



Solid-state lithium battery chemistries achieving high cycle performance at room temperature by a new garnet-based composite electrolyte



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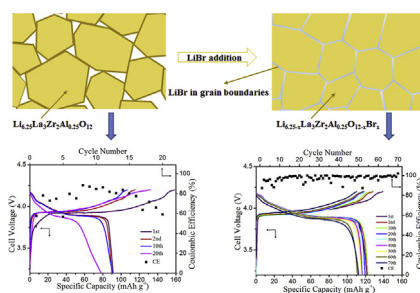
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HIGHLIGHTS

- Low-melting-point LiBr was incorporated into LLZO to form composite electrolytes.
- Anion doping at LLZO bulk and lithiated interface at LLZO grain boundary occurred.
- Ionic motion at the interface of composite electrolyte & electrode was accelerated.
- High cycle stability of a full cell using composite electrolyte was achieved at RT.
- Favorable contributions of LiBr addition towards solid-state cells were explained.

GRAPHICAL ABSTRACT



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ABSTRACT

LiBr has been incorporated into $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ garnet matrix to develop a new garnet-based composite electrolyte through high-energy ball milling followed by solid-state reaction. Of importance to note in the composite materials is joint occurrence of anion doping at $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ bulks and lithiated interface at $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ grain boundaries. Lattice distortion based on Br^- substitution at partial O^{2-} sites and high densification resulted from mergence effect of LiBr have been detected in the composite electrolytes. Li-ion conductivity and transport kinetics are thereby enhanced after LiBr incorporation. Also, LiBr addition into $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ causes the appearance of finely microporous feature for the composite materials without compromising pellet densification, which can favor interfacial contact and Li-ion motion between the composite electrolytes and electrode. A full cell with a Li metal anode, the newly developed solid electrolyte, tiny amount of liquid electrolyte, and a LiCoO_2 cathode has been assembled in sequence. High cycle stability of the full cell can be derived from capacity retention of 91.8% and high discharge capacity of 111.6 mAh g^{-1} after 70 cycles at room temperature. Consequently, favorable contributions of LiBr addition towards solid-state cell system can be further ascertained.

1. Introduction

Safety issues of traditional Li-ion batteries associated with the use of

flammable liquid electrolytes have attracted great attention to inorganic solid electrolytes [1–3] towards all-solid-state Li batteries (ASSLIBs). Among inorganic solid electrolytes, garnet-type cubic

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$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramics and their doped variants like $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ (LLZO) [4–8] possess one of the highest ionic conductivity ($\sim 10^{-4} \text{ S cm}^{-1}$) and excellently chemical stability against Li metal. From the thermodynamic viewpoint, cubic LLZO is unstable at room temperature (RT), transforming into tetragonal LLZO [9]. Thus, the ionic conductivity could be deteriorated by 1–3 orders of magnitude. Generally, supervalent doping of Al^{3+} [4,10,11] and Ga^{3+} [5] at the Li sites as well as Ta^{5+} [6,7,12] and Nb^{5+} [7] at the Zr sites has been conducted to stabilize the cubic garnet. After the supervalent doping, the ionic conductivity of the LLZO-related compounds could be increased owing to high stability of cubic phase, appropriate enhancement of Li vacancies, and disordered arrangement of cations.

Other than ionic conduction properties in the LLZO-related electrolytes itself, the most critical issue towards ASSLIBs is large interfacial resistance of the solid electrolytes with electrodes, especially at low temperature (e.g. RT), due to their rigid ceramic nature and poor wetting properties. Recently, several strategies have been performed in terms of preparation method [13], intermediate coating [14–17], hybrid electrolyte containing garnet [18], thermal annealing [19,20], etc., for decreasing the interfacial resistance. For example, Luo et al. [17] demonstrated that an ultrathin amorphous Si layer between garnet and Li metal decreased the resistivity of the garnet/Li interface due to the enhanced wettability of garnet surface. Sharafi et al. [20] employed wet polishing and heat treatments to remove carbonate and hydroxide surface contamination from $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, and thus there existed an ultra-low interfacial resistance. A typical gel electrolyte, namely a PVDF-HFP membrane soaked with liquid electrolyte [18], was used as an interlayer between garnet solid electrolyte and electrodes, significantly decreasing the interfacial resistance. Although the fundamental studies have made steady progress towards ASSLIBs, there has been little success in the development of high-performance ASSLIBs using the LLZO-related electrolytes.

In this work, we address our effort on developing a new LLZO-based composite electrolyte by LiBr incorporation into LLZO. The great interest associated with the utilization of LiBr mainly lies in the following several points: 1) The partial substitution with the larger ionic radii of Br^- (0.196 nm) for the smaller size of O^{2-} (0.140 nm) can be expected for creating Li vacancies and enlarging Li-ion conduction pathway in the composite electrolytes. Reports on Br^- doping at the O^{2-} sites of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials [21,22] have shown the good prospects in beneficially accelerating Li-ion diffusion. To the best of our knowledge, very few studies have adopted anion doping for enhancing Li-ion mobility in LLZO-related electrolytes until now. 2) LiBr, which has much lower melting point than LLZO, would serve as both an accelerator and a binder for interaction and densification among LLZO grains owing to the flow characteristic of liquid LiBr during high-temperature sintering. The incorporation of LiBr into LLZO matrix could thereby give rise to fast Li-ion migration in the LLZO-based electrolytes due to large contact area, effective bonding effect, and good wetting properties among LLZO grains. Moreover, the interfacial resistance between the LLZO-based electrolyte and electrode resulted from poor wetting properties and ineffective contact at the microscopic level could be reduced. 3) The concept of LLZO/LiBr composite electrolyte would make it possible to reduce the internal resistance of a cell using such an electrolyte. As we know, there has been no solid electrolyte that can meet all of the requirements such as wide electrochemical window, and low ionic area-specific and interfacial resistances. Thus, different types of electrolytes should be combined to integrate their advantages [23]. In this case, LiBr as a solid conductor, possessing a favorable ionic conductivity (about $10^{-7} \text{ S cm}^{-1}$ at RT [24]), could provide high-performance lithiated interfaces among LLZO grains. Although few works have been dedicated to LiBr addition into oxide solid electrolytes, LiBr has proved its feasibility and advantage for Li-ion conduction in $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ glass-ceramic solid electrolytes [25]. For these reasons above, the main aim of this study is to elucidate the influence of LiBr addition into LLZO solid electrolyte on intrinsic and interfacial Li-ion transport properties.

We also illustrate cyclic properties of full cells using such LLZO-based composite electrolytes.

2. Experimental

A typical LLZO powder with the chemical formula of $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$ was prepared by conventional solid-state reaction using stoichiometric amounts of Li_2CO_3 , La_2O_3 , ZrO_2 , and Al_2O_3 powders. A 10 mol% excess of Li_2CO_3 was added to compensate for Li volatilization during high-temperature sintering. The mixed powders were ball-milled in 2-propanol with zirconia balls at 600 rpm for 4 h by a high-energy ball miller (Fritsch P7), and heated at 650°C for 2 h and 900°C for 6 h, respectively. Subsequently, the uniform addition of LiBr powder into the mixture above was performed by another ball milling for 4 h to obtain LLZO/LiBr composite powder. LLZO/LiBr composite pellets were then prepared by isostatically pressing the composite powder at 300 MPa. Calcination of the pellets was carried out in air at 900°C for 6 h, at 1100°C for 6 h, and successively at 1200°C for 12 h. Each composite pellet was entirely buried in its mother powder (i.e. the corresponding LLZO/LiBr composite powder) during sintering to minimize Li evaporation and avoid Al inclusion from alumina crucible. After sintering, two surfaces of the pellets were polished with sandpaper down to P2000 to obtain LLZO-based electrolytes. After polishing, the LLZO-based electrolytes were heated up in a vacuum oven at 200°C for 2 h, and then stored them in the same vacuum oven at RT before being used or transferred into glove box. Pure LLZO electrolyte obtained from the same process route above without LiBr addition was prepared for comparison. Thus, several electrolyte samples were produced by adjusting the weight fraction with 0, 1, 3 and 5 wt% LiBr powder into the LLZO matrix, and the corresponding electrolytes were denoted as pure-LLZO, 1%LiBr-LLZO, 3%LiBr-LLZO, and 5%LiBr-LLZO hereafter.

The crystalline structures of the LLZO-based electrolytes were characterized by X-ray diffraction (XRD, Smartlab) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Field Emission Scanning electron microscopy (FESEM, ZEISS SUPRA55) equipped with an energy dispersive X-ray spectroscopy (EDX) detector was used to investigate the surface morphology and line composition of the electrolyte samples. Prior to Nitrogen adsorption/desorption isotherms measurements at 77 K, all of the electrolytes were grounded into powder and outgassed at 300°C for 6 h on a BEL BELSORP-max system. Then specific surface areas were calculated with the Brunauer-Emmet-Teller (BET) method and pore size distributions were confirmed by using the Barrett-Joyner-Halenda (BJH) model.

Li-ion conductivity of LLZO-based electrolytes with a desired thickness of about 1.0 mm was measured by electrochemical impedance spectroscopy (EIS) using an impedance analyzer (VMP3) in a frequency range of 10^6 – 10^{-1} Hz with an amplitude of 10 mV at open circuit voltage (OCV). Colloidal silver (SPI-paint) was painted on both faces of the electrolytes as Li-ion blocking electrodes to form symmetric cells. Equivalent circuits were used to fit the measured impedance spectra through Zsim 3.30d software. The temperature-dependent conductivities for the electrolytes were also determined through the impedance technique in a temperature range of 30 – 110°C . A stabilization time of 1 h at constant temperatures was utilized before the collection of the impedance data.

To address the effect of LiBr on the interface resistance, pure LLZO and 3%LiBr-LLZO samples were respectively used as solid electrolytes in full cells with LiCoO_2 cathode and metallic Li anode. Here, the thickness of LLZO-based electrolytes was controlled to be around 1.5 mm for studying the interfacial and cyclic performance of the full cells. The cathode slurry was obtained by mixing commercial LiCoO_2 powder, super P, and polyvinylidene fluoride (PVDF) at a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP). $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (LiTFSI) salts, as fast ion conductors used in composite cathodes of solid-state cells elsewhere [26–28], were also added to improve the ionic

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