

Supporting Information

**Impact of Air Exposure and Surface Chemistry on the Li-Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> Interfacial Resistance**

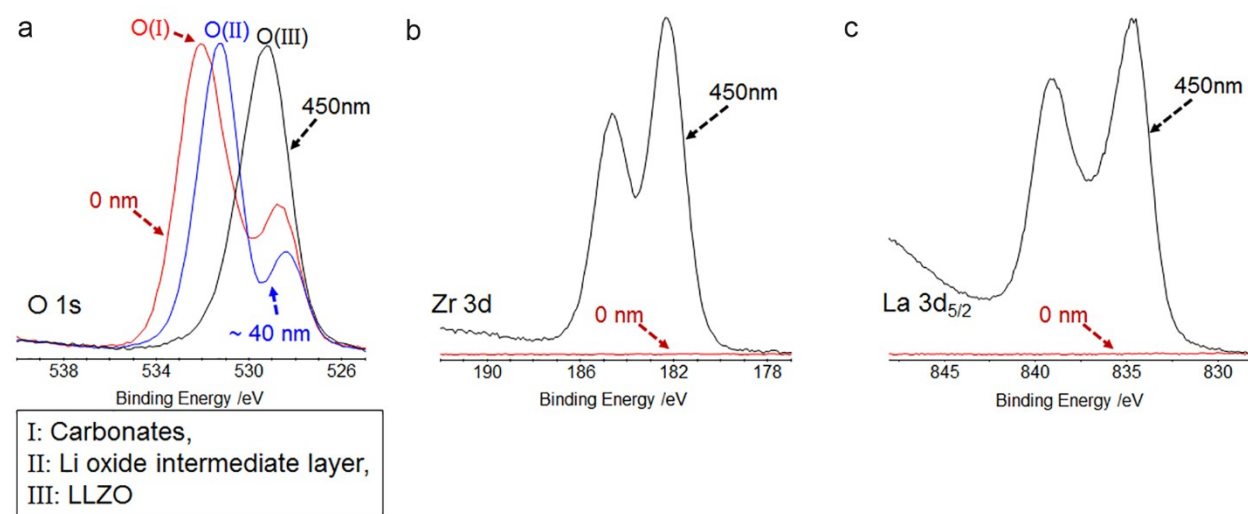
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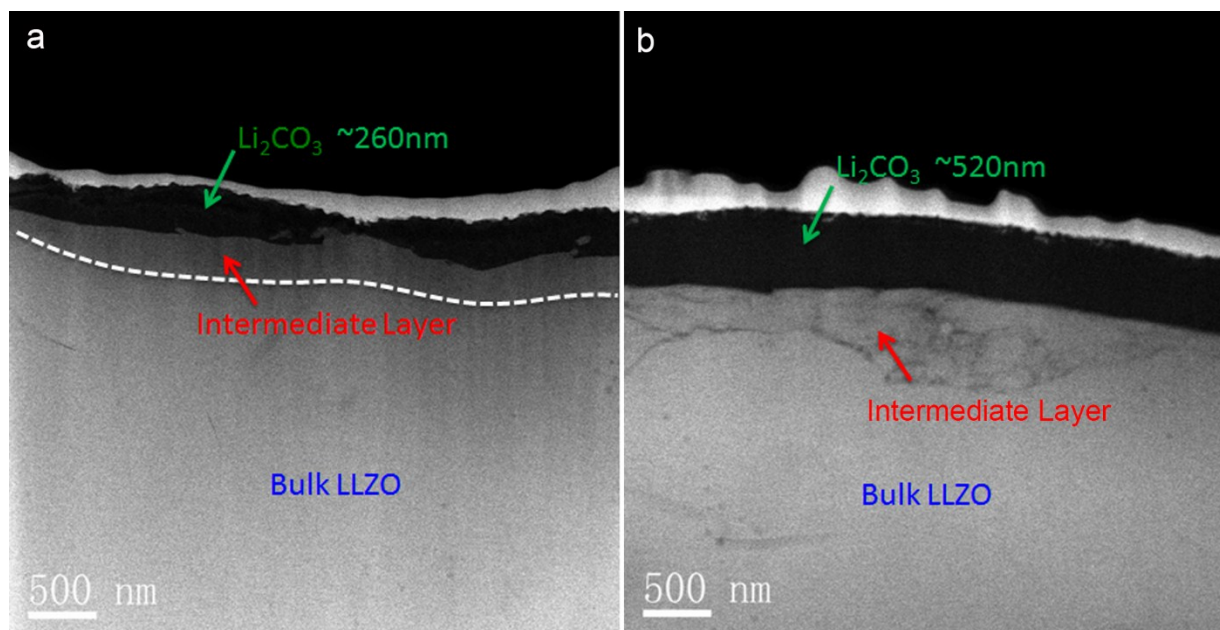
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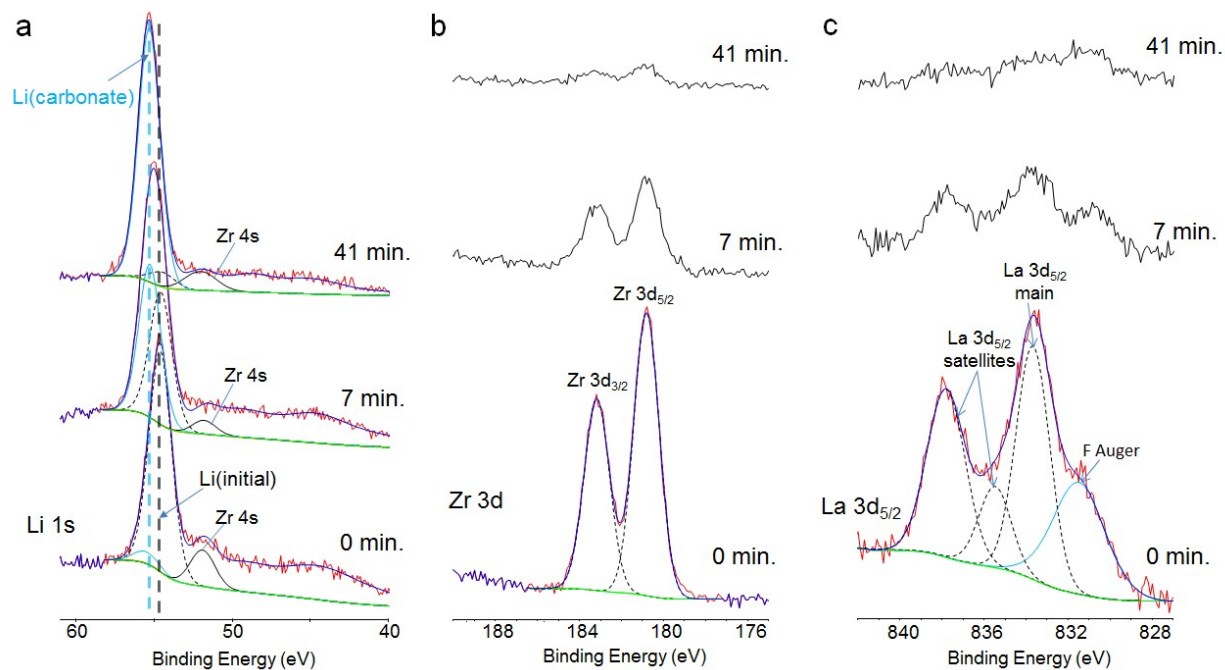
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**Fig. S1** XPS analysis of LLZO after sample preparation in ambient air. (a) O 1s and (b) Zr 3d, (c) La 3d<sub>5/2</sub> at different sputtering depths.

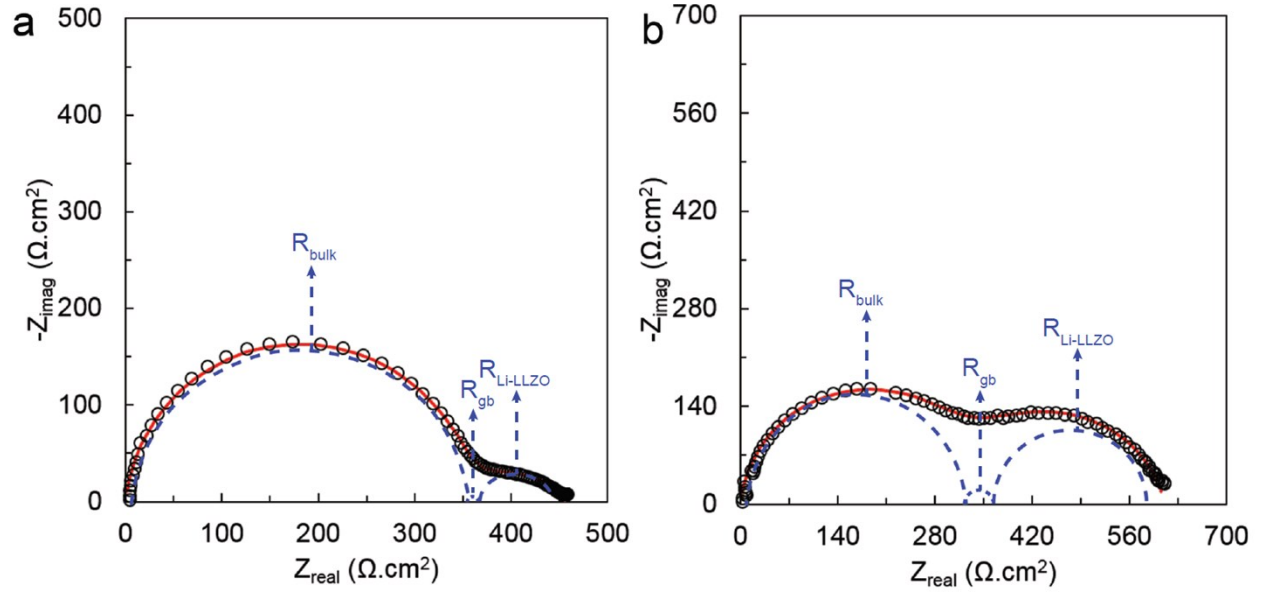


**Fig. S2** Cross sectional TEM image of LLZO pellet after (a) 120 h, and (b) 240 h air exposure to ambient air with 50 % RH (a), all the three layers (base layer, intermediate layer and dark layer) detected in LLZO after air exposure. The last layer above the dark layer is sputtered gold that was used on the exposed surface for protection.



**Fig. S3** XPS analysis of LLZO after polishing and exposure to ambient air for various exposure time (0 min to 41 min), (a) Li 1s, Zr 4s (b) Zr 3d 1s, and (c) La 3d<sub>5/2</sub>.

Based on the equivalent circuit modeling, upon exposure to air the grain boundary resistance increased, though not nearly as much as the Li-LLZO interfacial resistance. The higher grain boundary resistance could be caused by a change in grain boundary chemistry upon exposure to ambient air. Fig. S4 shows the effect of air exposure on the grain boundary resistance comparing LLZO with no exposure to LLZO after exposure to ambient air for 24 h.



**Fig. S4** Impedance spectra measured at room temperature for Li-LLZO-Li cells (a) with no air exposure, (b) after exposure to ambient air for 24 h. The open circles represent experimental data, the solid lines represent extrapolated data from equivalent circuit modeling, and the dashed semicircles represent estimated resistances of the respective transport phenomena.