried out at -20°C , a high reversible capacities of 100 mAh g^{-1} is still maintained at 1C rate. The present synergistic strategy with 1D nano-architectures and Cr modification on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material by electrospinning shows a great potential for energy-storage applications.

Acknowledgements

This study was supported by the National Science Foundation of China (Grant Nos. 51372060, 21676067 and 51402289) and the Opening Project of CAS Key Laboratory of Materials for Energy Conversion (KF2016005).

References

- [1] Z. Yang, J. Zhang, M.C. Kintner-Meyer, X. Lu, D. Choi, J.P. Lemmon, J. Liu, Electrochemical energy storage for green grid, *Chem. Rev.* 111 (2011) 3577-3613.
- [2] B. Zhao, R. Ran, M. Liu, Z. Shao, A comprehensive review of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based electrodes for lithium-ion batteries: the latest advancements and future perspectives, *Mat. Sci. Eng. R* 98 (2015) 1-71.
- [3] B. Zhao, X. Deng, R. Ran, M. Liu, Z. Shao, Facile synthesis of a 3D nanoarchitected $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode for ultrafast energy storage, *Adv. Energy Mater.* (2015) 1500924.
- [4] W. Xu, X. Chen, W. Wang, D. Choi, F. Ding, J. Zheng, et al., Simply AlF_3 -treated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite anode materials for stable and ultrahigh power lithium-ion batteries, *J. Power Sources* 236 (2013) 169–174.
- [5] L. Qi, S. Chen, Y. Xin, Y. Zhou, Y. Ma, H. Zhou, Self-supported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheet arrays for lithium ion batteries with excellent rate capability and ultralong cycle life, *Energy Environ. Sci.* 7 (2014) 1924-1930.
- [6] T.P. Zhou, X.Y. Feng, X. Guo, W.W. Wu, S. Cheng, H.F. Xiang, Solid-state synthesis and electrochemical performance of Ce-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials for lithium-ion batteries, *Electrochim. Acta* 174 (2015) 369-375.
- [7] M. Guo, H. Chen, S. Wang, S. Dai, L.X. Ding, H.H. Wang, TiN-coated micron-sized tantalum-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with enhanced anodic performance for lithium-ion batteries, *J. Alloys Compd.* 687 (2016) 746-753.
- [8] T. Yi, S. Yang, Y. Xie, Recent advances of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as promising next generation anode material for high power lithium-ion batteries, *J. Mater. Chem. A* 3 (2015) 5750-5777.
- [9] M. Guo, S. Wang, L.X. Ding, L. Zheng, H.H. Wang, Synthesis of novel nitrogen-doped lithium titanate with ultra-high rate capability using melamine as a solid nitrogen source, *J. Mater. Chem. A* 3 (2015) 10753-10759.
- [10] B. Tian, H. Xiang, L. Zhang, Z. Li, H. Wang, Niobium doped lithium titanate as a high rate anode material for Li-ion batteries. *Electrochim. Acta* 55 (2010) 5453-5458.
- [11] G.B. Xu, W. Li, L.W. Yang, X.L. Wei, J.W. Ding, J.X. Zhong, P.K. Chu,

Highly-crystalline ultrathin $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets decorated with silver nanocrystals as a high-performance anode material for lithium ion batteries. *J. Power Sources* 276 (2015) 247-254.

[12] C. Chen, Y. Huang, C. An, H. Zhang, Y. Wang, L. Jiao, H. Yuan, Copper-doped dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - TiO_2 nanosheets as high-rate and long cycle life anodes for high-power lithium-ion batteries, *ChemSusChem* 8 (2015) 114-122.

[13] X. Feng, H. Zou, H. Xiang, X. Guo, T. Zhou, Y. Wu, W. Xu, P. Yan, C. Wang, J.G. Zhang, Y. Yu, Ultrathin $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets as anode materials for lithium and sodium storage, *ACS Appl. Mater. Interfaces* 8 (2016) 16718-16726.

[14] C. Lin, X. Fan, Y. Xin, F. Cheng, M.O. Lai, H. Zhou, L. Lu, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based anode materials with low working potentials, high rate capabilities and high cyclability for high-power lithium-ion batteries: A synergistic effect of doping, incorporating a conductive phase and reducing the particle size, *J. Mater. Chem. A* 2 (2014) 9982-9993.

[15] M. Guo, S. Wang, L.X. Ding, C. Huang, H. Wang, Tantalum-doped lithium titanate with enhanced performance for lithium-ion batteries, *J. Power Sources* 283 (2015) 372-380.

[16] C. Chen, H. Xu, T. Zhou, Z. Guo, L. Chen, M. Yan, L. Mai, P. Hu, S. Cheng, Y. Huang, Integrated intercalation-based and interfacial sodium storage in graphene-wrapped porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers composite aerogel, *Adv. Energy Mater.* 26 (2016) 1600322.

[17] G. Xu, L. Yang, X. Wei, J. Ding, J. Zhong, P.K. Chu, MoS_2 -quantum-dot-interspersed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets with enhanced performance for Li and Na ion batteries, *Adv. Funct. Mater.* 26 (2016) 3349-3358.

[18] A.K. Haridas, C.S. Sharma, T.N. Rao, Electrochemical performance of lithium titanate submicron rods synthesized by sol-gel/electrospinning, *Electroanalysis* 26 (2014) 2315-2319.

[19] Y. Wu, M.V. Reddy, B.V.R. Chowdari, S. Ramakrishna, Electrochemical studies on electrospun $\text{Li}(\text{Li}_{1/3}\text{Ti}_{5/3})\text{O}_4$ grains as an anode for Li-ion batteries, *Electrochim. Acta* 67 (2012) 33-40.

- [20] R.J. Mi, Y.S. Jung, Y.M. Kang, Tailored $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers with outstanding kinetics for lithium rechargeable batteries, *Nanoscale* 4 (2012) 6870-6875.
- [21] H.W. Lu, Z. Wei, Y.S. Li, Z.W. Fu, Fabrication and electrochemical properties of three-dimensional net architectures of anatase TiO_2 and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers, *J. Power Sources* 164 (2007) 874-879.
- [22] Z. Yu, L. Tetard, L. Zhai, J. Thomas, Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions, *Energy Environ. Sci.* 8 (2015) 702-730.
- [23] Z. Yang, Q. Meng, Z. Guo, X. Yu, T. Guo, R. Zeng, Highly reversible lithium storage in uniform $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon hybrid nanowebs as anode material for lithium-ion batteries, *Energy* 55 (2013) 925-932.
- [24] H.S. Choi, T. Kim, J.H. Im, C.R. Park, Preparation and electrochemical performance of hyper-networked $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon hybrid nanofiber sheets for a battery-supercapacitor hybrid system, *Nanotechnology*, 22 (2011) 405402.
- [25] N. Zhu, W. Liu, M. Xue, Z. Xie, D. Zhao, M. Zhang, J. Chen, T. Cao, Graphene as a conductive additive to enhance the high-rate capabilities of electrospun $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for lithium-ion batteries, *Electrochim. Acta* 55 (2010) 5813-5818.
- [26] J. Liu, K. Tang, K. Song, P.A. van Aken, Y. Yu, J. Maier, Tiny $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles embedded in carbon nanofibers as high-capacity and long-life anode materials for both Li-ion and Na-ion batteries, *Phys. Chem. Chem. Phys.* 15 (2013) 20813-20818.
- [27] H. Xu, X. Hu, W. Luo, Y. Sun, Z. Yang, C. Hu, Y. Huang, Electrospun conformal $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C fibers for high-rate lithium-ion batteries, *ChemElectroChem* 1 (2014) 611-616.
- [28] H. Xu, X. Hu, Y. Sun, W. Luo, C. Chen, Y. Liu, Y. Huang, Highly porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C nanofibers for ultrafast electrochemical energy storage, *Nano Energy* 10 (2014) 163-171.
- [29] H. Park, T. Song, H. Han, U. Paik, Electrospun $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers sheathed with conductive $\text{TiN}/\text{TiO}_x\text{N}_y$ layer as an anode material for high power Li-ion batteries, *J. Power Sources* 244 (2013) 726-730.
- [30] J.G. Kim, D. Shi, M.S. Park, G. Jeong, Y.U. Heo, M. Seo, Y.J. Kim, J.H. Kim,

S.X. Dou, Controlled Ag-driven superior rate-capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes for lithium rechargeable batteries, *Nano Res.* 6 (2013) 365-372.

[31] X. Feng, C. Shen, N. Ding, C. Chen, Lithium chromium oxide modified spinel LiCrTiO_4 with improved electrochemical properties, *J. Mater. Chem.* 22 (2012) 20861-20865.

[32] H. Song, S.W. Yun, H.H. Chun, M.G. Kim, K.Y. Chung, H.S. Kim, B.W. Cho, Y.T. Kim, Anomalous decrease in structural disorder due to charge redistribution in Cr-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative-electrode materials for high-rate Li-ion batteries, *Energy Environ. Sci.* 5 (2012) 9903-9913.

[33] L. Wang, Q. Xiao, L. Wu, G. Lei, Z. Li, Spinel LiCrTiO_4 fibers as an advanced anode material in high performance lithium ion batteries, *Solid State Ion.* 236 (2013) 43-47.

[34] H.L. Zou, X. Liang, X.Y. Feng, H.F. Xiang, Chromium-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with a synergistic effect of bulk doping, surface coating, and size reducing, *ACS Appl. Mater. Interfaces* 8 (2016) 21407-21416.

[35] K. Tang, X. Mu, P.A.v. Aken, Y. Yu, J. Maier, “Nano-pearl-string” TiNb_2O_7 as anodes for rechargeable lithium batteries, *Adv. Energy Mater.* 3 (2013) 49-53.

[36] C. Wang, S. Wang, Y.B. He, L. Tang, C. Han, C. Yang, M. Wagemaker, B. Li, Q.H. Yang, J.K. Kim, Combining fast Li-ion battery cycling with large volumetric energy density: grain boundary induced high electronic and ionic conductivity in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spheres of densely packed nanocrystallites, *Chem. Mater.* 27 (2015) 5647-5656.

[37] K. Mukai, Y. Kato, Role of oxide ions in thermally activated lithium diffusion of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$: X-ray diffraction measurements and raman spectroscopy, *J. Phys. Chem. C* 119 (2015) 10273-10281.

[38] K. Mukai, Y. Kato, H. Nakano, Understanding the zero-strain lithium insertion scheme of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$: Structural changes at atomic scale clarified by raman spectroscopy, *J. Phys. Chem. C* 118 (2014) 2992-2999.

[39] Y.B. He, B. Li, M. Liu, C. Zhang, W. Lv, C. Yang, J. Li, H. Du, B. Zhang, Q.H. Yang, Gassing in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based batteries and its remedy, *Sci. Rep.* 2 (2011)

913–913.

- [40] P. Martín, M.L. López, C. Pico, M.L. Veiga, $\text{Li}_{(4-x)/3}\text{Ti}_{(5-2x)/3}\text{Cr}_x\text{O}_4$ ($0 \leq x \leq 0.9$) spinels: new negatives for lithium batteries, *Solid State Sciences*, 9 (2007) 521–526.
- [41] X. Feng, N. Ding, Y. Dong, C. Chen, Z. Liu, A chromium oxide solution modified lithium titanium oxide with much improved rate performance, *J. Mater. Chem. A* 1 (2013) 15310–15315.
- [42] X. Guo, H. F. Xiang, T. P. Zhou, X. K. Ju, Y. C. Wu, Morphologies and structures of carbon coated on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and their effects on lithium storage performance, *Electrochim. Acta* 130 (2014) 470–476.
- [43] H.F. Xiang, B. Tian, P. Lian, Z. Li, H. Wang, Sol–gel synthesis and electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite anode for lithium-ion batteries, *J. Alloys Compd.* 509 (2011) 7205–7209.
- [44] X. Guo, H. F. Xiang, T. P. Zhou, W. H. Li, X. W. Wang, J. X. Zhou, Y. Yu, Solid-state synthesis and electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite for lithium-ion batteries, *Electrochim. Acta* 109 (2013) 33–38.
- [45] Y. Yang, B. Qiao, X. Yang, L. Fang, C. Pan, W. Song, H. Hou, X. Ji, Lithium titanate tailored by cathodically induced graphene for an ultrafast lithium ion battery, *Adv. Funct. Mater.* 24 (2014) 4349–4356.
- [46] Z. Zhu, F. Cheng, J. Chen, Investigation of effects of carbon coating on the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /C nanocomposites, *J. Mater. Chem. A* 1 (2013) 9484–9490.
- [47] B. Wang, J. Wang, J. Cao, H. Ge, Y. Tang, Nitrogen-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets with enhanced lithium storage properties, *J. Power Sources* 266 (2014) 150–154.
- [48] C. Chen, Y. Huang, H. Zhang, X. Wang, G. Li, Y. Wang, L. Jiao, H. Yuan, Small amount of reduce graphene oxide modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles for ultrafast high-power lithium ion battery, *J. Power Sources* 278 (2015) 693–702.
- [49] C. Lai, Y.Y. Dou, X. Li, X.P. Gao, Improvement of the high rate capability of hierarchical structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ induced by the pseudocapacitive effect, *J. Power Sources* 195 (2010) 3676–3679.
- [50] G. Zhu, K. Wen, W. Lv, X. Zhou, Y. Liang, F. Yang, Z. Chen, M. Zou, J. Li, Y.

Zhang, Materials insights into low-temperature performances of lithium-ion batteries, J. Power Sources 300 (2015) 29-40.

[51] K. Chen, Z. Yu, S. Deng, Q. Wu, J. Zou, X. Zeng, Evaluation of the low temperature performance of lithium manganese oxide/lithium titanate lithium-ion batteries for start/stop applications, J. Power Sources 278 (2015) 411-419.

[52] Y. Tao, Y. Xing, C. Rui, Y. Zhou, Z. Shao, Synthesis of pristine and carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and their low-temperature electrochemical performance, J Power Sources 195 (2010) 4997-5004.

Figure captions

Fig. 1 SEM images of: (a) LTONF precursor and (b) LCTONF precursor, (c) LTONF and (d) LCTONF. The insets show the corresponding SEM images at high-magnification.

Fig. 2 TEM images of: (a) LTONF and (b) LCTONF; (c) HRTEM images, (inset: SAED pattern) and (d) the elemental maps of LCTONF.

Fig. 3 (a) XRD patterns and (b) Raman spectra of the as-prepared LTONF and LCTONF; and Rietveld refinement patterns of (c) LTONF and (d) LCTONF.

Fig. 4 XPS spectra of (a) LTONF and (b) LCTONF.

Fig. 5 (a) Voltage profiles of LTONF and LCTONF at 0.2C rate. (b) Incremental capacity plot of the first cycle for LTONF and LCTONF (inset: partial enlarged drawing).

Fig. 6 Voltage profiles of (a) LTONF and (b) LCTONF at different charge-discharge rates; (c) The rate capabilities of LTONF and LCTONF; (d) The cycling performance and relevant columbic efficiency of the LTONF and LCTONF at 5 C rate.

Fig. 7 Voltage profiles of (a) LTONF and (b) LCTONF anode at different temperatures with 1.0 C rate. (c) The cycling performance and relevant columbic efficiency of the LTONF and LCTONF at -10 °C with 1.0 C rate.

Fig. 8 Schematic illustration of the effects of Cr modification in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers.

Table 1 The lattice parameters and fitting coefficients of LTONF and LCTONF.

Fig. 1 SEM images of: (a) LTONF precursor and (b) LCTONF precursor, (c) LTONF and (d) LCTONF. The insets show the corresponding SEM images at high-magnification.

Fig. 2 TEM images of: (a) LTONF and (b) LCTONF; (c) HRTEM images, (inset: SAED pattern) and (d) the elemental maps of LCTONF.

Fig. 3 (a) XRD patterns and (b) Raman spectra of the as-prepared LTONF and LCTONF; and Rietveld refinement patterns of (c) LTONF and (d) LCTONF.

Table 1. The lattice parameters and fitting coefficients of LTONF and LCTONF .

Sample	Phase	Phase content (wt%)	Lattice parameter (Å)			Fitting coefficients	
			a	b	c	CHI ²	R _{wp} (%)
LTONF	Li ₄ Ti ₅ O ₁₂	75.55	8.354	8.354	8.354		
	rutile	14.96	4.595	4.595	2.953	1.142	10.45
	Li ₂ TiO ₃	9.49	5.055	8.759	9.742		
LCTONF	Li _{3.9} Cr _{0.3} Ti _{4.8} O ₁₂	98.01	8.351	8.351	8.351		
	rutile	1.31	4.585	4.585	2.966	1.434	20.46
	Li ₂ TiO ₃	0.68	4.906	8.801	9.619

Fig. 4 XPS spectra of (a) LTONF and (b) LCTONF.

Fig. 5 (a) Voltage profiles of LTONF and LCTONF at 0.2 C rate. (b) Incremental capacity plot of the first cycle for LTONF and LCTONF (inset: partial enlarged drawing).

Fig. 6 Voltage profiles of (a) LTONF and (b) LCTONF at different charge-discharge rates; (c) The rate capabilities of LTONF and LCTONF; (d) The cycling performance and relevant columbic efficiency of the LTONF and LCTONF at 5C rate.

Fig. 7 Voltage profiles of (a) LTONF and (b) LCTONF anode at different temperatures with 1.0 C charge-discharge rate. (c) The cycling performance and relevant coulombic efficiency of the LTONF and LCTONF at -10 °C with 1.0 C rate.

Fig. 8 Schematic illustration of the effects of Cr modification in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers.