

Supplementary Materials

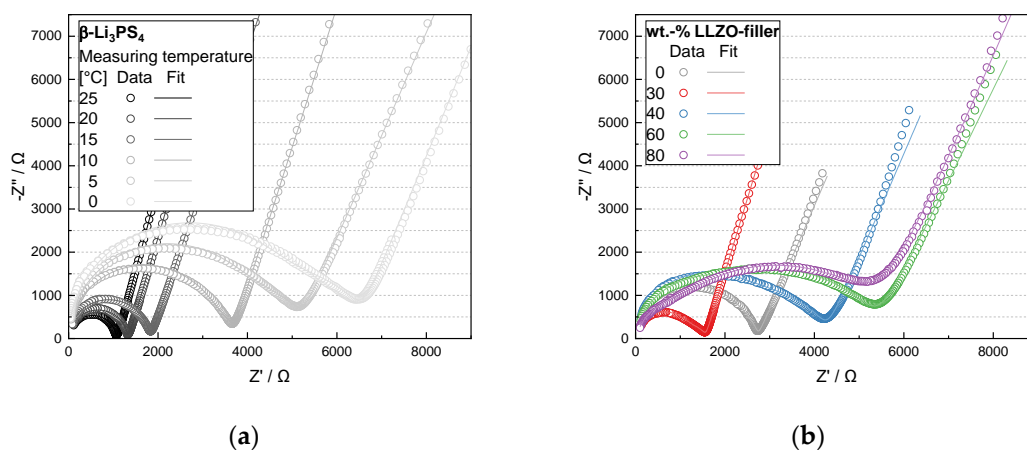


Figure S1: Nyquist plots of (a) LPS measured at different temperatures and (b) hybrid electrolyte pellets with varying LLZO filler content measured at 20 °C.

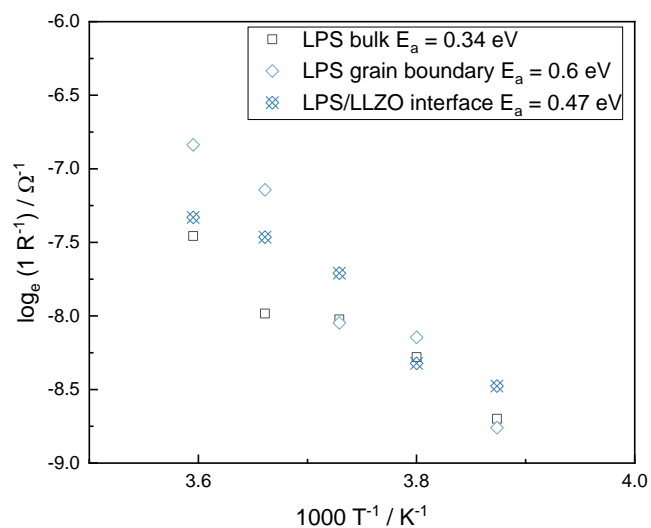


Figure S2: Transport properties of LPS hybrid electrolyte with 60 wt.-% LLZO filler. Arrhenius plot extracted from impedance data measured between 10 and 25 °C, separated into LPS bulk and grain boundary transport process as well as the LPS-LLZO interface transport process.

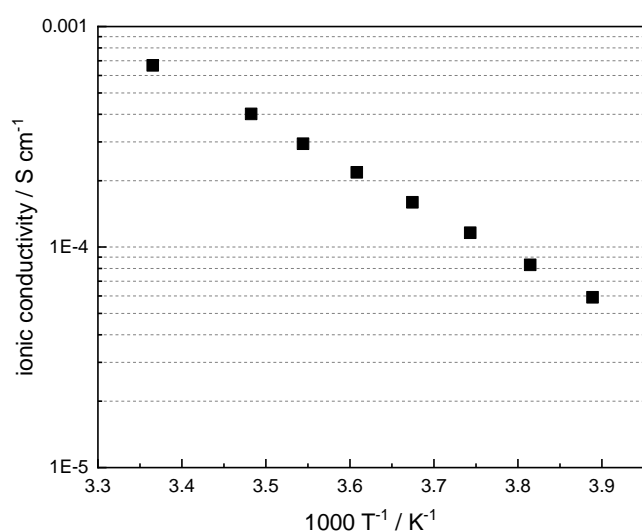


Figure S3: Ionic conductivity of LLZO pellets sintered above 1000 °C and polished by hand to achieve a good contact towards the blocking electrodes in the EIS measurement.

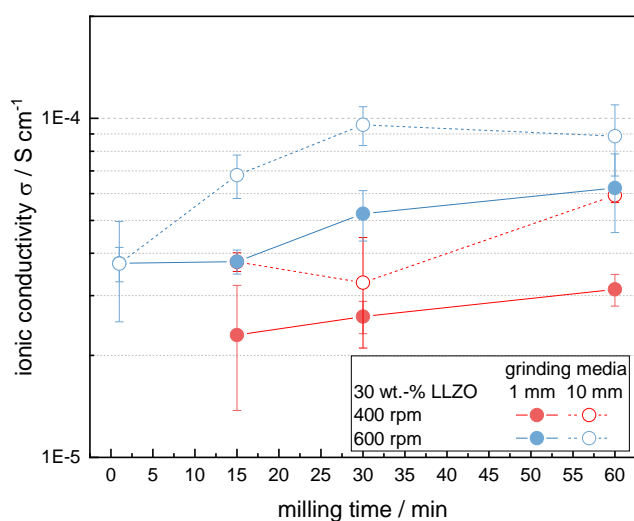


Figure S4: Ionic conductivity of LPS hybrid electrolyte pellets with 30 wt.-% LLZO filler contents processed by high-energy ball milling with ZrO_2 grinding media varying in size at 400 rpm and 600 rpm rotational speed. The increased energy input due to the higher rotational speed influences the lithium-ion conductivity of the hybrid electrolyte significantly.

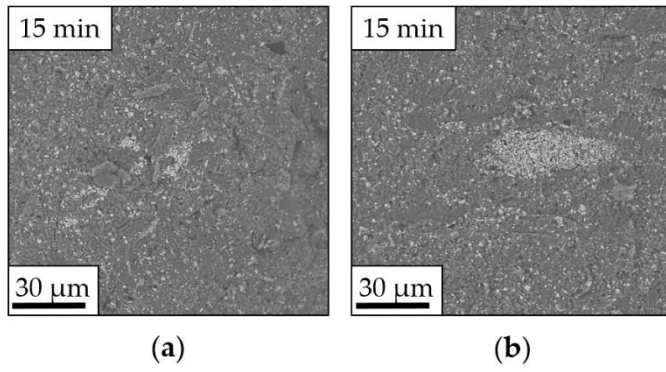


Figure S5: Microstructure of hybrid LPS with 30 wt.-% LLZO separator pellets processed by high-energy ball milling with 1 mm ZrO_2 grinding media at (a) 400 rpm and (b) 600 rpm rotational speed showing LLZO agglomerates within the LPS matrix, the light particles are the oxide compound.

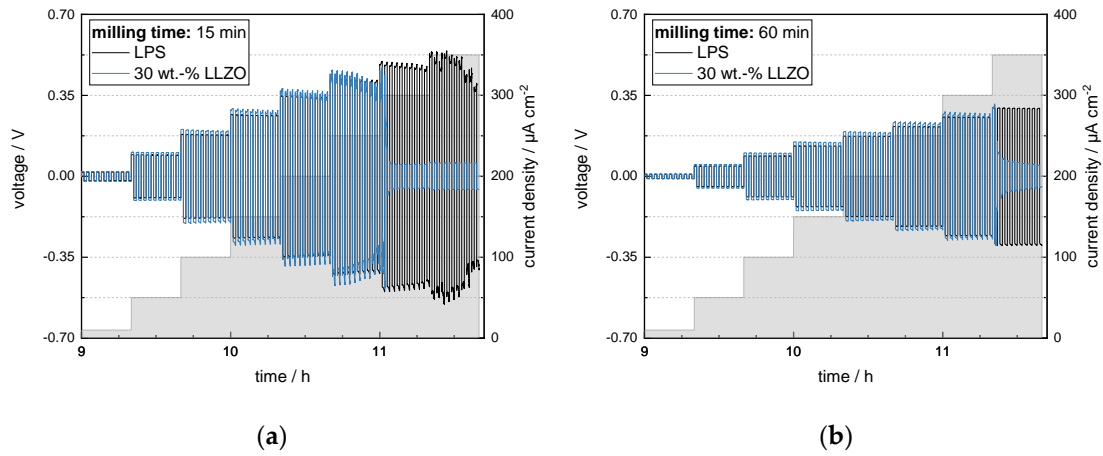


Figure S6: Critical current density of LPS hybrid electrolyte pellets with 30 wt.-% LLZO filler content processed by high-energy ball milling with ZrO_2 grinding media size of 10 mm at a rotational speed of 600 rpm. Representative samples at (a) 15 min milling time and (b) 60 min milling time. The sample of LPS after 60 min was started in a second test ranging from 100 to 800 $\mu\text{A cm}^{-2}$ and failed at 800 $\mu\text{A cm}^{-2}$.

Table S1: Ionic conductivity measured at different milling times and LLZO filler contents. Results displayed in Fig.4, 6, 10, and S4. The displayed samples were milled with a grinding media size of 10 mm and 600 rpm at 25°C unless otherwise indicated.

<i>Milling time / min</i>	<i>0</i>	<i>1</i>	<i>5*</i>	<i>15</i>	<i>30</i>	<i>60</i>	<i>60 + 5</i>
<i>LLZO filler content / wt.-%</i>	<i>Ionic conductivity / S cm⁻¹</i>						
<i>0</i>	4.1E-5 ± 2.0E-6	3.7E-5 ± 3.3E-7	2.3E-5 ± 5.1E-7	1.0E-4 ± 2.9E-5	1.2E-4 ± 1.0E-5	1.7E-4 ± 9.8E-6	
<i>10</i>						1.0E-4 ± 6.2E-6	
<i>20</i>			3.5E-5 ± 1.7E-6			1.0E-4 ± 9.4E-6	
<i>30</i>		3.7E-5 ± 4.3E-6	3.6E-5 ± 2.7E-6	6.8E-5 ± 9.9E-6	9.6E-5 ± 1.3E-5	8.9E-5 ± 2.1E-5	8.4E-5 ± 1.9E-5
<i>30**</i>				3.8E-5 ± 2.4E-6	3.3E-5 ± 1.2E-5	5.9E-5 ± 2.9E-6	
<i>40</i>			3.2E-5 ± 8.1E-7				
<i>60</i>			1.1E-5 ± 4.3E-7				
<i>80</i>			8.5E-6 ± 1.7E-6				

*20°C, **400 rpm