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$PbLi_2Ti_6O_{14}$: A novel high-rate long-life anode material for rechargeable lithium-ion batteries

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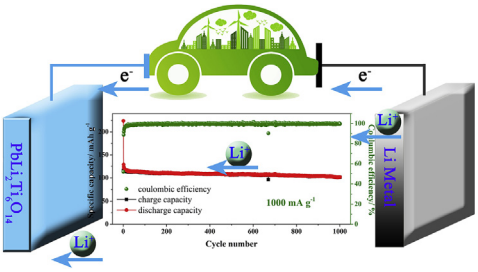
HIGHLIGHTS

- $PbLi_2Ti_6O_{14}$ is reported as lithium storage material for the first time.
- $PbLi_2Ti_6O_{14}$ exhibits outstanding cycle and rate performances.
- Capacity retention of 87.5% can be retained after 1000 cycles at 1000 mA g^{-1}.
- Reversibility of $PbLi_2Ti_6O_{14}$ is studied by in-situ and ex-situ methods.

GRAPHICAL ABSTRACT



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ABSTRACT

As a novel anode material, $PbLi_2Ti_6O_{14}$ is prepared by a traditional solid state method at a calcination temperature of 900 °C. Structural analysis and electrochemical tests prove that $PbLi_2Ti_6O_{14}$ possesses a good crystallinity and superior performance. $PbLi_2Ti_6O_{14}$, composed of particles with 400 nm in length and 300 nm in width, exhibits an initial charge capacity of 155.1 mAh g^{-1} at 100 mA g^{-1} and maintains at 147.9 mAh g^{-1} after 100 cycles, with capacity retention as high as 95.4%. Especially, the reversible capacity of $PbLi_2Ti_6O_{14}$ can stabilize at 101.6 mAh g^{-1} after 1000 cycles at a high current density of 1000 mA g^{-1}, with capacity retention of 87.5%. Besides, the lithium storage behavior in $PbLi_2Ti_6O_{14}$ is also studied by various in-situ and ex-situ methods. It is found that the lithiation/delithiation process in $PbLi_2Ti_6O_{14}$ is a highly reversible reaction. All these results demonstrate that $PbLi_2Ti_6O_{14}$ may be an impressive anode material in the near future.

1. Introduction

In modern society, the energy storage appliances are critical technologies to address the global energy shortage and emerging environmental issues [1,2]. As one of the most important energy storage systems, rechargeable lithium ion batteries (LIBs) attract great attention and have actively changed our lifestyles [3–9]. With widely application in grid storages, portable devices and electric vehicles, the LIBs still have many drawbacks such as low power, high cost and safety issues [10]. Like graphite, this anode material currently used in commercial LIBs has a small lithium diffusion coefficient and experiences large volume variation of 9% during the lithium insertion/extraction process [2,11]. Low Li-ion diffusion coefficient indicates a higher ion transportation resistance in the bulk electrode, while large volume change during lithium intercalation/de-intercalation signifies an inferior cycling stability [12,13]. These drawbacks will limit the electrochemical

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performance of LIBs by a large margin. In addition, the Li-ion operating potential of graphite (approaching 0.2 V vs. Li^+/Li) is close to the lithium electroplating potential, which could cause serious safety issues [14–18]. Furthermore, the low intercalation potential leads to electrolyte reduction and decomposition, which contribute to the formation of solid electrolyte interphase (SEI) layer, and could also introduce kinetic problems for fast charge and discharge [19,20]. Therefore, it is of great demand to develop new anode materials that possess the desired high lithium ion diffusion, good electrical conductivity and outstanding safety.

Among numerous explored anode materials, titanates especially like $A_2Ti_6O_{13}$ (A = H, Li, Na, K) [21–24], $Li_2MTi_3O_8$ (M = Zn, Co, Mg, Mn etc.) [25–30], and $Li_4Ti_5O_{12}$ [31–36] have gained large numbers of investigations due to their low cost, safety, stable structure, chemical stability and high Li-ion conductivity. Especially for $MLi_2Ti_6O_{14}$ (M = Sr, Ba, 2Na), there are recently new developed lithium storage compounds with a long and flat working potential platform at about 1.3 V [37–54]. The investigations of $MLi_2Ti_6O_{14}$ (M = Sr [37–43], Ba [43–47], 2Na [48–54]) provide new choices for the application of anode materials considering its superior electrochemical properties, such as low operating potential and high theoretical capacity. I. Belharouak *et al* [45] first reported the crystal structure and electrochemical properties of $MLi_2Ti_6O_{14}$ (M = Sr, Ba) as anode materials for secondary LIBs. They described that the $MLi_2Ti_6O_{14}$ (M = Sr, Ba) electrodes could deliver a stable reversible capacity of about 140 mAh g^{-1} with an operating platform at 1.4 V. H.S. Li *et al* [42] synthesized ultralong $SrLi_2Ti_6O_{14}$ nanowires by a simple electrospinning process. It is found that $SrLi_2Ti_6O_{14}$ nanowires show superior electrochemical performance with a retained capacity of 101 mAh g^{-1} at 10C after 1000 cycles, which makes it become possible alternative anode material to $Li_4Ti_5O_{12}$. X.T. Lin *et al* [41,47,53,54] also fabricated $SrLi_2Ti_6O_{14}$, $BaLi_2Ti_6O_{14}$ and $Na_2Li_2Ti_6O_{14}$ particles through solid state reaction and gave a detailed investigation of them, including their lithium-ion insertion/extraction mechanisms, structural evolutions and electrochemical properties during repeated charge/discharge cycles. Although $PbLi_2Ti_6O_{14}$ was initially presented by I. Koseva in 2005 [44], no report can be found about its lithium storage behaviors. Compared with $SrLi_2Ti_6O_{14}$ and $BaLi_2Ti_6O_{14}$, $PbLi_2Ti_6O_{14}$ is an isostructural titanate in the $MLi_2Ti_6O_{14}$ series. Therefore, it is expected that $PbLi_2Ti_6O_{14}$ may be also a good anode candidate for rechargeable LIBs.

In this paper, we fabricate the $PbLi_2Ti_6O_{14}$ particles via a simple solid state reaction method. The surface morphology, crystal structure, electrochemical property and lithium-ion insertion/extraction mechanism of $PbLi_2Ti_6O_{14}$ are thoroughly investigated by using various in-situ and ex-situ characterization techniques. The step-by-step lithium-ion transportation process in $PbLi_2Ti_6O_{14}$ is clarified during the charge/discharge cycles. The outstanding cycling and rate properties of $PbLi_2Ti_6O_{14}$ in our present work (101.6 mAh g^{-1} at 1000 mA g^{-1} after 1000 cycles) demonstrate that $PbLi_2Ti_6O_{14}$ is a promising high rate long life anode material.

2. Experimental

We adopt a simple solid-state reaction process to prepare $PbLi_2Ti_6O_{14}$ by using $(PbCO_3)_2{\cdot}Pb(OH)_2$ (Aladdin, 99.5%), Li_2CO_3 (Aladdin, 99.5%), and TiO_2 (Aladdin, 5–10 nm, 99.5%) as starting materials. The two-step synthetic process used to prepare $PbLi_2Ti_6O_{14}$ is schematically illustrated in Fig. 1a. In the first step, the stoichiometric amounts of $(PbCO_3)_2{\cdot}Pb(OH)_2$, Li_2CO_3, and TiO_2 were dispersed in anhydrous ethanol and then planetary ball

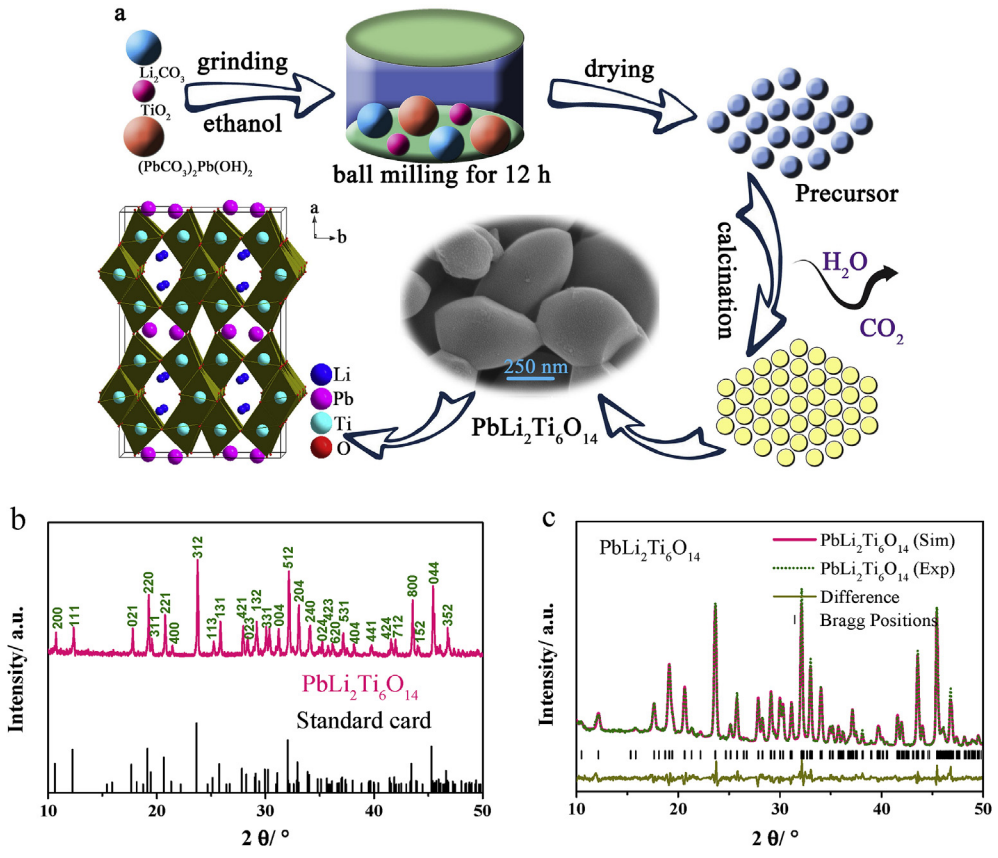

Fig. 1. (a) Schematic illustration of the formation of $PbLi_2Ti_6O_{14}$. (b) XRD pattern of $PbLi_2Ti_6O_{14}$. (c) XRD Rietveld refinement profile of $PbLi_2Ti_6O_{14}$.