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A Li-Garnet composite ceramic electrolyte and its solid-state Li-S battery

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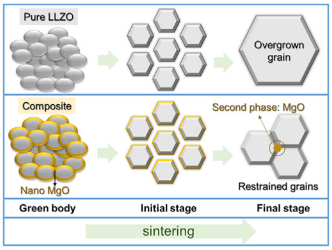
HIGHLIGHTS

- LLZTO-MgO composite Li-ion solid electrolyte is firstly studied in details.
- Second phase additive MgO can inhibit the grain growth of main phase LLZTO.
- Composite electrolyte shows high fracture strength and conductivity.
- Li-Sulfur battery is fabricated by solid electrolyte and shows good performance.

GRAPHICAL ABSTRACT



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ABSTRACT

A high strength Li-Garnet solid electrolyte composite ceramic is successfully prepared via conventional solid state method with $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ and nano MgO powders. Well sintered ceramic pellets and bars are obtained with 0–9 wt.% MgO. Fracture strength is approximately 135 MPa for composite ceramics with 5–9 wt.% MgO, which is ~50% higher than that of pure $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (90 MPa). Lithium-ion conductivity of the composite is above 5×10^{-4} S cm^{-1} at room temperature; comparable to the pure $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ material. SEM cross-sections of the composite ceramic shows a much more uniform microstructure comparing with pure ones, owing to the grain growth inhibition effect of the MgO second phase. A battery cell consisting of Li/composite ceramics/Sulfur-Carbon at 25 °C exhibits a capacity of 685 mAh g^{-1} at 0.2 C at the 200th cycle, while maintaining a coulombic efficiency of 100%. These results indicate that the composite ceramic $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$-MgO is promising for the production of electrolyte membrane and fabrication of Li-Sulfur batteries.

1. Introduction

High energy density lithium ion batteries (LIBs) are promising electrochemical energy storage devices and play an increasingly important role in the development of portable electronic devices as well as the electric vehicles and smart grids. New materials are being sought for next-generation batteries to provide higher energy density and lower cost factors comparing to conventional LIBs, such as Li-air and Li-S batteries [1]. In aqueous Li-Air batteries, the solid electrolyte membrane is essential to separate the lithium anode from the air cathode [2]. For Li-S [3] and redox mediators added aprotic Li-O_2 batteries [4], the internal "shuttle" phenomenon decreases the active mass utilization and reduces the coulombic efficiency. Novel configurations using the solid electrolyte membrane are found to block the shuttle effect and significantly prolong cycling without capacity fading [5]. Besides, all-solid-state lithium secondary batteries (ASSB) are considered to eliminate safety problems caused by flammable organic electrolyte used in conventional commercial LIBs. The key for

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developing new-generation lithium anode batteries is an excellent solid electrolyte membrane which has high relative density, high ionic conductivity, good chemical stability as well as good mechanical properties.

Recently, a novel class of lithium-stuffed garnet oxide (LLZO) has shown promise as a candidate for lithium anode batteries due to its high ionic conductivity, chemical stability vs. lithium metal and wide electrochemical window [6]. Elements such as Al, Ga, Y, Si, Ge, Nb, Ta and Te have been doped in order to stabilize the cubic phase and improve the ionic conductivity. Among them, the Ta-doped $Li_7La_3Zr_2O_{12}$ (LLZ) shows a high lithium ionic conductivity of 1×10^{-3} S cm^{-1}, which is much higher than that of pure LLZ [7]. At the same time, design and fabrication of ASSB using garnet-type electrolytes has been attempted [8–12]. However, it is still difficult for garnet oxides to meet the requisite conductivity and mechanical strength. Very large grains, which impair mechanical properties, are easily formed during sintering process of Li-garnet due to abnormal grain growth (AGG). In the field of ceramics, it is generally recognized that the strength of brittle polycrystalline materials are dependent on microstructure, especially porosity and grain size [13]. AGG will significantly degrade mechanical properties. Many second phase additives, such as MgO, CaO etc. [14,15], have been reported to restrain the grain growth in ceramics. But in the garnet-type electrolytes, results with second phase additions have not yet been reported.

In view of the above facts, it would be desirable to develop an economical process for improving the microstructure and enhancing the mechanical properties of garnet materials while providing the requisite conductivity. In this work, MgO was used to introduce a second phase to LLZTO. Murugan et al. reported that alkaline earth elements can be doped into cubic $Li_5La_3M_2O_{12}$(M = Nb and Ta) except Mg, which formed a second phase [16]. Application of hot-pressing method to sinter Li-Garnet can provide high relative density (> 97%) ceramics [17–20]. However, this method is not economical. A conventional solid state method was applied to obtain 3 × 4 × 30 mm LLZTO-MgO composite electrolyte ceramics. Mechanical strength, electrochemical properties and cross-sectional microstructure of these ceramics were studied and analyzed to show the effect of the second phase. Li/composite electrolyte/Au cells and Li-sulfur batteries were assembled using these composite ceramic pellets. The Li-Au cells were tested by cyclic voltammetry method to verify the electrochemical stability of composite electrolyte against Li metal and the Li-sulfur batteries were charged/discharged for 200 cycles to demonstrate application of the composite ceramic to batteries.

2. Experimental

2.1. The synthesis of composite solid electrolyte

Cubic phase $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) was synthesized from starting powders of $LiOH{\cdot}H_2O$ (AR), La_2O_3 (99.99%), ZrO_2 (AR), Ta_2O_5 (99.99%) with stoichiometry ratio. 2 wt.% excess of $LiOH{\cdot}H_2O$ added to compensate the lithium loss during the sintering process. Traces of moisture and adsorbed CO_2 were removed from La_2O_3 by heat treatment at 900 °C for 12 h. Raw materials were mixed via a wet grinding process in which yttrium stabilized zirconium oxide (YSZ) balls and isopropanol (IPA) were used as the milling media. The mixture was dried and calcined at 950 °C for 6 h in an alumina crucible following a second mixing step, and calcined at 950 °C for 6 h again to obtain pure cubic garnet phase powder. 0–9 wt.% MgO (50 nm, 99.9% metals basis, Aladdin Inc.) was added into synthesized LLZTO powder and the mixture was ball milled for 24 h following a 500 °C treatment for 1 h to evaporate solvent and moisture thoroughly. The powder was sealed in a Ar-filled glove box and dry milled for 24 h. The obtained fine powder was marked as LLZTO-xM (x = 0–9): referring to the weight ratio of added MgO. These powders were pressed into 5 × 7 × 40 mm green bars and sintered at 1250 °C for 10 h covered with LLZTO powder with 10 wt.% Li excess in platinum crucibles. Well sintered bars were ground to 3 × 4 × 30 mm and polished for mechanical tests.

2.2. Characterization of composite electrolyte

The mechanical strength of LLZTO-xM (x = 0–9) samples was determined by the three-point bending technique (Instron 3366). The bottom span was 20 mm and the loading rate was 0.02 mm min. Five samples were measured for each composition and averaged. The Vickers hardness was measured with a hardness tester (Wilson-Wolpert-Tukon 2100B). The average hardness of LLZTO-xM (x = 0–9) was determined using five indentations on the polished surface at the loads of 4.9 N with a loading time of 5 s. Separation distances of at least 500 μm were maintained between adjacent indentation sites.

Powder X-ray diffraction (PXRD, Rigaku, Ultima IV, nickel-filtered Cu-Kα radiation, λ = 0.1542 nm) was employed to determine the phase component of sintered LLZTO MgO composite electrolyte at room temperature in the 2θ range of 10°–80° with the step of 0.1° s^{-1}. The morphologies of the cross-section of ceramic bars were revealed by scanning electron microscopy (SEM, Hitachi, S-3400N). In order to clearly observe the grain boundaries, 2 mol L^{-1} HCl solution was used to etch the pristine cross-section for 3 min. The Mg distribution at cross-section of composite electrolytes was probed by SEM with the energy dispersive detector (Hitachi, S-3400N). The density of specimens was tested by the Archimedes method with the Mettler-Toledo density measurement attachments. The theoretical density of composite ceramics was calculated based on the XRD results.

The ionic conductivity was measured at room temperature by AC impedance analysis (Autolab, Model PGSTAT302N). The frequency ranged within 1 MHz–10 Hz and the electrical perturbation was set to 0.02 V. Before the test, both parallel surfaces were sputtered with gold as the lithium ion blocking electrode. The lithium ion conductivity activation energy was measured at the temperature range of 25 °C–110 °C and calculated from the slope of Arrhenius plot using the equation $\sigma T = A\exp(-Ea/kT)$, wherein σ is the conductivity, A is the pre-exponential parameter, Ea is the activation energy, T is the absolute temperature and k is the Boltzmann constant.

2.3. Fabrication of the batteries and characterization

Li/LLZTO-MgO/Au cell: The LLZTO-6M sample was selected to assemble batteries. All composite electrolyte pellets were dry polished with 400 followed by 1200 grit SiC sandpaper in an argon filled glovebox. One side of the pellet was sputtered with Au under 7–8 mA at 1.1–1.2 kV for 10 min, the other side was attached to Li foil and then sealed in an aluminum plastic film. The plastic film was isostatically pressed under 200 MPa to improve the contact between Li and electrolyte. This sandwich-type cell was packed in a CR2025 cell, and heated at 105 °C for 12 h. The electro-chemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests were conducted at 80 °C. The frequency range of EIS test was 1 MHz–10 Hz. The scanning speed and voltage range were 0.5 mV s and −0.5 V to 6.0 V (versus Li/Li^+), respectively.

Cathode: LLZTO powder was pulverized to sub-micro sizes by attrition milling method. Ketjen black (KB) and Sulfur were mixed according to the weight ratio of 1:4 by ball milling process in ethanol. The slurry was dried and sieved, and then heated to 155 °C under vacuum to obtain sulfur composite material. This 80 wt% composite was mixed with 10 wt% Super P conductive carbon black, 5 wt% Carboxy Methylated Cellulose and 5 wt% Styrene Butadiene Rubber binder in distilled water. This slurry was uniformly spread onto aluminum foil. The dried cathode on the foil was cut into sheets with 12 mm in diameter and further dried under vacuum. The sulfur loading is 1 mg cm^{-2}.

Battery configuration: The high interfacial resistance of Li metal and electrolyte was reduced by a thin Au interlayer sputtered onto the