



# Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub>@amorphous Li<sub>3</sub>OCl composite electrolyte for solid state lithium-metal batteries



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## ABSTRACT

Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) garnet-type oxide has become a promising inorganic electrolyte for solid-state lithium-ion batteries due to its high ionic conductivity and good chemical stability with the lithium metal. However, the poor wettability of LLZO garnet-type oxide with lithium metal and its incompact structure have impeded their extensive applications in solid-state lithium-ion batteries. Herein, Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub> (LLZTO) particles were embedded in the amorphous Li<sub>3</sub>OCl to form an integrated composite electrolyte (LLZTO-2wt.% Li<sub>3</sub>OCl) with compact and stable structure at 350 °C, which presents high ionic conductivity ( $2.27 \times 10^{-4}$  S cm<sup>-1</sup>), low interfacial resistance and high electrochemical stability (up to 10 V vs. Li/Li<sup>+</sup>) at room temperature. The amorphous Li<sub>3</sub>OCl acting as a binder, filler and bridge promotes the formation of an integrated composite electrolyte and continuous ionic conductive network among LLZTO particles. Furthermore, the Li<sub>3</sub>OCl with excellent affinity to lithium metal in-situ reacts with the lithium metal to form a stable and dense interfacial layer, which greatly decreases the interfacial resistance between the composite electrolyte and lithium metal (from 1850 to 90 Ω cm<sup>2</sup>). The interfacial layer allied compact composite electrolyte also effectively suppresses the lithium dendrite growth during lithium plating-stripping. The symmetrical Li/LLZTO-2wt.% Li<sub>3</sub>OCl/Li cell can stably cycle 1000 h without short circuit. The stable specific capacity of solid-state LiFePO<sub>4</sub>/LLZTO-2wt.% Li<sub>3</sub>OCl/Li battery is as high as 157.5 mAh g<sup>-1</sup> and 85.7 mAh g<sup>-1</sup> at 0.05 C and 0.5 C, respectively. Combining the garnet-type electrolyte with amorphous Li<sub>3</sub>OCl is a promising way to develop the compact garnet-type electrolyte at low temperature for solid-state lithium-ion batteries.

## 1. Introduction

Lithium-ion batteries have been widely applied in the electronic devices and electrical vehicles (EVs) owing to their excellent electrochemical properties, such as high energy density, long cycling life, low self-discharge, etc [1,2]. Whereas, commercial lithium-ion batteries with an organic liquid-based electrolyte still have some shortcomings, such as the high flammability of liquid electrolyte, which resulting in severe safety problem [3,4]. To address this issue, the inorganic solid-state electrolyte has attracted more and more attentions due to their outstanding advantages such as high mechanical strength, good chemical stability, high ionic conductivity and excellent safety performance [5–8]. The most common inorganic solid-state electrolyte can be divided into two groups including the sulfide-based electrolyte and

oxide-based electrolyte [9,10]. Owing to the instability of the sulfide-based electrolyte in air condition, the oxide-based electrolyte is becoming a research hotspot in the field of solid-state lithium-ion batteries [11,12]. Many types of the oxide-based electrolyte have been reported so far, including NASICON-type phosphates [13], perovskite-type titanates [14], lithium phosphorus oxynitride (LiPON) [15] and garnet-type frame oxides [16]. Compared to other oxide-based electrolyte, the garnet-type oxide of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) exhibits a high ionic conductivity ( $\sim 10^{-3}$  S cm<sup>-1</sup>) at room temperature [17], a wide electrochemical voltage window [18] and an excellent electrochemical stability with lithium metal anode [19]. Therefore, the LLZO is considered as a promising candidate solid-state electrolyte for the next generation of lithium-ion batteries. The LLZO has two crystal phases such as the tetragonal and cubic phases [20], and only the cubic LLZO possesses a

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high ionic conductivity at room temperature. The cubic LLZO can be prepared by co-precipitation [21] and sol-gel [22] methods. Besides, the element doping such as Al [23], Nb [24], W [25], Ga [26], Ta [27], Rb [28], can effectively improve the ionic conductivity of cubic LLZO.

However, the resistance among the LLZO particles in LLZO electrolyte with an incompact structure is quite larger due to a large amount of voids inside the electrolyte and discontinuous ionic conductive network, which greatly compromises the ionic conductivity of LLZO. Thus, the LLZO electrolyte sheets with compact structure are prepared as follows. First, the LLZO powders were synthesized under 900 °C, and then LLZO sheets with dense structure are obtained under high pressure and following calcinations for 36 h over 1200 °C [16]. The process is huge energy consumption and complex for practical applications. Therefore, developing a facile method preparing LLZO sheets with dense structure to decrease their voids and enhance the ionic conductivity is considerably significant for practical application of LLZO solid-state electrolyte. In addition, the high interfacial resistance between the electrode and LLZO is also one of the most critical factors to restrict the electrochemical performances of solid-state lithium-ion batteries. Accordingly, there is a huge interfacial resistance at the interface of the garnet-type electrolyte with lithium metal anode [29]. Owing to the rigid surface and non-metallic property, the surface of garnet-type electrolyte is hard to be wetted by the lithium metal, even for the melted lithium metal [30,31]. Furthermore, the LLZO would be destroyed by lithium dendrites formed at the grain boundaries due to the brittle nature of ceramic oxide [32,33]. Some research works have been done on the reduction of the interfacial resistance of the garnet-type electrolyte and lithium metal anode in recent years. One common method is depositing an interfacial layer between the garnet-type electrolyte and lithium metal anode. The interfacial layers include the aluminium oxide (Al<sub>2</sub>O<sub>3</sub>), [34] amorphous silicon (Si) [35], germanium metal (Ge) [36], nanoscale ZnO [37] and lithium-aluminium alloy [19], which can increase the wettability of lithium metal anode with LLZO and provide a good contact between the garnet-type electrolyte and lithium metal anode. The preparation methods of these interfacial layers include the chemical vapor deposition (CVD) and physical vapor deposition (PVD), which are too expensive and complex to be adopted for large scale applications. To reduce the cost of preparing process and improve the convenience of operation, more convenient modifying methods for improving the compatibility of the garnet-type electrolyte with lithium metal anode should be investigated and developed urgently.

The lithium-rich anti-perovskite of Li<sub>3</sub>OX (X=Cl and Br) has been exploited as a promising solid-state electrolyte for lithium-ion batteries, which displays a good electrochemical stability with lithium metal anode and a low melting temperature ( $T_m \approx 282$  °C [38–40]). In order to obtain a solid electrolyte with compact structure at low temperature using less energy consumption, in this work, the Li<sub>3</sub>OCl with an excellent affinity to lithium metal was introduced in the voids and boundaries of the Ta-doped Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub> (LLZTO) particles by a feasible and convenient melting-quenching method at 350 °C to form a novel all-solid-state composite electrolyte of LLZTO-xLi<sub>3</sub>OCl. We not only coated the amorphous Li<sub>3</sub>OCl layer onto LLZTO disk surface to improve the surface wetting with lithium metal, but also fill the amorphous Li<sub>3</sub>OCl into the voids of LLZTO disk to improve the surface wetting among LLZTO particles. As shown in Fig. 1, during the charge-discharge process, the Li<sub>3</sub>OCl in LLZTO-2wt.% Li<sub>3</sub>OCl in-situ reacts with the lithium metal to form a stable and dense interfacial layer, which not only greatly decreases the interfacial resistance between the LLZTO-2wt.% Li<sub>3</sub>OCl composite electrolyte and lithium metal electrode, but also effectively suppresses the growth of lithium dendrite on the surface of lithium metal anode during lithium plating-stripping. In addition, the LLZTO particles as framework of LLZTO-2wt.% Li<sub>3</sub>OCl were embedded in the amorphous Li<sub>3</sub>OCl with high lithium-ion conductivity, which acts as the binder, filler and bridge to promote the formation of an integrated composite solid-state electrolyte with

compact structure and continuous ionic conductivity network, leading to a reduced resistance and an enhanced ionic conductivity of composite solid-state electrolyte. Abundant Li ions transportation pathways in composite electrolyte are distributed in the LLZTO crystals and amorphous Li<sub>3</sub>OCl. As a result, the LLZTO-2wt.% Li<sub>3</sub>OCl composite electrolyte possesses high ionic conductivity ( $2.27 \times 10^{-4}$  S cm<sup>-1</sup>), low interfacial resistance with lithium metal anode (90 Ω cm<sup>2</sup>) and high electrochemical stability (up to 10 V vs. Li/Li<sup>+</sup>) at room temperature. The symmetrical Li/LLZTO-2wt.% Li<sub>3</sub>OCl/Li cell can stably cycle 1000 h without short circuit due to the suppression of lithium dendrite growth. The stable specific capacity of solid-state LiFePO<sub>4</sub>/LLZTO-2wt.% Li<sub>3</sub>OCl/Li battery is as high as 157.5 mAh g<sup>-1</sup> and 85.7 mAh g<sup>-1</sup> at 0.05 C and 0.5 C, respectively. This work provides a promising and convenient way to develop an integrated and compact garnet-type composite solid electrolyte at ultralow temperature (350 °C) for high performance of solid-state lithium-ion batteries.

## 2. Experimental

### 2.1. Preparation of LLZTO-2wt.% Li<sub>3</sub>OCl composite electrolyte

The cubic Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub> (LLZTO) solid-state electrolyte was prepared as follows: the starting materials of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and ZrOCl<sub>2</sub>·8H<sub>2</sub>O were mixed according to the stoichiometric ratios and dissolved in a Teflon reactor with the de-ionized water. The excess LiOH solution was added into the above mixed solution drop by drop to ensure a full precipitation of La<sup>3+</sup> and Zr<sup>4+</sup> ions. Then, the precipitate of LaZr(OH)<sub>n</sub> was isolated by a vacuum filtration procedure and washed with the de-ionized water for several times to remove the impurities. The obtained precipitate of LaZr(OH)<sub>n</sub> and the stoichiometric amount of Ta<sub>2</sub>O<sub>5</sub> particles were added into a mixed solution of LiOH and Li<sub>2</sub>CO<sub>3</sub> (10 wt% excess of lithium-ion), in which the lithium-ion molar ratio of LiOH to Li<sub>2</sub>CO<sub>3</sub> is 0.76:0.24. After that, the resulting mixture was heated at 80 °C and magnetically stirred until the de-ionized water had been evaporated. With the continuous volatilization of water, a homogeneous paste including the elements of Li, La, Zr, O and Ta was obtained. Then, the as-prepared paste was dried at 60 °C for 12 h to form the dry precursor. Finally, the precursor was heated at 450 °C for 3 h, and then was calcined at 900 °C for 8 h to obtain the powders of cubic LLZTO. The as-prepared cubic LLZTO powders were pressed into the pellets and sintered at 1200 °C for 6 h in an alumina crucible.

The anti-perovskite of Li<sub>3</sub>OCl electrolyte was prepared as follows: the LiOH and LiCl powders with stoichiometric ratio of 2:1 were ground for several minutes. The resulting mixture was placed in an alumina crucible and heated to 350 °C in a glove box filled with pure Ar gas (both the moisture and oxygen levels are below 0.1 ppm) for several days to form Li<sub>3</sub>OCl powders. The synthesized Li<sub>3</sub>OCl powder were pressed into the pellets and heated at 240 °C for 6 h in an alumina crucible.

The as-prepared LLZTO and Li<sub>3</sub>OCl powders with different mass ratios were ground for 0.5 h. The obtained solid-state mixture was pressed into the pellet with a thickness of 1 mm and a diameter of 16 mm. After that, the pellets of mixed electrolyte were reheated at 350 °C for 12 h and then quenched in a glove box to room temperature.

### 2.2. Structural and electrochemical characterization

A thin lithium metal foil with a thickness of 0.5 mm and in diameter of 1.2 cm was put on the solid-state electrolyte (LLZTO and LLZTO-2wt.% Li<sub>3</sub>OCl) pellets in a glove box filled with pure argon gas (both the moisture and oxygen are below 0.1 ppm). Then, the lithium metal foil was heated at 240 °C for 30 min. The cross-section scanning electron microscope (SEM) image of the solid-state electrolyte samples was analyzed by a field-emission scanning electron microscope (HITACHI S-4800). The X-ray diffraction (XRD) patterns was examined using

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