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Morphology control and its effect on the electrochemical performance of $Na_2Li_2Ti_6O_{14}$ anode materials for lithium ion battery application

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ABSTRACT

$Na_2Li_2Ti_6O_{14}$ was successfully prepared by a solvothermal method. The XRD patterns show that the as-prepared samples have good purity and crystallinity. Further Rietveld refinement and theoretical calculation suggested that lithium should occupy 16n and 8e sites of the lattice during the intercalation process, and nearly six lithiums can be inserted reversibly into the lattice. The amount of ammonium hydrogen carbonate added during the reactions have significant impacts on the structures and morphologies of the materials, and well-defined hierarchical and porous spheres can be obtained at a suitable condition. The electrochemical tests showed that the charge/discharge specific capacities of the four samples under a current density of 50 mA g^{-1} after 50 cycles are 103.9/104.3, 175.1/177.1, 191.9/194.1, and 138.4/140.4 mA h g^{-1}, suggesting that the performance of the NLTO-L-3 is much better than other samples. Furthermore, NLTO-L-3 also exhibits good cycling stability and rate capability, and its revisable capacity is about 93 mA h g^{-1} at 2.8 A g^{-1} after 500 cycles. The excellent performance can be attributed to the hierarchical structures and porous characteristics. These features are helpful for reducing the impedance and for improving the diffusion dynamics of materials, as further confirmed by EIS measurement.

1. Introduction

With the development of human society, the energy and environmental related issues have attracted extensive concerns, and the demand for green energy is increasing and becomes urgent nowadays [1]. As an important power source, lithium ion battery (LIB) have been applied in portable devices, electric vehicles, and large-scale energy storage grid [1–3]. It is well known that the safety and electrochemical performance of a LIB are two primary criterions for realistic applications. Although carbon-based materials were used as anode in the beginning, they were replaced by other anode materials because of their limited capacity, efficiency, and safety hazard [4]. Later efforts on searching safe and reliable anode materials led to the discovery of spinel $Li_4Ti_5O_{12}$ [5] and other titanium based materials [6–9].

Due to their structural stability, titanium-based materials have attracted much attention [10–12], and among then $Li_4Ti_5O_{12}$ have been commercialized. It was reported that $Li_4Ti_5O_{12}$ can be discharged down to 0 V (*v.s.* Li^+/Li) without causing any structural degradations [5]. Similarly, mixed alkali titanium oxides ($M_xLi_2Ti_6O_{14}$, M = Ba, Pb, Sr, Na_2) proposed recently are also consist of TiO_6 octahedrons assembling along the three dimensions [13–17]. In comparison to $Li_4Ti_5O_{12}$, the introduction of Na results in a much lower potential plateau (1.25 V *v.s.* Li^+/Li) [18], which will be beneficial for improving the open cell voltage and thus the energy density of a full battery. It was reported that $Na_2Li_2Ti_6O_{14}$ is built by a network of intercalated edge and corner-sharing distorted TiO_6 octahedrons, providing ion tunnels along b axis. This arrangement is suitable for the insertion, diffusion and storage of lithium ions [20]. Moreover, it can deliver a theoretical capacity of 281.6 mA h g^{-1} based on the total reduction of Ti^{4+} to Ti^{3+} in the structure [19]. However, $Na_2Li_2Ti_6O_{14}$ still suffers from a poor electric conductivity and limited diffusion dynamics [19].

To solve these problems, doping [18–21] and coating [22,27] techniques were introduced. It was reported that Na-site

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substitution by high valence metal ions (i.e. Cu^{2+}, Y^{3+}, Ce^{4+}, and Nb^{5+}) can effectively enhance the ionic and electronic conductivities of the materials [18]. Furthermore, recent reports also clearly showed that a small amount Mg^{2+} and Al^{3+} dopings at Li site can improve the electronic conductivity and ionic diffusion coefficient [19,20], while partial substitution of Li by Na^+, Mg^{2+}, and Cr^{3+} can effectively improve the lithium storage capability of materials [21]. As a result, the electrochemical performances of $Na_2Li_2Ti_6O_{14}$-based materials were improved significantly. Alternatively, controlling the morphology is proved to be a feasible way to improve the electrochemical performance of the materials. However, the synthesis of $Na_2Li_2Ti_6O_{14}$ reported at present is mainly based on the sol-gel method [23,29] or solid state reaction [24–28], which are difficult to control the shape, size, and dispensability of the materials and thus lead to unsatisfactory performances. To clarify the effect of morphology on the electrochemical performance of $Na_2Li_2Ti_6O_{14}$, further investigations were needed. Furthermore, the lithium storage mechanism in $Na_2Li_2Ti_6O_{14}$ system is also not very clear and still deserved our considerations.

In this paper, a solvothermal method was introduced, and ammonium hydrogen carbonate was added as a structure-directing agent to modulate the structures and morphology of $Na_2Li_2Ti_6O_{14}$. By investigating the amount of ammonium hydrogen carbonate added on the morphology and electrochemical performance of the as-prepared materials, the structural-performance relationship will be revealed. The method applied here provides a reference for the synthesis of relevant doping materials, being beneficial for the optimization of $Na_2Li_2Ti_6O_{14}$-based materials in the future.

2. Experimental section

2.1. Preparation of the samples

The procedure for the preparation of $Na_2Li_2Ti_6O_{14}$ samples was shown in Fig. 1. All chemical reagents are of A.R. grade and used without further purification. $Na_2Li_2Ti_6O_{14}$ samples were synthesized from lithium acetate ($CH_3COOLi \cdot 2H_2O$), sodium acetate (CH_3COONa), and tetrabutyl titanate ($Ti(OC_4H_9)_4$) with a molar ratio of 1.05: 1.05: 3 through a simple one-pot solvothermal process. Initially, 48 mmol tetrabutyl titanate ($Ti(OC_4H_9)_4$) was added drop by drop into 30 mL anhydrous ethanol (C_2H_5OH) with continuous stirring at room temperature. And then 16.8 mmol lithium acetate ($CH_3COOLi \cdot 2H_2O$) and 16.8 mmol sodium acetate (CH_3COONa) were slowly dropped into the $Ti(OC_4H_9)_4$ ethanol solution. After intense stirring for 30 min, the homogenized solution was transferred into a 100 mL Teflon-lined stainless steel autoclave together with different amount (0, 9.1, 27.3, and 45.5 mmol) of ammonium hydrogen carbonate (NH_4HCO_3), and the reactor was then kept in an electric oven at 180 °C for 12 h. When the reaction was finished, the white powders at the bottom of the reactor were separated by centrifugation and collected, followed by a washing step with ethanol for 3 times. The precursors were dried in an oven at 70 °C for 6 h and then ground to powder. After calcination at 800 °C for 10 h, the final products were obtained. For convenience, $Na_2Li_2Ti_6O_{14}$ samples obtained with different amount of ammonium hydrogen carbonate (0, 9.1, 27.3, and 45.5 mmol) were labeled as NLTO-L-1, NLTO-L-2, NLTO-L-3, and NLTO-L-4, respectively.

2.2. Characterization and performance tests

The crystal structures of the samples were studied by a Bruker D8 powder X-ray diffractometer with a filtered Cu Kα radiation ($\lambda = 1.54056$ Å). The morphology of samples was recorded by a Hitachi S-4800 scanning electron microscopy (SEM) and a JEOL 2100 transmission electron microscopy (TEM). Elemental compositions of the NLTO-L-3 sample were characterized via the energy dispersive spectroscopy (EDS) (Oxford INCA, Britain).

Electrochemical tests were performed by using the CR 2025-type coin cells with pure Li foils acting as counter electrodes. Typically, a mixture of the active material, carbon black, and polyvinylidene fluorides (PVDF) with a weight ratio of 8:1:1 was homogeneously dissolved in *N*-methyl-2-pyrrolidinone (NMP). The slurry was then pasted on a Cu foil current collector, followed by a vacuum drying process at 110 °C for 12 h. The dried foil was then cut into 14 mm diameter circular wafers, which were used as cathode to assemble the half cells in an argon-filled glove box. The oxygen and moisture in the glove box were both below 0.1 ppm. The electrolyte was a 1 mol L^{-1} $LiPF_6$ solution dissolved in a 1:1:1 (v/v/v) mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC). Celgard 2400 films were used as the separators. Galvanostatic charge/discharge performance was examined by a LAND CT2001A system between 0 and 3 V (vs Li^+/Li) at different rates. Electrochemical impedance spectroscopy (EIS) tests were performed by using a Princeton P4000 workstation over a frequency range from 0.01 Hz to 100 kHz at a potentiostatic signal amplitude of 5 mV. Cyclic voltammetry (CV) test was carried out on a CHI 1000C electrochemical workstation with a voltage between 0 and 3 V at a scanning rate of 0.1 mV s^{-1}.

3. Results and discussion

The crystalline structures of four samples were studied by the XRD patterns. As shown in Fig. 2, nine sharp and well-defined reflection peaks at 18.1°, 23.7°, 28.9°, 32.3°, 36.8°, 43.9°, 45.2°, 56.7°, and 64.9° can be indexed to the (111), (311), (113), (511), (222), (800), (024), (624), and (040) planes of $NaLiTi_3O_7$ (JCPDS card No.52-0690, space group: Fmmm (69)) [9,18,27], indicating that the purity and crystallinity of the as-prepared $Na_2Li_2Ti_6O_{14}$ are good. To

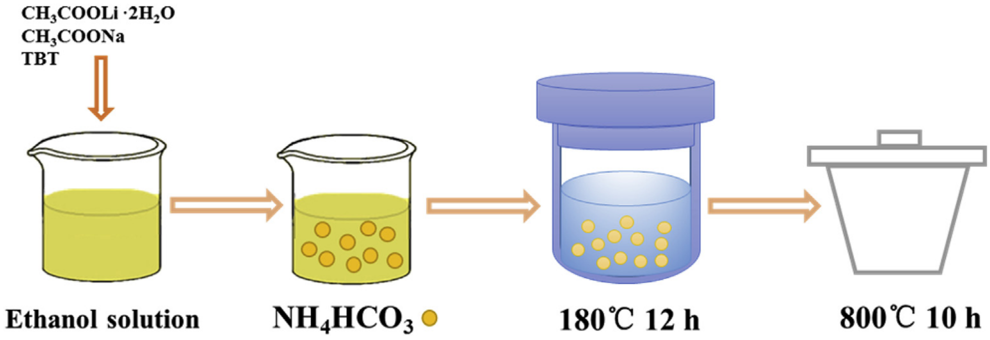

Fig. 1. Schematic diagram for the preparation of the mesoporous $Na_2Li_2Ti_6O_{14}$.