Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Dual Protective Layer on Lithium Metal Anodes for Improved Electrochemical Performance – In-Depth Morphological Characterization

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Experimental: Raman spectroscopy

Raman spectroscopy was performed on a LabRAM HR Evolution Raman spectrometer (Horiba Scientific). The following parameters were used for all measurements. A green laser (Nd:YAG, 532 nm) with a 5% laser intensity (corresponding to 1.5 mW), a 50x long distance objective (Olympus), a grating of 300 gr mm^{-1}, in a range of 3000 $cm^{-1} \geq \nu \geq$ 100 cm^{-1}. The acquisition time was set to 30 s with an accumulation of 5 s.

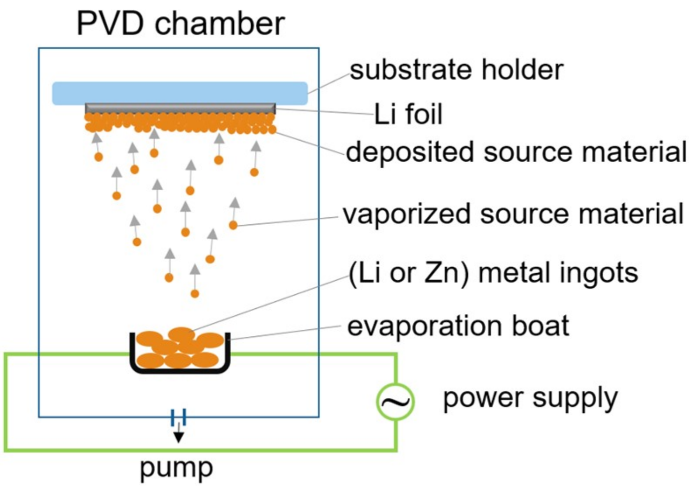

Figure S1: Schematic illustration of the PVD chamber. Interchangeable tungsten or tantalum boats are installed at the bottom of the chamber for the respective Li or Zn metal to be vaporized. Li metal foil at the substrate holder is coated with the vaporized source material.

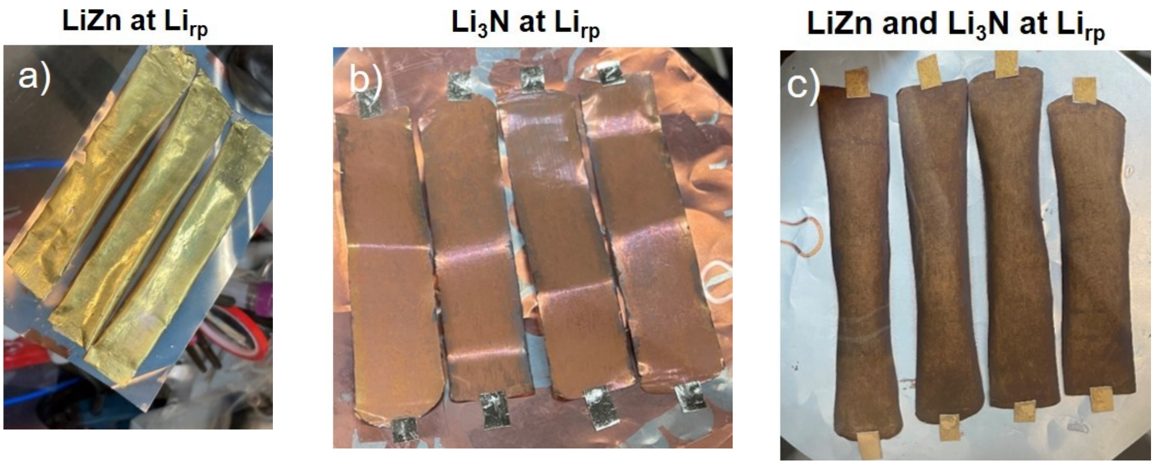

Figure S2: Optical images after thermal evaporation to form a) LiZn at Li_{rp} b) Li_3N at Li_{rp} and c) LiZn and Li_3N at Li_{rp} (dual layer, LZLN). The images were taken inside an argon-filled glovebox.

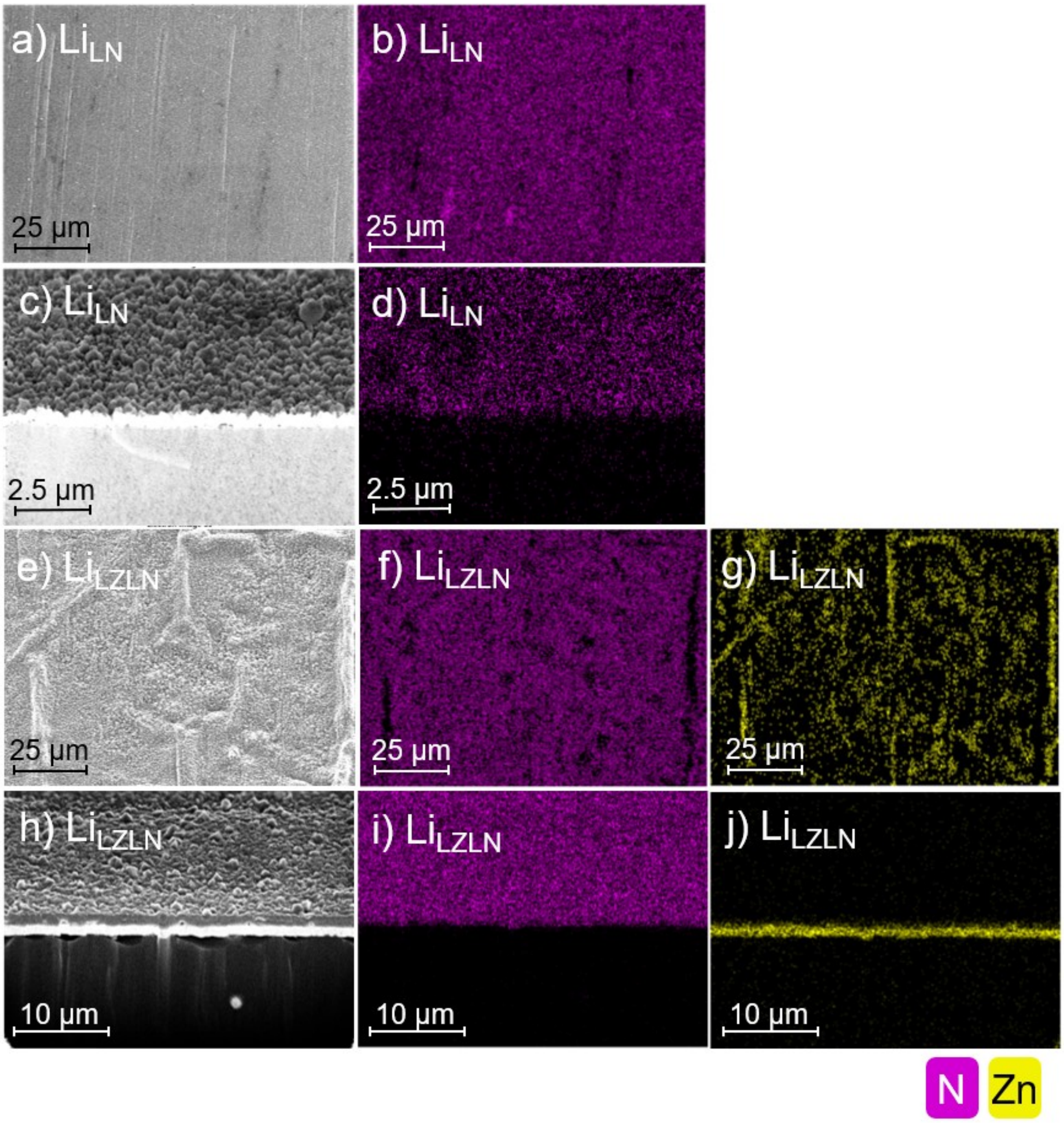

Figure S3: SEM images and corresponding elemental mapping of a-d) Li_3N layer on Li_{rp} and e-j) LZLN on Li_{rp} before cycling. a-b) Top-view and c-d) cross-section image of the Li_3N layer on Li_{rp}. e-g) Top-view and h-j) cross-section image of the LZLN layer on Li_{rp}.

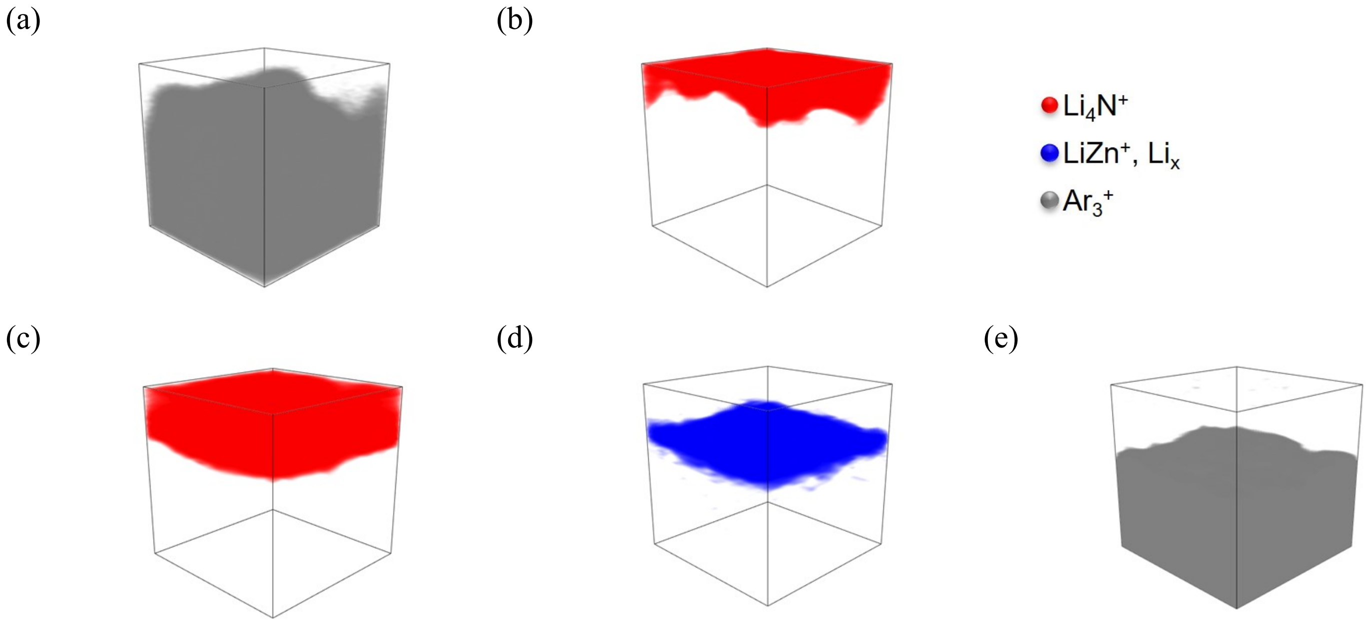

Figure S4: 3D reconstruction of corresponding ToF-SIMS depth profiles in an area of 100 x 100 μm^2 from a-b) Li_3N at Li_{rp} and c-e) LZLN at Li_{rp}. Individual spatial distributions of selected secondary ions are marked in red: Li_4N^+, blue: $LiZn^+$ and Li_x (x = 7-9) and grey: Ar_3^+. The multicolor overlay is represented in Figure 3.

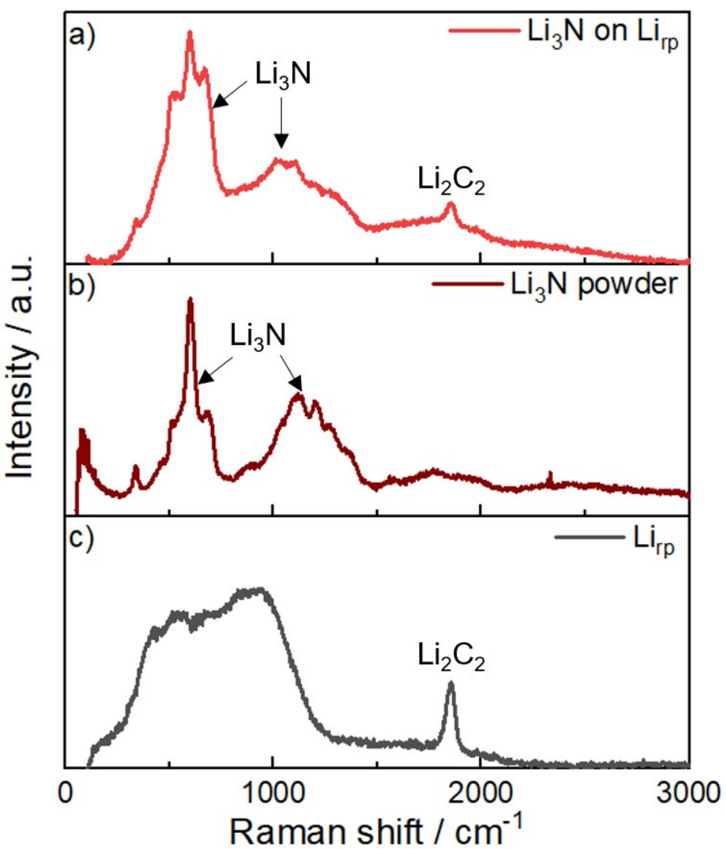

Figure S5: Raman spectra of (a) Li_{rp} coated with 100 nm Li via thermal evaporation and subsequent reaction with N_2 in the PVD chamber, (b) Li_3N powder and (c) Li_{rp} as reference.

Table S1: Cycle number of symmetric cells with Li_{rp}, Li_{LN} or Li_{LZLN} negative electrodes at the cut-off voltage (±1.5 V) for different current densities.

Current density	**Li_{rp} || Li_{rp}**	**Li_{LN} || Li_{LN}**	**Li_{LZLN} || Li_{LZLN}**
0.5 mA cm^{-2}	484	600	770
1.0 mA cm^{-2}	200	290	360
2.0 mA cm^{-2}	102	110	145

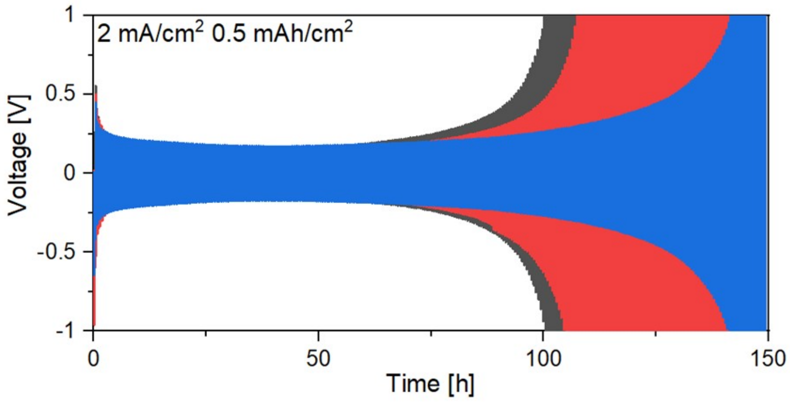

Figure S6: Galvanostatic cycling at a fixed current density of 2.0 mA/cm^2 with a capacity of 0.5 mAh/cm^2 of Li_{rp} (grey), Li_3N (red) and LZLN symmetric Li || Li cells.

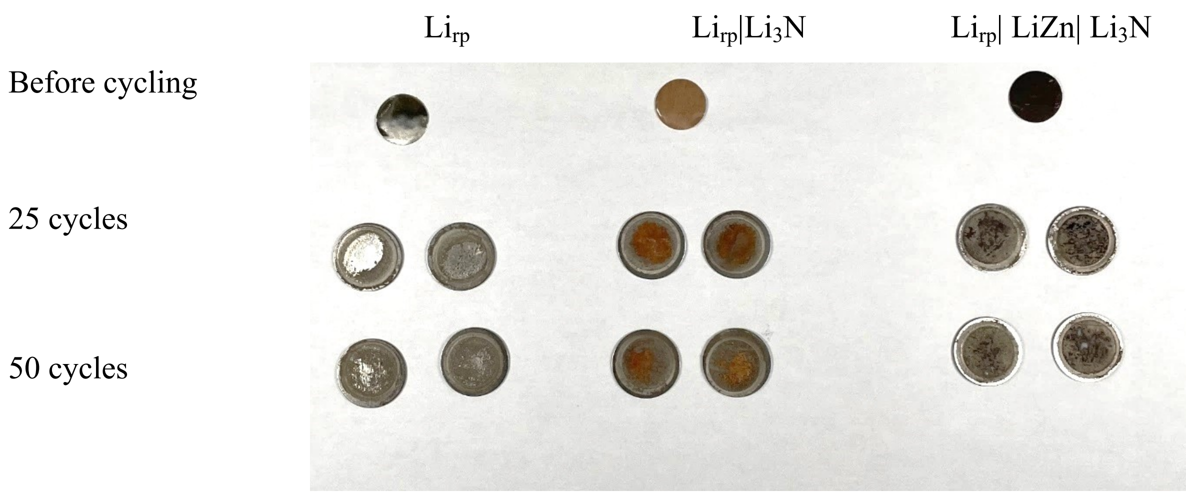

Figure S7: Optical images of Li_{rp}, Li_3N and LZLN before cycling and after 25 and 50 cycles. Cell disassembly, washing with dimethyl carbonate and photo capturing were pursued in the dry room.