Li–garnet solid-state batteries (SSBs) have attracted a great deal of attention due to their nonflammability, non-toxicity, and potential to achieve significantly higher energy and power densities compared to those of conventional Li-ion batteries. Research that began in 2007 and focused primarily on improving the Li-ion conductivity of Li-La₂Zr₂O₁₂ (LLZO) has since evolved into the development of Li–garnet SSBs, encompassing aspects of the LLZO/Li interface, the electrochemical voltage window of LLZO, and compatibility with current cathode chemistries. Nevertheless, an analysis of the literature shows that there is still no clear opinion in the research community on the configuration of future Li–garnet SSBs. In particular, opinions differ on the design of the LLZO-based anode layer that accounts for (i) the dynamic expansion and shrinkage of the Li metal (from up to 5–25 μm for the area capacity of 1–5 mAh cm⁻²) and (ii) the probability of void formation at the Li/LLZO interface.

It has been originally proposed that the problems of volume changes and void formation could be solved by the employment of the stack pressure at the LLZO/Li interface. However, the use of pressure inevitably incorporates nonactive components into the battery design and thus reduces the energy density. In addition, external stack pressure is considered a double-edged sword that can also lead to faster cell failure as the increased mechanical stress on LLZO SSE triggers crack propagation.

Recently, an alternative LLZO scaffold-type design of the anode layer has been proposed. The latter appears potent to address both problems: dynamic volume changes of the Li anode and the formation of voids. In addition, we analyze in detail other factors such as the change in current density during Li plating/stripping within the LLZO scaffold membranes compared to results for the Li host-free anode configuration based on dense LLZO membranes.

Among various possible cathode active materials (cathode-AM), this work focuses on LiNi₀·₁₀Mn₀·₅Co₀·₅O₂ (NMC) due to its high discharge voltage of 3.7 V vs Li⁺/Li and gravimetric and volumetric capacities (160 mAh g⁻¹ and 763 mAh cm⁻³). The effects of varying the thickness of the Li metal anode have also been investigated. Specifically, the configurations with 0 (anode-free), 10, and 50 μm Li metal anodes have been analyzed. As for the cathode side, the following compositions have been examined: 30–70, 40–60, 50–50, and 70–30 vol % solid-state electrolyte and NMC/CB/pVdF mixture, respectively. The choice of solid-state electrolytes is limited to Li₃P₂S₆ (LPS) and LLZO, which represent the compounds with low (ρLPS = 2 g cm⁻³) and high (ρLLZO = 5 g cm⁻³) densities. In all cases, it is assumed that there is no unoccupied pore volume. In order to assess the energy density of Li–garnet SSBs as realistically as possible, the conventional composition of the NMC/CB/pVdF mixture based on 95 wt % NMC active cathode material, 3 wt % carbon black, and 2 wt % of the pVdF binder is considered. The areal capacity of the studied cathodes is set to 3.5 mAh cm⁻². Additional parameters include the thickness of Cu, Al, and pouch-Al foils, and they are kept constant (Table S1). The gravimetric and volumetric energy densities of Li–garnet SSBs containing LLZO scaffolds. In addition, we analyze in detail other factors such as the change in current density during Li plating/stripping within the LLZO scaffold membranes compared to results for the Li host-free anode configuration based on dense LLZO membranes.

In the view of continuously strong impetus of academic and industrial research into various Li–garnet SSB configurations, herein we scrutinize the scaffold-like design, schematically shown in Figure 1. In particular, we aim to shed light on the feasibility of this approach from the gravimetric and volumetric energy density point of view, given the high density (5.1 g cm⁻³) of LLZO SSE and the significantly larger anode volume compared to a design with a fully dense LLZO membrane. We discuss the critical interplay among the thickness of the scaffold membranes, their porosity, and the theoretically achievable gravimetric and volumetric energy densities of Li–garnet SSBs.
and volumetric energy densities are calculated by considering the total weight or volume of 40 cathode/electrolyte/anode layers with credit size dimensions. The cell volume is calculated in the discharged state, i.e., the state in which the battery would be assembled. No kinetic or transport constraints have been considered in these calculations.

In Figure 2, the energy density of Li–garnet SSB based on LLZO scaffold with Li-anode-free configuration is plotted as a function of the thickness of the LLZO SSE and its porosity. The combination of LLZO thickness and porosity, allowing us to attain energy densities of 250, 275, 300, and 350 Wh kg\(^{-1}\) is shown as dashed lines. Another important curve, shown in blue, represents the minimum required combination of LLZO thickness and porosity of the porous LLZO layer. The batteries are composed of NMC (70 vol %)/SSE (30 vol %) cathodes, where SSE is based on LLZO or LPS.

Figure 2. Calculated gravimetric (a, b, d, e) and volumetric (c, f) energy densities of Li–garnet SSBs based on porous (a, b, c) and dense/porous (d, e, f) LLZO membranes vs the thickness and porosity of the porous LLZO layer. The batteries are composed of NMC (70 vol %)/SSE (30 vol %) cathodes, where SSE is based on LLZO or LPS.

side could achieve a much higher energy density of 321 Wh kg\(^{-1}\).

As to the volumetric energy densities, they are identical for batteries composed of cathodes with LPS or LLZO SSEs, since the volume of the batteries remains unchanged. Moreover, the porosity of the LLZO scaffold does not matter, since the occupied volume of the scaffold is defined only by its thickness. Interestingly, the achievable values are much higher than those for conventional Li-ion batteries (ca. 700 Wh L\(^{-1}\)), although the use of porous LLZO membranes significantly reduces the volumetric energy of LLZO SSBs. For example, with 33 μm 70% porous LLZO membranes, the volumetric energy density can reach the value of 1060 Wh L\(^{-1}\) (Figure 2c).

Next, we analyze LLZO SSBs composed of two-layer porous/dense LLZO membranes, where the dense part acts as an additional protective layer that mitigates possible cell short circuits during cell charging (Figure S1). From energy density considerations, the thickness of the dense part should be as small as possible. For instance, Figure 2 panels d–f show that employment of a 10 μm dense layer significantly decreases the energy density of Li–garnet SSBs. Specifically, the energy density of batteries composed of NMC/LLZO cathodes drops down by 27 Wh kg\(^{-1}\) (275 to 248 Wh kg\(^{-1}\)), 24 Wh kg\(^{-1}\) (260 to 236 Wh kg\(^{-1}\)), and 19 Wh kg\(^{-1}\) (240 to 221 Wh kg\(^{-1}\)) for 10 μm/33 μm, 10 μm/50 μm, and 10 μm/75 μm dense/porous LLZO membranes, respectively, at a constant porosity of the porous layers of 70% (Figure 2d). In the case of Li–garnet SSBs containing an NMC/LPS cathode and 10 μm/33 μm, 10 μm/50 μm, and 10 μm/75 μm dense/porous LLZO membranes, respectively (Figure 2e). Importantly, the use of a 10 μm dense LLZO layer significantly changes the achievable volumetric energy densities (Figure 2f). For instance, using 10 μm dense/33 μm porous LLZO membranes (with a porosity of 70% for the porous layer), one can achieve a volumetric energy density of only 975 Wh kg\(^{-1}\), which is 85 Wh L\(^{-1}\) lower than in the case without a dense layer (1060 Wh L\(^{-1}\)).

Interestingly, the employment of a Li metal anode has only a modest impact on the gravimetric energy densities (Figure S2). For example, in the case of a 10 μm Li anode, the gravimetric energy density of the Li–garnet SSB with a 33 μm thick and 70% porous LLZO membrane and an NMC/LLZO or NMC/LPS cathode only decreases by about 3–4 Wh kg\(^{-1}\) compared to that of the Li-free SSB configuration. At the same time, the use of a 10 μm Li anode significantly reduces the volumetric energy density by 82 Wh L\(^{-1}\). Further increasing the Li thickness of up to 50 μm reduces the gravimetric and volumetric energy density by about 15–20 Wh kg\(^{-1}\) and 309 Wh L\(^{-1}\), respectively. Interestingly, these data suggest that the employment of thin layers of Sb\(^{5}\), Sn\(^{31}\) or Si\(^{12}\) as alloying-type alternative anodes, might still be a feasible approach from a gravimetric energy density point of view.

Next, we analyze the dependence of the volumetric and gravimetric energy densities of SSBs on the volumetric content of solid-state electrolyte in the cathode. Figures S3–S5 show that when the SSE content in the cathode is increased, the achievable gravimetric and volumetric energy densities decrease significantly. For example, using a 33 μm thick LLZO scaffold with a porosity of 70% and NMC cathodes containing 40, 50, and 60 vol % LPS, the gravimetric and volumetric energy densities decrease to 302, 280, and 250 Wh kg\(^{-1}\) and 960, 848, and 725 Wh L\(^{-1}\), respectively. Interestingly, further increasing the volumetric content of LPS in the cathode...
leads to gravimetric energy densities much lower than 250 Wh kg\(^{-1}\). An even more drastic decrease in energy density can be expected if the volumetric content of LLZO in the cathodes is increased, considering high LLZO density (5.1 g cm\(^{-3}\)). The resulting gravimetric energy densities for 40, 50, and 60 vol % LLZO in NMC cathodes are 242, 209, and 172 Wh kg\(^{-1}\), respectively. However, despite these energy density constraints, it should also be noted that given the mediocre Li-ion conductivity of LLZO compared to that of liquid electrolytes (up to 1 mS cm\(^{-1}\) at RT), the use of high LLZO content in the cathode is mandatory to achieve high power densities. These energy/power density trade-off considerations point to severe limitations on the employment of LLZO in the solid-state cathodes for Li–garnet solid-state batteries.\(^{33}\)

Next, we analyze another key property of the porous LLZO structures: the possibility to increase the critical current density of the Li plating, i.e., the maximum current density at which Li dendrites are not yet formed. This feature is related to the fact that the actual current density applied at the LLZO/Li contact area changes dynamically when Li metal is incorporated into the porous LLZO membranes, as the LLZO/Li contact area increases. This process is schematically illustrated in Figure 3a,

![Figure 3a](image)

Figure 3. Illustration of Li plating/stripping at the Li/LLZO interface for porous and dense LLZO SSE.

where the pores are shown in the form of parallel cylinders. Although the geometric shape of the pores is highly simplified and the experimentally fabricated porous membranes have much more complex microporosity, this approach provides a qualitative estimate of the actual current density at the LLZO/Li interface during Li plating/stripping within LLZO scaffolds.

The results of these calculations are summarized in Figure 4, showing the changes in the actual current density applied to the LLZO/Li interface in the case of 50% porous LLZO membranes. The current density is plotted as a function of the pore size and the amount (thickness) of Li plated inside the LLZO scaffold. As shown in Figure 4a, the actual current density at the LLZO/Li interface is not constant but changes dynamically. At the very first moment of Li plating, the current density for 50% porous LLZO membranes is twice that of fully dense LLZO membranes (2 mA cm\(^{-2}\) vs 1 mA cm\(^{-2}\)). This is due to the twice lower LLZO/Li contact area compared to that of fully dense LLZO (Figure 3b). However, when Li is further intertwined within the LLZO scaffold up to 15, 30, and 50 \(\mu\)m, the actual current density drops drastically to 80, 40, and 25 \(\mu\)A cm\(^{-2}\) for porous LLZO membranes with a pore size of 5 \(\mu\)m (Figure 4b). For LLZO scaffolds with higher porosity and smaller pore size, the actual current densities are expected to have even lower values. The summary of achievable current densities for LLZO scaffolds with 60%, 70%, 80%, and 90% porosity can be found in Figures S6–S9. Importantly, this assessment also suggests that infiltration of metallic Li into porous membranes down to 5 \(\mu\)m, which can be implemented prior to SSB assembly, can significantly reduce the initial Li plating current density to 0.21, 0.19, 0.17, 0.15, and 0.13 mA cm\(^{-2}\) (at a set value of 1 mA cm\(^{-2}\)) for 50%, 60%, 70%, 80%, and 90% porous LLZO scaffolds (with a pore size of 5 \(\mu\)m), respectively.

**SUMMARY AND OUTLOOK**

The eventual design of the commercial Li–garnet SSB has yet to be determined. Drastic fluctuations in the volume of Li during the battery operation must be factored into the design of the cell. Although the commonly reported tests on LLZO-based symmetrical cells demonstrate relatively high critical current density, areal capacity, and cycling stability, the viability of these data for commercial solid-state battery architecture is questionable since most experiments were performed on millimeter thick pellets combined with high pressure and elevated temperature.

In this context, for addressing the issues of volume change of Li upon plating/stripping and the formation of voids at the Li/LLZO interface at high current densities, the fabrication of the battery based on self-standing porous LLZO membranes appears as a highly feasible design approach. Our calculations show that the use of LLZO scaffolds instead of dense LLZO membranes not only could serve to accommodate large amounts of Li upon plating and thus avoid cell volume variation problems but also could provide an effective avenue for mitigating the formation of Li dendrites as a consequence of the lower actual current density during Li plating.

Nevertheless, a careful analysis of the reported data points to the issues to be addressed. First, the thicknesses of the porous LLZO membranes have previously been reported mainly in the range 100–150 \(\mu\)m, rather than the 30–50 \(\mu\)m required (depending on porosity) to achieve the high energy density of >275 Wh kg\(^{-1}\). Importantly, the volumetric energy density of Li–garnet SSBs with 30–50 \(\mu\)m thick LLZO scaffolds is still very high (930–1080 Wh L\(^{-1}\)) compared to that of conventional Li-ion batteries (700 Wh L\(^{-1}\)), although the use of LLZO scaffolds creates additional volume, which reduces the overall volumetric energy density.

Another problem is the brittleness of LLZO and low fracture toughness, which might require special technological solutions...
for handling thin LLZO membranes with large dimensions and arranging them in layers. So far, research has been conducted with membranes of maximum 1 cm$^2$ size in a single layer. In this context, unlike current liquid electrolyte systems, the manufacturability and cost of the material components of such a solution are unknown, so the value of these features must be analyzed accordingly.

**ASSOCIATED CONTENT**  
* Supporting Information*  

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/accountsr.2c00004. Parameters for energy density calculations, charging process schematics, calculated gravimetric and volumetric energy densities, calculated current densities vs pore sizes (PDF)

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**Notes**  

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