

Supplementary Material

**Novel “sandwich” configuration with ALD-coating layers on electrode/electrolyte interfaces for durable all-solid-state lithium metal batteries with high-voltage cathodes**

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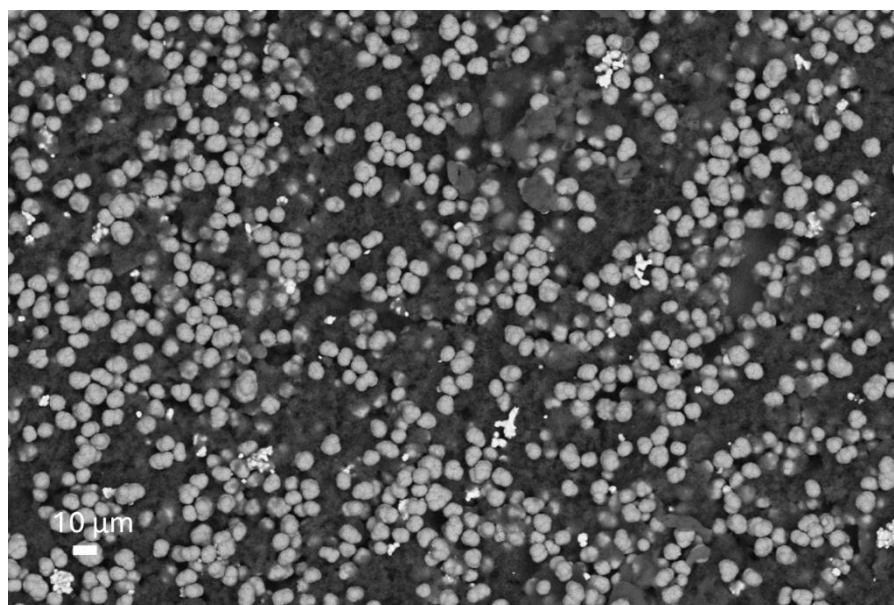
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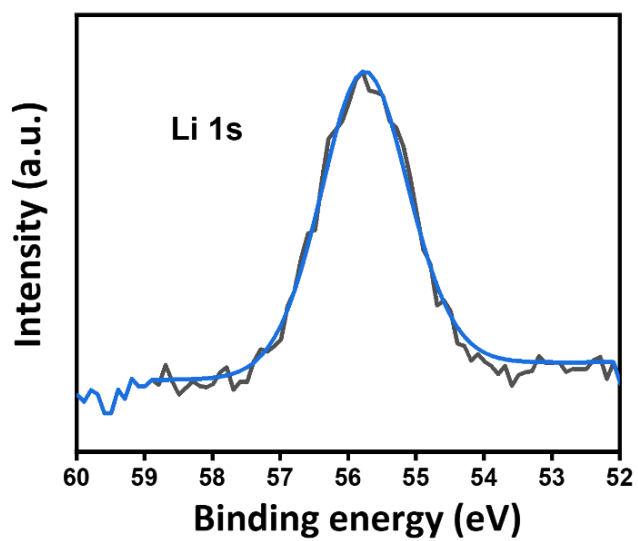
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## RESULTS AND DISCUSSION

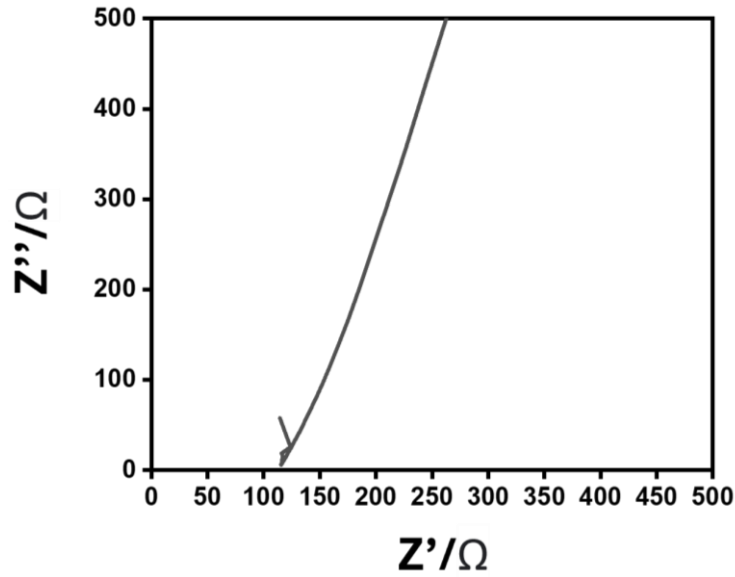


**Supplementary Figure 1.** SEM image of the uncoated NCM811 cathode.



**Supplementary Figure 2.** Li 1s XPS spectra of the LLZO/PEO/LiTFSI film.

**Supplementary Figure 2** displays the Li 1s XPS, which is contributed from both Li<sup>+</sup> in LiTFSI and LLZO, which is assigned to Figure 2.

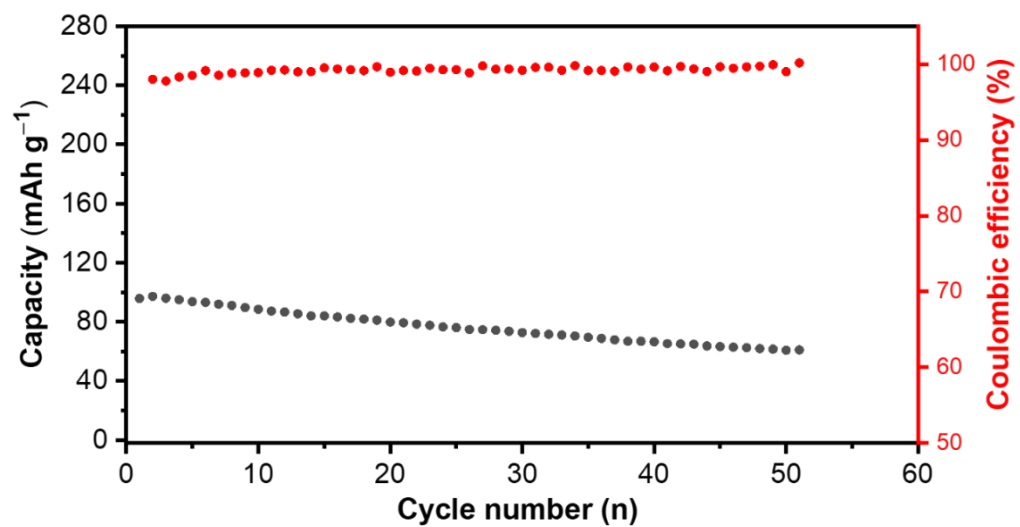


**Supplementary Figure 3.** Electrochemical impedance of the LLZO/PEO/LiTFSI film carried out at 50 °C.

The ionic conductivity is acquired from the electrochemical impedance spectroscopy (EIS) at 50 °C as displayed in **Supplementary Figure 2**. According to the formula:

$$\sigma = L / (R_b \times A) \quad (S1)$$

as presented in EXPERIMENTAL SECTION, the active area (A) is 0.0314 cm<sup>2</sup>, R<sub>b</sub> is 105 Ω, the thickness (L) is 100 μm, thus the calculated ionic conductivity (σ) is 1.28×10<sup>-4</sup> S/cm.



**Supplementary Figure 4.** Cycling performance of LMA-Alucone|LLZO/PEO/LiTFSI|Alucone-NCM811 at 0.2 C at room temperature.