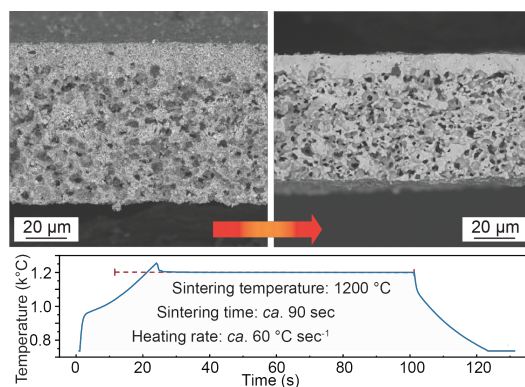


## Ultrafast-sintered self-standing LLZO membranes for high energy density Li-garnet solid-state batteries

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Towards building non-flammable and temperature-tolerant Li-ion batteries with high energy density,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) has recently attracted considerable attention as a compelling solid-state Li-ion electrolyte (SSE) due to its high thermal stability, Li-ion conductivity of up to  $1 \text{ mS cm}^{-1}$  (RT), and a wide electrochemical operation window of 0–6 V vs.  $\text{Li}^+/\text{Li}$ .<sup>[1, 2]</sup> Additionally, unlike other Li-ion soft solid conductors such as those based on sulfides, LLZO SSE can be manufactured with a bilayer dense-porous microstructure, which prevents the issues of dynamic volume change of the Li anode and the formation of voids at the Li/SSE interface during cycling and thus eliminates the need for external pressure.<sup>[3, 4]</sup> Here we report a facile, ultrafast sintering methodology for the fabrication of LLZO solid-state electrolyte in the form of self-standing bilayer dense-porous LLZO membranes. The thickness of the produced dense and porous layers was ca. 8  $\mu\text{m}$  and 55  $\mu\text{m}$ , which hypothetically allows to achieve high gravimetric and volumetric energy densities of Li-garnet batteries of  $218 \text{ Wh kg}^{-1}$  and  $769 \text{ Wh L}^{-1}$  (in combination with an NMC811/LiFSI-Pyr<sub>13</sub>FSI cathode). Electrochemical measurements confirmed that produced LLZO membranes possess high critical current density up to  $1.7 \text{ mA cm}^{-2}$  and cycling stability of over 160 cycles at a current density of  $0.4 \text{ mA cm}^{-2}$ .



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[2] Semih Afyon, Kostiantyn V. Kravchyk, Shutao Wang, Jan van den Broek, Christian Hänsel, Maksym V. Kovalenko, Jennifer L. M. Rupp, *J. Mater. Chem. A* **2019**, 7, 21299.

[3] Kostiantyn V. Kravchyk, Faruk Okur, M. V. Kovalenko, *ACS Energy Lett.* **2021**, 2202.

[4] Kostiantyn V. Kravchyk, Huanyu Zhang, Faruk Okur, Maksym V. Kovalenko, *Acc. Mater. Res.*, **2022**, 3, 4, 411-415.