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Supporting Information

A novel layered titanoniobate as anode material for long-life sodium-ion batteries

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Experimental

1. Materials

Niobium (V) oxide (Nb_2O_5 , AR), titanium dioxide (TiO_2 , AR) and cesium carbonate (Cs_2CO_3 , AR) were purchased from Aladdin (Shanghai). Hydrochloric acid (HCl, 36%), and tetrabutylammonium hydroxide (TBAOH, 10% in water) were obtained from Sinapharm chemical reagent Co., Ltd (Shanghai). All the chemicals were analytic grade and used as received without further purification.

2. Synthesis of the protonated derivative HTi_2NbO_7

Layered $\text{CsTi}_2\text{NbO}_7$ materials were prepared by solid-state calcination at 1373K for 12h using Cs_2CO_3 , TiO_2 and Nb_2O_5 as raw materials in a molar ratio of 1.1: 4: 1. A 10% molar excess of Cs_2CO_3 were added to compensate for loss due to their volatilization at high temperature.

The proton exchange reaction was carried out by adding 1g $\text{CsTi}_2\text{NbO}_7$ to 100ml acid solution (1M) under magnetic stirring at 60°C. The solution was renewed with fresh one every 8h for ensuring the concentration of acid during the reaction. The solutions were kept stationary at ambient temperature for 4h after stirred 24h. Then the precipitate was filtered, washed with pure water three times. Finally, the HTi_2NbO_7 was obtained by heating the precipitate at vacuum 423K for 2h.

3. Characterization

The crystalline structure of the as-prepared samples were characterized by powder X-ray diffraction (XRD, D8) with $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) from 7 to 90°. The scanning electron microscopy (SEM, SU-70) was used to characterize the microscope morphology of the samples. The N_2 adsorption/desorption tests were determined by Brunauer–Emmett–Teller (BET) measurements using an ASAP-2020 surface area analyser.

4. Electrode fabrication and electrochemical characterization

HTi₂NbO₇ was tested as an anode electrode material in CR2032 coin cell. Typically, the electrodes were fabricated by spreading a slurry of HTi₂NbO₇ (70%), conductive carbon black (20%) and PVDF (10%) mixed in N-methyl pyrrolidinone (NMP) onto a Cu foil. After drying in air at 60 °C for 5 h, the working electrode would be further dried at 110 °C under vacuum one night. Coin cells were assembled in an Ar-filled glove box with a 1 M NaClO₄ in ethylene carbonate (EC)/propylene carbonate (PC) (1:1 w/w) as the electrolyte, glass-fiber (Whatman GF/D) separator and Na sheet as the cathode electrode. All the coin cells were tested at the range of 0.01-3 V. The electrochemical performance a cyclic voltammogram (CV) was obtaining by using electrochemical workstation (Solartron Analytical 1400) at a scan rate of 0.01 mV S⁻¹. Galvanostatic charging/discharging cycles were tested at different rates on Land BT2013A battery testing system.

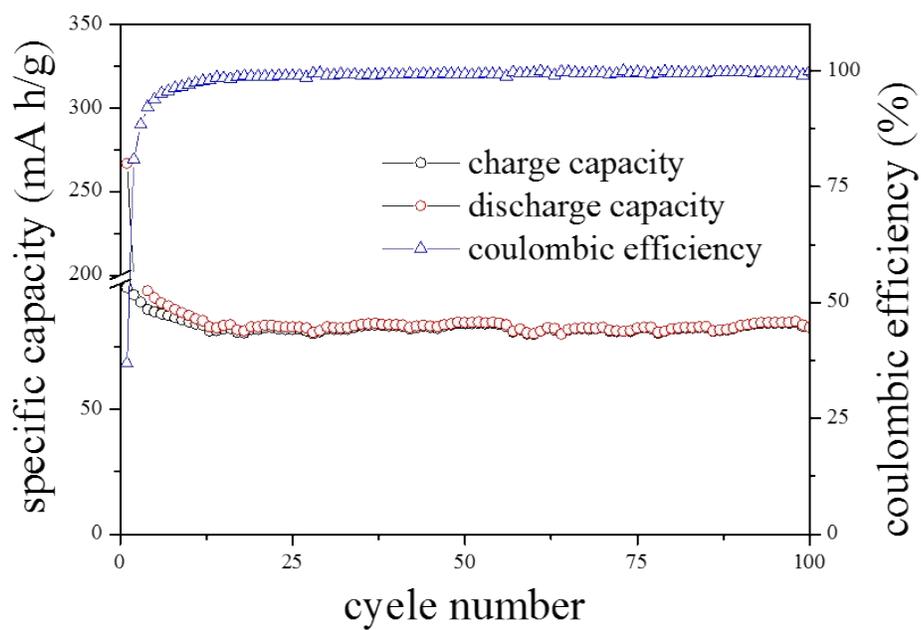


Figure S1 Cycle performance of conductive carbon at 100 mA g⁻¹.

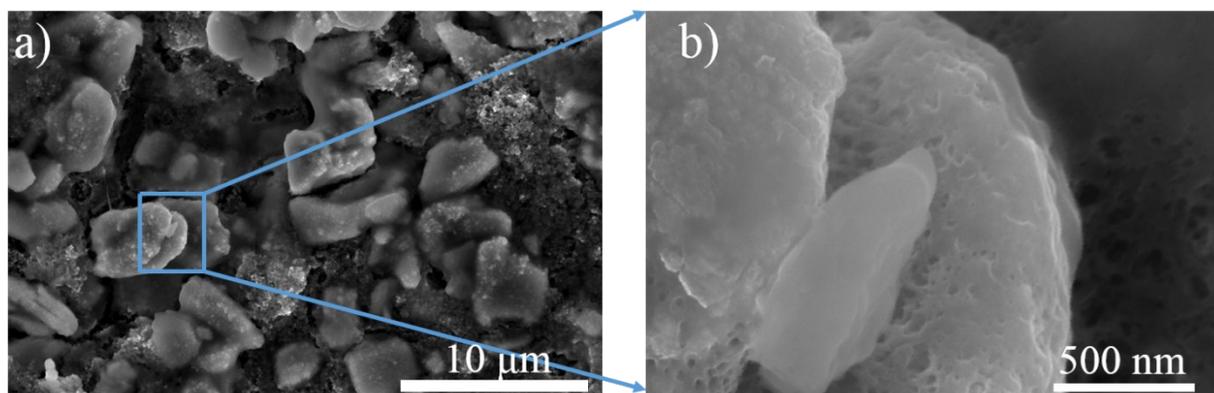


Figure S2 SEM images of the HTi_2NbO_7 after 2000 cycles.