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A novel and safety lithium thermal battery electrolyte - $Li_7La_3Zr_2O_{12}$ prepared by solid state method

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ABSTRACT

In this paper, a garnet-related type $Li_7La_3Zr_2O_{12}$ material is synthesized by using a solid-state method. Then, the obtained $Li_7La_3Zr_2O_{12}$ is investigated by X-ray diffraction method and field emission scanning electron microscopy. The prepared $Li_7La_3Zr_2O_{12}$ material is first used as the lithium thermal electrolyte for its good ionic conductivity and safety at 550 °C. Compared with LiCl-LiBr-LiF molten salt electrolyte, the lithium thermal batteries using $Li_7La_3Zr_2O_{12}$ material as the electrolyte have longer discharge time and higher melting point, resulting an increasing of the utilization rate of active substance by 20% at 550 °C under 80 mA/cm^2. In addition, there was no $Li_7La_3Zr_2O_{12}$ electrolyte overflowing during this discharge process, and which is beneficial to prolong the lithium thermal battery life and improve the lithium battery safety.

1. Introduction

Lithium thermal batteries have been used as power sources in rockets, air-to-air missiles and emergency escape system. They have higher operating temperature, shorter activation time and larger discharge current. Normally, the electrolyte used in thermal batteries was molten salt electrolyte which was solid at room temperature [1,2]. Currently, alkali metal halides, such as LiCl-LiBr-LiF materials, are used as the thermal battery electrolytes [3–5]. As the temperature rises to 430 °C, this electrolyte will melt and has a high ionic conductivity of 1.89 S/cm, which can conduct lithium ions between the anode and cathode. However, at a higher temperature, for 550 °C, the melting of the alkali metal halides may overflow, resulting in a short circuit between the anode and cathode of the thermal battery, and even leading to a safety accident. In order to avoid or reduce this problem, some inert substances (such as MgO, SiO_2) were added to the molten salt electrolyte [2]. However, the addition of these substances will reduce the conductivity of the molten salt electrolytes.

Solid state electrolyte is a novel kind of material used in all-solid-state lithium batteries. This kind of electrolyte has lattice defects or special structures, so that can form migration channels which lithium ions can rapidly pass through [6–10]. The environment-friendly, low cost, lithium ion conductivity and good thermal and chemical stability of garnet-type electrolyte - $Li_7La_3Zr_2O_{12}$ (LLZO) stands out among all solid-state electrolytes. Several studies on LLZO synthesis (such as solid-state reactions and sol-gel methods) have been reported. In the earliest LLZO report [11], a solid-state process, involving the heating of a powder mixture of LiOH, La_2O_3, ZrO_2, was used to prepare LLZO powder. Following this, some researchers [12–15] have successfully prepared LLZO by solid state methods, while the preparation temperature is higher than 1000 °C and the preparation time is longer than 48 h. The tetragonal LLZO sample obtained by Awaka et al. [16] exhibited a grain-boundary Li-ion conductivity of 5.59×10^{-7} S/cm. In 2015, Rosenkiewitz et al. [17] reported that the LLZO had an ionic conductivity of 10^{-5} S/cm. However, the ionic conductivity of LLZO electrolyte is relatively lower than that of molten salt electrolyte. In order to improve the Li^+ conductivity of $Li_7La_3Zr_2O_{12}$, predecessors study on the chemical substitution using various cation species, such as Ta^{5+} [16–19], Al^{3+} [20,21], Fe^{3+} [22], Ca^{2+} [23], Ga^{3+} [24,25]. Generally speaking, the reasons for doping metal ions to increase Li^+ conductivity are that: (1) the ionic is inert to metallic lithium; (2) it is able to broaden the ion channel; (3) it can lower the lithium content, thus raising the lithium vacancy concentration, which is beneficial to the enhancement of Li^+ conductivity [22].

The future of solid electrolyte in lithium-ion batteries will focus on improving their ionic conductivity, while for lithium thermal battery, it is necessary to find a new safety electrolyte material with non-conductive at room temperature and higher conductivity at higher temperature. Compared with molten salt electrolyte, this solid electrolyte is an alternative for its safety and thermal stability. In a previous work,

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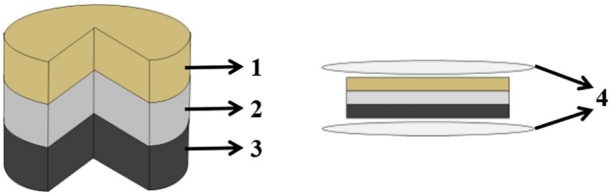

Fig. 1. The schematic illustration of the thermal battery, 1 - $NiCl_2$ cathode, 2 - electrolyte, 3 - Li-B alloy anode, 4 - nickel sheet.

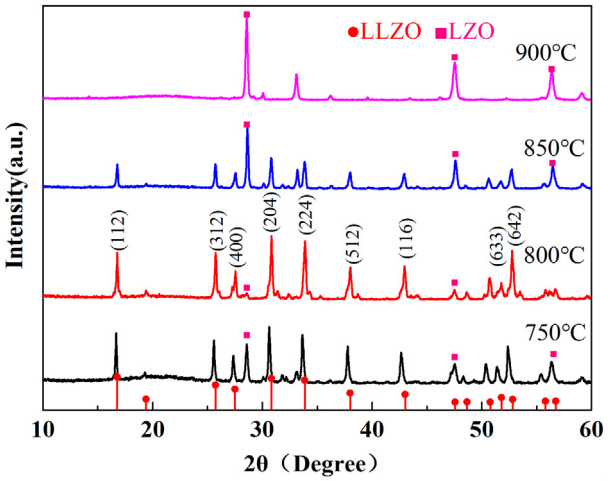

Fig. 2. XRD patterns of LLZO materials synthesized at various sintering temperatures.

LLZO with garnet-like electrolyte and predominantly ionic conduction holds the promise of increasing conductivity as temperature increases [11], which may make it as an ideal candidate for lithium thermal battery electrolyte. It has a high melting point and will not melt at the high working temperature (for 550 °C), which can overcome tough challenges of poor safety. However, there are few reports on the application of solid state electrolyte to lithium thermal batteries.

In this study, a garnet-type solid electrolyte — $Li_7La_3Zr_2O_{12}$ (LLZO) is synthesized by a simple solid-state method using $LiOH{\cdot}H_2O$, La_2O_3, ZrO_2 as the raw materials at the optimum synthesis conditions. The obtained LLZO was then used as the electrolyte in lithium thermal batteries for the first time. Moreover, we expect using this LLZO electrolyte to solve the short circuit and safety problems of lithium thermal batteries caused by molten salt overflowing.

2. Material and methods

2.1. Synthesis and characterization of LLZO material

$Li_7La_3Zr_2O_{12}$ was prepared by a solid-state method. Lithium hydroxide (analytical reagent 95%), lanthanum oxide (99.99% purity), and zirconium oxide (analytical reagent 99.5%) powders were used as raw materials. A 10 wt% excess of LiOH was provided to compensate for the volatilization of Li during the LLZO synthesis. Thus, the appropriate stoichiometric amount of lithium hydroxide, lanthanum oxide, and zirconium oxide was chosen as Li:La:Zr = 7.1:3:2. And these stoichiometric raw materials (Li:La:Zr = 7.1:3:2) were mixed in a planetary mill (ND70.4) with agate balls for 3 h using ethanol as a solvent. After drying in a crucible and grinding in an agate mortar, the precursors were calcined at 800 °C for 12 h in air in a muffle furnace (SX2-5-10). In order to get the target product, the sintering temperature was set in the range of 750–900 °C.

The obtained LLZO was examined by X-ray diffraction method (XRD) with CuKα radiation source at the room temperature. The date

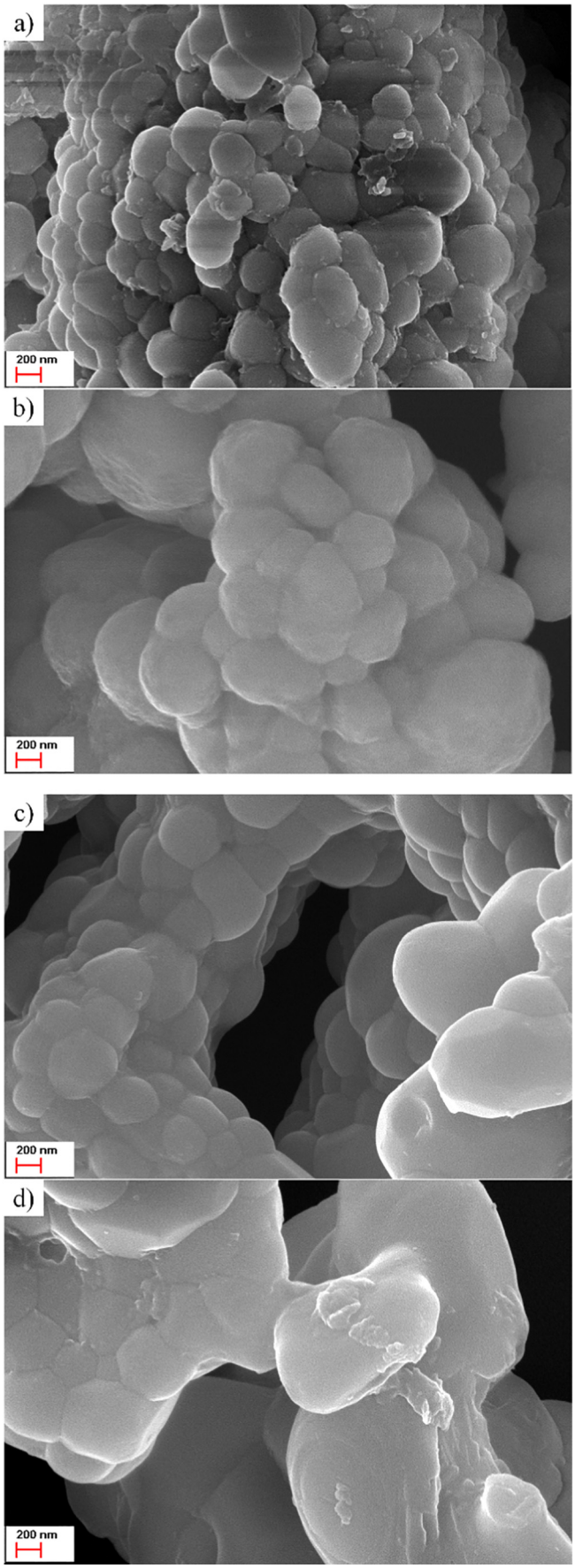

Fig. 3. FE-SEM images for LLZO materials synthesized at various temperatures a) 750 °C, b) 800 °C, c) 850 °C, d) 900 °C.

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