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Gd-doped $Li_7La_3Zr_2O_{12}$ garnet-type solid electrolytes for all-solid-state Li-Ion batteries

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ABSTRACT

$Li_7La_3Zr_2O_{12}$ (LLZO) garnet is one of the most promising Li-ion solid electrolytes for all-solid-state Li-ion batteries, owing to its high chemical stability against Li metal and relatively high Li-ion conductivity. In order to further enhance the conductivity of LLZO, Gd^{3+} is used to dope LLZO at the Zr^{4+} site, in order to enable excess Li to occupy the octahedral sites, which could facilitate Li-ion transport and increase ionic conductivity. In this study, $Li_{7+x}La_3Zr_{2-x}Gd_xO_{12}$ (LLZGO, x = 0–0.5) solid electrolytes with cubic phase and high relative densities are prepared at 1220 °C using a solid-state reaction method. It is found that LLZGO garnets with x from 0.1 to 0.2 deliver higher conductivities than pristine LLZO. Among these, the $Li_{7.2}La_3Zr_{1.8}Gd_{0.2}O_{12}$ (LLZG2O) sample achieves the highest room-temperature total conductivity of $2.3 \times 10^{-4}\ S\ cm^{-1}$. X-ray diffraction characterization confirms that LLZG2O is chemically stable against Li metal at room temperature for half a month. Cyclic voltammetry shows that LLZG2O possesses good electrochemical stability and reversibility of Li dissolution and deposition reactions. Symmetrical cells using a LLZG2O solid electrolyte and two Li metal electrodes are cycled galvanostatically under various current densities. The results demonstrate that the cell can achieve excellent cycling stability and low overpotentials for the dissolution and deposition reactions of Li. The substitution of Gd^{3+} for Zr^{4+} is effective in improving the Li-ion conductivity of LLZO, and $Li_{7+x}La_3Zr_{2-x}Gd_xO_{12}$ could be promising as solid electrolytes for high-performance all-solid-state Li-ion batteries.

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1. Introduction

The rapid development of electric vehicles (EVs) requires that the energy densities and safety of current Li-ion batteries (LIBs) can be further improved. All-solid-state Li-ion batteries (ASSLIBs), with Li metal anodes and solid state electrolytes, instead of the conventional graphite-based anode and combustible liquid electrolytes, can offer superior energy densities and safety to LIBs and meet the requirements of EVs [1]. Li-stuffed garnet-type oxides are one of the most promising solid electrolytes because they are able to accommodate excess Li^+, and uncommonly possess both high ionic conductivities (~$10^{-4}\ S\ cm^{-1}$) and high stabilities against Li metal, air, and moisture. So far, garnet-type solid electrolytes have exhibited better overall performance, in contrast to some other inorganic solid state electrolytes such as sulfides [2], nitrides [3], NASICON [4], and perovskite oxides [5]. Additionally, garnets can also be coupled with high-voltage cathodes, owing to their wide electrochemical stability window (~6 V) [6]. Typical Li-stuffed garnets are $Li_xA_3B_2O_{12}$-type oxides, in which A sites are generally occupied by La cations in 8-fold coordination, and B sites are occupied by pentavalent Nd^{5+} or Ta^{5+} cations, or by tetravalent Zr^{4+} cations in 6-fold coordination. $Li_5La_3M_2O_{12}$ (M = Nb, Ta) [7] and $Li_7La_3Zr_2O_{12}$(LLZO) [8] are promising chemical compositions among garnet-type solid electrolytes, and they have attracted intense research interests. The latter has a higher Li content and occupancy of octahedral sites, which can enhance Li-ion conduction. LLZO garnet oxides have been thereby regarded as an ideal solid electrolyte material for ASSLIBs [9,10].

LLZO is reported to have two polymorphs: the tetragonal phase is a low-temperature stable form, with a relatively low conductivity

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(~10^{-6} S cm^{-1}), and the cubic phase is a high-temperature stable form, with a two orders higher conductivity [11]. The garnet framework structure of cubic LLZO is composed of dodecahedral LaO_8 and octahedral ZrO_6, which corresponds to 8-coordinate La^{3+} and 6-cordinate Zr^{4+}, respectively. Two LiO_4 tetrahedrons are bridged by a LiO_6 octahedron, forming a migration pathway for Li^+ [12]. In cubic LLZO garnet, the Li atoms are located in the tetrahedral 24d (Li1) site and distorted octahedral 96h (Li2) site, respectively. The Li2 site is vacant in the ideal garnet structure, and the Li1 site is fully occupied. O'Callaghan et al. [13] report that increasing the lithium content in a garnet Li-ion conductor leads to an increased concentration of Li in the octahedral (Li2) site. The Li-ion conduction in the garnet structure occurred exclusively via a network of an edge-linked, distorted octahedral oxide, and the tetrahedrally coordinated Li (Li1) played no part in the transport properties [13]. Awaka et al. [14] further reported that the Li-ion migration pathway was a loop constructed by the Li1 and Li2 sites. The loop linked to another one, whereas only the Li1 site was shared by two loops as a junction. A three-dimensional network of the Li-ion migration pathway is then formed, which results in the very short Li-Li distance in this migration pathway. The full occupation of the Li1 site and the disordering and partial occupation of the Li atoms at the Li2 site are the significant features of cubic $Li_7La_3Zr_2O_{12}$ that can achieve good Li-ion conduction. Cubic LLZO is usually sintered at ~1230 °C [8]. Chemical substitutions can effectively reduce the preparation temperature to around 1100 °C and increase the Li-ion conductivity [15]. A wide range of elements have been used to dope LLZO, and several substitution schemes have been put forward. Super valent cations are favored for substitution because their mixed charge valence allows for easy formation of Li vacancy. One of the replacement schemes is to substitute Li^+ with super valent cations Al [16], Ga [17], and Fe [18], which can reduce Li content and increase Li vacancy concentration, thus stabilizing the cubic structure with a good Li-ion conductivity. However, this may impair the Li^+ transport [19]. In contrast, doping LLZO with Nb [20], Ta [21], and Sb [22] pentavalent cation on the B site can also increase Li vacancy and stabilize the cubic structure, and the conductivity can be increased without blocking the Li^+ pathway. Substitution of low-valent alkaline earth cations (Ba^{2+} [23], Ca^{2+} [24], and Sr^{2+} [25]) for La^{3+} at A sites is another effective approach to improve the Li-ion conductivity. Unlike the above two schemes, the alkaline earth substitution leads to an increase in Li content. The excess Li may partially occupy the Li2 sites, which can encourage Li-ion conduction [26]. Recently, a novel Li-stuffed garnet-type $Li_{5+2x}La_3Ta_{2-x}Gd_xO_{12}$ electrolyte was reported, by substituting a low-valent Gd^{3+} for Ta^{5+} cation on B sites in $Li_5La_3Ta_2O_{12}$ [27]. The size of Gd^{3+} (6-coordination) is about 0.94 Å, relatively bigger than that of Ta^{5+} (0.64 Å in 6-coordination), which results in the increased lattice constant of $Li_5La_3Ta_2O_{12}$ after doping. The Li-ion conductivity of $Li_{5+2x}La_3Ta_{2-x}Gd_xO_{12}$ is higher than its parent counterpart; this is attributed to the increased Li-ion concentration as well as the weak chemical interaction between the Li-ions and other ions in the lattice. The size of Zr^{4+} in 6-coordination is about 0.72 Å, close to that of Gd^{3+}, which suggests that the substitution of Gd^{3+} at the Zr^{4+} site in LLZO should be feasible and may accordingly enable excess Li to occupy the Li2 sites. To the best of the authors' knowledge, Gd-doped LLZO has not been reported yet among Li-stuffed garnet-type solid electrolytes.

Here for the first time it is reported that the preparation of Gd-doped LLZO, composed of $Li_{7+x}La_3Zr_{2\text{-}x}Gd_xO_{12}$ (LLZGO, x = 0–0.5) as the Li-ion solid electrolytes. The conductivities, chemical and electrochemical stabilities of LLZGO as well as their cycling performance in symmetrical cells are systematically studied. It is expected that, by substituting Gd^{3+} at the Zr^{4+} site in LLZO, the partial occupation of the excess Li at the Li2 site would accelerate the Li^+ migration and thereby increase the Li-ion conductivity.

2. Experimental session

Preparation: $Li_{7+x}La_3Zr_{2\text{-}x}Gd_xO_{12}$ (LLZGO, x = 0–0.5) powders were prepared by the conventional solid-state reaction process. All the raw materials were purchased from Shanghai Macklin Biochemical Co. The starting materials of Li_2CO_3, $La(OH)_3$, ZrO_2, and Gd_2O_3 were mixed by planetary ball-milling in an ethyl alcohol medium for 24 h, using the stoichiometric ratio. 10 wt% excess of Li_2CO_3 was added to compensate for lithium loss during calcination. The precursor powders were heated at 950 °C for 12 h in air to obtain the LLZGO powder. Then the calcined powders were pressed into green pellets of 15 mm in diameter under a uniaxial pressure of 175 MPa. The green pellets were subsequently surrounded by the as-calcined LLZGO powder and sintered in air at 1220 °C for 36 h at a heating rate of 3 °C min^{-1}. The relative densities of the sintered samples were about 93–95%, determined by Archimedes' method. For identification purposes, the final LLZO-based garnet oxides received a denomination of LLZGO, according to their equivalent gadolinium content in mol%. Thus, LLZG20 represented a sample with 0.2 mol% of Gd^{3+} in LLZO, i.e., $Li_{7.2}La_3Zr_{1.8}Gd_{0.2}O_{12}$. The denomination of other compositions can be seen in Table S1 in detail.

Material Characterizations: The mixed starting powders composed of Li_2CO_3, $La(OH)_3$, and ZrO_2 for preparing LLZO were examined by thermogravimetry (TG)/derivative thermogravimetry (DTG) from 25 to 1350 °C, in order to determine the sintering schedule. The X-ray diffraction (XRD) measurements were performed according to internal standard method. The Gd-Doped $Li_7La_3Zr_2O_{12}$ (LLZGO) solid electrolyte pellets sintered at 1220 °C for 36 h were ground and mixed with 20 wt% pure silicon powder (Shanghai Macklin Biochemical Co. Ltd.) which is used as the internal standard substance. The XRD analysis of the mixture of LLZGO and Si powders were tested by a Rigaku D/max-2500 X-ray diffractometer, using Cu Kα radiation. The XRD patterns were then calibrated by the diffraction peaks of Si standard substance. The morphologies of the LLZG20 electrolytes were examined by field-emission scanning electron microscopy (Hitachi S4800). The interfacial stability of LLZG20 with Li metal electrodes was investigated in CR2032 coin cells at room temperature, assembled by directly sandwiching LLZG20 electrolyte between two Li metal electrodes. After storage for 15 days, the test cell was disassembled in the argon glove box, and the surface of LLZG20 was examined by XRD.

Electrochemical evaluation: The ionic conductivities of LLZO-based pellets were measured from room temperature to 250 °C by AC impedance, using a CHI 660 Electrochemical Work Station. The applied frequency range was from 1 MHz to 1 Hz, with a 5 mV AC amplitude. For measuring the conductivity, both sides of the pellets were finely polished and painted with silver paste to form the current-collector layers. The geometric area of Ag electrode was about 0.28 cm^2. Electrical contacts were made to each of the electrodes, using Ag paste and Ag wire. To evaluate the electrochemical performance and stability of the LLZG20 solid electrolyte, symmetrical cells of Li|LLZG20|Li configuration were assembled in coin cells (CR2032) in an Ar-filled glovebox, using Li metal chip as the electrodes. A small amount of silver paste was applied between the Li electrodes and the electrolyte to reduce the contact resistance between them. The geometric area of the Li electrode in the symmetrical cells was about 0.79 cm^2. Cyclic voltammetry (CV) of symmetrical cells was conducted with a CHI 660 Electrochemical Work Station, under a scanning rate of 0.1 mV s^{-1} within −0.5–0.5 V. The impedance of the symmetrical cells was examined under the same condition as that applied in conductivity

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