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Synthesis of TiO₂ hollow nanofibers by co-axial electrospinning and its superior lithium storage capability in full-cell assembly with olivine phosphate†

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We report the formation and extraordinary Li-storage properties of TiO₂ hollow nanofibers by co-axial electrospinning in both the half-cell and full-cell configurations. Li-insertion properties are first evaluated as anodes in the half-cell configuration (Li/TiO₂ hollow nanofibers) and we found that reversible insertion of ~0.45 moles is feasible at a current density of 100 mA g⁻¹. The half-cell displayed a good cyclability and retained 84% of its initial reversible capacity after 300 galvanostatic cycles. The full-cell is fabricated with a commercially available olivine phase LiFePO₄ cathode under optimized mass loading. The LiFePO₄/TiO₂ hollow nanofiber cell delivered a reversible capacity of 103 mA h g⁻¹ at a current density of 100 mA g⁻¹ with an operating potential of ~1.4 V. Excellent cyclability is noted for the full-cell configuration, irrespective of the applied current densities, and it retained 88% of reversible capacity after 300 cycles in ambient conditions at a current density of 100 mA g⁻¹.

Introduction

Since the commercialization of lithium-ion batteries (LIB) by Sony in 1991, carbonaceous materials (especially graphite) have dominated as ideal anodes due to their appealing properties like good capacity (~372 mA h g⁻¹), lower insertion potential (<0.1 V vs. Li), eco-friendliness, good cyclability and chemical stability.^{1–8} However, such anodes endure the problem of lithium plating during high current operation which hinders possibility of using them in high power applications like hybrid electric vehicles (HEV) and electric vehicles (EV).^{9–11} Hence, the development of a new insertion host with appealing properties, like a lower insertion potential (vs. Li), high capacity, safety, higher thermal stability, low cost and eco-friendliness are anticipated. To fulfil the desired properties stated above, titanium based binary and ternary oxides are proposed as

prospective anode materials for LIB applications due to the possible utilization of a Ti^{4+/3+} redox couple irrespective of the nature of the crystal structure.^{12–16} Thus far, a variety of Ti based compounds such as spinel Li₄Ti₅O₁₂ (~175 mA h g⁻¹),¹² spinel LiCrTiO₄ (~157 mA h g⁻¹),^{16–18} super cubic TiP₂O₇ (~121 mA h g⁻¹),^{16,19} NASICON type LiTi₂(PO₄)₃ (~138 mA h g⁻¹),^{20,21} anatase TiO₂ (~335 mA h g⁻¹)²² and monoclinic TiO₂-B (~335 mA h g⁻¹)²³ *etc.* were explored as possible insertion anodes and those materials exhibit a bi-phase reaction mechanism during Li-insertion/extraction processes. Among the insertion hosts mentioned, anatase TiO₂ is found to have promising characteristics, like the highest theoretical capacity with less volume change during Li-insertion/extraction (~3.7%).^{15,22} Apart from its electrochemical properties, TiO₂ is abundant in Earth's crust, environmentally benign and low cost, and expected to deliver a highly durable cycling performance with much greater safety.²⁴ To develop high performance LIBs, utilization of nanostructured materials are crucial to replace conventional bulk or micro scale materials owing to their shorter diffusion time, which is proportional to the square root of the diffusion length and inversely proportional to the diffusion coefficient, which thereby improves the battery characteristics. Numerous nanostructured materials with a variety of morphologies such as nanoparticles, nanowires, nanotubes, nanosheets, nanobelts *etc.* were engaged as electrode materials for LIB.^{25,26} Among these nano architectures, one dimensional (1D) nanofibers are found attractive by virtue of their unique structure, chemical stability and high specific surface area, which may benefit from a higher flux of lithium ion across the electrode/electrolyte interface leading to the facile diffusion of cations.^{26,27}

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Several reports are available on the Li-insertion properties of anatase TiO_2 as anode materials in LIB with different nanostructured morphologies,^{12–16,22} however only very few works are available on the electrochemical properties of one dimensional electrospun TiO_2 nanofibers in the half-cell configuration in either a native or composite form with either carbon nanotubes and graphene.^{28–32} To the best of our knowledge, there is no report available on electrospun anatase TiO_2 hollow nanofibers as anode materials in the full-cell configuration. Herein, we demonstrate a template synthesis of TiO_2 hollow nanofibers by co-axial electrospinning and post annealing. Electrospinning is a convenient and scalable technique to produce high-performance one-dimensional fibers with desirable structures by tuning the concentration, applied voltage, distance between the collector *etc.*^{31,32} The prepared TiO_2 hollow nanofibers were employed as an anode in the half-cell (Li/TiO_2) and full-cell assemblies with olivine phosphate ($\text{LiFePO}_4/\text{TiO}_2$) to evaluate their battery characteristics. Extensive electrochemical characterization and optimization of mass loading of the electrodes was carried out and the obtained results are presented in detail.

Experimental

Materials preparations

Titanium tetraisopropoxide [TIP , $\text{Ti}(\text{O}^i\text{Pr})_4$; 97%], solvents *N,N*-dimethylformamide (DMF, 99.8%), absolute ethanol (100%) and acetic acid (99.7%) were purchased from Aldrich. All chemicals were used as received without further purification. An indigenously developed core-shell spinneret was set up with two needles of size 27G (core) and 21G (shell), fixed co-axially according to the schematic representation given in Fig. 1a. Two precursor gels, preferably polymers were chosen in such a way that they were immiscible in nature, one for the core liquid and another for the shell liquid. The precursor solution for the shell side was prepared by dissolving 1.8 g of polyvinyl pyrrolidone (PVP, $M_w = 100\,000$, Aldrich) in 20 ml of ethanol followed by the addition of 5 ml acetic acid. TIP (3 g) was then added to PVP solution under vigorous stirring for 12 h. The precursor for the core fluid was prepared by dissolving 0.5 g of polyethylene oxide (PEO, $M_w = 900\,000$, Aldrich) in 5 ml of DMF under heating at 50 °C. As-prepared two precursor gels were loaded into two plastic syringes (5 ml) and connected to a co-axial core-shell spinneret (Fig. 1a). A high-voltage power was applied to the needle tip, and the flow rate for core and shell fluids was set to 0.2 and 0.6 ml h^{-1} , respectively. The electric field strength was fixed to 15 kV and an aluminum foil wrapped plate collector was placed at 12 cm below the needle tip for collection of the fiber mat. Then as-spun core-shell nanofibers mat were calcined at 450 °C for 1 h at a heating rate of 2 °C min^{-1} to decompose the polymers and subsequently yield the single phase TiO_2 hollow nanofibers in an air atmosphere.

Materials characterizations

The morphological features of the samples were examined by a field emission scanning electron microscope (FE-SEM; JEOL, 6701F). The microstructure of the samples was characterized by

transmission electron microscopy (TEM; JEOL, 3010) and selected area electron diffraction (SAED) at an applied potential of 200 kV. The crystallographic nature of the samples was investigated using X-ray diffraction (XRD) using Bruker AXS, D8 Advance equipment with $\text{Cu-K}\alpha$ radiation at $\lambda = 1.54056 \text{ \AA}$. Surface area and pore volumes of the annealing TiO_2 hollow nanofibers are determined by nitrogen adsorption-desorption (BET, Micromeritics Tristar 2000, surface area and pore size analyzer).

Electrochemical measurements

All the electrochemical studies were conducted in standard two-electrode coin-cell (CR 2016) configuration. The composite electrodes were formulated with an accurately weighed 10 mg of active materials (TiO_2 hollow fibers or LiFePO_4), 1 mg of conductive additive (super P), and 2 mg of Teflonized acetylene black (TAB-2) as binder. Then the composite film was pressed on a area of 200 mm^2 stainless steel mesh, under a pressure of 200 kg cm^{-2} , which acts as a current collector and were subsequently dried at 60 °C for 24 h before assembling the coin-cell under an Ar-filled glove box (MBraun, Germany). The electrodes were separated by a microporous glass fiber separator (Whatman, Cat. no. 1825-047, UK) and filled with 1 M LiPF_6 in an ethylene carbonate (EC)/diethyl carbonate (DEC) (1 : 1 wt%), DAN VEC) mixture as electrolyte. Cyclic voltammetric (CV) traces were recorded using a Solartron, 1470E and SI 1255B impedance/gain-phase analyzer coupled with a potentiostat in a two electrode configuration at a slow scan rate of 0.1 mV s^{-1} . Galvanostatic cycling profiles were recorded using an Arbin 2000 battery tester at a constant current density of 100 mA g^{-1} for both half and full-cell configurations in ambient temperature conditions.

Results and discussion

Fig. 1a illustrates a schematic representation of the complete process of hollow nanofiber synthesis by the electrospinning technique. The insets correspond to optical images of the co-axial electrospinning system and the core-shell spinneret, respectively. During the electrospinning process, core and shell fluids are highly electrified and the induced charges are dispersed over the surface of core and shell droplets at the tip of the spinneret due to the high applied voltage between the tip and collector. Core and shell droplets are distorted and transformed into a conical shape (Taylor cones) with compound jets at the edge of spinneret nozzles, which is attributed to electrostatic forces caused by the repulsion of surface charges and the pull of the external electric field. When the electrostatic force overcomes the surface tension of the solutions, the compound Taylor cones are stretched by bending instability. The solvents from core and shell solutions are evaporated rapidly due to the set-humidity level of 50%. Concentrated core and shell solutions in the traveling path lead to the formation of solidified PEO and PVP core and shell nanofiber frames, respectively (Fig. 1b). Simultaneously, the hydrolysis of TIP catalyzed by acetic acid and condensation of titanium alkoxides

Fig. 1 (a) Schematic representation of the synthesis of TiO_2 hollow fibers by co-axial electrospinning and (b) magnified view of the formation of core-shell nanofiber Taylor cones. (i) Photo image of electrospinning setup.

also takes place to form amorphous TiO_2 in the shell according to the reaction process given here

$R = i\text{-propyl}$

The as-spun core-shell (PEO-PVP/ TiO_2) nanofibers are calcined at 450°C in an air atmosphere to yield single phase TiO_2 hollow nanofibers. During the calcination process of core-shell nanofibers, PEO and PVP were decomposed and well-developed crystalline anatase TiO_2 hollow nanofibers were formed (Fig. 1a). The feed rate of core and shell liquids plays an important role in the shape and size of hollow nanofibers. By

optimizing the feed rate of core and shell liquids, uniform hollow nanofibers can be obtained by the core and shell feed rate ratio of 1 : 3.

The morphological and micro structural properties of the as-spun core-shell (PEO-PVP/ TiO_2) were examined by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), respectively. Fig. 2a shows the FE-SEM image of as-spun core-shell fibers with a smooth surface morphology and exhibiting a fiber diameter of ~ 150 to 200 nm. The TEM image of an as spun fiber is given as the inset of Fig. 2a, which clearly shows a thin layer of the single TiO_2 -PVP composite shell covering uniformly the entire length of the PEO core nanofibers without any noticeable porosity, and suggests the amorphous TiO_2 is in the shell layer. The diameters of the core and shell parts of the fibers are measured to be 120 ± 20 and 170 ± 30 nm, respectively. An FE-SEM image of a bundle of TiO_2 hollow nanofibers after calcination at 450°C in air for 1 h is illustrated in Fig. 2b. The TiO_2 hollow nanofibers showed a

Fig. 2 (a) FE-SEM image of the as-spun core shell PEO-PVP/TiO₂ nanofiber and the corresponding inset TEM image shows the single as-spun core-shell (PEO-PVP/TiO₂) nanofiber, (b) FE-SEM image of a TiO₂ hollow nanofiber after calcination at 450 °C and the inset image corresponds to a magnified view of the TiO₂ hollow nanofiber, (c) TEM image of a bundle and individual (inset images with high magnification) TiO₂ hollow nanofiber after calcinating at 450 °C, (d) HR-TEM image of the anatase TiO₂ hollow nanofibers, (e) SAED pattern of TiO₂ hollow fibers, (f) Rietveld refined X-ray diffraction pattern of TiO₂ hollow nanofibers after calcination at 450 °C in air.

special layer-by-layer nanonet structure and the corresponding inset clearly shows the formation of a hollow TiO₂ structure after calcination. The formation of a hollow TiO₂ structure is well supported by the TEM images presented in Fig. 2c. The inset image clearly shows the typical microstructure of the TiO₂ hollow nanofiber. This kind of hollow structure is formed when the PEO and PVP are removed from the core and shell layer, respectively, during the calcination process without destroying the morphology. The inner diameter of TiO₂ hollow nanofibers after calcination is found to be 80 ± 20 nm, whereas the outer diameter of TiO₂ hollow nanofibers is 150 ± 30 nm (Fig. 2c). The shrinkage of the inner and outer diameter after the calcination process can be attributed to the removal of PEO and PVP from core and shell layers and simultaneously leads to the crystallization of TiO₂ in the outer shell to form hollow structures. A high resolution TEM image of the TiO₂ hollow nanofibers is shown in Fig. 2d. It is revealed that the TiO₂ hollow nanofibers

possess a highly ordered crystalline structure and the observed lattice fringes have an interplanar spacing of 3.5 Å, corresponding to the (1 0 1) plane of the anatase phase of TiO₂. This indicates that the growth of TiO₂ takes place along the (1 0 1) direction. Well-ordered diffraction rings of (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 0 4) planes are noted in the selected area electron diffraction (SAED) patterns (Fig. 2e) which confirm presence of the anatase phase. This also demonstrates that the TiO₂ hollow nanofibers were polycrystalline. We believe that such a unique morphology facilitates the faster diffusion of Li-ions during the electrochemical reaction and enables a higher contact area towards the electrode/electrolyte interface, thereby providing good electrochemical performance. Fig. 2f depicts the X-ray diffraction pattern of TiO₂ hollow nanofibers. The observed XRD reflections are indexed according to the tetragonal structure with the *I4₁/amd* space group. The XRD pattern clearly reveals the formation of a phase-pure structure without any noticeable impurity traces. Rietveld refinement is also conducted using TOPAS V3 software for the observed X-ray reflections to calculate the lattice parameters, which are found to be $a = 3.787$ (8) Å and $c = 9.507$ (9) Å which is consistent with the literature values (JCPDS 89-4203). The BET surface area of TiO₂ hollow nanofibers is also measured and found to be 118 m² g⁻¹.

Electrochemical Li-insertion properties of TiO₂ hollow nanofibers were investigated in the half-cell configuration (Li/TiO₂) by cyclic voltammetry (CV) between 1 and 3 V at a slow scan rate of 0.1 mV s⁻¹ in room temperature and illustrated in Fig. 3. For CV measurement, metallic lithium acts as both the counter and reference electrode. First, test electrodes are discharged to 1 V vs. Li, during such a cathodic sweep Li-insertion takes place in the anatase TiO₂ crystal lattice, whereas in the anodic scan Li-ions are extracted from the crystal lattice. In the first cathodic sweep, the Li-insertion potential is noted at ~1.57 V vs. Li which corresponds to the reduction of Ti⁴⁺ to Ti³⁺. The oxidation process of Ti³⁺ in to Ti⁴⁺ occurs at ~2.08 V vs. Li by a subsequent anodic scan. From second cycle onwards, the cathodic peak potential is shifted towards the higher voltage region (~1.67 V vs. Li), but there is no deviation in the peak

Fig. 3 Cyclic voltammogram of Li/TiO₂ hollow nanofibers cells cycled between 1 and 3 V at scan rate of 0.1 mV s⁻¹, in which metallic lithium serves as both counter and reference electrode.

potential is evidenced during the anodic scan. Variation in the peak potential is mainly due to structural re-arrangement or so-called formatting cycles.¹⁸ The sharp constructive and overlapping peak potential during the Li-insertion/extraction process indicates excellent reversibility during electrochemical cycling and corresponds to a two-phase reaction mechanism according to the following equilibrium,

Charge–discharge studies of Li/TiO₂ half-cells were conducted galvanostatically between 1 and 3 V vs. Li at a current density of 100 mA g^{−1} (Fig. 4). Typical galvanostatic charge–discharge curves of the first two cycles of TiO₂ hollow nanofibers are illustrated in Fig. 4a. It is evident that the discharge traces were composed of a sharp decay followed by a long distinct plateau then monotonous curves which are ascribed to solid-solution formation, a two-phase region and interfacial storage, respectively. The cell delivered a capacity of ~184 (0.55 moles lithium) and ~150 (0.45 moles lithium) mA h g^{−1} for the first discharge and charge, respectively. An irreversible capacity of ~34 mA h g^{−1} is noted, which is common in the case of anatase TiO₂.³³ Here, the reversible capacity 150 mA h g^{−1} is assumed to be 1 C, so the applied current density is equal to 0.67 C. Li-insertion into anatase TiO₂ hollow nanofibers induces the phase transition from the tetragonal (*I*₄₁/*amd*) to the orthorhombic (Li_{0.5}TiO₂, space group *Pnm*2₁) phase. This phase transition occurs along with a spontaneous phase separation of a lithium-

poor (Li_{0.01}TiO₂) into a lithium-rich (Li_{0.5}TiO₂) phase. The long distinct plateau at ~1.7 and 1.94 V vs. Li during the discharge and charge process correlates to the bi-phase reaction mechanism and is consistent with the peak potential noted in CV analysis.¹⁶ The cycling profiles of Li/TiO₂ hollow nanofiber half-cells tested for 300 cycles are given in Fig. 4b. It is apparent that the cell delivered more stable cycling profiles with a meager amount of capacity fading. After 300 galvanostatic cycles, the test cell retained 84% of its reversible capacity at a current density of 100 mA g^{−1}. The observed capacity is one of the best values obtained on electrospun TiO₂ fibers, for instance Nam *et al.*²⁸ reported an electrochemical performance of Au- and Ag-embedded anatase TiO₂ nanofibers by electrospinning, and delivered a discharge capacity of ~150 mA h g^{−1} at a low current density of 33 mA g^{−1}. Electrospun TiO₂ fibers delivered a reversible capacity of ~120 mA h g^{−1} at a current density of 150 mA g^{−1} and retained only 77% capacity after 50 cycles, as reported by Reddy *et al.*²⁹ Zhu *et al.*³⁴ reported the long term cyclability of electrospun TiO₂ nanofibers with 12% rutile phase impurities and displayed a reversible capacity of ~144 mA h g^{−1} at a current density of 150 mA g^{−1}. Further, the electrospun TiO₂ hollow fibers are capable of delivering very stable cycling profiles irrespective of the current rates which is clearly evident from the rate capability studies (Fig. S1†). This clearly showed our electrospun single phase anatase TiO₂ hollow nanofibers out-performed the rest of these electrospun nanofibers in terms of phase purity and battery performance. Such an enhanced performance is mainly due to the presence of voids (hollow structure) in the fibers, which allow the penetration of electrolyte solution and thereby enable facile Li⁺ transport properties compared to solid interiors prepared through conventional single needle electrospinning (Fig. S2†). Further, the observed value is one of the best cyclabilities reported on the electrochemical performance of anatase phase TiO₂ irrespective of the morphology, which is clearly evident from the recent review by Kavan²² and Yang *et al.*¹⁵ On the other hand, the high surface area of TiO₂ hollow fibers (118 m² g^{−1}), the retention of the fibrous morphology after cycling and the Li-diffusion co-efficient cannot be ruled out as responsible for such performance, which increase the electrode/electrolyte interface area. The Li-diffusion co-efficient of electrospun TiO₂ hollow fibers was obtained from the CV traces recorded at various scan rates (Fig. S3†). It is apparent to notice the shifting of peak potential towards higher and lower voltages during Li-extraction and insertion reactions, respectively. The Li-diffusion co-efficient has been calculated using the following equation, $i_p = (2.69 \times 10^5)n^{3/2}C_0AD^{1/2}\nu^{1/2}$, where *n* is the number of electrons transferred, *i_p* is the current density in A g^{−1}, *D* is the diffusion coefficient of the rate limiting species (lithium ion) in cm² s^{−1}, *A* is surface area of the active material (cm² g^{−1}), *ν* is the scan rate (V s^{−1}), and *C₀* (mol cm^{−3}) is the maximum lithium concentration (*C₀* = 0.024 mol cm^{−3} for *x* = 0.5 moles of Li).^{35,36} By fitting the slope of peak current density (*i_p*) vs. the square root of the scan rate (Fig. S3-b†) into said relation, the lithium diffusion coefficient in the anatase titanium oxide hollow fibers during extraction process is estimated and found to be 3.91×10^{-17} cm² s^{−1}, which is consistent with the previous report by Kavan *et al.*³⁵

Fig. 4 (a) Initial charge–discharge curves of the Li/TiO₂ hollow nanofiber cell cycled between 1 and 3 V at a current density of 100 mA g^{−1} at room temperature, and (b) plot of capacity vs. cycle number.

Most of the research reports based on TiO_2 anodes (irrespective of the synthesis routes) end up with the half-cell configuration and there are no extensive reports available on the electrochemical performance of such anodes in the full-cell assembly with any of the commercial cathodes (LiCoO_2 , LiMn_2O_4 or LiFePO_4) to evaluate its compatibility towards an intercalation host. By employing TiO_2 as an anode in the full-cell configuration, the net energy density of the battery will be decreased to $\sim 250 \text{ W h kg}^{-1}$ when compared to metallic lithium, because of the higher insertion potential ($\sim 1.67 \text{ V vs. Li}$). In this line, we made an attempt to develop high performance Li-ion cells based on electrospun anatase TiO_2 hollow nanofibers with the LiFePO_4 cathode. The operating potential of the LiFePO_4 cathode ($\sim 3.45 \text{ V vs. Li}$) will be reduced to less than half while employing TiO_2 as the anode. The net operating potential is only around $\sim 1.4 \text{ V}$, but is still higher than other commercial rechargeable systems like lead–acid, Ni–Cd, Ni–MH and magnesium.^{1,37,38}

Mass balance between the electrodes is necessary before conducting the full-cell assembly, hence we made a half-cell for the cathode (Li/LiFePO_4) to evaluate the electrochemical performance by CV and galvanostatic cycling studies (ESI Fig. S4 and S5[†]). Based on the galvanostatic charge–discharge studies under the same current density of 100 mA g^{-1} , mass loading of the electrodes was optimized and the ratio of anode (TiO_2) to cathode (LiFePO_4) was fixed as 1 : 1.31. The full-cell delivered an open circuit potential of $\sim 180 \text{ mV}$. Fig. 5 depicts typical CV traces of $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers full-cell cycled between 0.9 and 2.5 V at a slow scan rate of 0.1 mV s^{-1} along with the CV signatures of the individual electrodes of LiFePO_4 and TiO_2 hollow nanofibers for comparison. Full-cell, $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers exhibited a well defined sharp oxidation peak at $\sim 1.74 \text{ V}$ which corresponds to Li-ion extraction from the cathode and simultaneous insertion of Li-ions into the TiO_2 lattice. The reduction peak at 1.38 V is ascribed to the removal of Li-ion from the anode and the successive reversible insertion

Fig. 5 Cyclic voltammogram (CV) of $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers cells (pink line) cycled between 0.9 and 2.5 V at scan rate of 0.1 mV s^{-1} ; the green line and orange line indicate the CV profiles of Li/TiO_2 hollow nanofibers and Li/LiFePO_4 cells, respectively.

of Li-ion into the FePO_4 lattice. Extraction of Li-ions is due to the oxidation of Fe^{2+} to Fe^{3+} (LiFePO_4) and simultaneous reduction of Ti^{4+} into Ti^{3+} (TiO_2), whereas during discharge the trend has been reversed according to the following equilibrium, $\text{LiFePO}_4 + \text{TiO}_2 \leftrightarrow \text{FePO}_4 + \text{LiTiO}_2$. Constructive overlapping of the CV curves with sharp redox peaks corresponds to the excellent reversibility of the full-cell during electrochemical cycling.

Fig. 6a illustrates the galvanostatic cycling performance of full-cell $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers cycled between 0.9 and 2.5 V at constant current density of 100 mA g^{-1} in ambient temperature for 100% depth-of-discharge. Two distinct voltage plateaus can be observed during the charge/discharge process, which is in good agreement with the CV traces obtained in Fig. 5. The discharge curves in full-cell configurations are similar to TiO_2 hollow nanofibers in the half-cell assembly and divided into three regions, which is consistent with previous report by Choi *et al.*³⁹ The full cell of $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers delivered a reversible capacity of 103 mA h g^{-1} at a current density of 100 mA g^{-1} with a Coulombic efficiency of 68%. The lesser Coulombic efficiency in the initial cycle is expected, since a huge amount of irreversible capacity loss ($\sim 34 \text{ mA h g}^{-1}$) is noted in half-cell configuration for TiO_2 hollow nanofibers. The applied current density of 100 mA g^{-1} is equal to 0.97 C, since the reversible capacity is found to be 103 mA h g^{-1} . A plot of discharge capacity vs. cycle number is presented in Fig. 6b, with Coulombic efficiency. It is evident that, $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers presented excellent cyclability up to the 300 cycles tested. The $\text{LiFePO}_4/\text{TiO}_2$ hollow

Fig. 6 (a) Typical galvanostatic charge–discharge curves of $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers cells cycled between 0.9 and 2.5 V at a current density of 100 mA g^{-1} at room temperature, and (b) plot of the discharge capacity vs. cycle number of $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers cells with Coulombic efficiency, in which red squares and pink circles correspond to the discharge capacity and Coulombic efficiency, respectively.

nanofibers cell retained 88% of its reversible capacity after 300 galvanostatic cycles. The Coulombic efficiency is increased to over 99% within 10 cycles and thereafter the same efficiency was maintained for the measured 300 cycles, which indicates the excellent reversibility during cycling. At low current rates (50 mA g^{-1}), the full-cell $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofibers delivered a reversible capacity of $\sim 140 \text{ mA h g}^{-1}$, whereas only $\sim 30 \text{ mA h g}^{-1}$ was obtained at the current density of 1 A g^{-1} (Fig. 7). It is very difficult to compare the state-of-art LIB based on TiO_2 anodes due to the slightly higher insertion potential, and hence less research work has been reported. Choi *et al.*³⁹ reported the electrochemical performance of homemade $\text{LiFePO}_4/\text{graphene-TiO}_2$ composite cells and delivered a stable reversible capacity over a reported 700 cycles at a 10 C rate. The performance of electrospun TiO_2 nanofibers with LiMn_2O_4 cathodes were reported by Suresh Kumar *et al.*³² and the test cell experienced a capacity fade of 19% after 100 cycles at a current density of 150 mA g^{-1} . The net operating potential of this $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofiber cell is found to be only $\sim 1.4 \text{ V}$ and hence this cell can be used effectively for miniature and stationary applications. Recently, Hassoun *et al.*⁴⁰ reported the performance of a $\text{LiFePO}_4/\text{TiO}_2$ -rutile phase configuration with a PEO-based dry solid polymer electrolyte and experienced a capacity fade during cycling, but no long term cyclability was reported. On the other hand, the liquid electrolyte comprising full-cell configuration ($\text{LiFePO}_4/\text{TiO}_2$ -rutile phase) delivered better cyclability than the solid polymer electrolyte system with a reversible capacity of $\sim 150 \text{ mA h g}^{-1}$ at a current rate of C/3. The performance of mesoporous $\text{TiO}_2\text{-C}$ nanospheres in a full-cell assembly with LiFePO_4 was reported by Cao *et al.*⁴¹ However, the full-cell assembly is fabricated without any proper optimization. Further, the inclusion of an excess amount of anode has also

been carried out which results in the consumption of more Li. As a result, a reversible capacity of $\sim$ only 100 mA h g^{-1} (based on the anode mass) was obtained and this also delivered the worst rate capability compared to our present system. More importantly, the working potential of the present configuration is still higher than aqueous based rechargeable battery systems like lead-acid, Ni-Cd and Ni-MH.¹ In addition, the full-cell system is made up of completely eco-friendly, low cost materials and can possibly be explored for heavier applications like EV and HEV in near future by making stacks.³⁸ Further studies are in progress to improve the cell potential based on the TiO_2 hollow nanofiber anode by employing high voltage cathodes such as LiMn_2O_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ *etc.*

Conclusion

A simple co-axial electrospinning approach was adopted for the synthesis of one dimensional anatase TiO_2 hollow nanofibers. Firstly, TiO_2 hollow nanofibers were characterized in the half-cell configuration and subsequently employed as anode in the full-cell configuration. The full-cell was fabricated using TiO_2 hollow nanofibers as the anode and olivine phase LiFePO_4 as the cathode under optimized mass loading. The $\text{LiFePO}_4/\text{TiO}_2$ hollow nanofiber cell exhibited a relatively high reversible capacity of 103 mA h g^{-1} at a current density of 100 mA g^{-1} and retained 88% of its reversible capacity after 300 cycles. The unique structure, with a large surface area and short diffusion pathways of the electrospun TiO_2 hollow nanofibers played a vital role for such excellent performance. This technique can be extended for other transition metal oxides to employ them as prospective electrode materials for Li-ion battery applications.

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Fig. 7 (a) Galvanostatic charge-discharge curves of $\text{LiFePO}_4/\text{TiO}_2$ cells cycled between 0.9 and 2.5 V at various current densities from $0.05\text{--}1 \text{ A g}^{-1}$ in room temperature, and (b) plot of discharge capacity vs. cycle number.

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