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Electrochemical kinetics of $Na_2Ti_3O_7$ as anode material for lithium-ion batteries

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ABSTRACT

In this work, $Na_2Ti_3O_7$ is fabricated as lithium storage material *via* one-step solid state reaction. Worked as anode material, $Na_2Ti_3O_7$ delivers a stable electrochemical performance with good lithium storage capability. Structural analyses show that $Na_2Ti_3O_7$ anode experiences slight volume change during electrochemical lithiation/delithiation process. Moreover, the reversibility of structural evolution is further demonstrated by *in-situ* X-ray diffraction technique. All these evidences prove the cycling stability of $Na_2Ti_3O_7$ as lithium storage material. Besides, the kinetic properties of the Li^+ ion storage in $Na_2Ti_3O_7$ are systematically investigated. The observed results reveal that $Na_2Ti_3O_7$ delivers the lithium ions diffusion coefficient in the range of 10^{-14}–10^{-12} cm^2 s^{-1} during the discharge process and 10^{-15}–10^{-12} cm^2 s^{-1} during the recharge process. It suggests that $Na_2Ti_3O_7$ has good lithiation/delithiation kinetics in rechargeable batteries.

1. Introduction

Energy is not only the most important basis of the progress of human society, but also one of the basic driving forces of economic development. However, the short of fossil energy arouses serious energy crisis all over the world, which drives the material scientists to develop new energy sources. As a novel energy storage and conversion system, rechargeable lithium-ion batteries have been widely used in electronic equipments in the past twenty years. It becomes the main power of the portable electronic devices due to its considerable energy density, long cycle calendar life and low self-discharge [1–9]. Graphite is a traditional anode material for commercial lithium-ion batteries. However, it suffers from safety issues due to low operating potential (0.1 V *vs.* Li^+/Li). Thus, alternative anode materials are developed to replace graphite. Recent years, titanium-based oxides have been put forward to be the distinguished substitutions because of their high working potential and stability electrochemical property [10–12].

Among titanium-based oxides, $Na_2Ti_3O_7$ has been used as a possible anode material for rechargeable batteries since its ability to store sodium was first found in 2011 [13]. Since the discovery of its electrochemical activity in 2011, $Na_2Ti_3O_7$ has attracted much attention because of the great potential as anode material [14–16]. It is found that $Na_2Ti_3O_7$ can store two moles of sodium ions per formula to form $Na_4Ti_3O_7$ in sodium-ion batteries [17]. However, $Na_2Ti_3O_7$ suffers from poor electrochemical activity. Hence, various methods have been used to improve its sodium storage ability. Recently, carbon-encapsulated $Na_2Ti_3O_7$ particles have been testified successfully in increasing the electrochemical property of the anode material [18]. Employing the spray-drying method, Li et al. prepared micro-spherical $Na_2Ti_3O_7$ which has high sodium storage capacity and stable cycle performance [19,20]. As well-known, the alkali titanium, having the general formula of $A_2Ti_nO_{2n+1}$ (A = alkali metals; $2 \leq n \leq 9$), can also show high Li^+ ion conductivity and storage capability. Preliminary investigation reveals that $Na_2Ti_3O_7$ anode material has high and flat working platform (about 1.6 V) in lithium-ion batteries [21]. However, detailed electrochemical research and lithium storage behaviors have not been reported.

In this article, well-crystallized $Na_2Ti_3O_7$ is synthesized by a solid-state method and its Li storage performance is evaluated. It is found that $Na_2Ti_3O_7$ has good structural stability as anode material for lithium-ion batteries. No obvious structural changes can be observed from the *in-situ* XRD observation. In addition, the lithium ions diffusion coefficient in $Na_2Ti_3O_7$ is also studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods. The observed data show that $Na_2Ti_3O_7$ has good electrochemical kinetics in lithium-ion batteries.

2. Experimental

2.1. Synthesis of $Na_2Ti_3O_7$

$Na_2Ti_3O_7$ was synthesized by a traditional solid-state reaction method. All the chemical reagents were analytical grade in the experiment.

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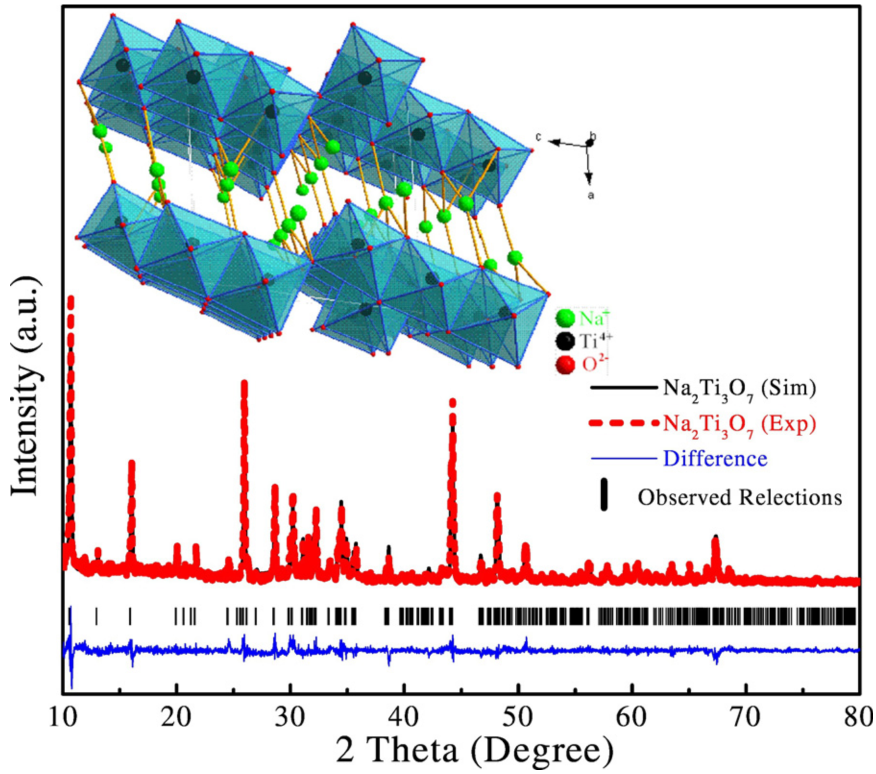

Fig. 1. XRD pattern of $Na_2Ti_3O_7$ powder.

TiO_2 (Aladdin Chemical, 99.8%) and anhydrous Na_2CO_3 (Aladdin Chemical, 99.0%) were used as starting materials. Then the precursor powders were mixed with ethanol and ground in the planetary ball mill for 12 h. The resultant specimen was transferred into a muffle furnace and heat-treated at 800 °C for 10 h in air atmosphere. After cooling down to room temperature naturally, the final product was formed.

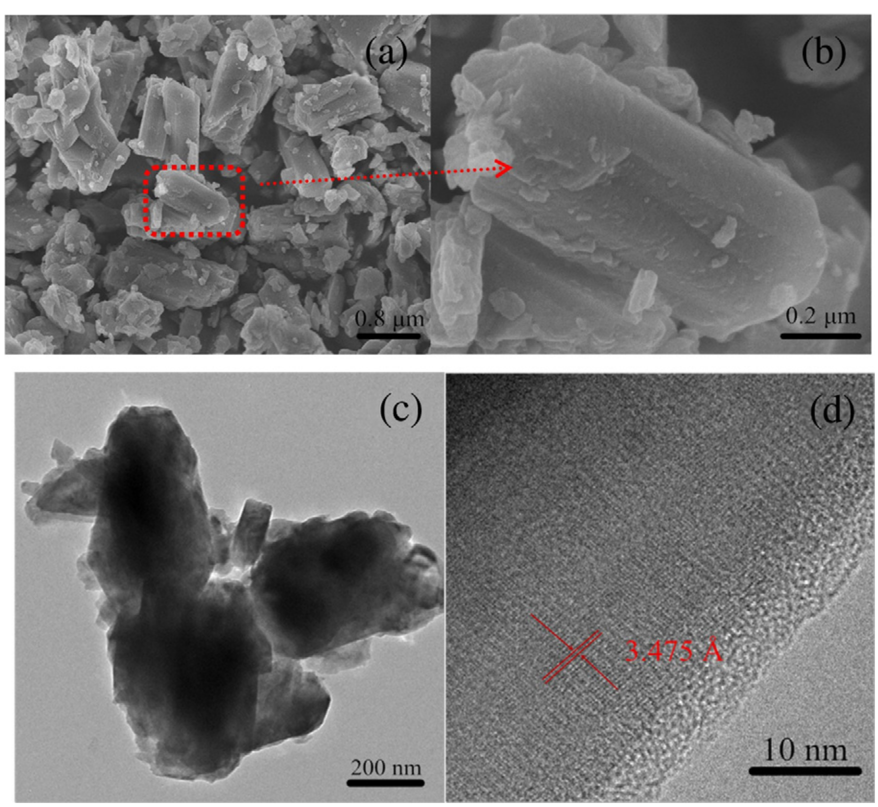

Fig. 2. (a, b) SEM and (c, d) TEM images of $Na_2Ti_3O_7$ powder.