



Long life anode material sodium titanate synthesized by a moderate method

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ABSTRACT

A sodium titanate-carbon ($\text{Na}_2\text{Ti}_3\text{O}_7/\text{C}$) composite as an anode material for sodium-ion batteries (SIBs) is successfully synthesized via a moderate method (500 °C). It can deliver charge capacities of 161 mA h g^{-1} and 91 mA h g^{-1} at current densities of 0.05 C and 10 C, respectively. The material can be cycled at 0.2 C for 400 cycles without capacity or voltage decay. This low cost and environmentally friendly $\text{Na}_2\text{Ti}_3\text{O}_7/\text{C}$ exhibits excellent electrochemical performance.

1. Introduction

Lithium ion batteries (LIBs) have been intensively pursued as power sources for portable electronics and electric vehicles (EVs) owing to their high energy and power density [1–3]. However, the depletion in lithium resources may restrict their perspective applications in large-scale energy storage [4]. On the other hand, the amount of sodium distributed in the ocean is almost unlimited [5,6]. Therefore, sodium-ion batteries have attracted much attention in recent years. Significant progress has been made in developing SIBs cathodes [7–11], but the major obstacle is the absence of suitable anode materials.

Layered sodium titanium oxide $\text{Na}_2\text{Ti}_3\text{O}_7$ (NTO) with a low intercalation potential of around 0.3 V (vs. Na^+/Na) is a promising anode material for SIBs because of its chemical stability, non-toxicity and abundant resources [12–14]. However, it suffers from poor electronic conductivity and poor long-cycle performance. Besides, high temperature (> 800 °C) and/or long synthesis time (> 48 h) are usually adopted to synthesize NTO [15–18]. In this work, we use a facile low-temperature method (500 °C) to synthesize a $\text{Na}_2\text{Ti}_3\text{O}_7$ -carbon network composite with excellent cycling performance. Moreover, different from the synthesis of other carbon-coated electrode materials (e.g. $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$) which needs an extra carbon source (e.g. sugar) in the starting materials, the carbon network here is directly derived from an alkoxide precursor of titanium. Such an in-situ formed carbon may be more homogeneously mixed with the active electrode materials, that results in good electrochemical properties.

2. Experimental

Here, $\text{Na}_2\text{Ti}_3\text{O}_7/\text{C}$ was fabricated by a moderate method. Stoichiometric CH_3COONa (1.6406 g, Sinopharm, AR) and tetrabutyl titanate (TBT) (10.2108 g, Sinopharm, CP) were added into 200 ml ethanol under stirring. The obtained solution was heated in a water bath at 60 °C to form a white gel, which was further dehydrated at 120 °C in an oven to obtain an xerogel. Then $\text{Na}_2\text{Ti}_3\text{O}_7$ (NTO-A) and $\text{Na}_2\text{Ti}_3\text{O}_7/\text{C}$ (NTO-N) were prepared by annealing the grinded xerogel at 500 °C for 7 h under air atmosphere and N_2 atmosphere, respectively.

The carbon content of NTO-N was measured with an Infrared Carbon-sulfur analyzer (CS-8800C, Jinbo). It was also analyzed by Raman spectroscopy (Renishaw inVia Raman Microscope). The crystal structures of NTO-A and NTO-N were characterized using powder X-ray powder diffraction (XRD, Rigaku TTR-III) in the 2θ range from 10° to 50° at a scanning rate of 4° min^{-1} . Their morphologies were examined by a scanning electron microscope (SEM, JSM-6390 LA, JEOL) and a high resolution transmission electron microscope (HRTEM, JEM-2100).

The electrochemical properties of NTO-N, and NTO-A were measured by assembling CR2032 half cells in an argon filled glove box (MBraun Labmaster 130) and tested on a multi-channel battery cycler (NEWWARE BTS-610). The electrodes were prepared by coating the slurry containing 70 wt% NTO-N or NTO-A, 20 wt% carbon black and 10 wt% PVDF (dissolved in N-methyl-2-pyrrolidinone) onto a Cu foil, followed by drying in a vacuum oven at 80 °C for 12 h. The electrolyte was 1.0 M NaClO_4 dissolved in ethylene carbonate (EC) and dimethyl

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carbonate (DMC) (EC: DMC=1:1 V/V, Zhuhai Smoothway Electronics Materials Co. Ltd). Glass fiber was used as the separator (Whatman™), and a sodium foil as the counter electrode. The cells were cycled in the voltage range of 0.005–2.5 V at room temperature. For the rate performance test, the cells were also cycled at current densities of 0.05–10 C, (1 C=178 mA h g⁻¹), respectively. The electrochemical impedance spectroscopy (EIS) was also conducted on a CHI 604A electrochemical workstation.

3. Results and discussion

The SEM morphologies of NTO-A and NTO-N (Fig. 1a–b) show that the particle size of NTO-N distributes from 200 nm to 3 μm, much smaller than that of NTO-A due likely to the presence of carbon in NTO-N. The organic functional groups in TBT may form in-situ carbon network during the thermal treatment under N₂ atmosphere, which can wrap NTO particles and avoid them from further growth. The carbon content in NTO-N determined with an Infrared Carbon-sulfur analyzer is about 5.52 wt%. The TEM and HRTEM images of NTO-N (Fig. 1c–d) confirm the presence of carbon in the powder. With a higher resolution, the lattice fringes can be observed. The distance of the lattice fringes are about 0.56 nm and 0.35 nm, corresponding to the (101) and (011) planes of NTO crystals. In addition, the presence of carbon in NTO-N is also confirmed by its Raman analysis (Fig. S1), where the two characteristic D band at about 1300 cm⁻¹ and G band at 1560 cm⁻¹ are clearly observed.

The XRD patterns of NTO-A and NTO-N (Fig. 2) are indexed to Na₂Ti₃O₇ (JCPDS#31-1329) without any impurity phase. The relatively low intensity of NTO-N peaks can be ascribed to the low temperature thermal treatment adopted in this work and the carbon component is amorphous.

The initial discharge/charge capacities (Fig. 3a) of NTO-A and NTO-N at 0.05 C are 291.6/105.9 and 340.5/161.1 mA h g⁻¹, respectively. The shape of curves of the two materials are similar, but the

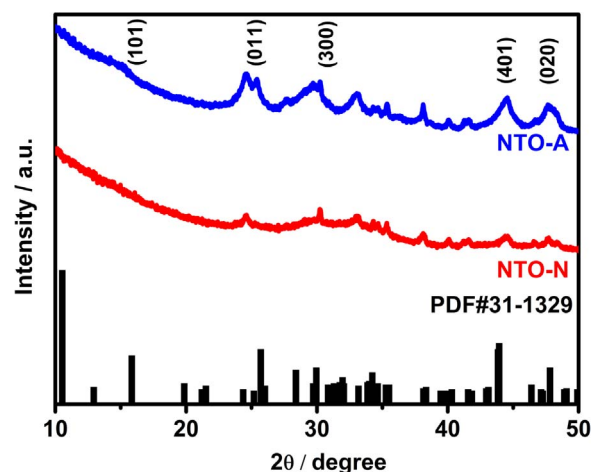


Fig. 2. X-ray diffraction patterns of NTO-A and NTO-N.

capacity of NTO-A is much lower than NTO-N, which can be ascribed to the relatively large polarization of NTO-A. The large irreversible capacities of the two materials are caused by the formation of surface layer and the irreversibility of the conductive additive. The initial coulombic efficiency (ICE) of NTO-N is 47.3% and it increases dramatically upon cycling, reaching 98% after 7 cycles and about 100% after 13 cycles (Fig. 3b). However, the ICE of NTO-A is only 36.3% and it is always lower than that of NTO-N during subsequent cycling, implying that the presence of carbon network can effectively reduce the contact of NTO particles and electrolyte, avoiding irreversible side-reactions. The capacity retention of NTO-A is 96.7% after 200 cycles while the cycleability of NTO-N is even better. For NTO-N, except for the initial discharge profile, the profiles of other cycles are overlapped, meaning that not only the capacity of NTO-N does not fade, but also the voltage of the material remains almost the same even

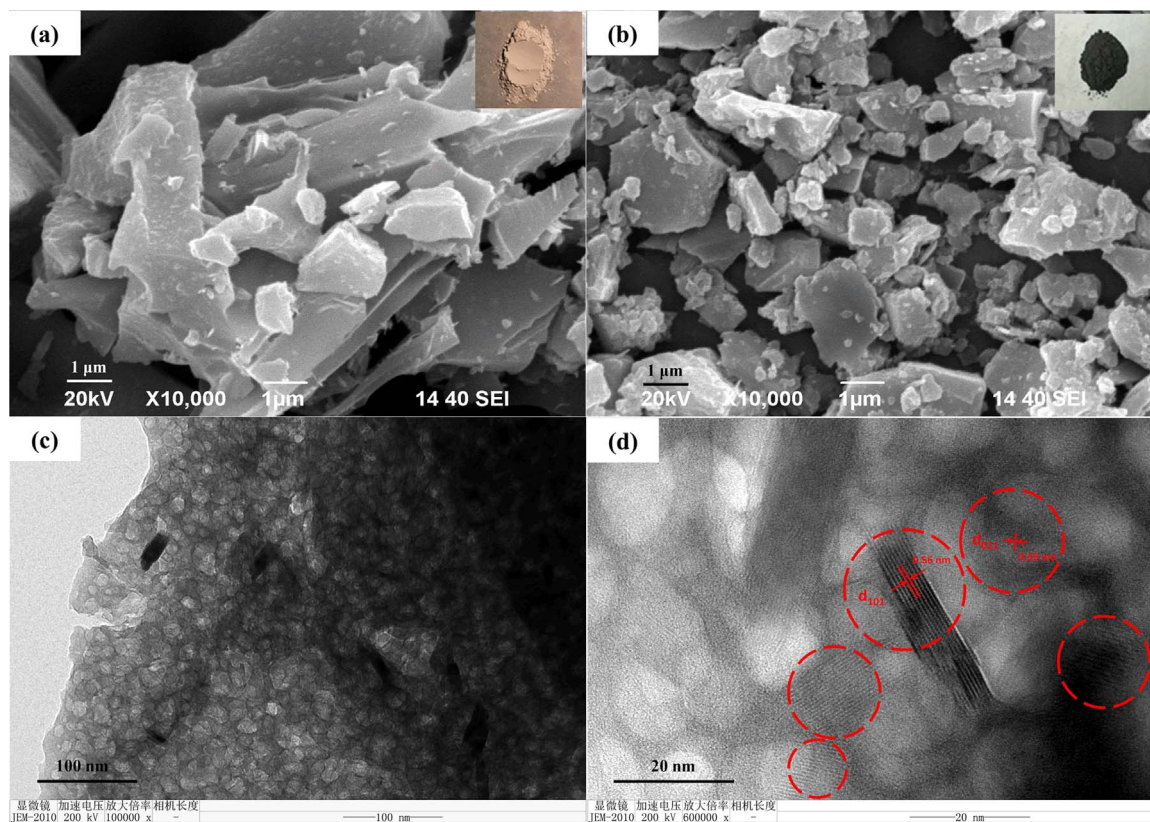


Fig. 1. SEM images of NTO-A (a) and NTO-N (b), TEM (c) and HRTEM (d) images of NTO-N. The insets in (a) and (b) show the colors of NTO-A and NTO-N.

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