Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Effect of calcination temperature on morphology and electrochemical performance of $PbLi_2Ti_6O_{14}$

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ARTICLE INFO

Keywords:
$PbLi_2Ti_6O_{14}$
Electrochemical behavior
Lithium ion batteries
In-situ observation
Anode material

ABSTRACT

As a promising anode material, $PbLi_2Ti_6O_{14}$ has attracted the attention of many researchers. In this work, a series of $PbLi_2Ti_6O_{14}$ are prepared by solid state method at five different calcination temperatures and used as anode materials in lithium ion batteries. Through a series of tests, the results show that the phase purity, morphology and electrochemical performance of $PbLi_2Ti_6O_{14}$ can be seriously influenced by calcination temperature. When the calcination temperature is 900 °C, the phase-pure $PbLi_2Ti_6O_{14}$ can be obtained with relatively small particle size, excellent cycle performance and outstanding lithium ion diffusion behavior. It provides an initial charge capacity of 151.3 mA h g^{-1} at 100 mA g^{-1}. After 100 cycles, it shows a reversible capacity of 142.0 mA h g^{-1} with superior capacity retention of 93.85%. In contrast, $PbLi_2Ti_6O_{14}$ formed at 800 °C displays an unsatisfactory performance due to the presence of impurity, even though it has the smallest particle size and the largest lithium ion diffusion coefficient among the five samples. The reversible capacity is only 82.6 mA h g^{-1} after 100 cycles with capacity retention of 53.9%. In order to further study the lithium ion diffusion behavior of $PbLi_2Ti_6O_{14}$, the in-situ X-ray diffraction technique is also implemented. It is found that during the lithiation/delithiation process, the stable framework can effectively inhibit the volume change and ensures the excellent electrochemical performance of $PbLi_2Ti_6O_{14}$.

1. Introduction

Excessive use of fossil fuels has accelerated the depletion of the earth energy. As an energy storage and conversion devices, rechargeable lithium ion batteries (LIBs) play a significant role in solving the existing problems of energy depletion and environmental pollution. Now, LIBs have been widely used in people's production and life [1,2]. The demand for outstanding LIBs in various portable electronic devices continues to grow. However, most of the current LIBs use graphite, soft carbon, hard carbon and other single intercalated lithium carbon materials as anode materials. These carbonaceous materials exhibit high capacities but with poor rate performance. During the past few years, numerous efforts have been made to develop new anode materials with high capacity and super cycle stability to replace carbonaceous materials.

Recently, titanates occupy an important position among multitudinous explored materials [3]. As a well-known anode material, $Li_4Ti_5O_{12}$ has obtained comprehensive attention due to its stable structure and exceptional electrochemical performance [4,5]. Since a new phase composed of Sr, Li and Ti was discovered from the SrO-TiO_2-$LiBO_2$ system by Koseva in 1991 [6]. Various types of titanate materials have been noted as the high voltage anode materials. The single crystal of $SrLi_2Ti_6O_{14}$ has been grown by the flux method and its structure was determined in 2002 [7]. A novel family of isostructural titanates $MLi_2Ti_6O_{14}$ (M = Ba, Sr, Pb) was reported by Koseva, which can be one of promising materials to replace graphitic anodes in LIBs [8]. According to the previous literature reported by Dambournet, the electrochemical performance of $SrLi_2Ti_6O_{14}$ is superior to those of $BaLi_2Ti_6O_{14}$ and $Na_2Li_2Ti_6O_{14}$ under the same conditions [9].

As a member of titanates family, $PbLi_2Ti_6O_{14}$ also exhibits excellent electrochemical performance. Li ever reported the electrochemical performance of $PbLi_2Ti_6O_{14}$ obtained from solid state preparation. It suggests that $PbLi_2Ti_6O_{14}$ can express remarkable cyclability and rate performance. After 1000 cycles, $PbLi_2Ti_6O_{14}$ only shows 12.5% capacity fading of the first cycle at 1000 mA g^{-1} [10]. However, they did not detail the impact of calcination temperature on the morphology and electrochemical properties of $PbLi_2Ti_6O_{14}$. Therefore, further investigation on the influence of calcination temperature for $PbLi_2Ti_6O_{14}$

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https://doi.org/10.1016/j.ceramint.2018.02.169
Received 11 February 2018; Received in revised form 21 February 2018; Accepted 21 February 2018

Please cite this article as: Zhang, J., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.02.169

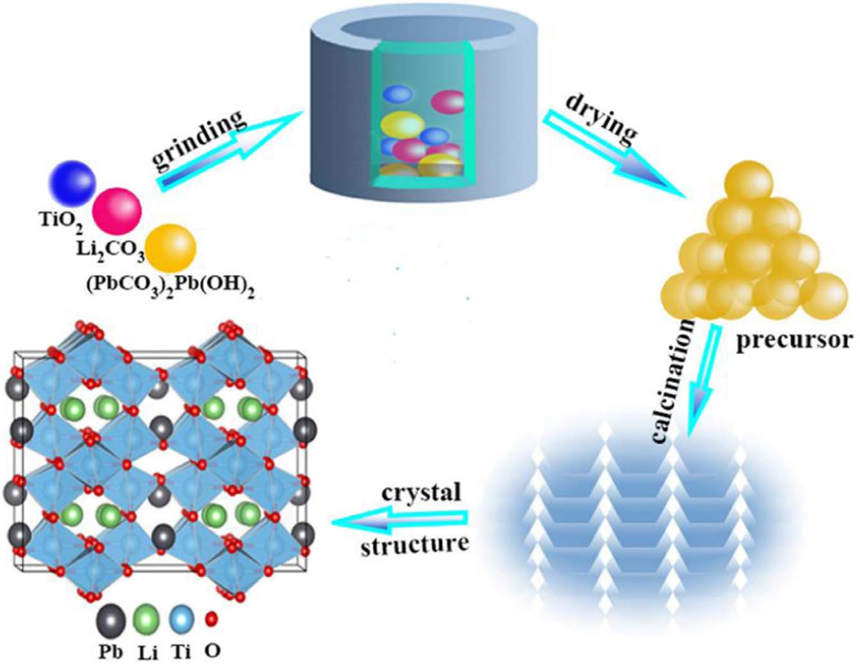

Fig. 1. Schematic illustration of the formation for PbLi$_2$Ti$_6$O$_{14}$.

still needs to be carried out. In this work, PbLi$_2$Ti$_6$O$_{14}$ is synthesized by the solid state methods at the various calcination temperatures ranged from 800 to 1000 °C. In order to elucidate the morphology, electrochemical performance and lithium storage behavior, a series of measurements are performed thoroughly. The optimum calcination temperature of PbLi$_2$Ti$_6$O$_{14}$ is finally determined.

2. Experimental

The schematic illustration of the formation of PbLi$_2$Ti$_6$O$_{14}$ via solid state reaction is illustrated in Fig. 1. The raw materials were Li$_2$CO$_3$ (Aladdin, 99.5%) (PbCO$_3$)$_2$·Pb(OH) (Aladdin, 99.5%) and TiO$_2$ (Aladdin, 99.5%). They were mixed by ball milling in anhydrous ethanol for 12 h and the molar ratio of Li/Pb/Ti was 2.02:1:6. After that, the precursor was obtained. The precursor was dried in an oven at 80 °C and then calcined in a muffle furnace. The calcination was divided into two steps. In the first step, the precursor was pre-calcined at 600 °C for 4 h. In the second step, the powder obtained in the first step was subsequently calcined at 800, 850, 900, 950 and 1000 °C for 15 h, respectively. Finally, the target compounds were obtained. In the process of calcination, an excess of 2% Li salt was added in order to compensate for the loss of Li source under high temperature conditions. The structures of five samples were identified on a Bruker D8 Focus X-ray diffraction (XRD) instrument with Cu Kα radiation from 10° to 50° in a sweep speed of $0.02^{\circ}\,s^{-1}$. The surface morphologies of samples were measured on a Hitachi S4800 scanning electron microscopy (SEM).

The electrochemical performances of the samples are evaluated in Swagelok-type cells with lithium disk as the counter electrode and Whatman glass fiber as separator. The working electrode was prepared by mixing the active material, acetylene black as conductive agent, and polyvinylidene fluoride as adhesive at a ratio of 8:1:1. Then, the homogenous slurry was cast onto copper foil and subsequently dried in a vacuum oven at 120 °C for 24 h. All the cells were assembled in a glovebox filled with argon. The electrolyte was a mixture which was obtained by 1 M LiPF$_6$ dissolved in EC-DMC (1:1, v/v, EC was ethylene carbonate and DMC was methyl carbonate).

The charge/discharge cycles were tested on the Wuhan Land battery test system with operating voltage range of 0.5–2.0 V. Cyclic voltammetry (CV) test was measured by CHI1000B electrochemical workstation from 0.5 to 2.0 V at a scan rate of $0.1\,mV\,s^{-1}$. The electrochemical impedance spectroscopy experiment was carried out by CHI660D electrochemical workstation. The working frequency range was 10^{-2}–10^{5} Hz.

3. Results and discussion

Fig. 2 demonstrates XRD patterns of samples which were

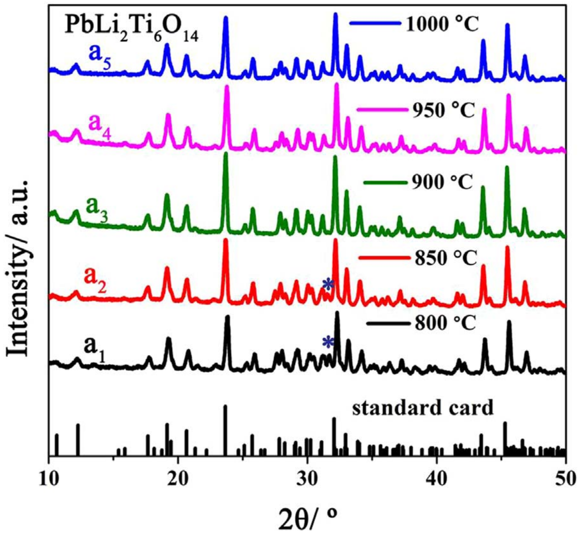

Fig. 2. XRD patterns of PbLi$_2$Ti$_6$O$_{14}$ at different temperature. (a$_1$) 800 °C, (a$_2$) 850 °C, (a$_3$) 900 °C, (a$_4$) 950 °C, (a$_5$) 1000 °C.