SUPPORTING INFORMATION

Nano-scaled Degradation Analysis of Sulfide Solid Electrolyte Around Cycled Cathode Material by STEM-EELS Technique

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Method S1.

Sulfide solid electrolyte (SSE) with a composition of Li3PS4 was prepared by mechanochemical milling in a ball mill (PL-7, Fritsch Ltd., Germany).4 The starting materials of Li2S (1.38 g, Furuuchi Chemical Ltd., Japan) and P2S5 (2.22 g, Merck Ltd., Germany) were placed in a zirconia vessel (internal volume: 80 ml) containing zirconia balls (diameter: 5 mm, total amount: 106 g) and dehydrated heptane (11.7 ml, FUJIFILM Wako Pure Chemical Ltd., Japan), and Li3PS4 coarse powder was formed by mechanochemical milling for 20 h at a rotation speed of 500 rpm. Then, the Li3PS4 coarse powder (2 g) was placed in a zirconia vessel (internal volume: 80 ml) containing zirconia balls (diameter: 1 mm, total amount: 80 g), dehydrated heptane (26 ml) and dibutyl ether (0.5 ml, FUJIFILM Wako Pure Chemical Ltd., Japan), and Li3PS4 fine powder was formed by mechanochemical milling for 20 h at a rotation speed of 200 rpm. Pellet-type half-cells were prepared in the following manner: First, a separator layer was formed by uniaxial compression of the SSE coarse powder at a pressure of 31 MPa. A mixture5 of a LiNbO3-coated6 Li(Ni0.8Co0.1Mn0.1)O2 cathode active material (140 mg), finely-ground SSE5 (60 mg) and a conductive material powder (acetylene black, 10 mg, Kishida Chemical Ltd., Japan) with a weight ratio of 66.6 : 28.6 : 4.8 was formed as a cathode electrode layer by pressing on one side of the separator layer at 216 MPa. Finally, a Li foil (thickness: 100 µm, diameter: 8 mm, Nilaco Ltd., Japan) and an In foil (thickness: 200 µm, diameter: 4 mm, Honjo Metal Ltd., Japan) were attached to the opposite side of the separator layer by pressing at 92 MPa. All processes were performed in a dry Ar atmosphere.

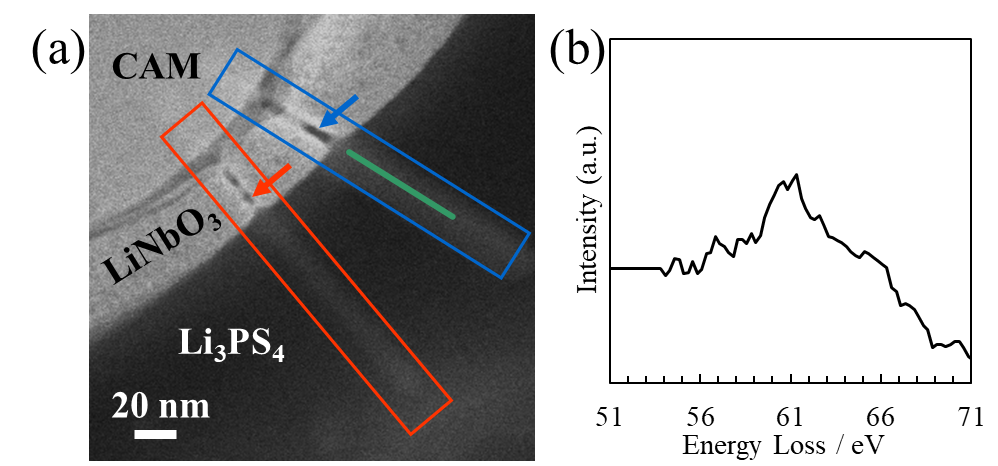


Figure S2. (a) ADF STEM image of degraded cell after EDX and EELS analysis. The red rectangle corresponds to the data acquisition area in Fig. 2 and Fig. 3, and the blue rectangle shows the line-scanning area for the EDX and EELS analysis. The green line corresponds to the acquisition location of the Li K-edge EEL spectrum after background subtraction, as shown in (b). The analysis conditions for the bule rectangle were the same beam current and accumulation time as in Fig. 2 and Fig. 3, but the scanning pitch was set to 1 nm. The SSE remained in the red and bule rectangle. The traces of the EDX and EELS analysis in the LiNbO3-coat were observed. The damage of the SSE by electron beam irradiation was less than the damage of the LiNbO3-coat. At the 1 nm scanning pitch (bule arrow), a clear hole was observed and the intensity of the Li K-edge EEL spectrum in (b) was low. It is suggested that the too-narrow scanning pitch increased the current density in the electron irradiation area and the higher current density caused drilling of the LiNbO3 and knock-on of lithium in the SSE.

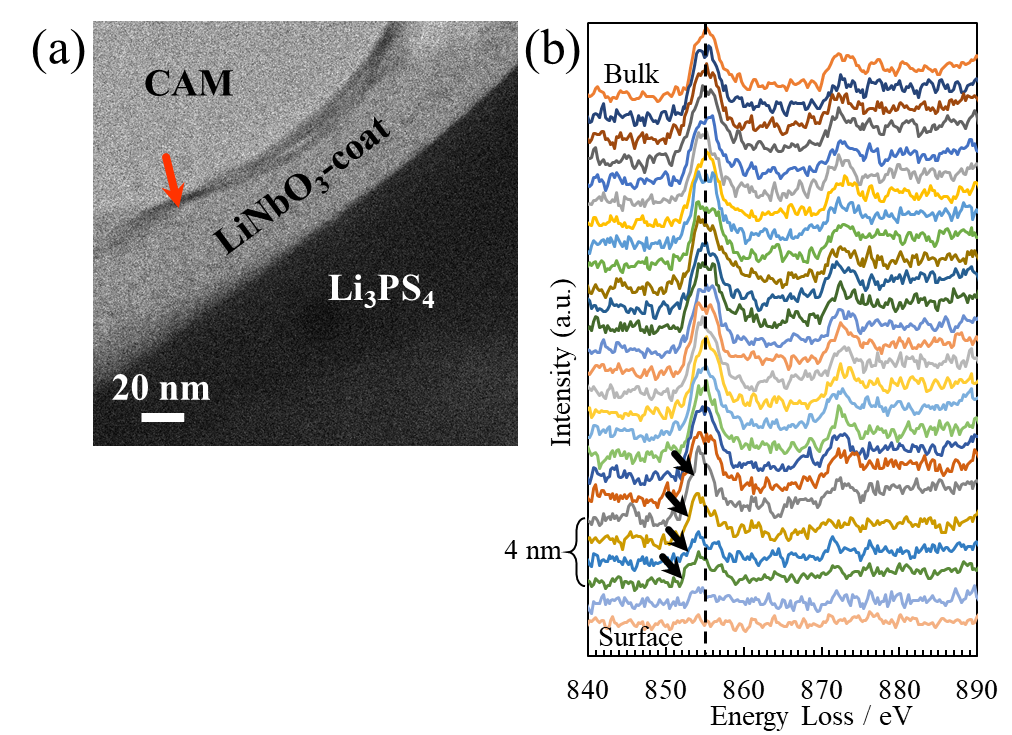


Figure S3. (a) ADF STEM image and (b) Ni L-edge EEL spectra after background subtraction for the degraded cell. The red arrow in the ADF image shows the position of the EELS analysis. The EELS data were acquired with a scanning pitch of 1 nm. The Ni L-edge spectra in the surface region shows that the peak positions shift to the low energy loss side. This peak shift indicates reduction of nickel. Using STEM-EELS, a previous study18 reported that nickel reduction of bare Li(Ni0.8Co0.1Mn0.1)O2 as a CAM in sulfide-based all-solid-state batteries was widely observed. Compared to that study18, a short nickel reduction region was observed in our study. It is thought that the LiNbO3-coat prevents reduction of nickel in the charge/discharge cycle.

**References**

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