H₂Ti₃O₇ Nanorods Synthesized H Cation-exchange in Na₂Ti₃O₇ for Stable Sodium Storage

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Abstract: To overcome poor interfacial stability and slow ion transport rate of Na₂Ti₃O₇, H₂Ti₃O₇ nanorods are synthesized by acidification of Na₂Ti₃O₇ with low concentration of strong acid. The dominated pseudo-capacitive behavior significantly improved rate capability with fast electron and ion storage kinetics. When used as anode for sodium-ion batteries, H₂Ti₃O₇ delivers a stable specific capacity of 103.5 mAh g⁻¹ after 500 cycles with a capacity retention rate of 49.3%, and high rate performance (70.5 mAh g⁻¹ at 2 A g⁻¹).

1. Introduction

With the rapid consumption of fossil energy, as well as the unstable wind/solar energy, the energy storage systems have aroused widespread concern to alleviate energy pressure. Due to the abundant resources and similar chemical properties to lithium, sodium ion batteries (SIBs) are considered to be one of the good substitutes for lithium ion batteries (LIBs) [1]. Na₂Ti₃O₇ is considered as a promising anode material for SIBs because of its rich resource reserves, low price, low working voltage, high energy density and stable structure [2]. However, the low electronic conductivity, poor interface stability and Z-shaped curved layered crystal structure result in the slow ion transport in Na₂Ti₃O₇, further leading to poor electrochemical performance for SIBs anodes.

Wang et al. designed a single crystal Na₂Ti₃O₇ nanorods, which provided 103 mAh g⁻¹ at 0.1 C (~17.7 mA g⁻¹) after 20 cycles [3]. Wu et al. introduced parts of tunnel-typed Na₂Ti₆O₁₁ into Na₂Ti₃O₇ to fabricate mixed rod-like structure, which retained a discharge capacity of 81 mAh g⁻¹ after 100 cycles at a current density of 20 mA g⁻¹ [4]. Two-dimensional Na₂Ti₃O₇ nanoflakes were synthesized by a hydrothermal method, which showed excellent electrochemical properties for SIBs anode owing to high specific surface area and optimized structure [5]. The complex synthesis processes bring about uneven materials. Chen et al. proposed ion exchange F-doped Na₂Ti₃O₇ materials, which achieved a specific capacity of 75 mAh g⁻¹ after 800 cycles at 100 mA g⁻¹ [6]. Further, H-cation exchange was adopted to prepare H₂Ti₃O₇, and a stable capacity of 168 mAh g⁻¹ after 1000 cycles [7]. Few researches have been reported on completely protonated Na₂Ti₃O₇ for SIBs anodes.

Herein, H₂Ti₃O₇ nanorods were obtained by H cation-exchange treatment of Na₂Ti₃O₇ with low concentration of strong acid for a long time. Through H cation-exchange, the crystal plane spacing of the material was increased, which made it easier for intercalation/deintercalation of Na⁺. In addition, the high pseudo-capacitive contribution rate significantly improved the sodium storage kinetics, and achieved stable electrochemical performance as the anodes for SIBs.
2. Materials and Methods

2.1. Synthesis of Na₂Ti₃O₇ and H₂Ti₃O₇

1.2 g TiO₂ powder was added to 100 mL deionized water, with ultrasonic for 30 min. Then added 0.88 g CH₃COONa powder to the solution (according to the molar ratio of TiO₂:CH₃COONa is 3:2, while CH₃COONa excess 5 %). Raised to 80 °C until the water was completely volatilized. The remaining solids was heated in a muffle furnace with a rate of 5 °C min⁻¹ to 500 °C for 3 h, and then calcined at 800 °C for 12 h. The final product was Na₂Ti₃O₇ (NTO).

1.2 g NTO powder was added to 100 mL 1 M hydrochloric acid solution and stirred violently for 48 h. After that, wash with deionized water and ethanol for several times, and collect the precipitate. The precipitate was calcined at 200 °C for 3 h to obtain the final product H₂Ti₃O₇ (HTO).

2.2. Materials characterization

X-ray diffraction (XRD) was performed on DMAX-2400 diffractometer (Cu-Kα radiation, wavelength of 1.5406 Å) over the range of 5~75°. The microstructures and morphologies of the samples were characterized by Quanta 600 field emission scanning electron microscope (SEM). The micro-morphology and crystal structure characteristics of samples were characterized by Tecnai G2 F20 S-TWIN transmission electron microscope (TEM), and the structure of the sample was deeply analyzed by selected area electron diffraction (SAED).

2.3. Electrochemical measurements

Working electrodes were prepared by mixing the active material (70%), acetylene black (20%) and polyvinylidene fluoride (PVDF, 10%) to form a uniform slurry that was then coat on copper foil. The resulting electrodes were dried at 80 °C for 24 h. The electrochemical properties of the NTO and HTO anodes were evaluated with CR2032 coin cells. Pure sodium foils were used as counter electrodes, and 1.0 M NaClO₄ in EC/PC (1:1, v/v) were used as the electrolyte. Galvanostatic charge/discharge tests were carried at room temperature on Land CT2001A. Cyclic Voltammetry (CV) was performed on CHI 604e electrochemical workstation (Chen Hua Instruments Co.). The CV data was acquired over the range of 0~2.5 V.

3. Results and Discussion

The XRD patterns of HTO were shown in Figure 1, suggesting good crystalline structure. Notably, the peaks at 9.8, 11.2, 16.4, 24.3, 29.8, and 43.9 ° correspond to the crystal planes of H₂Ti₃O₇ (PDF #47-0561) (001), (200), (201), (110), (003), and (204), respectively. However, some unmatched peaks at 35 ~ 48 ° (purple marked) may be related to the blue shift of the peaks, or impurities formed during the subsequent acid treatment.

![Figure 1. XRD patterns of the HTO](image-url)
Figure 2a-b show the SEM images of H$_2$Ti$_3$O$_7$ and Na$_2$Ti$_3$O$_7$, and both samples hold the similar rod-like morphology. The unchanged morphologies of H$_2$Ti$_3$O$_7$ after acid treatment indicate the acidification is a slow and subtle ion exchange process. TEM was conducted to confirm the rod-like structure of H$_2$Ti$_3$O$_7$ with a width of about 200 nm. The high resolution TEM (HRTEM) image shows the lattice stripes of H$_2$Ti$_3$O$_7$ (Figure 2d), where the spacings of 0.296, 0.306, 0.368 and 0.399 nm correspond to the planes of H$_2$Ti$_3$O$_7$ (003), (310), (110) and (400), respectively. The clear lattice stripes further confirm the good crystallinity of H$_2$Ti$_3$O$_7$, which is consistent with the previous results XRD patterns. Figure 2e presents a selection of specific areas of the H$_2$Ti$_3$O$_7$ morphology, and show the diffracted lattice diffraction spots in Figure 2f. The single crystal properties of H$_2$Ti$_3$O$_7$ can be clearly seen and the corresponding (400), (401) and (001) crystal planes are calculated by the spacing between the spots.

Figure 2. SEM images of (a) HTO and (b) NTO; HTO: (c) TEM images; (d) HRTEM images; (e) Selection of specific areas; (f) Diffracted lattice diffraction spots

The electrochemical performance of the HTO and NTO was tested as SIBs anodes. Figure 3a-b exhibit the selected charge/discharge curves of two electrodes. The discharge specific capacity of HTO is 489.4 mAh g$^{-1}$ in the first cycle and 209.8 mAh g$^{-1}$ in the second cycle (Figure 3a). Large amount of capacity loss is due to the irreversible reaction and the formation of SEI film in the first cycle. The capacity of HTO remained virtually unchanged from the 2rd to 10th cycle, but NTO (Figure 3b) lost 28% capacity of the second cycle. The characteristics of the CV curve of HTO (Figure 3c) are basically consistent with the charge/discharge curve. The rate performance of HTO and NTO samples were tested at different current densities from 50 to 2000 mA g$^{-1}$ (Figure 3d). HTO shows the discharge specific capacity of 193.6, 172.3, 137.6, 119.5, 92.7 and 70.5 mAh g$^{-1}$ at current densities of 50, 100, 200, 500, 1000 and 2000 mA g$^{-1}$, respectively. However, NTO could only provide the discharge specific capacity of 128.2, 92, 72, 56.7, 38.9 and 29.9 mAh g$^{-1}$, respectively. When the current density is back to 50 mA g$^{-1}$, the discharge specific capacity of HTO reaches to 170.6 mAh g$^{-1}$. The above results show excellent rate performance of the acidified HTO, which mainly originates from the expansion of ion channels after acidizing treatment to promote the transport of sodium ions. The cycling performance of HTO and NTO was carried at 100 mA g$^{-1}$ (Figure 3e). The first cycle discharge specific capacity of HTO is 489.4 mAh g$^{-1}$, and the coulomb efficiency is 37.4%. The first discharge capacity of NTO is 297.4 mAh g$^{-1}$, and the coulomb efficiency is 46.9%. Higher first-cycle discharge specific capacity and lower first-cycle coulomb efficiency mean that a large number of side reactions happen between HTO and electrolyte during the first cycle, which may be caused by the more micropores or mesopores in HTO. The coulomb efficiency of HTO is close to 100% from the 43rd
cycle, but the coulomb efficiency of NTO is close to 99% from the 50th cycle, indicating that HTO maintains higher electrochemical activity and electrochemical stability than NTO. After 100 cycles, HTO provides a discharge specific capacity of 138 mA h g\(^{-1}\), but NTO can only provide 65 mAh g\(^{-1}\). After 500 cycles, HTO delivers a discharge specific capacity of 103.5 mAh g\(^{-1}\), but NTO can only provide 48 mAh g\(^{-1}\). The results show excellent electrochemical performance of the acidified HTO anodes, owing to the interlayer spacing of (001) crystal plane is enlarged (H\(_2\)Ti\(_3\)O\(_7\), 9.01 Å; Na\(_2\)Ti\(_3\)O\(_7\), 8.4 Å) after H\(^+\) replaced Na\(^+\), which increases the transport rate of sodium ions. Meanwhile, the original inert Na\(^+\) site is released, improving electrochemical activity in the subsequent process of sodium intercalation and storage.

Figure 3. Selected charge/discharge curves of (a) HTO and (b) NTO; (c) CV curves of HTO at 0.1 mV s\(^{-1}\); (d) Rate performance test of HTO and NTO; (e) Long-term performance of HTO and NTO at 100 mA g\(^{-1}\).

The sodium storage kinetics of HTO were investigated according to the CV curve at different scanning rates (Figure 4a). The current \(i\) and the scan rate follows the formula [8-9]:

\[
i = a v^b
\]  

where \(i\) represents the current density, \(v\) represents the scanning speed, \(a\) and \(b\) represent constants. It indicates that the diffusion behavior is dominant when the \(b\) value is 0.5, while \(b\) value is 1.0, the surface diffusion process is dominant. Through the calculation, the \(b\) values at 0.6, 0.7 and 0.8 V in the anode peak region are 0.84, 0.95 and 0.98, respectively (Figure 4b). The \(b\) values are 0.77 (0.2 V), 0.81 (0.3 V), 0.83 (0.4 V) and 0.84 (0.5 V), respectively (Figure 4c). The \(b\) values are between at 0.5~1.0, indicating the diffusion and capacitive behavior simultaneously appear in the HTO electrodes. The capacitive contribution can be calculated by the following formula:

\[
i(V) = k_1 v + k_2 v^{1/2}
\]  

where \(k_1\) and \(k_2\) are fitting parameters. The pseudo-capacitive contribution rate of HTO pseudo-capacitive is 49.8% at 0.2 mV s\(^{-1}\) (Figure 4d). Similarly, the pseudo-capacitance contribution rates of 0.5, 1, 2 and 5 mV s\(^{-1}\) are 56.3%, 64.6%, 73.3% and 89.2%, respectively (Figure 4e). Therefore, the sodium storage of HTO anode is mainly capacitive process at 5 mV s\(^{-1}\). This further confirmed that
acidification treatment hydrogen ion exchange can optimize the surface and promote ion diffusion and charge transfer, achieving high rate performance and good cycle stability.

Figure 4. (a) CV scurves of HTO at 0.1, 0.2, 0.5, 1, 2 and 5 mV s\(^{-1}\); The fitting curves of the b value (b) Anodic areas, (c) Cathodic areas; (d) The capacitive contribution at 0.2 mV s\(^{-1}\); (e) The ratios between capacitive and diffusion contributions at different scan rates.

4. Conclusion
In summary, HTO with good crystalline structure was prepared by solid-state synthesized NTO with low concentration of strong acid for a long time. The HTO electrodes showed good cycle performance and rate performance for anode in SIBs. After 500 cycles, it still provides a specific capacity of 103.5 mAh g\(^{-1}\) with a capacity retention rate of 49.3% at 100 mA g\(^{-1}\). Besides, the HTO anodes showed excellent rate performance, which delivers a capacity of 70.5 mAh g\(^{-1}\) at 2 A g\(^{-1}\). The dominated pseudo-capacitive contribution behavior of the materials significantly improves the sodium storage kinetics. The facile and simple H cation-exchange process improves the discharge specific capacity and cycle stability. This work provides the possibility for the practical application of sodium titanate as the negative electrode for SIBs.

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