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Supporting Information

Pseudo-capacitive performance of titanate nanotubes as a supercapacitor electrode

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Experimental

1. Preparation of the titanate nanotubes

The synthesis of titanate $H_2Ti_3O_7$ nanotubes was similar to our previous reports.[10] Typically, 0.1 g of TiO_2 (P25) was dispersed in a 50 mL of 10 M aqueous NaOH solution. Then, the suspension was transferred into a Teflon-lined stainless steel autoclave with a capacity of 75 mL. The autoclave was kept at 120 °C for 48 h and then cooled to room temperature. The resulting precipitate was acid-washed with 0.1 M HCl solution until pH value of 1-2 was reached, then stirred at a solution with its pH value of 5-6 to make the ion-exchange completely, and again washed with alcohol for some times. Finally, the white product was dried at 70 °C for 12 h in air.

2. Sample Characterization

The power X-ray diffraction (XRD) patterns were recorded on PANalytical X'Pert spectrometer using the Co-Kα radiation and the data were changed to Cu-Kα data. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were taken on a Hitachi S4800 instrument and a FEI F20 S-TWIN instrument, respectively. Surface area was determined by Brunauer–Emmet–Teller (BET) method using ASAP 2020 from Quanta Chrome. Fourier Transform Infrared (FT-IR) transmission spectra were taken on a BRUKER-EQUINOX-55 IR spectrophotometer. Differential scanning calorimetry (DSC) was performed using the Setsys Evolution instrumentation with a temperature increment of 10 ℃ min^{-1} under ambient conditions.

3. Sample Tests

For the electrochemical measurements, 70 wt% active material was mixed and grounded with 20 wt% polyvinylidene fluoride (PVDF) powder as a binder and 10 wt% acetylene back carbon (AB) powder as the conductive assistant materials. The mixture was added to N-methyl-2-pyrrolidinone solvent to form homogeneous slurry and pressed on Al foil circular flakes as the working electrode, and dried at 100°C for 24 h under vacuum conditions. Metallic lithium foils were used as the counter electrodes. The electrolyte was 1 M $LiPF_6$ in a 1:1:1 (volume ratio) mixture of ethyl carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC). The separator was an UP 3093 (Japan) macroporous polypropylene membrane. The cells were assembled in a glove box filled with highly pure argon gas (O_2 and H_2O levels <1 ppm), and charge/discharge tests were performed in the voltage range of 1-2.5V (Li^+/Li) at different current densities on a Land automatic batteries tester (Land CT 2001A,Wuhan, China). The cyclic voltammetry (CV) measurements were performed on an IM6 Electrochemical Workstation (Zahner) at a scan rate of 5 mVs^{-1} in a range of 1-2.5 V *vs*. Li/Li^+. The electrochemical impedance spectroscopy (EIS) was performed on IM6 Electrochemical Workstation (Zahner). The EIS data were collected with an AC voltage of 10 mV amplitude in the frequency range from 1 MHz to 100 mHz. The discharge specific capacitance was calculated according to the following equation (1)

$$C_{\mathrm{s}p} = \frac{I \times \Delta t}{m \times \Delta U} \qquad (1)$$

where I (A) is the applied current, E (V) is the tested potential range, t (s) is the discharge time, and m (g) is the mass of single electrode active materials. The energy density value was calculated according to Equation (2)

$$E = \frac{1}{2} C V^2 \qquad (2)$$

where C is the capacitance (Fg^{-1}) of supcapacitor and V is its operating potential window, respectively. The average power density value was calculated according to Equation (2) and (3):

$$P = \frac{E}{\mathrm{t}} \qquad (3)$$

where t is the discharge time (s).

TG-DTA and IR analysis

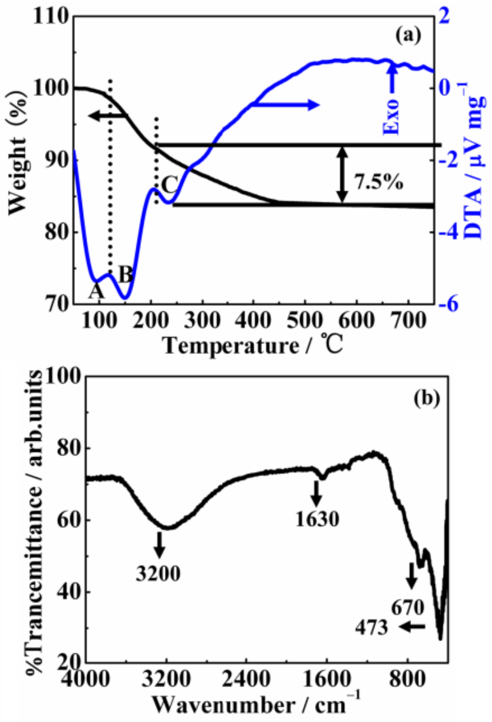

Fig. S1 (a) TG-DTA curves and (b) IR spectrum of the titanate nanotubes.

Fig. S1a shows the TG-DTA curves of the titanate nanotubes. There are three endothermic peaks on the DTA curve, corresponding to the three thermal decomposition stages on the TG curve. The first range between 50–120°C and the second range between 120–200°C are attributed to the evaporation of surface water and interlayered water,[1] whereas the third stage between 200–500°C is ascribed to the loss of the constitution water that arises from the formation of TiO_2.[2] The percentage of the constitution water loss is nearly 7.5% at approximately 250°C, which is close to the theoretical structural water loss of 7.0% for the thermal decomposition of $H_2Ti_3O_7$.[3] Fig. S1b shows the IR spectrum of the titanate nanotubes. The broad bands at ca. 3200 and 1630 cm^{-1} are attributed to the O–H stretching vibration and H–O–H bending vibration, respectively, indicating that the bonded H exists within the material. Two absorption bands locate at 473 and 670 cm^{-1}, corresponding to stretching Vibrations of the octahedral $[MO_6]$ lattice, respectively. The IR measured results are good in agreement with the reports about $H_2Ti_3O_7$ titanate.[4,5]

References

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The ragone plot of the titanate electrodes

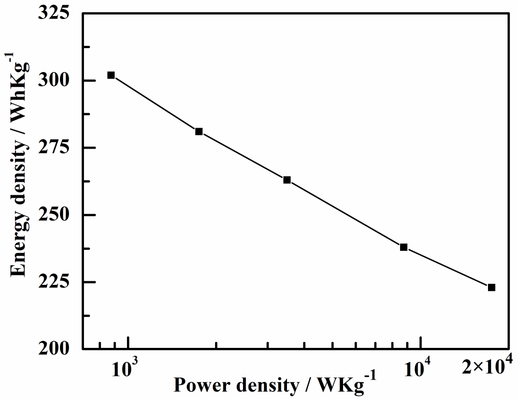

Fig. S2 The ragone plot (energy density vs. power density) of the titanate electrodes.

The HRTEM image of the titanate nanotubes

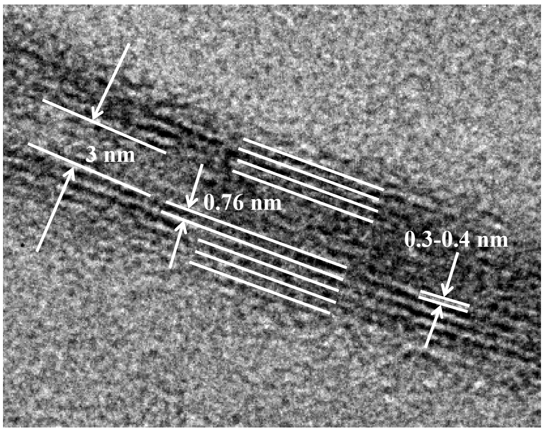

Fig. S3 The HRTEM image of the titanate nanotubes.

EIS plots of the titanate electrodes

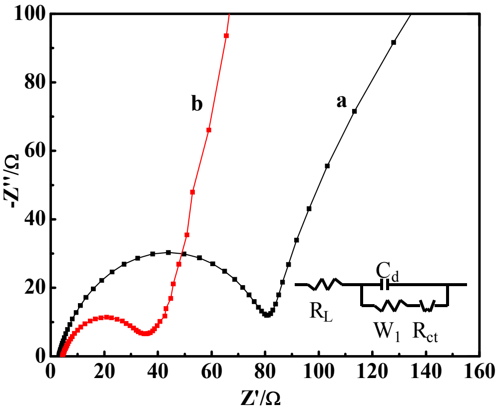

Fig. S4 EIS plots of the electrodes (a) the 10th cycle and (b) the 1000th cycle. (Inset: the corresponding equivalent circuit model).