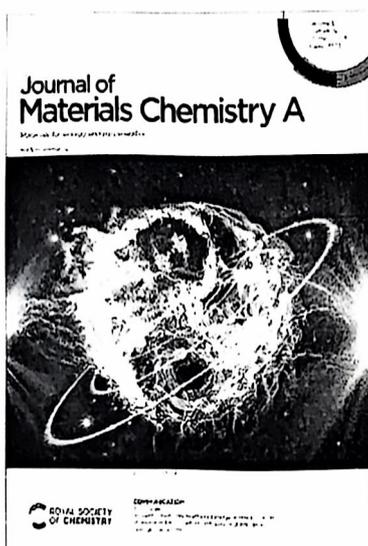


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Mortise-tenon-like ionic/electronic conductive interface facilitates long-cycle solid-state lithium metal batteries

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The high energy density and superior safety of solid-state lithium metal batteries (SSLMBs) has been recognized as a next-generation energy storage system with great attention. Garnet-type oxide solid-state electrolytes, especially $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO), with high ionic conductivity, low activation energy and superior stability with Li, are among the most promising solid-state electrolyte materials. However, high interfacial resistance, uneven lithium deposition and lithium dendrite growth between Li/LLZTO interfaces have hindered the industrialization development of SSLMBs. In this work, a novel mortise-tenon-like hybrid ionic/electronic conductive interface (Li/LZFC@LLZTO) is constructed, which is composed of LiF, LiCl, and Li-Zn alloy through an *in situ* transformation reaction. As expected, the interfacial impedance of Li|LZFC@LLZTO|Li is significantly reduced from $128 \Omega \text{ cm}^2$ to $2.7 \Omega \text{ cm}^2$ and the critical current density increases from 0.3 mA cm^{-2} to 2.1 mA cm^{-2} , as well as prominent cycling performance of 6600 h at 0.2 mA cm^{-2} or 900 h at 0.4 mA cm^{-2} . Consequently, both the Li|LZFC@LLZTO|LiFePO₄ and Li|LZFC@LLZTO|LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ full cells exhibit excellent rate performance. Furthermore, Li|LZFC@LLZTO|LiFePO₄ can maintain a high discharge specific capacity close to 140 mAh g^{-1} at 0.2 C after 150 cycles of stable cycling. This work lays the foundation for developing garnet-based SSLMBs with high critical current density, low interfacial impedance and long-term cycling performance.

Introduction

As human technology and the standard of living are advancing by leaps and bounds, society's demand for new energy storage systems with higher energy density, greater security, and longer cycle times is becoming increasingly urgent.¹ The energy density of traditional lithium-ion batteries with graphite as anode is close to the theoretical limit of 300 Wh kg^{-1} , posing a challenge to current battery system.^{2,3} Li metal has a high theoretical specific capacity of 3860 mAh g^{-1} and a low chemical potential (-3.04 V vs standard hydrogen electrode). Thus, replacing the traditional graphite anode with Li metal can dramatically increase the energy density.⁴ Unfortunately, conventional organic electrolytes are flammable, explosive, and have inferior stability against Li anode, which can lead to complicated side reactions. Moreover, the decomposition products of these side reactions can result in an unstable solid electrolyte interface (SEI), which may bring inhomogeneous Li plating/stripping and stimulate Li dendrites to penetrate the separator, thus causing safety hazards.⁵

Solid-state lithium metal batteries (SSLMBs) are expected to be one of the best candidates for next-generation energy storage systems with higher energy density, security and outstanding cycle life, which is mainly attributed to the superior stability of solid-state electrolytes (SSEs) against Li anode.⁶ Among these electrolytes, garnet-type SSEs, especially Ta-doped LLZTO ($\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$), exhibit favorable comprehensive performance, including high Li⁺ conductivity, thermal stability, electrochemical window and Young's modulus. The wide electrochemical window and high mechanical strength mean that LLZTO is not only compatible with high-voltage cathode materials, but also helps to inhibit the growth of lithium dendrites, thereby improving the energy density and safety of the battery. More importantly, LLZTO manifests excellent chemical and electrochemical stability to Li, which is hard to achieve with other SSEs.^{7,8} Nevertheless, the "point-to-point" interfacial contact cannot provide uniform Li deposition/stripping between Li and LLZTO. Furthermore, the uneven Li⁺ flux distribution can induce the growth of lithium dendrites, which penetrate the electrolyte and ultimately lead to cell failure, significantly hindering the practical application of garnet-based solid-state lithium metal

