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3D lithium metal anodes hosted in asymmetric garnet frameworks toward high energy density batteries

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ABSTRACT

Solid-state electrolytes (SSEs) have been widely studied to enable applications of high-energy Li metal anodes in batteries with high safety and stable performance. However, integration of SSEs into batteries is hindered by the infinite volume change of Li metal anodes upon cycling, the unstable resistance between Li and SSE, and low battery energy densities. To address these challenges, we developed a porous-dense bilayer structured garnet SSE as a 3D ionic framework for Li metal. The framework consists of one porous layer as a volume-stable host of Li metal with a large contact area, and one dense layer as a solid-state separator preventing short-circuits. The flatness of the dense layer enables simple battery manufacturing by laying a pre-made cathode on top of the bilayer framework. The thicknesses of the porous and dense layers are well controlled at 50 and 20 μm, respectively, to improve the battery energy density. Based on the bilayer garnet framework and highly loaded $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ (NMC) cathodes (32 mg/cm^2), we developed solid-state Li-NMC batteries with energy densities (329 W h/kg and 972 W h/L) significantly higher than all of the state-of-art garnet-based Li metal batteries. The bilayer framework design provides a promising strategy towards solid-state Li metal batteries with high energy densities because of its well-optimized thickness, stable cycling performance, and feasibility to be integrated with high-energy cathodes.

1. Introduction

Lithium metal is the ultimate choice for battery anodes because it has the highest specific capacity (3860 mA h/g) and the lowest electrochemical potential (−3.04 V *vs*. standard hydrogen electrode) among all anode materials [1,2]. However, there are challenges regarding the safety and stability of Li metal anodes in conventional batteries with liquid electrolytes, including dendrite formation [3], unstable solid electrolyte interface (SEI) [4], and infinite anode volume change upon cycling [5]. Strategies have been developed for Li metal anode protection, such as electrolyte additives [6], artificial SEI [7–9], and nano-structural engineering on the surface of Li metal [10,11]. These strategies can improve the stability of electrolytes against Li and suppress unstable SEI formation, but cannot completely prevent Li metal dendrite penetration. Inorganic solid-state electrolytes (SSEs) have been developed to intrinsically solve the safety issues of Li metal batteries by mechanically blocking Li metal dendrites due to their high shear moduli [12–14]. Besides, SSEs have other superior safety performances to liquid electrolytes, such as wide electrochemical windows and high thermal stabilities [15]. Various types of SSEs have been developed during the past few years, including oxynitrides, sulfides, and oxides [16–20]. Among all viable SSEs, garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) is promising for Li metal batteries due to its wide electrochemical window (0 ~ 6 V vs. Li^+/Li), high ionic conductivity (10^{-3} S/cm), and high chemical and electrochemical stabilities against Li metal [21–25]. However, one of the remaining obstacles to integrating garnet SSEs into Li metal batteries is the unstable interfacial resistance between Li and garnet while cycling. This instability can be attributed to the significant volume change at the Li metal electrode during platting and stripping [26–28]. Another challenge is the large thickness and mass of garnet electrolytes fabricated by traditional powder-sintering processes. It is difficult to reduce the thickness of garnet electrolyte below 100 μm for battery applications and processing, which both adds significant internal

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resistance and hinders the resultant volumetric energy density. Thick garnet with a density of 4.97 g/cm^3 occupies a high mass ratio in the full cell and results in a low gravimetric energy density [29].

Researchers have developed 3D frameworks for Li metal anodes from carbon [30,31], metals [10,32], and polymers [33] for batteries with liquid electrolytes, which can prevent the significant volume change for Li metal anodes. However, since liquid electrolytes are still employed, it is difficult to extend these host designs into solid-state Li batteries, and the dendrite formation and unstable SEI issues of Li metal anode remain unsolved. In this work, we developed a garnet-based asymmetric 3D framework with a porous-dense bilayer structure as a solid-state Li metal host to address the unstable anode volume and limited energy density issues of solid-state Li metal batteries. Such a bilayer structural design is promising for safe and high-energy-density Li metal batteries, as it provides not only highly conductive and continuous ionic pathways for Li-ion transport but also a mechanically and electrochemically stable and porous framework for Li metal anode. The integration of the Li metal host (porous layer) and the solid-state electrolyte/separator (dense layer) into a single slice with a high flatness on the dense side also enables easy assembly of a highly loaded $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ (NMC) cathode. The solid-state Li/bilayer-garnet/NMC batteries demonstrate stable electrochemical performances because of the firm volume of the framework and the constant resistance between Li metal and garnet. High battery energy densities can be achieved due to the optimized structure of the bilayer framework with a significant reduction in solid-state separator thickness (20 μm *vs.* 100 μm or more) and the highly loaded cathode. The bilayer garnet framework provides a promising strategy for solid-state Li metal anodes, which can be easily integrated with various types of cathode chemistries for batteries with high energy densities.

2. Results and discussions

The framework is composed of one dense layer and one porous layer which are combined by co-sintering (Fig. 1a). The two layers were fabricated by tape-casting and then sintered together into a bilayer structure, based on the similar technique to our previous work on trilayer garnet structure [34]. The porosity of the porous layer is 70%, which is realized by controlling the volume ratio of sacrificial polymer pore-formers in the tape. (Detailed fabrication information in the Methods section.) We developed a 3D Li metal anode based on the bilayer framework by infiltrating molten Li into the porous garnet at 250 °C. Zinc oxide is coated through the porous layer by atomic layer deposition before Li infiltration, as reported in our previous work, for better contact between the molten Li metal and garnet [35]. Li metal is distributed through the whole layer with continuous contact to the framework after infiltration because of the highly porous structure (Fig. 1b). The amount of Li and the infiltration time are optimized so that large empty spaces remain in the framework for full cell integration with lithiated NMC cathodes.

Based on the integrated Li metal anode, a battery can be assembled by laying a pre-made cathode film on the dense side of the bilayer framework (Fig. 1c). The ionic conductivity between garnet and the cathode is achieved by a gel interlayer, using techniques from our previous research [36]. This direct assembly strategy enables easy integration between the solid-state Li metal anode and conventional battery cathodes. Fig. 1d displays the structure of the solid-state battery with the Li metal anode hosted by the garnet framework. In the full cell, high mass loading cathodes can be integrated with the bilayer garnet framework because of the porous layer with high areal specific capacity and the Li^+-conductive gel interlayer. The highly loaded cathode and the garnet framework with an optimized structure provide high gravimetric and volumetric energy densities for solid-state batteries. Different types of cathodes can be applied together with the bilayer framework, which gives a broad practicability of solid-state electrolytes in high-energy Li metal batteries.

Fig. 2 shows the morphologies of a bilayer garnet framework by scanning electron microscopy (SEM) before and after Li metal infiltration. The thicknesses of the dense and porous layers are controlled to 20 μm and 50 μm, respectively (Fig. 2a). The dense layer without open pores effectively prevents short-circuiting and provides high chemical stability for the hosted Li metal. The dense side of the bilayer framework has a flat top surface with no defects, providing a continuous interface for the cathode (Supporting Information Fig. S1a). The porous layer with a 3D structure hosts Li metal and transports Li^+ ions between the anode and the cathode. There are open holes uniformly distributed on top of the porous layer (Supporting Information Fig. S1b), enabling Li metal infiltration into the framework. Fig. 2b exhibits the morphology of the porous garnet layer. The garnet grains are firmly sintered together to form continuous ionic pathways with high conductivity. The large empty space in the porous layer provides a high capability of Li metal in the framework. The

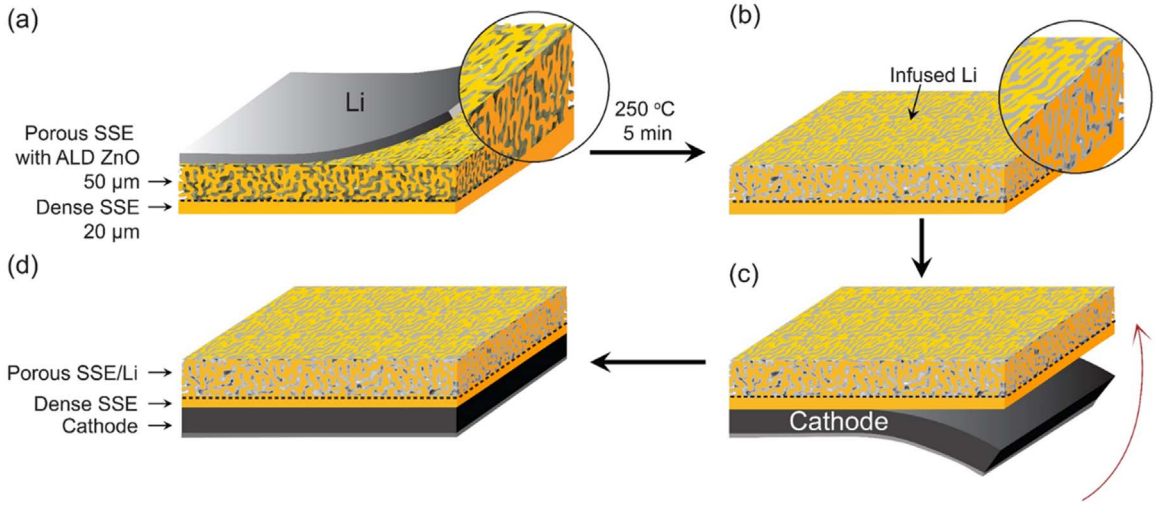

Fig. 1. Process of developing a solid-state Li metal battery based on the bilayer garnet framework**.** (a) Diagram of a bilayer garnet framework composed of a dense layer and a porous layer. The two layers are integrated together by co-sintering the precursor tapes. Li metal foil is coated on the porous side for infiltration. Zinc oxide (30 nm) is coated onto the surface of the porous framework by ALD method to help Li metal infiltration. (b) 3D Li anode based on the framework, developed by infusing molten Li metal into the porous layer. The porous layer functions as the host for Li metal, and the dense layer works as the solid-state separator between the two electrodes. (c) A battery is integrated by laying a pre-made cathode on the dense side of the bilayer garnet framework. (d) The accomplished Li metal battery based on the bilayer garnet framework. The battery is composed of the 3D Li metal anode, garnet solid-state electrolyte, and a cathode pre-made by conventional techniques.

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