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Thermal convection induced TiO₂ microclews as superior electrode materials for lithium-ion batteries†

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One great challenge of lithium-ion battery (LIB) commercialization is to achieve high rate capacity at large mass loading density. Here, a thermal-convection hydrothermal method was newly designed and developed to synthesize TiO2 microclews (TiO2 MCs) for their use as LIB electrode materials. The unique MC architecture could be immobilized on a carbon cloth collector uniformly to form a 3D flexible conductive network (TiO2 MCs@CC), which facilitates fast Li-ion and electron transport and promotes continuous lithiation reaction during the charge-discharge process. With these merits, TiO₂ MCs@CC with high loading density (up to 4 mg cm⁻²) exhibits ultrahigh rate performance (75 mA h g^{-1} at an extremely high current density of 4000 mA g^{-1}), outstanding long-cycling life (74 mA h g^{-1} over 1000 cycles at a specific current density of 2000 mA g⁻¹) and a high initial coulombic efficiency (ICE) of 82%. The demonstrated advantages open up possibilities for fabricating ultrafast rechargeable LIBs with potential industrial applications.

Introduction

Long cycle life and high rate capability are expected in highperformance rechargeable lithium-ion batteries (LIBs) to meet the growing demands for consumer products such as mobile phones, tablet computers and electric vehicles.¹⁻³ Ti-based electrode materials, *e.g.* Li-titanates and titanium dioxide (TiO_x), having stable capacities and outstanding cycling stability are earth-abundant and have attracted a lot of attention as an ideal anode for the Li-ion insertion/extraction host in LIBs.⁴⁻¹⁰ However, the poor electrical conductivity and inferior Li-ion diffusivity in the materials hold back the battery rate performance.¹¹⁻¹³ Conductive agents including carbon nanoparticles, graphene nanosheets and carbon nanotubes have to be bonded to improve the electrode conductivity and a layered structure has been proposed in the design of electrodes to improve the Liion diffusivity.¹⁴⁻²⁰ In addition, a three-dimensional (3D) porous electrode is proposed, which can enhance the contact between the electrode and electrolyte to provide a fast Li-ion diffusion pathway at highrate capacity.²¹⁻²⁸ It is reported that 3D $TiO_{2-\delta}$ nanomembranes exhibit a remarkable rate capability of 75 mA h g^{-1} under 20C.²² Ultrafine TiO₂ nano-crystals based on porous graphene foam show a high capacity of 125 mA h g^{-1} at 10 000 mA g^{-1} .²³ Carbon-coated TiO₂ nanotubes exhibit a high capacity of 150 mA h g⁻¹ under 100C.²⁴ However, the mass loading of active materials in such structures is usually very low (less than 2 mg cm $^{-2}$), because the thicker active material layer will dramatically retard the electrolyte penetration and reduce the specific capacity of LIBs especially at high rates.²⁹⁻³¹ In this regard, increasing the mass loading density of LIBs and maintaining a high rate capacity are the major challenges of LIB research.

In this paper, we present TiO₂ microclews (MCs) for highperformance LIB electrode applications. The as prepared TiO_2 MCs are actually composed of tangled TiO₂ nanobelts with a width of about 50 nm, obtained by a thermal-convection hydrothermal (TCH) method. The TiO2 MCs can exhibit superior electrochemical performance with a high initial coulombic efficiency (ICE) of 82%, stable high-rate capacity of 235–75 mA h g^{-1} at varied current rates of 50–4000 mA g^{-1} and long-cycling life over 1000 cycles at a current density of 2000 mA g⁻¹ (charge/ discharge within 3 minutes). More significantly, the mass loading of the electrode can be high up to 4 mg cm^{-2} . The high performance can be attributed to the intrinsic porous structure of the MCs that facilitates fast Li-ion and electron transport. Furthermore, the production scale of MCs by the TCH method can be raised to 20 g L^{-1} , implying that the synthesis strategy may have a promising commercial application prospect. The

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TCH method can also provide great guidance for the massive synthesis of other kinds of nano-materials in the applications of catalysis, energy storage and conversion.

Experimental procedure

Preparation of TiO₂ MCs

Commercial TiO₂ powder from Dongyi Chemistry Factory (10 g) was firstly dispersed in NaOH aqueous solution (500 mL, 5 M) with continuous stirring and ultrasound sonication for 1 h, respectively, until homogenous milky solutions were formed. Then, the solution was transferred into a self-convection hydrothermal Teflon-lined cylindrical hydrothermal autoclave and the autoclave was heated at a temperature of 190 $^\circ C$ for 24 h. After the hydrothermal reaction, the autoclave was cooled to room temperature. The product, sodium titanate, was collected by natural settling, washed with diluted HCl solution (0.1 M) several times to attain a pH value of 1. During these processes, the Na⁺ ions were replaced by H⁺ ions. After that, the suspension was washed with deionized water several times to reach a pH value of 7 to generate hydrogen trititanate HTO MC materials. Finally, the wet HTO MCs were subjected to freezedrying for 24 h to obtain the HTO MC powder. The as-prepared HTO MC powder was annealed at 300 °C for 3 h to obtain the TiO₂ MC powder.

Characterization

The morphology and structure of the as-synthesized samples were characterized by field emission scanning electron microscopy (FESEM, JEOL JSM-6340F). Transmission electron microscopy (TEM, JEOL JEM-2100F) performed at 200 kV was used to further confirm the detailed nanostructures. The crystal phase of the samples was measured by XRD on a D/MAX-2500 diffractometer. Raman spectroscopy characterization was performed using an Andor 500i spectrograph with a 532 nm laser. The specific surface area was calculated by the Brunauer– Emmett–Teller (BET) method.

Electrochemical measurements

The electrochemical measurements were conducted *via* CR 2032 coin-type cells with lithium foil as the counter and reference electrodes. The working electrode was fabricated by mixing TiO₂ MCs, carbon black, and polymer binder (polyvinylidene fluoride) in a weight ratio of 80 : 10 : 10. After intensive mixing, the paste was spread on commercial flexible carbon cloth and then subjected to thermal treatment at 110 °C in a vacuum. The mass loading of electrode materials was around 4.0 mg cm⁻². The concentration of the electrolyte was 1 M.

The electrolyte was LiPF_6 in a 50 : 50 (w/w) mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in a glove box with oxygen and water contents below 1.0 ppm and 0.5 ppm, respectively. Charge/discharge cycles were performed between 1.0 and 3.0 V vs. Li⁺/Li at varied current densities with a LAND battery test system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted using an electrochemical analyzer (IM6).

Results and discussion

The schematic illustration of the TCH technique for the synthesis of TiO₂ MCs is shown in Fig. 1. 500 mL aqueous solution of sodium hydroxide mixed with commercial TiO₂ nanoparticles (NPs) was filled into a vertically placed 1 L reactor with a specially elongated length of 60 cm (Fig. 1a). A resistanceheater to raise the temperature was equipped at the bottom of the reactor to form a temperature gradient from bottom to top (Fig. 1b). After the hydrothermal reaction, the as-prepared products (Fig. 1c) were collected and immersed in diluted HCl solution to obtain hydrogen trititanates by ion exchange (Fig. S1[†]). Fig. 2a shows the clew-like shaped product with a diameter of around 2-5 µm, which is labeled HTO MCs. The channels in the MCs can improve the electrode/electrolyte contact area and shorten the Li⁺ diffusion pathway. Fig. 2b shows the magnified detail view of the HTO MCs, which is a nanoporous network composed of three-dimensional (3D) branched nanobelts with an average width of around 50 nm. The MCs composed of 3D branched nanobelts can further enhance the electrode conductivity and provide more Li⁺ storage active sites. In order to avoid the structural damage induced by the surface tension of water, the HTO MCs were freeze dried and annealed at 300 °C in air for 3 h to obtain shape-retained TiO_2 MCs as shown in Fig. 2c and S2.[†] A large specific surface area of 135 m² g⁻¹ for MCs measured by the Brunauer-test indicates that the micro-nano structures are well maintained (Fig. S3[†]). The high-resolution TEM (HRTEM) image of the MC fragment reveals the lattice distance of 0.35 nm, corresponding to (101) planes of the anatase TiO_2 phase (Fig. 2d). The XRD patterns in Fig. 2e identify the diffraction peaks of anatase TiO₂ (PDF#21-1272) and rutile TiO₂ (PDF#21-1276) in the samples. The TiO2 MCs possess similar XRD patterns to the raw powder of TiO₂ NPs. The rutile TiO₂ phase in TiO₂ MCs corresponds to the nanoparticles on the surface of MCs (Fig. S4[†]). In HTO MCs, the peaks at 10°, 32° and 46° show a diagnostic gallery spacing for the layered protonic



Fig. 1 Schematic illustration of the TCH technique. (a) The real photo of the apparatus. (b) The thermal convection and the formation process of TiO₂ MCs from TiO₂ nanoparticles dispersed in NaOH aqueous solution. (c) SEM image of the obtained HTO MCs. (d) Digital photograph of the TiO₂ MCs (10 g).



Fig. 2 Material characterization of the HTO MCs before and after thermal treatment: (a) SEM image of the as-prepared HTO MC structure. (b) High-magnification SEM image of the HTO MCs. (c) SEM image of TiO₂ MCs. (d) TEM image of the TiO₂ MCs. (e and f) The XRD patterns and Raman spectra of TiO₂ NPs, HTO MCs and TiO₂ MCs. In (e), "A" represents anatase, "R" represents rutile, "T" represents layered protonic titanates, and the bottom green and pink lines are the standard XRD patterns of anatase TiO₂ (PDF#21-1272) and rutile TiO₂ (PDF#21-1276), respectively.

titanates.^{32,33} Fig. 2f shows the Raman spectra of TiO_2 NPs, HTO MCs and TiO_2 MCs. The strong peak at 274 cm⁻¹ in HTO MCs belongs to Ti–OH bonds in sodium titanate, indicating the existence of titanate nanobelts.^{33,34} The Raman spectra of TiO_2 MCs and TiO_2 NPs exhibit the characteristic anatase-type and rutile-type phonon modes, agreeing well with the XRD results.

In order to understand the formation of the MCs in the TCH process, the holding time-dependent synthesis was performed (Fig. 3 and S5[†]). It was found that short titanate branches appeared from TiO_2 NPs at a holding time of 4 h (Fig. 3a and b). The amount of nanobelts increased gradually with increasing the holding time from 8 h to 20 h, and finally MCs were obtained (Fig. 3c-f). Based on this observation, we proposed the mechanism of MC formation as shown in Fig. 3g. When the temperature of the reactor bottom increased, the reactant at the bottom would be firstly heated, yielding a density gradient between the top and the bottom solution due to various thermal expansions by temperature gradient. Gravity then acts to pull the cooler and denser liquid from the top to the bottom (Fig. 1b). A thermal-convection induced spontaneous liquid flow was then formed continuously in the reactor, which could accelerate the dissolution of TiO2 NPs and recrystallization of planar fragments (dissolved, kinetic product) to nanobelts (Fig. S6[†]).³⁵ In fact, Chen's group has reported elongated bending TiO₂ nanowires by mechanical force-driven methods.³⁶



Fig. 3 SEM images of the products at the hydrothermal holding time of (a) 0 h, (b) 4 h, (c) 8 h, (d) 16 h, (e) 20 h and (f) 24 h. (g) The proposed formation mechanism of the MCs with a 3D structure.

The liquid flow could prevent the sedimentation of solid reactants, as well as facilitate the growth of products into elongated nanobelts.

The thermal-convection in the reactor is further known as Rayleigh-Bénard convection.37,38 Benefitting from the localized convection cells, the nanobelts tangled and subsequently evolved into MC structures (Fig. 1c, 3c, d and S1[†]). When thermalconvection is eliminated by constant magnetic stirring, elongated TiO2 nanobelts with 2-10 µm can be clearly observed and less clew structure could be found, indicating that the heat convection in the hydrothermal reactor is an essential factor for the synthesis of the clew structure (Fig. S7[†]). In order to clarify the role of thermalconvection in TCH, the whole reactor was heated to 190 °C and compact products instead of MCs were obtained (Fig. S8[†]). The reason is that the solid reactant is sedimented without liquid flow, which will be more prominent in massive preparation. This indicates that the heating position is an important factor to form the temperature gradient and liquid convection.^{39,40} Once the appropriate parameters are configured, the mass production of TiO₂ MCs becomes very easy and feasible, independent of the slight change of the raw materials (Fig. S9[†]). The MC production scale in this work is high up to 20 g L^{-1} (Fig. 1d), suggesting the potential industrial application of this method.

For the performance test of LIBs, the HTO precursor was annealed at 300 °C (Fig. S10[†]) and carbon cloth was chosen as the current collector for the TiO₂ MC loading (TiO₂ MCs@CC) and Li foil was used as the counter and reference electrodes. As demonstrated in Fig. S10 and S2,† annealing at 300 °C could result in the best rate performance because of the achieved clew structure. The rate capability of the electrode is investigated at different charge-discharge rates (Fig. 4a). TiO2 MCs@CC exhibits extraordinary cycling specific capacities of 235, 200, 175, 160, 140, 110 and 75 mA h g^{-1} when the current density gradually increases from 50, 100, 200, 500, 1000, 2000 to 4000 mA g^{-1} , respectively (Fig. S11†). After high-rate cycling at 4000 mA $\mathrm{g}^{-1},$ a specific capacity of 185 mA h g^{-1} could be restored when the current density was set back to 100 mA g^{-1} , demonstrating the excellent electrochemical kinetics and lithium storage properties of the electrode. The initial



Fig. 4 Electrochemical performance of the TiO_2 -MCs@CC electrode. (a) Rate performance of the TiO_2 MCs@CC, TiO_2 NPs@CC and TiO_2 MCsB@CC electrodes. (b) The comparison of areal capacity *versus* active material loading in the TiO_2 MCs@CC electrode with that of the electrodes recently reported in ref. 11, 22, 25 and 41–46. (c) The first 5 cycles of CV curves at a scan rate of 0.1 mV s⁻¹. (d) Long-term cycling performance at a high current density of 2000 mA g⁻¹.

discharge/charge curves of the TiO2 MCs@CC electrode show that the first discharge and charge capacity are 283 and 232 mA h g⁻¹, respectively, corresponding to an ICE of 82% (Fig. S12^{\dagger}), which indicates that the obtained TiO₂ MCs@CC electrode can catch up with potential industrial applications. In the conventional TiO2 nanoparticles loaded electrode (TiO2 NPs@CC), much lower specific capacities of 100–10 mA h g^{-1} at a current density of 50–4000 mA g^{-1} can be observed (Fig. 4a). The low capacity of TiO₂ NPs@CC can be attributed to the sluggish ion diffusion kinetics and poor electronic conductivity caused by the agglomeration of TiO2 NPs (Fig. S13[†]).²⁹ In contrast, the TiO₂ MCs composed of branched nanobelts can be well distributed in the carbon cloth to achieve a high active surface and fast electron transfer. As a verification, the structure destroyed TiO2 MCs (TiO2 MCs-B) was prepared by mechanical milling. The TiO₂ MCs-B were broken into short nanobelts (Fig. S14[†]) which exhibits decadent cycling performance when loaded in the carbon cloth electrode (TiO₂ MCs-B@CC). Moreover, TiO₂ nanobelts obtained from the common hydrothermal reaction under the same loading show much lower capacity (Fig. S15[†]), indicating that the MC structure is a crucial factor for the high rate capacity (Fig. S16[†]). Compared with the results of the most recently reported TiO₂-based electrode, the TiO₂ MCs@CC electrode illustrates superior areal capacity at different current densities (Fig. 4b).^{11,22,25,41-46} More importantly, the rate capacity has caught up with the results of various reported Ti-based technologies though the mass loading density of the electrode reaches high up to 4 mg cm⁻² (Table S1[†]). Fig. 4c shows the representative cyclic voltammetry (CV) of the TiO₂ MCs@CC electrode with a mass loading of 4.0 mg cm⁻². The voltammograms were obtained with a scan rate of 0.1 mV s⁻¹ in a cut-off voltage window of 1.0-3.0 V. The well-defined redox reaction peaks observed at approximately 1.75 V/2.0 V (vs. Li⁺/Li) can be associated with the insertion/ extraction process of Li⁺ for anatase TiO₂.^{11,47} It should be pointed out that the peak current curves demonstrate no significant change after the first cycle, suggesting a quite stable electrochemical reversibility of the TiO₂ MCs@CC electrode. Moreover, the TiO₂ MCs@CC electrode can exhibit excellent cycling performance at 2000 mA g^{-1} (Fig. 4d) and it also retains 67% of its initial capacity (110 mA h $g^{-1})$ after 1000 cycles with almost 100% coulombic efficiency. Apparently, the structure of the TiO₂ MCs@CC electrode with relatively high loading is beneficial to obtain superior cycling performance as well as high areal capacity for lithium storage.

The excellent performance of the TiO_2 MCs@CC electrode can be elucidated by the synthetic effect of the unique MC structure and the 3D conductive network of carbon cloth. On the one hand, the MC structure shortens the ion diffusion length and provides sufficient electrode–electrolyte contact area for pseudocapacitive lithium storage reactions. On the other hand, the carbon cloth collector is composed of robust carbon nanofibers with a diameter of about 10 µm and length of hundreds of micrometers (Fig. S17†), which can provide a flexible framework for TiO₂ MC loading without apparent fractures. The continuous porous carbon cloth is conducive to offer more active material loading and interconnected ion conductive pathways, therefore the TiO₂ MC loading density in carbon cloth can be up to 4 mg cm^{-2} by the common scraper stretching process (Fig. S17[†]). Moreover, the rate capability of TiO₂ MCs on a common Cu foil collector with the same loading density (TiO₂ MCs@Cu) shows much lower specific capacities especially at high current rate (2000 mA g^{-1}) (Fig. S18[†]). As a result, the TiO₂ MC filled carbon cloth achieved more excellent electrochemical performances due to the large surface area, short ion transport length, and enhanced electron conductivity.¹¹ Furthermore, the robust and flexible texture of carbon nanofibers possesses a good sticking effect, making it possible to be used in industrial high-speed roll-to-roll coating processes.³⁰ The kinetic process of lithium insertion in the electrode was investigated by electrochemical impedance spectroscopy (EIS), as shown in Fig. 5a. In the Nyquist plots, the first semicircle observed at relatively high frequencies can be attributed to the parallel combination of surface film resistance R_f and surface film capacitance $C_{\rm f}$ (Fig. S19a[†]). The second medium-frequency is associated with the interfacial charge transfer, represented by the charge transfer resistance (R_{ct}) and the double-layer capacitance (C_d).⁴⁸ The first semicircle of the TiO₂ NPs@CC electrode could be generally attributed to surface phenomena such as the irreversible decomposition of electrolyte accompanying the formation of the solid electrolyte interface (SEI). This obvious difference compared to other two electrodes might be caused by the differences of exposed crystal facets among TiO₂ MCs@CC, TiO₂ NPs@CC and TiO₂ MCs-B@CC (Fig. 2e), which could influence the chemical reactivity as well as the irreversible decomposition of electrolyte.49,50 That's why TiO2 NPs@CC exhibits relatively low coulombic efficiency in the first cycle (67.3%) (Fig. S19b[†]) compared to TiO₂ MCs@CC (82%) and TiO₂ MCs-B@CC (80%). Furthermore, TiO₂ MCs@CC exhibits lower R_{ct} values than TiO₂ NPs@CC, indicating that the MC structure possesses more active interfaces with the electrolyte (Fig. S16[†]).⁵¹ The increased R_{ct} values in TiO₂ NPs@CC are attributed to the agglomeration of the particles which has eliminated most active interfaces for the lithium storage



Fig. 5 Kinetic analysis of the TiO_2 MC electrode. (a) EIS analysis and (b) the Warburg coefficient of the TiO_2 NPs@CC, TiO_2 MCs@CC and TiO_2 MCs-B@CC electrodes. (c and d) Schematic diagram of TiO_2 MCs on the flexible carbon cloth conductor and the ion and electron transport within the electrode.

(Fig. S13[†]). Although the MC structure is transformed into short nanobelts in TiO₂ MCs-B@CC, the R_{ct} can still maintain close values to those in MCs. The reason would be that short nanobelts can be uniformly dispersed in the carbon cloth without agglomeration (Fig. S14[†]). In spite of the differences of high and medium-high frequency resistance among the three electrodes, the low-frequency Warburg contribution of the impedance response is usually used to determine the Li-ion diffusion coefficient (D_{Li}) at various states of discharge in the electrode; the D_{Li} values of TiO2 MCs@CC and TiO2 MCs-B@CC have been demonstrated to be higher than that of the TiO₂ NPs@CC electrode (Fig. S20[†]).³⁰ As a result, the EIS under different discharge capacities reveals that the TiO2 MCs@CC exhibits low electronic resistance dynamic change and high ion-diffusion coefficient at different charging states, which is critical for high-rate LIBs (Fig. S21[†]). The schematic diagram of the 3D carbon cloth conductor and ion transport within the TiO₂ MCs@CC reveals the improved electrochemical performance of the TiO₂ MCs@CC electrode as shown in Fig. 5c and d. We also used commercial pure anatase TiO₂ (A-TiO₂ NPs) to synthesize the MC structure (A-TiO₂ MCs). The products exhibited a similar microclew structure (Fig. S9^{\dagger}), composed of the anatase TiO₂ phase (Fig. S22a^{\dagger}). The similar outstanding electrochemical performance of A-TiO2 MCs (Fig. S22b^{\dagger}) to that of TiO₂ MCs confirms that the high electrochemical performance is mainly attributed to the unique MC nanostructure. TiO2 MCs@CC exhibits outstanding electrochemical performances with high loading density, high rate capacity and stable cycling capability, which makes it a very promising anode for advanced energy storage applications.

Conclusions

In summary, we have designed a TCH method for the first time to prepare TiO₂ MCs on a large scale. The mechanism of TiO₂ MC formation can be attributed to the thermal convection flow in the TCH process. The novel TiO₂ MCs were loaded on carbon cloth with a high loading mass of up to 4.0 mg cm⁻² and exhibited high rate capacity and long cycling life in the LIB test. The electrode can deliver a high initial coulombic efficiency of 82%, and a large rate capacity of 110 mA h g⁻¹ at 2000 mA g⁻¹ with a capacity retention of 67% after 1000 cycles. The outstanding electrochemical performance is attributed to the unique MC structure for the fast electron and ion transport in a 3D conductive network of carbon cloth. We believe that this synthetic strategy could be extended to the fabrication of a wide variety of functional nanomaterials in industry and provides new avenues for the future development of ultrafast rechargeable LIBs.

Conflicts of interest

There are no conflicts to declare.

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