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A Simple Synthesis of Porous Titanium Dioxide Nanofibres with a Large Specific Surface Area by Electrospinning as High-Performance Anode Materials for Lithium-Ion Batteries

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Anatase titanium dioxide is considered a promising anode material for lithium-ion batteries (LIBs), however its application is restricted due to the poor Li⁺ transport. Nano-crystallization and pore creation are regarded as two effective strategies for solving the above shortcomings. This study aims to realize the combination of the two strategies by synthesizing porous anatase TiO₂ nanofibres by electrospinning with camphene as the pore-creating agent. Porous anatase TiO₂ nanofibres as anode materials for LIBs demonstrated excellent electrochemical performance when a suitable content of camphene was added. The results indicated that a larger specific surface area ($72 \text{ m}^2 \cdot \text{g}^{-1}$) was obtained in anatase TiO₂ nanofibres with 12 wt.% camphene than in those without camphene ($61 \text{ m}^2 \cdot \text{g}^{-1}$). The former exhibited a higher initial discharge specific capacity ($518.71/294.99 \text{ mAh} \cdot \text{g}^{-1}$) than the latter ($305.56/114.68 \text{ mAh} \cdot \text{g}^{-1}$). Moreover, the former demonstrated outstanding cycle performance due to the higher retention rate of 21.7% obtained after 100 cycles. Meanwhile, an excellent rate performance was also achieved due to a larger average discharging specific capacity ($58.96 \text{ mAh} \cdot \text{g}^{-1}$) being when the current density increased from 0.5 C to 10 C and recovered to 0.5 C ($145.71 \text{ mAh} \cdot \text{g}^{-1}$). The improvement in electrochemical performance should be attributed to the low charge transfer resistance (R_{ct}) and large transportation rate of Li⁺ resulting from the obtained high specific surface area.

Keywords: Electrospinning, porous anatase titanium dioxide, Camphene, Lithium-ion battery anode

1. INTRODUCTION

Lithium-ion batteries (LIBs) have attracted wide attention due to their light weight, small size, good safety, high working voltage, high energy density, and long service life. Anode materials are considered an essential factor responsible for their service performance[1-5]. Graphite, as a traditional commercial anode material is applied to LIBs; however, its electrochemical performance is seriously restricted due to its low theoretical capacity (372 mAh·g⁻¹), abundant reactions, poor structural

stability, and low charge-discharge platform[6-8]. Titanium dioxide (TiO₂) is regarded as a very promising anode material for LIBs owing to its low cost, good safety, small volume expansion (4%) and high potential of discharge-charge platforms (1.5-1.8 V (vs. Li/Li⁺)). However, the low lithium ion diffusion rate and poor electronic conductivity limit its practical application[9-11].

Nano-crystallization and pore creation have been regarded as two effective strategies for solving the above shortcomings. TiO_2 with nanostructures (nanofibres, nanotubes, nanorods, nanoparticles, etc.) was fabricated to improve its electrochemical performance. R. Oing et al.[12] prepared TiO₂ nanofibres by electrospinning followed by calcining in air or a flowing argon atmosphere. The electrode made of TiO₂ subjected to calcination in an argon atmosphere exhibited a discharging specific capacity of 250 mAh·g⁻¹ at 10 C, which was increased by 27% compared with that of the air-calcined TiO₂ electrode. O. Fasakin et al.[13] synthesized anatase TiO₂ nanotubes via hydrothermal treatment. The TiO₂ electrode demonstrated a discharge specific capacity of 142 mAh·g⁻ ¹ at 36 mA·g⁻¹ after 100 cycles, which was superior to that obtained in the pristine material (38 mAh·g⁻¹) 1 at 36 mA $\cdot g^{\text{-1}}$ after 100 cycles). Y. Liu et al.[14] prepared rutile/anatase TiO_2 nanorods via a hydrothermal method. The electrode exhibited a higher retained discharge specific capacity of 102.7 mAh·g⁻¹ after 1000 cycles at 10 C, which was higher than that of pure rutile/anatase TiO₂ (45.8) $mAh \cdot g^{-1}$ at 10 C after 1000 cycles). H. Liu et al.[15] prepared TiO₂ (n)-T (n and T are the hydrothermal reaction time and calcination temperature) nanoparticles by a template method. The TiO₂ (48)-550 sample showed a superior rate performance of 165 mAh \cdot g⁻¹ at 10 C and 116 mAh \cdot g⁻¹ at 60 C. Moreover, there are many investigations into porous TiO₂ to improve the electrochemical performance of TiO₂ electrodes. W. Wu et al.[16] successfully synthesized mesoporous TiO₂ (MT) by a hydrothermal method with a template (a nonionic copolymer template, a cationic template, or an anionic template) approach, and investigated the effect of template type and addition amount on the electrochemical performance of MT. The results indicated that the MT-3F (F refers to the template type) sample had a high discharge specific capacity of approximately 131.2 mAh \cdot g⁻¹ at 1 C after 1000 cycles. S.I. Choi et al.[17] prepared lotus-root shaped meso-/macroporous TiO₂ (LR-TiO₂) through calcination at different temperatures. LR-TiO₂ calcined at 450 °C with the highest anatase ratio and largest specific surface area showed the best discharge specific capacity of 120 mAh·g⁻¹ after the first cycle and the highest retention rate of 74% after 100 cycles. All these studies proved that nanocrystallization and pore creation endowed TiO₂ with a larger specific surface area and more active sites, further improving its electrochemical performance.

In this work, nano-crystallization and pore creation were combined to successfully synthesize porous A-TiO₂ nanofibres via simple electrospinning followed by calcining with camphene as the pore-creating agent. The morphology of TiO₂ nanofibres was changed by adding different loading amounts of camphene, and the morphological structures of TiO₂ nanofibres were characterized by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and N₂ adsorption–desorption patterns. The electrochemical performances of TiO₂ nanofibres used as electrode materials in lithium-ion batteries were determined by cyclic voltammetry, and galvanostatic charge-discharge tests. Hence, this work provides a simple synthesis of porous anatase TiO₂ nanofibres with promising high-performance for use as anode materials in LIBs.

2. EXPERIMENTAL PART

2.1 Preparation of porous anatase TiO₂ nanofibres

Porous anatase TiO₂ nanofibres were prepared by electrospinning and subsequent heat treatment. First, the precursor solution was prepared by adding 2 mL tetra-n-butyl titanate (TBOT, 99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), 2 mL acetic acid (99.5%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), 0.3 g polyvinylpyrrolidone (PVP, MW: 1300000 g·mol⁻¹, Aladdin Industrial Corporation, Shanghai, China) and different contents of camphene (95%, Aladdin Industrial Corporation, Shanghai, China) to 6 mL absolute ethyl alcohol (99.7%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) with stirring overnight. The relative mass percent of camphene in the solution was regulated to be 0 wt.%, 8 wt.%, 12 wt.%, and 16 wt.%, and the finally obtained TiO₂ nanofibres were named PT-1, PT-2, PT-3 and PT-4, respectively. Next, the prepared precursor solution was put in a 20 mL plastic syringe with a 23-gague stainless-steel nozzle. The applied voltage between the drum and the syringe tip was 8 kV, and the distance between them was maintained at 15 cm. The rotation speed of the drum was kept at 50 rpm, and the flow rate was 0.01 mL·h⁻¹. The filaments sprayed from the solution were collected on a drum collector covered with aluminium foil. The obtained as-spun nanofibres were stabilized at 150 °C for 24 h and then heat-treated at 400 °C, 500 °C and 600 °C for 3 h in air.



Figure 1. Schematic diagram of electrospinning apparatus.

2.2. Electrochemical measurements of the coin cells

To prepare the anodes, the active materials, carbon black, and polyvinylidene fluoride (PVDF) with a mass ratio of 8:1:1 were stirred in a ball mill for three minutes, and then N-methyl-2-pyrrolidone (NMP) was added to form a uniform slurry. The slurry was coated on a copper foil with a coating machine. The coated copper foil was moved into a vacuum oven, dried at 60 °C for 12 h, and then punched into a 12 mm diameter electrode sheet with a punching tool. Pure lithium foil was used as the counter electrode. A solution composed of 1 M lithium hexafluorophosphate (LiPF₆), ethylene

carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte. The coin cells were assembled in a glove box full of argon (Super 1220/750/900, Shanghai Mikrouna Electromechanical Technology Co., Ltd, Shanghai, China).

Galvanostatic charge-discharge tests were carried out using an electrochemical workstation (CT 4008, Neware Electronics Co., Ltd, Shenzhen, China) with a potential window of 0.05 to 3.0 V (vs. Li/Li⁺) at a current density of 0.5 C for 100 cycles (1C=168 mAh·g⁻¹). The rate performance was evaluated at different current densities of 0.5 C, 1 C, 2 C, 5 C and 10 C. Cyclic voltammetry (CV) tests were performed on an electrochemical workstation (CHI 760E, CH Instruments Ins, Shanghai, China) with a potential window of 0-3.0 V (vs. Li/Li⁺) at 0.1 mV·s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed with an electrochemical workstation (Autolab-PGSTAT302N, Metrohm, Herisau, The Netherlands) at room temperature with a perturbation amplitude of 5 mV applied over a frequency window from 0.1 MHz to 0.01 Hz to probe the kinetic properties of the materials.

2.3. Materials characterizations

The phase constituents of the samples were identified by utilizing X-ray diffraction (XRD, D2-PHASER, Bruker, Karlsruhe, Germany) with Cu K α radiation(γ =0.1540560 nm). The morphologies and structures of the samples were analysed by a field-emission scanning electron microscopy (FESEM, S-4800, HITACHI, Tokyo, Japan) and a transmission electron microscopy (TEM, JEM-2100F, JOEL, Tokyo, Japan) coupled with energy dispersive spectroscopy (EDS, X-MAX 65T, OXFORD, England, UK). The specific surface area was measured by obtaining Brunauer Emmett Teller nitrogen adsorption-desorption isotherms (JW-BK200B, Beijing JWGB Sci&Tech Co., Ltd., Beijing, China) at 77 K.

3. RESULTS AND DISCUSSION

3.1 Characterization of nanofibres

Fig.1 shows the XRD patterns of the PT-2 nanofibres subjected to heat treatment at different temperatures (400 °C, 500 °C, and 600 °C). By comparing the d values with standard values from JCPDS cards, the nanofibres treated at 400 °C can be identified as single anatase TiO₂ (JCPDS, No. 00-021-1272)[18]. However, two weak peaks at 27.4° and 35.9° appear when the temperature is elevated to 500 °C, which confirms the formation of rutile TiO₂. The relative content of rutile TiO₂ further increased with increasing temperature to 600 °C because the three peaks related to rutile TiO₂ were observed. Two characteristic peaks associated with anatase (101) and rutile (110) can be applied to calculate their relative contents (90% and 85% anatase TiO₂ at 500 °C and 600 °C, respectively) according to the following Spurr-Myers formula[19]:

$$X_{A} = \frac{100}{\left(1 + 1.265 \frac{I_{R}}{I_{A}}\right)}$$
(1)

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Where X_A denotes the mass percent of anatase TiO₂, I_A and I_R refer to the intensities of the (101) peak related to anatase TiO₂ and the (110) peak related to rutile TiO₂, respectively.



Figure 2. XRD patterns of the PT-2 nanofibers treated at different temperatures.

The results indicate that elevated temperature can promote the transformation from metastable anatase TiO₂ to stable rutile TiO₂. Such a transformation will further have a significant effect on the electrochemical performance of nanofibres due to their difference in crystal structure. Compared with rutile TiO₂, more defects and vacancies are involved in the lattice structure of anatase TiO₂, which allows the latter to trap more electrons. Moreover, anatase TiO₂ can provide wide bidirectional channels or the insertion/extraction of Li⁺ unlike rutile TiO₂ with a narrow channel 4 nm in radius, so anatase TiO₂ has a the higher lithium intercalation capacity than rutile TiO₂ [20,21]. The samples subjected to heat treatment at 400 °C will be selected for subsequent studies to achieve more anatase TiO₂ with better activity recovery.



Figure 3. The SEM images of (a) PT-1, (b) PT-2, (c) PT-3 and (d) PT-4.



Figure 4. Changes in nanofiber morphology with different camphene.

FESEM testing was performed to investigate the evolution in morphology with varying the content of camphene (shown in Fig. 3). The morphology is closely related to the content of camphene. The camphene free nanofibres are uniform and approximately 200 nm in diameter, and their surfaces are very smooth (Fig. 3(a)). A high-magnification image reveals that the nanofibres are mainly composed of numerous tightly connected particles (Fig. 3(b)). There are almost no changes in the diameter of nanofibres when the camphene content is increased to 8 wt.% (Figs. 3(c) and (d)); however, their surfaces and cross-sections become rougher. The roughness of the nanofibres with 12 wt.% camphene is further increased, so that many wrinkled patterns are formed on their surfaces. Two other changes are also observed, corresponding to the formation of some pores and the reduction in the diameter of nanofibres (approximately 150 nm). Moreover, the addition of more camphene (16 wt.%) results in a further reduction in diameter (to approximately 120 nm); however, the nanofibres again become smooth and dense, coupled with the disappearance of pores. The change in morphology with changing the content of camphene can be clearly demonstrated by the schematic diagram (Fig. 4). When the nanofibres with camphene undergo heat treatment, the camphene will be thermally decomposed from nanofibres, which may result in the formation of some pores. A low content of camphene (lower than 8 wt.%) hardly has an obvious effect on the morphology of nanofibres. However, the pores are gradually clearly observed when the content of camphene reaches 12 wt.%, at which the point structure of nanofibres cannot be stably maintained and collapses. The nanofibres are correspondingly shrunken and deformed, causing a reduction in the diameter and the formation of a wrinkled pattern on their surfaces. Nevertheless, their collapse will become more serious in the nanofibres with 16 wt.% camphene due to the presence of more pores, which results in the disappearance of pores and structural reconstruction during subsequent heating. Consequently, the nanofibres become finer, and their structure becomes denser. The above results imply that the suitable content of camphene (12 wt.%) will contribute to the improvement in the electrochemical performance of TiO₂ nanofibres due to the increase in specific surface area.



Figure 5. (a) TEM images of PT-3, and (b-c) HRTEM images, and (d) SAED patterns.

Transmission electron microscopy images of titanium dioxide nanofibres with a load of 12 wt.% camphene are shown in Fig. 5. TEM images provide detailed information on the nanostructure of titanium dioxide. Fig. 5(a) shows that the diameter of the fiber is approximately 150 nm, which as agrees with the SEM result. Many bright spots can be observed in nanofibres (Fig. 5(b)), which are supposed to be fine pores caused by camphene acting as a pore marker. In an HRTEM image (Fig. 5(c)), the orderly lattice fringes with a spacing of approximately 0.347 nm can be assigned to the (101) plane of anatase TiO₂. The selected electron diffraction (SAED) diagram (Fig. 5(d)) obtained from a fibre shows many concentric diffraction rings, which correspond well with the planes of anatase TiO₂ (JCPDS, No. 00-021-1272). This is consistent with the XRD results, which clarifies its high crystallinity; comparing the SEM and XRD; results shows that camphene only has a morphological structure, but the crystal structure is not affected.



Figure 6. N₂ adsorption-desorption isotherms of PT-1 and PT-3.

The N₂ physical adsorption-desorption isotherm and BJH pore-size distribution (inner figure) are shown in Fig. 6. Two samples without camphene and with 12 wt.% camphene exhibit type IV patterns with an H3 hysteresis loop in terms of the Brunauer, Deming, Deming, and Tellers (BDDT) classification, which is associated with a large number of fine pores resulting from the aggregation of particles. The pore diameter distributions are similar, with a range from 2 nm to 10 nm. However, the average pore diameter is slightly reduced from 6.64 nm to 5.79 nm after introducing 12 wt.% camphene. Moreover, the specific surface area of nanofibres is increased by approximately 14.3%, which is in accordance with the SEM and TEM results.

3.2 Electrochemical performance



Figure 7. (a) The CV curve of all samples for the 1st cycle and (b) Nyquist plot and equivalent circuit of the sample for EIS.

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Fig. 7(a) shows the cyclic voltammetry (CV) curve obtained at a scan rate of 0.1 mV·s⁻¹. With respect to all samples, a very strong reduction peak can be clearly observed at 1.625 V (vs. Li/Li⁺) during the cathodic scan, accompanied by a corresponding oxidation peak at 2.055 V (vs. Li/Li⁺) during the anodic scan. The redox peak is closely related to the insertion and extraction of lithium in the anatase lattice, which can be described as follows[22,23]:

$$TiO_2 + xLi^+ + xe^{-1} \leftrightarrow Li_x TiO_2 (0 < x < 1)$$

$$\tag{2}$$

where x is the lithium insertion coefficient of TiO_2 (the theoretical capacity of anatase is 168 mAh·g⁻¹, so the maximum value is 0.5).



Figure 8. (a) The galvanostatic charge-discharge curve of all samples for the 1st and (b) PT-3 for the 1st, 2nd, 3rd and 4th. (c) Cycle performances of all samples at 0.5 C. (d) Rate performances of all samples at 0.5-10 C.

In addition to the basic characteristic reversible redox peaks, a weak reduction peak can be detected at approximately 1.45 V, and no corresponding oxidation peak appears in the reverse scan, which may be attributed to an irreversible Li⁺ insertion reaction occurring beyond the tetragonal/orthorhombic phase boundary[24]. The peak currents present a regular change with changing the content of camphene, namely, they first increased and then reduced. The highest peak currents are recorded for the PT-3 sample. This phenomenon should be associated with the change in the specific surface area of the samples. As mentioned above, the largest specific area was obtained for the PT-3 sample, which will provide more active sites for Li⁺ insertion/extraction and greatly shorten the diffusion path of Li⁺. Moreover, a large number of fine pores in the sample will offer considerable

tunnels to accelerate the diffusion of Li^+ into the interior of the sample. The synergistic effect resulting from the above factors causes more drastic Li^+ insertion/extraction reactions. The EIS results provide strong evidence of this. As shown in Fig. 7(b), Nyquist plots can be divided into two regions, the highfrequency region (a semicircle) and the low-frequency region (a straight line). The equivalent circuit model was simulated based on the Nyquist plots (the inset in Fig. 7(b)). R_s is the ohmic resistance in the electrolyte, which can be assessed by the intercept of the semicircle and the real (Z') axis. The value hardly changed (approximately 3 Ω) among the four samples. R_{ct} represents the interfacial charge transfer resistance, which is associated with the diameter of the semicircle. It is clear that the PT-3 sample has the lowest value (50.8 Ω) because it exhibits the smallest semicircle diameter among all the samples, followed by PT-2 (124.6 Ω), PT-1 (158.4 Ω) and PT-4 (162.2 Ω). Z_W is the impedance element that is related to the linear slope; PT-3 has a steeper slope than the other samples. The changes in R_{ct} and Z_w are mainly connected with the specific surface area[25-27]. A larger specific surface area will offer more active sites for lithium insertion and extraction and shorten the transportation path of Li⁺.

Fig. 8(a) shows the galvanostatic charge-discharge curve of the first circle with a cut-off voltage of 0.05-3 V (vs. Li/Li⁺) at a current density of 0.5 C. All samples demonstrate two clear discharging/charging platforms at 1.625 and 2.055 V, corresponding to the insertion/extraction of lithium ions in the A-TiO₂ lattices[28-30]. This is consistent with the results obtained in the CV tests. The discharge specific capacity, charge specific capacity and coulombic efficiency of PT-3 can be calculated to be 518.71 mAh·g⁻¹, 294.99 mAh·g⁻¹ and approximately 62.1%, which are higher than those of the other samples (PT-1: 305.56 mAh \cdot g⁻¹, 114.68 mAh \cdot g⁻¹ and 37.4%; PT-2 :402.87 mAh \cdot g⁻¹, 250.06 mAh·g⁻¹ and 55.2%; PT-4: 387.77 mAh·g⁻¹, 176.99 mAh·g⁻¹ and 45.7%, respectively). The reason for the low initial coulombic efficiency is the irreversible loss of Li⁺, and the loss of partial Li⁺ is mainly attributed to the formation of the solid electrolyte interface (SEI) layer by the reaction between the electrolyte and the negative electrode material on the solid-liquid interlayer during the first discharge cycle. Although the SEI layer will cause irreversible capacity loss, the stable SEI layer will facilitate the decomposition of the electrolyte and prevent the formation of lithium dendrites[31,32]. Fig. 8(b) demonstrates the charge-discharge curves obtained during the initial four cycles. The charge-discharge curves gradually tend to overlap with each other, implying that the electrode possesses good cycling stability. Moreover, the coulombic efficiency is also gradually increases from 62.1% (first circle) to 96.7% (fourth circle), which indicates that the electrode has excellent reversibility.

Fig. 8(c) shows the cycle performance of all samples subjected to 100 cycles at a current density of 0.5 C. PT-3 demonstrates the best cycling stability due to its higher retained discharging specific capacity of 110.11 mAh·g⁻¹ after 100 cycles, followed by PT-2 (92.96 mAh·g⁻¹), PT-4 (54.64 mAh·g⁻¹) and PT-1 (51.44 mAh·g⁻¹). PT-3 also exhibits a high retention rate of 21.47%, which is similar to that of PT-2 (23%), and which is superior to that of PT-4 (14.1%) and PT-1 (17.1%). All samples possess an extremely high coulombic efficiency of nearly 100%, indicating their excellent reversibility. The decay in discharge specific capacity is mainly associated with the structural change and mass loss of the active substance suffering from long-term cycling. For the given four samples, the mass loss may be responsible for the change in cycling stability because they possess the same phase

constituents. For compact PT-1 with fewer pores, its volume variation resulting from discharging and charging will be severely constrained, causing a portion of active substances to undergo the fatigue failure and exfoliate from the electrode with an increase in the number of cycles [33,34]. Consequently, the discharge specific capacity is drastically reduced. When a suitable content of camphene was introduced into TiO₂, a large number of fine pores formed on the nanofibres or in their interor. The pores will accommodate the volume change of active substances during charge-discharge, implying that less active substances are lost due to their good structural integrity. This will result in the excellent cycling stability of PT-3.

Fig. 8(d) shows the rate performance of all samples at different current densities (0.5 C to 10 C). The average discharge specific capacity of the TiO₂ electrode without camphene is sharply reduced from 114.2 mAh·g⁻¹ to 19.6 mAh·g⁻¹ as the current density from 0.5 C to 10 C with a very low retention rate of approximately 17.1%. When the current density is recovered to 0.5 C, only 37.1% of the initial value is retained. It is clear that the introduction of camphene into TiO₂ can significantly improve the rate performance of the TiO₂ electrode. When a suitable content of camphene (12 wt.%) is introduced, a high average discharge specific capacity of 145.71 mAh·g⁻¹ is maintained when the current density is increased to 10 C with a retention of rate 21.6 %. Moreover, the value can reach 145.71 mAh·g⁻¹ with a retention rate of approximately 53.3 % when the current density is recovered to 0.5 C. The excellent rate performance of PT-3 should be ascribed to its large specific surface area, which greatly shortens the transportation path of Li⁺ and allows Li⁺ to diffuse in the active substances at a more rapid rate.

Ref	Materials	Discharge/charge Capacity	Cycle performance	Rate Performance
				$136.12 \text{ mAh} \cdot \text{g}^{-1} \text{ at}$ $168 \text{mA} \cdot \text{g}^{-1}$
This	12wt.%	$518.71/294.99 \text{ mAh} \cdot \text{g}^{-1}$ at	110.11 mAh·g ⁻¹ after 1	$\frac{106.88 \text{ mAh} \cdot \text{g}^{-1} \text{ at}}{336 \text{ mA} \cdot \text{g}^{-1}}$
wor k	camphene	$84 \text{ mA} \cdot \text{g}^{-1}$	00 cycles at 84 mA \cdot g ⁻¹	$78.99 \text{ mAh} \cdot \text{g}^{-1} \text{ at } 840 \\ \text{mA} \cdot \text{g}^{-1}$
				57.90 mAh·g ⁻¹ at 1680 mA·g ⁻¹
[13]	TiO ₂	160 mAh·g ⁻¹ at 36 mA·g ⁻¹	142 mAh·g ⁻¹ after	122 mAh·g ⁻¹ at
	nanotubes		100 cycles at 36 $mA \cdot g^{-1}$	$144 \text{ mA} \cdot \text{g}^{-1}$
[17]	LR-TiO ₂	$120 \text{ mAh} \cdot \text{g}^{-1} \text{at } 0.5 \text{C}$	89 mAh·g ⁻¹ after 100 cycles at 0.5C	$67 \text{ mAh} \cdot \text{g}^{-1} \text{ at } 2$ C
[35]	TiO ₂ -NCs	298.9 mAh·g ⁻¹ at 44.5 mA·g ⁻¹	242.1 mAh·g ⁻¹ after 100 cycles at 44 mA·g ⁻¹	$70 \text{ mAh} \cdot \text{g}^{-1} \text{ at } 1780 \\ \text{mA} \cdot \text{g}^{-1}$
[36]	TiO ₂ rods	262/221 mAh·g ⁻¹ at 100 mA·g ⁻¹	213 mAh \cdot g ⁻¹ after 40 cycles at 100mA \cdot g ⁻¹	-

Table 1. The initial discharge/charge capacity, cycle performance and rate performance ofnanostructured TiO2 reported in some related references

	TiO ₂	263/229 mAh·g ⁻¹ at 10.05		$56 \text{ mAh} \cdot \text{g}^{-1} \text{ at } 1005$
[37]	nanospheres	$mA \cdot g^{-1}$	-	$m A \cdot g^{-1}$
[38]	TiO ₂	204.7 mAh·g ⁻¹ at 170 m	151.9 mAh·g ⁻¹ after 60	151.7 mAh·g ⁻¹ at 340
	mesocrystals	$A \cdot g^{-1}$	cycles at 170mA · g ⁻¹	$mA \cdot g^{-1}$
[39]	TiO ₂	$355/249 \text{ mAh} \cdot \text{g}^{-1}$ at 33.6		66 mAh·g ⁻¹ at 1680
	microspheres	$mA \cdot g^{-1}$	—	$mA \cdot g^{-1}$
[40]	TiO ₂ -B	$413/216 \text{ mAh} \cdot \text{g}^{-1}$ at 33.5	203 mAh·g ⁻¹ after 35	
	nanobelts	$mA \cdot g^{-1}$	cycles at 33.5 mA·g ⁻¹	-
[41]	TiO ₂	$505/225 \text{ mAh} \cdot \text{g}^{-1}$ at $0.1C$	195 mAh·g⁻¹ after	132 mAh·g ⁻¹ at 1C
	microspheres		20cycles at 0.1C	

In order to evaluate the electrochemical performance of the TiO_2 nanofibres with 12 wt.% camphene synthesized in this work, we compared it with that of TiO_2 reported in the relative references [13,17 35-41]. As shown in Table 1, the initial discharge/charge capacity acquired in this work is higher than that reported in those references. With respect to the cycle performance, it is difficult to evaluate which is better due to the difference in selected cycling number or current density between our work and above-mentioned references. When the cycling number is small or the current density is low, the resultant value is usually large, and vice versa. For the rate performance, the retained discharge capacity in our work is usually superior to that reported in those references, indicating that the synthesized TiO_2 nanofibres with 12 wt.% camphene demonstrate more outstanding rate performance. Based on the above comparison, it can be concluded that TiO_2 nanofibres possess excellent electrochemical performance by introducing 12 wt.% camphene into those.

4. CONCLUSIONS

Porous anatase TiO₂ nanofibres with a very large specific surface area were successfully synthesized by introducing camphene as the pore-creating agent through the electrospinning followed by calcination at a suitable temperature. The TiO₂ electrode with 12 wt.% camphene demonstrated an outstanding electrochemical performance in terms of its capacity, rate performance and cycling performance because it exhibited the largest specific area surface of approximately 72 m²·g⁻¹. Its initial discharge specific capacity was 518.71 mAh·g⁻¹, which was approximately 1.7 times that obtained in the TiO₂ electrode without the addition of camphene. The former also had a higher average discharge capacity of 273.27 mAh·g⁻¹ and a larger retention rate of 21.6% when the current density was gradually increased from 0.5 C to 10 C. Moreover, the discharge capacity recovered to a higher value of approximately 145.71 mAh·g⁻¹, and the retention rate of 53.3%. In addition, the highest discharging capacity remains at 114.41 mAh·g⁻¹, and the retention rate is 21.7% when the sample is subjected to 100 cycles at 0.5 C, which is larger than that of the electrode without camphene (51.44 mAh·g⁻¹, 17.1%).

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