Building flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT lithium-ion battery anodes with superior rate performance and ultralong cycling stability

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Abstract

Nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT composite particles were synthesized using an aerosol spray drying process followed by thermal annealing. After assembling into CNT networks, lightweight, flexible and binder-free $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT anodes were fabricated for lithium-ion batteries. Electrodes fabricated from these nanocomposites showed effective electron and ion transport and, more importantly, more robust structure compared to traditional binder-bonded electrodes. The electrodes delivered a high reversible capacity and superior rate performance up to an extremely high rate of 100 C. Moreover, ultralong cycling stability was attained through 8000 rapid charge-discharge cycles with 89 % capacity retention. These results demonstrate the feasibility of ultrafast batteries.

KEYWORDS: Carbon nanotube, Lithium-ion battery, Flexible electrode, Lithium titanate

Introduction

Lightweight and flexible energy storage devices have attracted increasing attention because of their promising applications in smart electronics, wearable devices and rollup displays [1, 2]. Of particular interest are flexible lithium-ion batteries (LIBs) due to their high energy storage densities. A common approach to preparing battery electrodes is to mix active materials with carbon black and polymeric binders and press them onto metal substrates [3]. Such electrodes usually have little flexibility due to their rigid structure. Moreover, a significant amount of inert components (*e.g.*, binders) and cumbersome current collectors are used in the electrodes, inevitably compromising the devices' energy densities. Lightweight flexible substrates such as textiles [4] or plastics [5] have been proposed to replace the metal collectors. Such substrates, however, are not conductive, or, at best, less conductive than metal substrates. As an alternative approach, metal substrates and polymeric binders are eliminated; conductive nanocarbon materials [6], particularly carbon nanotubes (CNT) [7] and graphene [8] are used to make flexible electrodes. However, the design and fabrication of reliable flexible electrodes with high storage capacity, high rate capability and excellent stability remains challenging

Engineering reliable flexible CNT-based electrodes requires building of effective and robust transport of electrons and ions in electrodes. One most direct method is growing active materials on CNTs, which enables binder-free electrodes [9]. Such electrodes mostly have improved rate performance due to the intimate contacts between the active materials and the CNTs. Nevertheless, due to the hydrophobic interfacial properties, phase separation of CNTs leads to difficult fabrication of such electrodes. To circumvent this problem, several groups have proposed to deposit active materials on CNT substrates using atomic layer

deposition [10], chemical vapor deposition [11], and other deposition methods [12, 13]. However, the expensive equipments and high synthesis costs limit their applications. Simple mixing of active materials with CNTs may be a viable solution. If properly engineered, robust flexible electrodes can be built with high electron conductivity and intimate interfacial contacts. Recently, mechanical mixing TiO_2 nanoparticles with CNTs result in binder-free electrode with much better rate performance. However, binder-free electrodes using nanoparticles usually exhibit low stability due to the too heightened reactivity at their excessive exposed interfaces. When using bulk particles, reduced interfacial areas result in slower ion transport kinetics, leading to limited rate performance.

Here, we reported the fabrication of high-performance flexible LIB anodes based on CNT networks and nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT composite particles. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was chosen as an anode material because of its stability in repeated lithium insertion/extraction reactions [15-18]. In our synthesis, nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT composites were prepared using aerosol spray drying process followed by high-temperature annealing. As illustrated in Figure 1a, CNTs were dispersed into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ precursor solution. An aerosol spray drying process generated droplets of the precursor and CNTs, which were then condensed into solid particles by solvent (ethanol) evaporation. The aerosol particles produced were collected and annealed at 800 °C for 24 h, forming nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT composites. Vacuum filtration of the nanocomposite particles with CNTs yielded binder-free, flexible LIB anodes.

Figure 1b is a schematic of as-synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT nanocomposites. Compared to previously reported work [19-25], the nanocomposites exhibit several unique features. First, conductive CNTs were directly condensed into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spheres, forming intimate and robust interfacial contacts between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the CNTs. Next, the converted $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystals were small with short solid-state ion diffusion length and the nanocrystal networks had

interconnected channels which enabled facile electrolyte transport. Furthermore, the binder-free anodes based on highly entangled CNT networks provided a flexible, conductive and porous scaffold, facilitating ion and electron transport.

Experimental

Material synthesis

The multi-walled CNTs used were produced from a chemical vapor deposition (CVD) process and purified using an 18 % HCl solution and a 20 % HF solution in sequence to remove residual catalyst. The purified CNTs were washed using de-ionized water and then transferred into an $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2=4:1$ volume ratio) to oxidize the surface at 0 °C for 2 h [26]. 75 mg of these weakly oxidized CNTs were dispersed into 40 mL of isopropyl alcohol using ultrasonication for 0.5 hr. Then, 3.7060 g of tetra-n-butyltitanate, 0.6036 g of lithium acetate and 0.3378 g sucrose were dissolved into 60 mL of isopropyl alcohol, forming a precursor solution. To prepare $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ nanocomposites, 40 mL of the aforementioned CNT dispersion, 60 mL of precursor solution and additional 20 mL of isopropyl alcohol were mixed. The dispersion was then sent through an atomizer using nitrogen as a carrier gas. The aerosol droplets produced passed through a glass tube heated to 450 °C; as-formed particles were collected using a filter. Then, the collected particles were annealed at 800 °C under argon for 24 h, forming the final $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ nanocomposites.

The 80 wt-% of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composite particles and 20 wt-% extra CNTs were dispersed in N-methyl-2-pyrrolidone (NMP) to form a uniform dispersion. Freestanding composite films were formed by vacuum filtration. As-obtained films were dried in a vacuum oven at 100 °C for 12 hr before use. To make traditional electrodes for comparison, 80 wt-% of aerosol-synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composite particles, 10 wt-% carbon black, and 10 wt-% polyvinylidene fluoride (PVDF) were mixed with NMP to form slurries. The

homogenous slurries were coated on steel substrates and dried under vacuum at 100 °C for another 12 h.

Material characterization

X-ray diffraction (XRD) was conducted on a Panalytical X'Pert Pro x-ray powder diffractometer using Cu-K_α radiation ($\lambda=1.54 \text{ \AA}$). Raman spectroscopy were performed on a Horiba Jobin Yvon Lab RAMHR800 Raman spectrometer with He-Ne laser excitation at 633 nm. Thermalgravimetric analysis (TGA) was conducted on a TGA Q50 instrument at a ramp rate of $20^\circ \text{ min}^{-1}$ under oxygen gas. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method using a desorption branch in a relative pressure (P/P_0) range from 0.04 to 0.25. Scanning electron microscopy (SEM) experiments were conducted on a JEOL JSM-6700 FE-SEM instrument operated at 3.0 kV. Transmission electron microscopy (TEM) experiments were carried out on a JEOL JEM-2010 operated at 120.0 kV. The volume conductivity measurements of the composite film and binder-bonded electrodes under bending were conducted using a 266 Clamp Meter.

Electrochemical measurement

To test the electrochemical performance of the flexible anodes, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composite films were cut into desired sizes. The flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ anodes were then assembled into 2032-type coin cells, where glass fibers (Whatman) were used as separators and lithium foils were used as both counter and reference electrodes. The electrolyte solution was 1 mol L^{-1} LiPF_6 in propylene carbonate (PC). All the cells were assembled in an argon-filled glovebox. Cyclic voltammetry (CV) measurements were performed on a Bio-Logic VMP3 electrochemical workstation at a scan rate of 0.2 mV s^{-1} in a voltage range between 1.0 and 2.8 V (vs. Li/Li^+). Electrochemical impedance spectroscopy (EIS) tests of cells were carried

out on a Solartron 1860/1287 Electrochemical Interface. The constant-current charge and discharge measurements were conducted using a LAND CT2000 at various current densities.

Results and discussion

Figure 2a shows the low-magnification scanning electron microscope (SEM) images of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ nanocomposites. It exhibits that the nanocomposites are spherical granules with diameters largely distributed around ~ 400 nm (Figure S1 of Supplementary Information). Their texture is rough, with threading CNTs visible on their surfaces (Figure 2b). Close observation of transmission electron microscope (TEM) images (Figure 2c) shows that lots of CNTs interpenetrated into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanocrystal networks. The nanocomposites exhibit direct interfacial contact between the CNT and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ components. The interlayer spacing of crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and CNTs is also given by Figure 2d. The lattice spacing of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystals corresponding to the (111) crystal plane is 0.486 nm, which demonstrates that the active material is well-crystallized $\text{Li}_4\text{Ti}_5\text{O}_{12}$, as confirmed by X-ray diffraction (XRD) characterization.

Figure 3a shows the XRD pattern of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composites. They exhibit intense diffraction peaks of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with characteristic diffraction peaks at 18.3 , 35.5 , 43.5 , 47.6 , 57.2 , 63.0 and 66.2° , corresponding to the (111), (311), (400), (331), (333), (440) and (531) crystal faces (JCPDS card no. 49-0207) [27]. The XRD results suggest the successful conversion of the aerosol spray products into crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composites after annealing. Note that the characteristic CNT diffraction peak of (002) crystal face at 26.2° was not obvious. Consistent with morphology characterization, however, Raman spectroscopy (Figure 3b) detected the existence of carbons with high graphitization. Characteristic peaks of the D and G bands corresponding to the disordered and graphitized carbons were observed at 1350 and 1580 cm^{-1} respectively, which could be ascribed to the

existence of CNTs, as well as decomposed carbons [28]. The mass fractions of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and carbons were estimated to be ~ 89 and ~ 11 wt-% in the nanocomposite particles.

In addition, nitrogen sorption isotherms of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ nanocomposites suggest interconnected porous channels exist in the composites (Figure 3c). The surface area of the powder samples was measured to be $42.7 \text{ m}^2 \text{ g}^{-1}$ with broad pore sizes distributed around 20-60 nm. Such pore structure facilitates electrolyte transport, a key factor affecting an electrode's rate performance.

A homogeneous dispersion of nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composites and CNTs were prepared, which was used to produce flexible electrodes based on a simple vacuum filtration method (Figure 4a). The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ particles were well entangled with the high-aspect-ratio CNTs, forming free-standing electrodes without the introduction of any polymeric binders (Figure 4b). These highly entangled electrodes possess good mechanical strength. Figure 4c shows the stress-strain curve of an electrode containing 80 wt-% composite particles and 20 wt-% CNTs, where a tensile strength of 1.2 MPa at a strain of 0.97 % was attained. The strength ensured the electrodes' mechanical stability. The robust structure was further confirmed through electrical conductivity measurements under bending (Figure 4d). Indeed, flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ electrodes had a constant resistance under different degrees of bending. Traditional binder-bonded electrodes had much greater resistance under bending. The difference was ascribed to the entanglements of CNT networks with $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ particles within the electrodes, which was observed under SEM technique (Figure 4e). By comparison, the pathways constructed by polymeric binders and carbon black in traditional electrodes were limited in flexibility and conductivity (Figure S2).

Spray synthesis of nanostructured composites are important to increase the packing density [29, 30], thus yielding electrodes with high loading of active materials, which is

essential to ensuring high energy density of electrodes. The packing density of our flexible composite electrode was 1.1 g cm^{-3} , which is comparable to that of graphite (1.0 g cm^{-3} for graphite). Figure S3 shows thermogravimetric analysis (TGA) of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composite electrodes in oxygen gas, 70 % of the weight is attributed to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ loading in the electrode. In comparison, direct mixing of nano-sized active materials for high rate performance usually requires a large quantity of conductive carbons and polymeric binders which inevitably compromises the total electrode performance [31]. Alternatively, direct growth of active $\text{Li}_4\text{Ti}_5\text{O}_{12}$ on CNTs resulted in low active loading and even phase separation [32, 33]. Here, the demonstrated method was simple and effective, encountering none of the aforementioned issues.

Coin-cells were constructed to measure electrochemical performance of the fabricated flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ electrodes. Figure 5a shows the cyclic voltammetry (CV) profile at a scan rate of 0.2 mV s^{-1} . The cathodic peak for the first cycle was weak because the fresh cell was not fully charged. However, after fully charged from the second cycle, the current peaks of CV curves increased and became highly reversible. Consistent with previous literatures [34], well-defined redox peaks of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were observed at around 1.55/1.42 V associated with Li insertion/extraction in anodic and cathodic regions. Figure 5b shows initial three galvanostatic charge/discharge profiles of the electrode between the cutoff voltages of 1.0 and 2.8 V vs Li^+/Li at an electrode current density of 20 mA g^{-1} . The charge/discharge curves have a pair of distinguished plateaus, which reflects one-stage Li^+ insertion/extraction behavior. The initial charge and discharge capacities calculated for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ component in the flexible anodes were 172 and 167 mAh g^{-1} respectively, corresponding to a high Coulombic efficiency of 97 %. In general, nanostructured hybrid anode materials, such as metal oxides [35], have high capacities but low Coulombic

efficiencies because of the formation of solid electrolyte interphases (SEI) and side reactions occurring at the electrode/electrolyte interfaces. Nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT composite could circumvent this effect due to their higher voltage windows.

Figure 5c illustrates the impressive rate-capability of flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT electrodes. At a current density of 1 C (corresponding to 100 mA g^{-1} for the total mass of electrode), the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ component in the composite electrodes had a discharge capacity of 163 mAh g^{-1} . At an increased current density of 10 C, they had a capacity of 143 mAh g^{-1} . Even at super-high rates of 100 C, the capacity still approached 108 mAh g^{-1} , corresponding to 66 % capacity retention from 1 C. By comparison, the discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in traditional electrode is much lower, only 74 mAh g^{-1} at 100 C. The overall CNT contribution to capacity within the electrode was less than 5.2 %, which was relatively small compared to that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the voltage of 1.0-2.8 V (Figure S4). We also compared the rate performance of electrodes with different compositions (Figure S5). The results showed that the electrodes with 23 and 30 wt-% carbon contents had comparable discharge capacity based on the total mass of electrodes. However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ component in the electrodes with 30-wt% carbon contents had higher discharge capacity if deducting CNT contribution. Moreover, further increase of active materials reduced the electrochemical performance due to reduced conductivity (Figure S5). Upon returning back to a rate of 10 C after 90 cycles at various rates, the composite anodes still delivered the same capacity of 143 mAh g^{-1} , suggesting excellent reversible stability. The excellent rate performance is ascribed to the significantly enhanced storage kinetics of flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT electrodes and their facile lithium ion diffusion and electron transport, which was confirmed using electrochemical impedance measurements. The impedance spectra of the flexible electrodes were compared with traditional electrodes over the frequency range of 100 kHz to 0.1 Hz (Figure 5d). As

expected, the flexible electrode displayed an approximately 80° inclined line in the low-frequency range, which can be attributed to Warburg impedance, associated with the lithium-ion diffusion in the electrode. A small semicircle is present in the high-frequency range, which is related to the charge transfer resistance [36, 37]. The results (Figure S6 and Table S1 in Supplementary Information) showed that the flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ electrodes exhibited higher electron conductivity and lower ion transport resistance. The rate-capability of our flexible electrodes exceeds most reported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based electrodes [38-46], and is comparable to porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated by N-doped carbon (129 mAh g^{-1} at 10 C) [15], carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ microspheres (123 mAh g^{-1} at 100 C) [47], graphene-supported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanosheets (130 mAh g^{-1} at 100 C) [8], hydrogenated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanowire arrays (121 mAh g^{-1} at 30 C) [48], self-supported nanosheet arrays (99 mAh g^{-1} at 100 C) [49] and other nanostructured composites [50-52]. Such electrodes are being developed for next-generation hybrid supercapacitor applications due to their superior rate performance [53].

The long-term cycling stability of the flexible electrodes was measured at an electrode current density of 1 A g^{-1} (Figure 6a). The discharge capacity of the total electrode reached 103 mAh g^{-1} . The electrode avoids the use of polymer binders ($\sim 10 \text{ wt-\%}$ in total weight) which do not contribute to lithium storage capacity, and hence provide higher overall storage density. Stable performance was attained in 8000 cycles, with a discharge capacity decay of less than 0.0014% per cycle, which, to our knowledge, was never achieved before [49, 54]. By comparison, due to the lower structure flexibility, the capacity of traditional electrodes drops by 25% after 6000 cycles (Figure S7). Note that the stability criterion is of great importance for the realization of the flexible devices in practice. The stability of the designed electrode is comparable or even superior to that of all-carbon supercapacitors [55-57], and they possess higher energy storage capability. Their charge/discharge efficiencies

approached 100 % during cycling, indicating good reversibility. To further confirm the electrodes' structural integrity, after 8000 cycles, they were taken out of the batteries and examined under electron microscopies. As shown in Figure 6b, the electrodes retained their macroscopic flexibility and their hierarchical porous structure, indicating the ultralong life of such anodes at the high rates. These results demonstrate that the flexible anodes described herein are both highly stable and highly reliable.

Conclusions

In summary, we have demonstrated a simple yet effective process to synthesize ultrastable, flexible, and binder-free $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composite anodes for LIBs. Nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composites were successfully prepared using an aerosol technique, and were then entangled into CNT networks and used to prepare anodes. The fabricated LIB anodes had superior rate performance and ultrastable cycling performance through 8000 rapid charge-discharge cycles. The synthetic method developed herein may be extended to other systems to fabricate additional high-performance flexible electrodes.

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References

- [1] G. Zhou, F. Li, H.-M. Cheng, *Energy Environ. Sci.* 7 (2014) 1307-1338
- [2] F.-R. Fan, Z.-Q. Tian, Z. Lin Wang, *Nano Energy* 1 (2012) 328-334.
- [3] N. Li, G. Zhou, F. Li, L. Wen, H.-M. Cheng, *Adv. Funct. Mater.* 23 (2013) 5429-5435.
- [4] L. Hu, M. Pasta, F.L. Mantia, L. Cui, S. Jeong, H.D. Deshazer, J.W. Choi, S.M. Han, Y. Cui, *Nano Lett.* 10 (2010) 708-714.
- [5] F. Meng, Y. Ding, *Adv. Mater.* 23 (2011) 4098-4102.
- [6] D. Wei, P. Hiralal, H. Wang, H. Emrah Unalan, M. Rouvala, I. Alexandrou, P. Andrew, T. Ryhänen, G.A.J. Amaratunga, *Nano Energy* 2 (2013) 1054-1062.
- [7] X. Jia, C. Yan, Z. Chen, R. Wang, Q. Zhang, L. Guo, F. Wei, Y. Lu, *Chem. Commun.* 47 (2011) 9669-9671.
- [8] N. Li, Z. Chen, W. Ren, F. Li, H.-M. Cheng, *Proc. Natl. Acad. Sci. U. S. A.* 109 (2012) 17360-17365.
- [9] X. Jia, C. Yan, Z. Chen, R. Wang, Q. Zhang, L. Guo, F. Wei, Y. Lu, *Chem. Commun.* 47 (2011) 9669-9671.
- [10] S. Boukhalfa, K. Evanoff, G. Yushin, *Energy Environ. Sci.* 5 (2012) 6872-6879.
- [11] L.-F. Cui, L. Hu, J.W. Choi, Y. Cui, *ACS Nano* 4 (2010) 3671-3678.
- [12] M.D. Lima, S. Fang, X. Lepró, C. Lewis, R. Ovalle-Robles, J. Carretero-González, E. Castillo-Martínez, M.E. Kozlov, J. Oh, N. Rawat, *Science* 331 (2011) 51-55..
- [13] S.W. Lee, J. Kim, S. Chen, P.T. Hammond, Y. Shao-Horn, *ACS Nano* 4 (2010) 3889-3896.
- [14] Z. Chen, D. Zhang, X. Wang, X. Jia, F. Wei, H. Li, Y. Lu, *Adv. Mater.* 24 (2012) 2030-2036.
- [15] L. Zhao, Y.S. Hu, H. Li, Z. Wang, L. Chen, *Adv. Mater.* 23 (2011) 1385-1388.
- [16] E.M. Sorensen, S.J. Barry, H.-K. Jung, J.M. Rondinelli, J.T. Vaughey, K.R. Poeppelmeier, *Chem. Mater.* 18 (2006) 482-489.

- [17] Y.B. He, B.H. Li, M. Liu, C. Zhang, W. Lv, C. Yang, J. Li, H.D. Du, B.A. Zhang, Q.H. Yang, J.K. Kim, F.Y. Kang, *Sci. Rep.* 2 (2012).
- [18] H.G. Jung, M.W. Jang, J. Hassoun, Y.K. Sun, B. Scrosati, *Nature Commun.* 2 (2011).
- [19] Y. Tang, L. Yang, S. Fang, Z. Qiu, *Electrochim. Acta* 54 (2009) 6244-6249.
- [20] A. Nugroho, S.J. Kim, W. Chang, K.Y. Chung, J. Kim, *J. Power Sources* 244 (2013) 164-169.
- [21] W. Liu, D. Shao, G. Luo, Q. Gao, G. Yan, J. He, D. Chen, X. Yu, Y. Fang, *Electrochim. Acta* 133 (2014) 578-582.
- [22] Y. Ma, B. Ding, G. Ji, J.Y. Lee, *ACS Nano* 7 (2013) 10870-10878.
- [23] S.-L. Chou, J.-Z. Wang, H.-K. Liu, S.-X. Dou, *J. Phys. Chem. C* 115 (2011) 16220-16227.
- [24] 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.
- [25] L. Yu, H.B. Wu, X.W. Lou, *Adv. Mater.* 25 (2013) 2296-2300.
- [26] X. Jia, Q. Zhang, M.-Q. Zhao, G.-H. Xu, J.-Q. Huang, W. Qian, Y. Lu, F. Wei, *J. Mater. Chem.* 22 (2012) 7050-7056.
- [27] Z. Liu, N. Zhang, K. Sun, *J. Mater. Chem.* 22 (2012) 11688-11693.
- [28] B. Li, C. Han, Y.-B. He, C. Yang, H. Du, Q.-H. Yang, F. Kang, *Energy Environ. Sci.* 5 (2012) 9595-9602.
- [29] D.S. Jung, Y.N. Ko, Y.C. Kang, S.B. Park, *Adv. Powder Technol.* 25 (2014) 18-31.
- [30] X. Jia, Z. Chen, X. Cui, Y. Peng, X. Wang, G. Wang, F. Wei, Y. Lu, *ACS Nano* 6 (2012) 9911-9919.
- [31] C. Jiang, M. Wei, Z. Qi, T. Kudo, I. Honma, H. Zhou, *J. Power Sources* 166 (2007) 239-243.

- [32] Y.R. Jhan, J.G. Duh, J. Power Sources 198 (2012) 294-297.
- [33] H. Ni, L.-Z. Fan, J. Power Sources 214 (2012) 195-199.
- [34] L. Shen, X. Zhang, E. Uchaker, C. Yuan, G. Cao, Adv. Energy Mater. 2 (2012) 691-698.
- [35] Z.-S. Wu, G. Zhou, L.-C. Yin, W. Ren, F. Li, H.-M. Cheng, Nano Energy 1 (2012) 107-131.
- [36] Y. Shi, J. Gao, H.D. Abruña, H. Liu, H. Li, J. Wang, Y. Wu, Nano Energy 8 (2014) 297-304.
- [37] X. Jia, Z. Chen, A. Suwarnasarn, L. Rice, X. Wang, H. Sohn, Q. Zhang, B.M. Wu, F. Wei, Y. Lu, Energy Environ. Sci. 5 (2012) 6845-6849.
- [38] A. Nugroho, W. Chang, S. Jin Kim, K. Yoon Chung, J. Kim, RSC Adv. 2 (2012) 10805-10808.
- [39] X. Guan, X. Chen, G. Li, Y. Zang, H. Lin, D. Luo, L. Li, RSC Adv. 3 (2013) 3088-3094.
- [40] W. Zhang, J. Li, Y. Guan, Y. Jin, W. Zhu, X. Guo, X. Qiu, J. Power Sources 243 (2013) 661-667.
- [41] A.S. Prakash, P. Manikandan, K. Ramesha, M. Sathiya, J.M. Tarascon, A.K. Shukla, Chem. Mater. 22 (2010) 2857-2863.
- [42] X. Li, H.-C. Lin, W.-J. Cui, Q. Xiao, J.-B. Zhao, ACS Appl. Mater. Interfaces 6 (2014) 7895-7901.
- [43] K.S. Park, A. Benayad, D.J. Kang, S.G. Doo, J. Am. Chem. Soc. 130 (2008) 14930-14931.
- [44] J.R. Li, Z.L. Tang, Z.T. Zhang, Electrochem. Commun. 7 (2005) 894-899.
- [45] L. Shen, C. Yuan, H. Luo, X. Zhang, L. Chen, H. Li, J. Mater. Chem. 21 (2011) 14414-14416.
- [46] H. Pan, L. Zhao, Y.-S. Hu, H. Li, L. Chen, ChemSusChem 5 (2012) 526-529.

- [47] H.-G. Jung, S.-T. Myung, C.S. Yoon, S.-B. Son, K.H. Oh, K. Amine, B. Scrosati, Y.-K. Sun, *Energy Environ. Sci.* 4 (2011) 1345-1351.
- [48] L. Shen, E. Uchaker, X. Zhang, G. Cao, *Adv. Mater.* 24 (2012) 6502-6506.
- [49] S. Chen, Y. Xin, Y. Zhou, Y. Ma, H. Zhou, L. Qi, *Energy Environ. Sci.* 7 (2014) 1924-1930.
- [50] L.F. Shen, H.S. Li, E. Uchaker, X.G. Zhang, G.Z. Cao, *Nano Lett.* 12 (2012) 5673-5678.
- [51] J. Liu, K.P. Song, P.A. van Aken, J. Maier, Y. Yu, *Nano Lett.* 14 (2014) 2597-2603.
- [52] Y.M. Jiang, K.X. Wang, H.J. Zhang, J.F. Wang, J.S. Chen, *Sci. Rep.* 3 (2013).
- [53] K. Naoi, W. Naoi, S. Aoyagi, J.-i. Miyamoto, T. Kamino, *Acc. Chem. Res.* 46 (2012) 1075-1083.
- [54] 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.
- [55] X. Li, B. Wei, *Nano Energy* 2 (2013) 159-173.
- [56] X. Xiao, T. Li, Z. Peng, H. Jin, Q. Zhong, Q. Hu, B. Yao, Q. Luo, C. Zhang, L. Gong, J. Chen, Y. Gogotsi, J. Zhou, *Nano Energy* 6 (2014) 1-9.
- [57] G. Ning, Z. Fan, G. Wang, J. Gao, W. Qian, F. Wei, *Chem. Commun.* 47 (2011) 5976-5978.

Figure 1 Schematic of a) aerosol spray drying process and b) the prepared nanostructured Li₄Ti₅O₁₂/CNT composites.

Figure 2 a, b) SEM and c, d) TEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composite particles at different magnifications.

Figure 3 a) XRD pattern, b) Raman spectrum and c) nitrogen-sorption isotherms and BJH

pore size distribution (inset) of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composite particles.

Figure 4 a) Structure and fabrication of the flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ electrode. b) A photograph of the flexible electrode and its low-magnification SEM image (inset). c) Stress-

strain curve of the flexible electrodes. d) Resistance changes of the flexible electrode in comparison with that of traditional electrode. e) Cross-sectional SEM morphology of the flexible electrode, showing intimate entanglement between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT composite particles and CNTs.

Figure 5 a) CV curves of flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNT electrode at a scanning rate of 0.2 mV s^{-1} . b) Galvanostatic charge/discharge curves of the flexible electrode at an electrode current density of 20 mA g^{-1} between 1.0-2.8 V. c) Rate performance and d) electrochemical impedance spectra of the flexible electrode compared with traditional electrode.

Figure 6 a) Cycling stability and Coulombic efficiency of flexible $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ electrode at a current density of 1 A g^{-1} . b) Morphology of the flexible electrode after cycling (Inset is the digital photograph of the electrode after 8000 cycles).

Graphical Abstract

Nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ composite particles were synthesized and assembled into CNTs, leading to formation of light-weight, flexible and binder-free electrodes with superior rate performance and ultralong cycling stability.

Personal Portrait Photo and Biosketch

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