



Short communication

# Honeycomb-alumina supported garnet membrane: Composite electrolyte with low resistance and high strength for lithium metal batteries



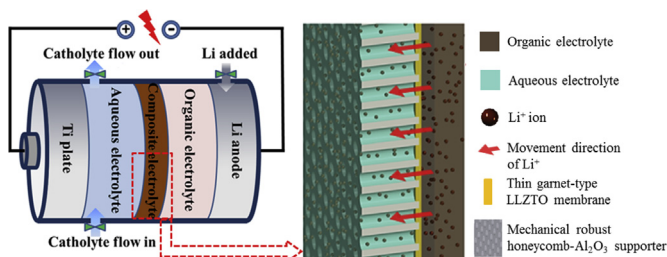
Kai Liu, Chang-An Wang\*

State Key Lab of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

## HIGHLIGHTS

- Composite design disentangles thinness–strength dilemma in garnet.
- Simple and efficient mechanical strength and gas impermeability test method.
- Electrical property of the composite electrolyte verified in a Li–H<sub>2</sub>O<sub>2</sub> cell.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 15 December 2014

Received in revised form

12 January 2015

Accepted 5 February 2015

Available online 7 February 2015

## Keywords:

Lithium metal battery

Composite electrolyte

Garnet

Ionic resistance

Mechanical strength

## ABSTRACT

Li-ion ceramic electrolyte material is considered the key for advanced lithium metal batteries, and garnet-type oxides are promising ceramic electrolyte materials. To disentangle the thinness–strength dilemma in garnet-type Li<sub>6.4</sub>La<sub>3</sub>Zr<sub>1.4</sub>Ta<sub>0.6</sub>O<sub>12</sub> (LLZTO) electrolyte, we designed and successfully synthesized a ceramic–ceramic composite electrolyte, i.e. a honeycomb–Al<sub>2</sub>O<sub>3</sub> pellet supported LLZTO membrane. The honeycomb–Al<sub>2</sub>O<sub>3</sub> pellet acts as a supporter to the thin LLZTO membrane and makes the whole composite electrolyte strong enough, while the straight holes in the Al<sub>2</sub>O<sub>3</sub> supporter can be filled with liquid electrolyte and acts as channels for Li<sup>+</sup> transportation. Such a composite design eliminates the concern over the LLZTO membrane's fragility, and keeps its good electrical property.

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## 1. Introduction

Breakthrough in portable electronic devices and electric vehicles requires high-energy and safe electrochemical storage. Lithium metal batteries (LMBs), such as Li–O<sub>2</sub> [1–3], Li–S [4–6] and Li–redox flow batteries [7], are currently attractive storage technologies due to their high cell voltage, high energy density and large

capacity, and are considered as next generation battery technology. To enhance safety and reliability of LMBs, the highly reactive lithium metal anode must be strictly protected and the lithium dendrite growth in charging process should be blocked [8]. Li-ion conducting ceramic electrolyte, due to its dense microstructure, high mechanical modulus, good stability and non-flammability, is an ideal material that can provide reliable lithium metal protection and lithium dendrite blocking, and it is considered the key for high performance LMBs [9]. The foremost requirement for the ceramic electrolyte is a mechanically robust plate with a low ionic resistance [2], and a great deal of research has been conducted to meet

\* Corresponding author.

E-mail address: [wangca@mail.tsinghua.edu.cn](mailto:wangca@mail.tsinghua.edu.cn) (C.-A. Wang).

the requirement [10–14]. However, ionic resistance of ceramic electrolyte is still quite large and results in a poor battery performance. A better ceramic electrolyte with lower ionic resistance is urgently needed to further improve the performance of LMBs.

Ionic resistance of the ceramic electrolyte ( $R$ ) can be calculated as follows:

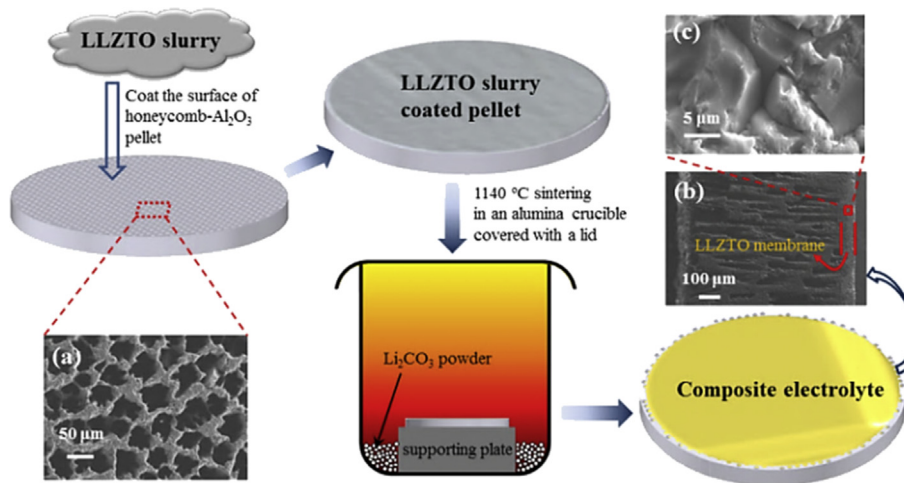
$$R = \frac{L}{\sigma \cdot S} \quad (1)$$

where  $L$ ,  $\sigma$  and  $S$  represent thickness, ionic conductivity and cross-sectional area of the ceramic electrolyte, respectively. The ionic resistance can be lowered by both increasing  $\sigma$  and decreasing  $L$ . Most studies on ceramic electrolytes focus on the high ionic conductivity. Among the ceramic electrolytes that have been reported, garnet-type metal oxides are considered the most promising ones [15]. Ta-doped garnet, with an apparent formula as  $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$  (LLZTO), shows a  $\text{Li}^+$  ionic conductivity of  $\sim 1.0 \cdot 10^{-3} \text{ S cm}^{-1}$  at room temperature [16]. This is almost the highest level of ionic

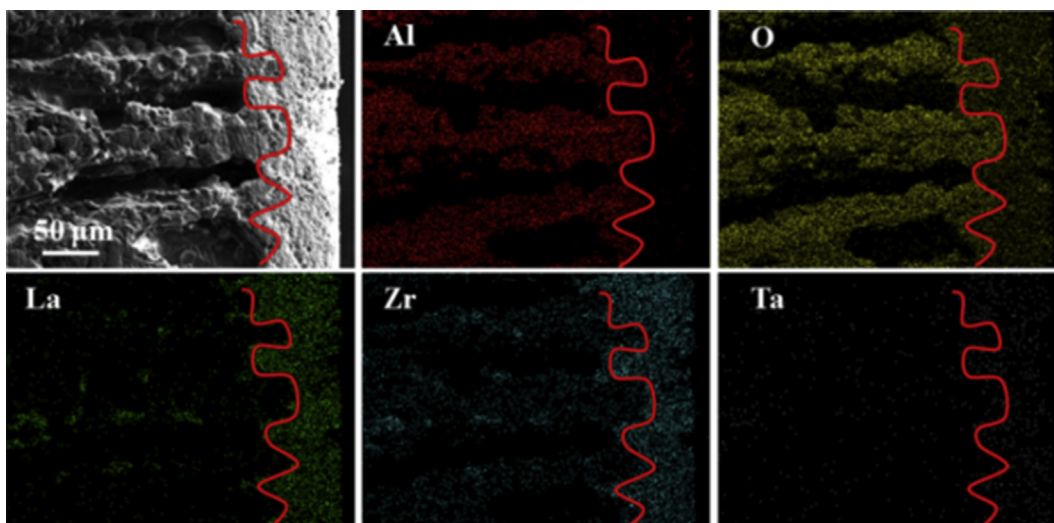
conductivity which ceramic electrolyte can reach till now, but it still lags behind what high performance LMBs desire, and further improvement seems to have hit a plateau. Thus, we tried to adopt another strategy to lower the ionic resistance: decreasing thickness ( $L$ ). To this end, ceramic electrolytes are usually applied as thin sheets in the LMBs. For instance, the widely used commercial LTAP sheet has a thickness of only  $150 \mu\text{m}$  [2,17,18], and the LLZTO sheet used in our former work was  $200 \mu\text{m}$  thick [19].

However, the thinner the ceramic electrolyte, the more fragile it is. A fragile thin sheet, such as the  $200 \mu\text{m}$  thick LLZTO sheet, is inconvenient to handle and can hardly stand against stress in practical operation conditions. As a result, even though the thin LLZTO sheet shows low ionic resistance, its application is severely limited due to its weakness and fragility. It's a big challenge to make the ceramic electrolyte plate thin enough and strong enough at the same time.

In this study, we adopt a conventional strategy introducing a porous mechanical robust supporter [20,21] to disentangle such a new thinness-strength dilemma. We design a ceramic–ceramic



**Fig. 1.** Schematic representation of the fabrication process of composite electrolyte and SEM images of the sample in different stages of the process. (a) Surface of the honeycomb  $\text{Al}_2\text{O}_3$  supporter; (b) a side view of the composite electrolyte, between the two red lines is the LLZTO membrane; (c) close-up of the dense membrane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Electron-energy dispersive spectroscopies of the composite electrolyte in the side view. The red line marks the boundary between honeycomb  $\text{Al}_2\text{O}_3$  pellet and LLZTO membrane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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