Electrochemical performance and lithium-ion insertion/extraction mechanism studies of the novel Li_2ZrO_3 anode materials

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A B S T R A C T

Li_2ZrO_3 anode materials were prepared by the conventional solid-state reaction. The crystal structure has been determined by X-ray diffraction. Electrochemical tests show that Li_2ZrO_3 anode materials process a excellent cycle performance and rate capability due to the good structural stability and high lithium diffusion coefficients. For the Li_2ZrO_3 anode material, the change of the unit cell volume is only $\sim$0.3% at discharge or charge process. Except for the first several cycles, the coulombic efficiency of the Li_2ZrO_3 electrode was nearly 100% at a discharge/charge rate of 0.3 C. The lithium diffusion coefficients of Li_2ZrO_3 for the reduction and oxidation process are calculated to be 3.165×10^{-6} and $1.919 \times 10^{-6}\,cm^2\,s^{-1}$ respectively which is much higher than that of the $Li_4Ti_5O_{12}$ anode material (about 10^{-9} to $10^{-13}\,cm^2\,s^{-1}$). In situ XRD results, combined the sloping character of the charge/discharge voltage profiles and the lithium ion diffusion controlled mechanism in the charge and discharge process, show that the insertion/extraction mechanism of Li^+ for Li_2ZrO_3 can be interpreted as a solid-solution behavior.

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1. Introduction

With the imminent exhaustion of fossil fuel resources and increasing environmental problems, a variety of renewable and clean energy sources, such as the wind and sun, are growing rapidly. Efficient energy storage systems are needed for the electricity generated from intermittent, renewable sources. In addition, considering the substitution of alternative energy sources for fossil fuels, the development of electric vehicles also require the large scale energy storage device as power sources. Among various energy storage technologies, the lithium ion battery technique is one of the most promising means for storing electricity on a large-scale because of the flexibility, high energy conversion efficiency and simple maintenance [1]. As the key part of the lithium ion battery, the anode materials can be divided into three main categories according to the reaction mechanisms: the alloy-type, typically as Si- and Sn- based alloys and their composites; the conversion reaction type, mainly referring to transition metal oxides; the insertion/extraction type, such as graphite, Ti-based oxides [2–6]. The alloy-type Si anode materials are attractive because of its ultra-high capacities (accommodating about 4.4 mol Li for per mol Si) and low raw materials cost. However, the huge volume changes caused by the accommodation of so much lithium lead to lattice stress and consequential cracking and deteriorated the contact between the anode material and the current collector, which leads to an abrupt loss in capacity within a few charge/discharge cycles [7,8]. The conversion type materials can deliver a high capacity too, but the Li insertion potential is relatively high. This makes the use of conversion type material impractical in a high energy battery system. The insertion/extraction type anode materials, due to the high reversibility and high energy efficiency, have been considered to be the most promising anode materials. As the typical representative, graphite has remained the dominant anode in rechargeable lithium-ion batteries for twenty years [9–11]. However, due to the small lithium diffusion coefficient, large volume variation during the Li insertion/extraction process, the safety issues of dendritic lithium growth produced by its low potential (only about 0.2 V versus Li+/Li) and the kinetic problems for fast charge and discharge caused by the thick solid electrolyte interphase (SEI) layer on its surface, the application of the graphite are more and more restrictions. In addition, the spinel $Li_4Ti_5O_{12}$ is another well recognized insertion type anode known for its minimal structure change, good lithium ion mobility, high reversibility upon Li insertion/extraction and low cost and safety. However, its potential is still relatively higher, about 1.6 V (versus Li+/Li), thus resulting the poor energy efficiency

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[12,13]. So, it would be of great interest to find a new insertion/extraction type anode materials with appropriate intercalation potential.

As is well known, the ionic conductivity of electrode materials plays a major role in the rate performance of batteries since the diffusion of lithium ion within the electrode materials acts as the rate-limiting step during the charge–discharge process. So, it is necessary to find an new electrode material with high lithium diffusion coefficient for improving the electrochemical performance of anode material at high current densities. Monoclinic Li_2TiO_3, a layered material with a three-dimensional path for Li ions diffusion, has been reported to be capable of stabilizing the structure of high-capacity cathode materials such as $LiMnO_2$, $LiCrO_2$ and $LiNiO_2$ [14–16]. However, the poor electrical conductivity, on the order of $10^{-7}\,S\,cm^{-1}$ at 400 K, prohit its use as a electrode material [17]. Monoclinic Li_2ZrO_3 which is isomorphous to Li_2TiO_3 is another excellent Li ions conductor, As an insertion/extraction type anode candidate material, its structure was first reported by Dittrich by X-ray diffraction, but only the Zr and O atoms were located. Later, using neutron profile refinement, Hodeau et al. located the Li ions and solved the structure in space group C2/c [18,19]. Because of the high ionic conductor, thermodynamically stable against Li, chemical inert in common nonaqueous electrolyte and a good diffusion pathway for the lithium ion, at present, Li_2ZrO_3 is often used as coating material to suppress the dissolution of cathode material, such as spinel $LiMn_2O_4$, $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$, at high charge potential [20,21]. To our knowledge, no experimental results relating to Li_2ZrO_3 as anode material has been reported.

In the present study, we report the preparation, structure and electrochemical performance of the Li_2ZrO_3 as anode material for Li-ion batteries. The main objective of this paper is to explore the electrochemical performance of Li_2ZrO_3 as anode for Li-ion battery and the possible charge/discharge mechanism, which may be benefit to further study on improving the electrochemical performance of Li_2ZrO_3.

2. Experimental

Li_2ZrO_3 samples were synthesized via conventional solid-state reaction using required amounts of Li_2CO_3 and ZrO_2 as starting materials. The mixed powder were ground to sufficient homogenization in a mortar and then heated at 350 °C for 6 h. The obtained powder was re-ground and pressed into pellets of 10 mm in diameter and 3–4 mm in thickness. The pallets were was heated again at a rate of 2 °C/min to 950 °C and held for 10 h in air to get the final samples.

Powder X-ray diffraction (XRD) patterns of the products were recorded at room temperature with a Philips X-ray diffractometer equipped with Cu Kα radiation in a continuous-scanning mode. For refinement samples, the data was collected by a step-scanning mode over the range 10–90° with a step size of 0.02° and a dwell time of 2 s.

The in situ XRD data for lithium storage into Li_2ZrO_3 were collected at room temperature with a Philips X-ray diffractometer in a continuous-scanning mode. In our in situ X-ray cell, Beryllium was used as window because of its relative transparency to X-rays. Where, the studied material (the mixing of the Li_2ZrO_3 samples with acetylene black and PVDF binder) was painted on the Be window as the working electrode. In situ X-ray cell were assembled in a Mikrouna glove box filled with high-purity argon, where the lithium metal foil were used as the counter electrode, Celgard® 2320 as a separator, and 1 M $LiPF_6$ in EC:DMC (1:1 vol.%) were used as an electrolyte. The discharge/charge of in situ cell was carried on an automatic battery tester system (Land®, China) in a voltage range of 0.1–2.5 V at a current rate of C/10.
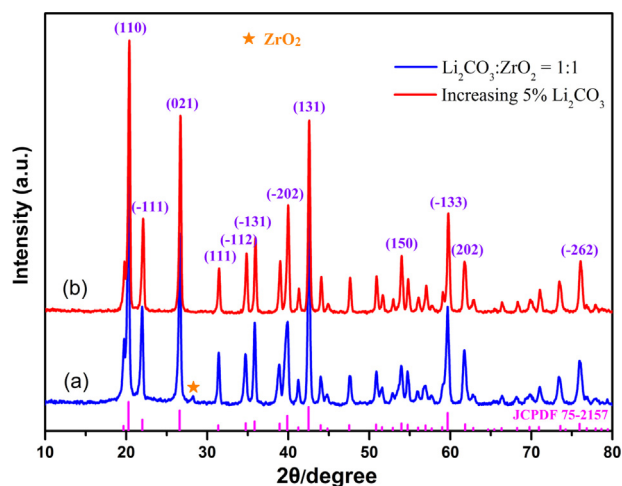

Fig. 1. XRD patterns of the Li_2ZrO_3 samples synthesized using different amount of Li_2CO_3 and ZrO_2: (a) Li_2CO_3: ZrO_2 = 1:1; (b) Li_2CO_3: ZrO_2 = 1.05:1

For electrochemical measurements, the anode was prepared by mixing the as-prepared samples with acetylene black and polyvinylidiene fluoride (PVDF) binder in a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP). The obtained slurry was coated onto copper foil current collector, dried at 50 °C for 24 h and pressed (5 MPa) respectively. Then, the electrodes fabricated were dried again at 90 °C for 12 h in a vacuum and cut into disc with a diameter of 14 mm using a punch where about 5 mg of active materials was hold on it. Coin cells were assembled in a Mikrouna glove box filled with high-purity argon, where the lithium metal foil were used as the counter electrode, Celgard® 2320 as a separator, and 1 M $LiPF_6$ in EC:DMC (1:1 vol.%) were used as an electrolyte. The electrochemical performance of the prepared samples was evaluated with the coin cell by an automatic battery tester system (Land®, China) at room temperature and the electrochemical capacity of samples was evaluated based only on the active material weight.

Cyclic voltammetric (CV) tests were performed on an AUTOLAB PGSTAT100 type electrochemical workstation (Metrohm AG company). CV tests were carried out at a scan rate of $0.02\,mV\,s^{-1}$ on the potential interval 0.1–2.5 V (vs. Li^+/Li). All tests were performed at room temperature.
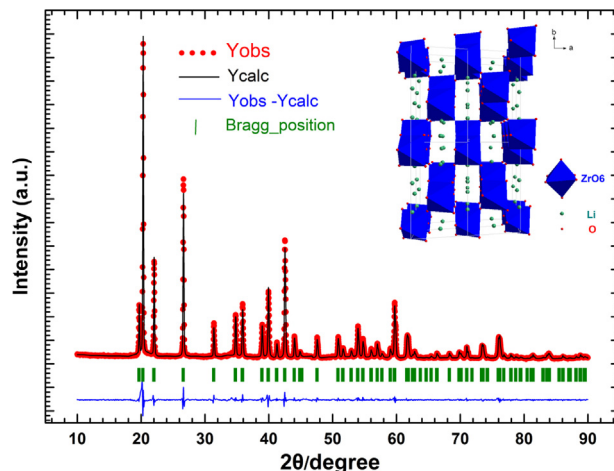

Fig. 2. XRD refinement results of Li_2ZrO_3. Inset shows the crystal structure of Li_2ZrO_3.