Supporting Information

In situ Observation of Lithium Metal Plating into Sulfur-based Solid Electrolyte for All-solid-state Batteries

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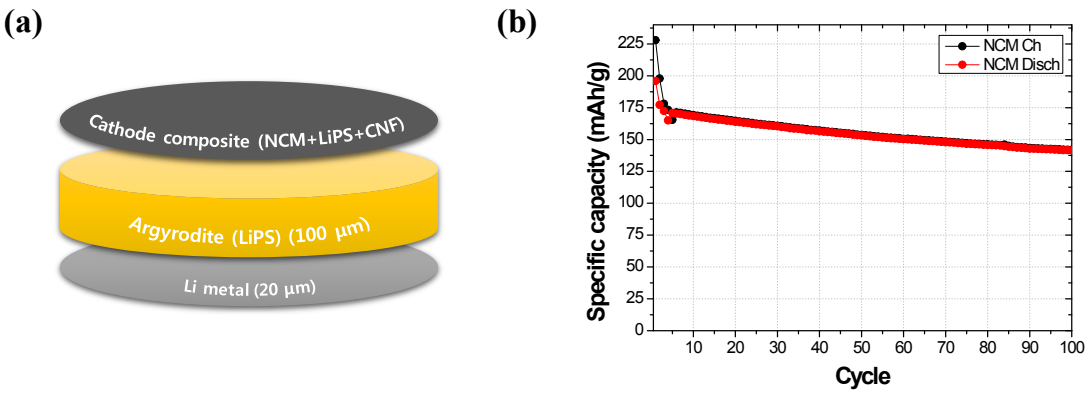

Figure S1. (a) Schematic of the NCM/LiPS/Li ASSB cell structure, and (b) cycle performance result of NCM/LiPS/Li ASSB cell at a charge/discharge rate of 0.22/0.35 C at 25 ℃. (Initial 4 cycles were performed at discharge rates of 0.033, 0.22, 0.35, and 0.7 C and a charge rate of 0.066 C.)

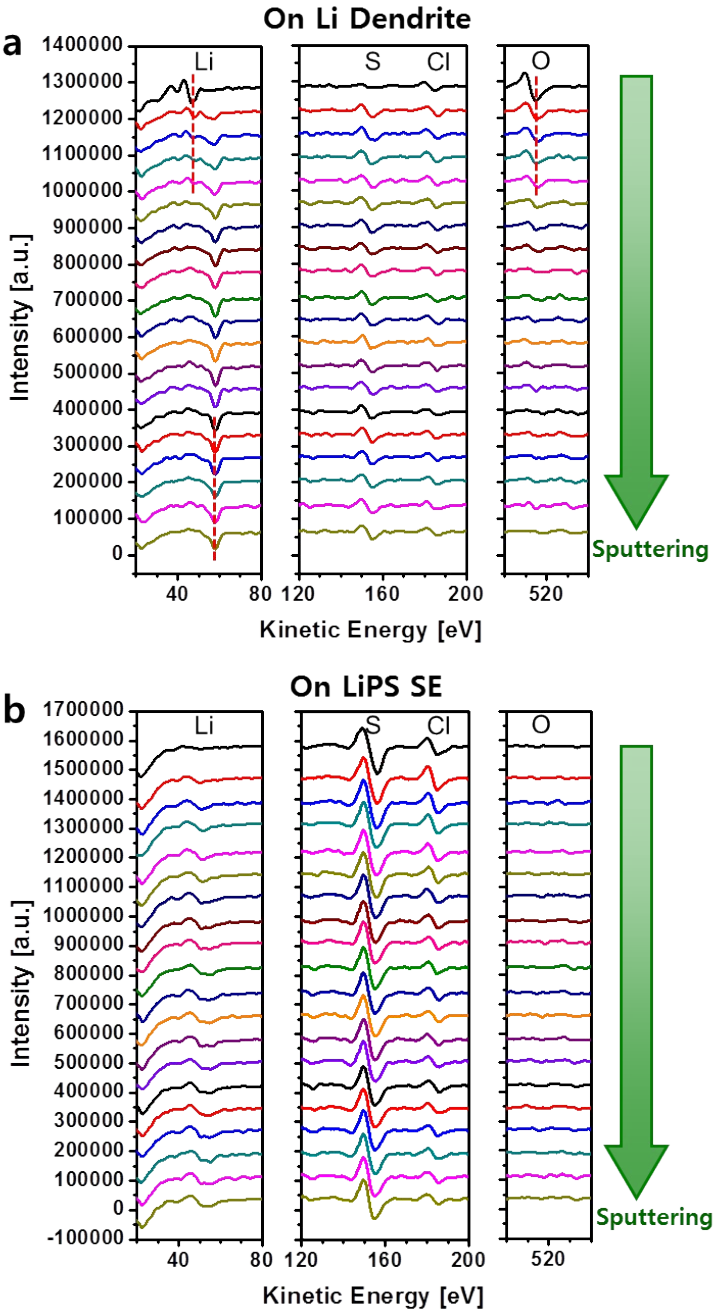

Figure S2. (a), (b) AES depth profiles acquired on the Li dendrite (A) and on the LiPS (B) regions, respectively, in Figure 4(f). The sputtering was performed with an Ar^+ beam voltage of 2 kV and a raster scan size of 1 mm × 1 mm. The time interval between two adjacent spectra is 2 min.

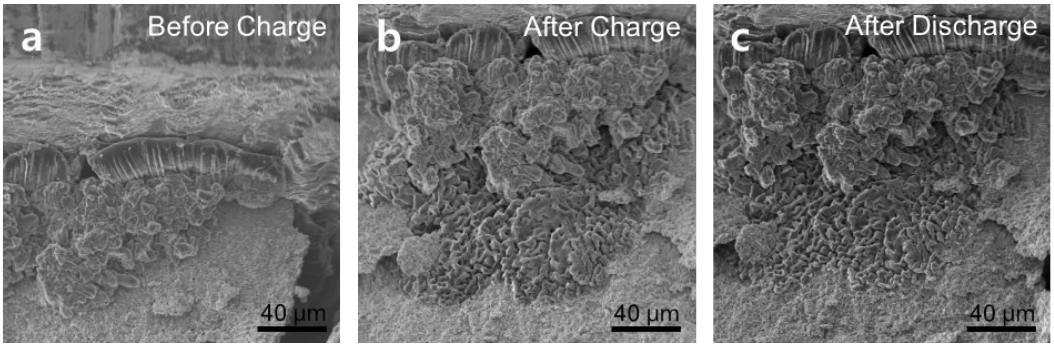

Figure S3. Series of cross-sectional SEM images for the NMC/LiPS/Li ASSB sample during the second charge/discharge cycle. (a) Before, (b) after the charge and (c) after the discharge process.

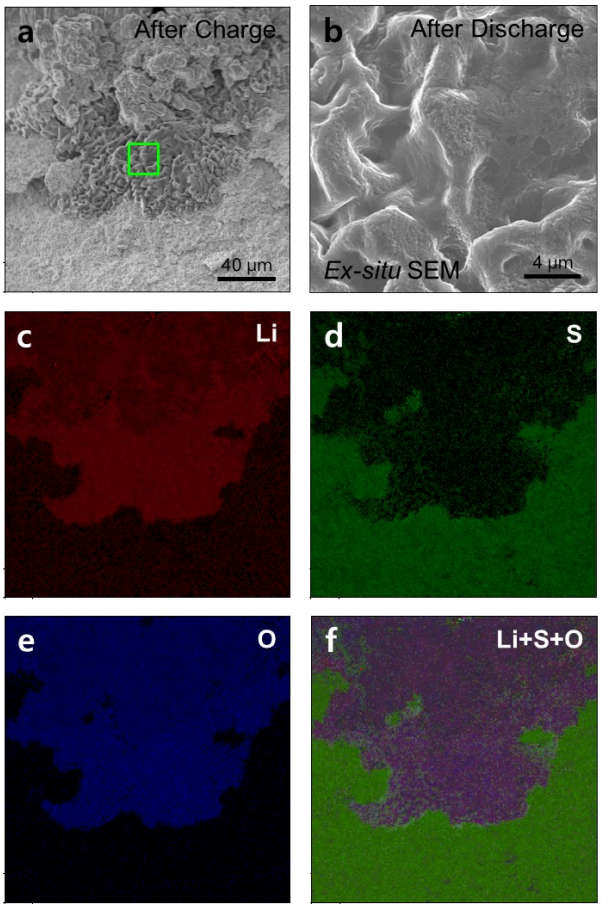

Figure S4. (a) SEM image of the NMC/LiPS/Li ASSB sample after the charge process. (c), (d), (e), (f) Corresponding elemental maps. (b) *Ex situ* high-resolution SEM image for the area indicated by the green rectangle in (a).

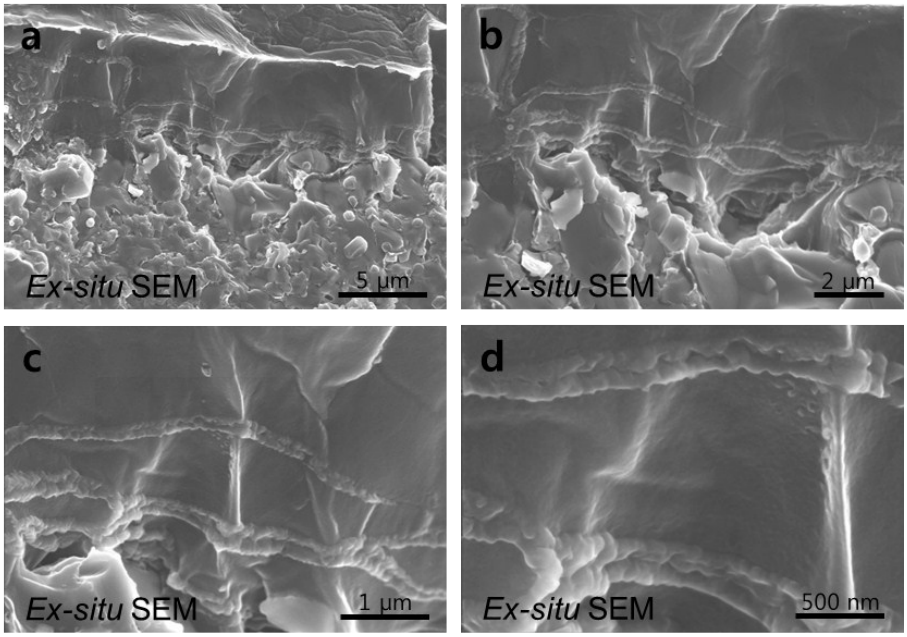

Figure S5. SEM images with increasing magnifications for the narrow cracks formed on the surface of the Li metal anode.

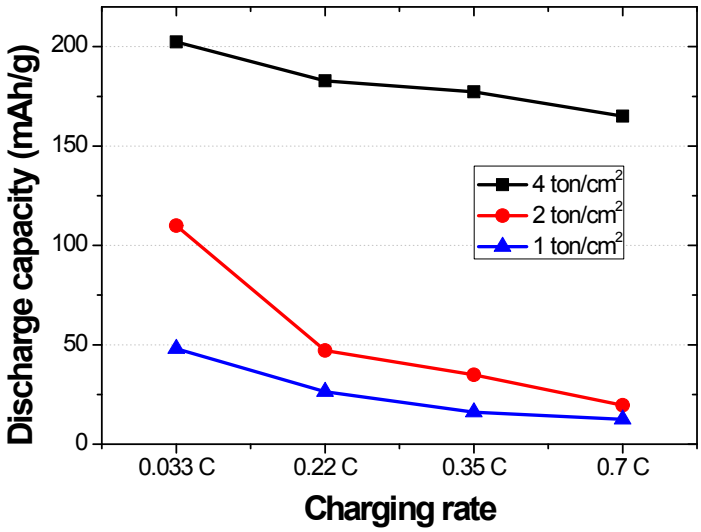

Figure S6. Rate capability of the NCM/LiPS/Li ASSB cell with various cell pressures (1, 2, and 4 ton/cm^2).

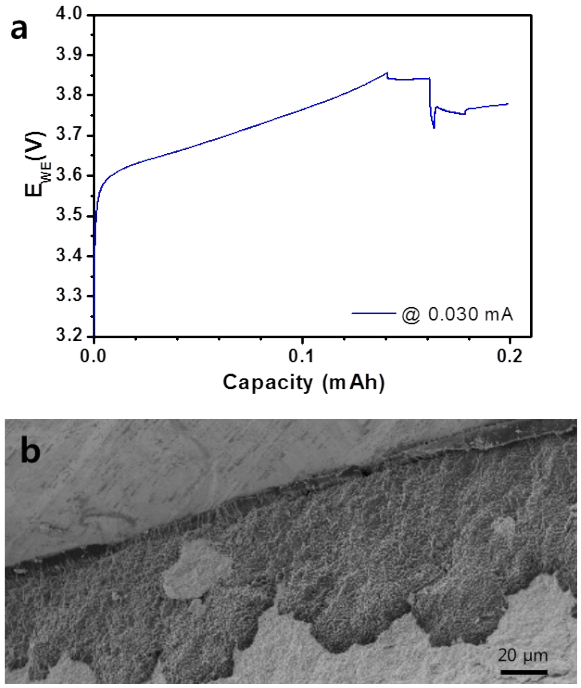

Figure S7. (a) Electrochemical charge result after repeated charge/discharge cycles in the *in situ* AES/AEM setup, which shows the typical failure of the charge process due to the electrical short circuit. (b) SEM image showing a considerable Li dendrite growth on the short-circuited sample in (a).