Unravelling the Chemistry and Microstructure Evolution of a Cathodic Interface in Sulfide-Based All-Solid-State Li-Ion Batteries

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Experimental Section

Preparation of NMC-LGPS cathode composites: Commercial NMC811 with/without ALD $LiNbO_x$ coating are selected as cathode active materials. Detailed synthetic process of ALD $LiNbO_x$ thin film was reported in our previous studies.[1] As-prepared NMC811, LGPS (99.95%, MSE supplies, LLC) and acetylene black (AB) at a weight ratio of 65:30:5 were mixed to obtain the NMC811-LGPS cathode composites.

All solid-state Li-ion cell assembly: LGPS powder (65 mg) was firstly pressed under 240 MPa with 10 mm diameter to form a pellet. The cathode composite powder (10 mg) was then uniformly spread onto the surface of the LGPS electrolyte and pressed under 360 MPa to form a two-layer pellet. Finally, indium foil was put successively onto the other side of the pellet with Cu foil and pressed together. The three-layered pellet was sandwiched between two stainless-steel rods as current collectors for both positive and negative electrodes. For the In-LGPS-In battery, the LGPS electrolyte was pressed under 360 MPa firstly. After that, indium foil was put onto both side of the LGPS pellet with Cu foil and pressed together. For operando synchrotron XANES studies, custom designed coin cells CR-2032 with a 5 mm hole opening on the cathode side is employed. A polymer thin film covers the coin and allows for beam penetration. To assemble the all-solid-state battery in coin cell, the formed three-layered pellet should be dropped out from the pellet pressing model cautiously to avoid the break of pellet. The pellet was then added stainless steel spacers as current collectors at two sides (the spacer at cathode side has 5 mm hole in the center) and sealed in coin cell compactly. All the processes were performed in an Ar-filled glove box.

Electrochemical characterization: Charge-discharge characteristics were galvanostatically tested in the range of 2.0 V-3.8 V, corresponding to 2.6 V and 4.4 V vs. Li/Li^+, under 0.1 C at room

temperature using a multichannel battery tester (LAND CT-2001A, Wuhan Rambo Testing Equipment Co., Ltd.). Cyclic voltammograms were collected on a versatile multichannel potentiostation 3/Z (VMP3) using a scan rate of 0.1 mV s^{-1} between 2.0 V-3.8 V. Electrochemical impedance spectroscopy (EIS) was also performed on the versatile multichannel potentiostat 3/Z (VMP3) by applying an AC voltage of 10 mV amplitude in the 7000 kHz to 1000 mHz frequency range.

Physical characterization: Morphology and microstructure of NMC811 cathodes and LGPS SSEs before cycling were characterized using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive spectrometer (EDS), and high-resolution transmission electron microscopy (HRTEM) (JEOL 2010 FEG). The morphology and microstructure of NMC811 cathodes after cycling were checked by focused ion beam (FIB, Helios NanoLab 460HP, FEI)/FESEM (FE-SEM; JEOL JSM-7001F) for a detailed structural analysis. The FIB technique can cut samples and expose the cross sections of samples. The obtained FIB samples were further investigated by aberration-corrected scanning transmission electron microscopy (STEM, Titan Cubed Themis G2 300) and EELS (Enfinium ER Model 977). To avoid contamination of samples, the NMC-LGPS particles after cycling are scratched from the pallet and sealed in a glovebox under Ar firstly, and subsequently transferred to the corresponding techniques quickly for further measurements. The crystalline structure of as-prepared cathodes and SSEs are conducted via X-ray diffraction system (XRD) (Bruker D8 Advance, Cu K α X-ray source).

Synchrotron-based X-ray absorption spectroscopy measurement: Synchrotron-based X-ray absorption near edge structure (XANES) was carried out at the Canadian Light Source (CLS). S, Ni, Mn, and Co K-edge XANES was collected using fluorescence yield mode using a Si crystal on the Soft X-ray Microcharacterization beamline (SXRMB) at CLS. For ex-situ XANES

experiments, raw NMC811 powder, LGPS powder, and as-prepared pellets before and after battery testing were prepared in a vacuum environment prior to synchrotron measurements. To avoid sample oxidation, the samples are firstly sealed by Mylar polymer thin film in a glovebox under Ar, and subsequently transferred to the corresponding beamline for further measurements. For operando synchrotron studies, an ambient table setup was used at the SXRMB beamline. The chamber was filled with helium gas to reduce scattering at low energies. Charge-discharge characteristics of operando cells were galvanostatically tested at 0.05 C in the range of 1.9 V-3.8 V (V vs. Li-In) at room temperature using a LAND Battery Test. The XANES measurements have been done at the shortest time around 10-20 min scans with good quality data at SXRMB beamline.

REFERENCES

(1) Wang, B.; Zhao, Y.; Banis, M. N.; Sun, Q.; Adair, K. R.; Li, R.; Sham, T.-K.; Sun, X. Atomic Layer Deposition of Lithium Niobium Oxides as Potential Solid-State Electrolytes for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2018,** *10,* 1654-1661.

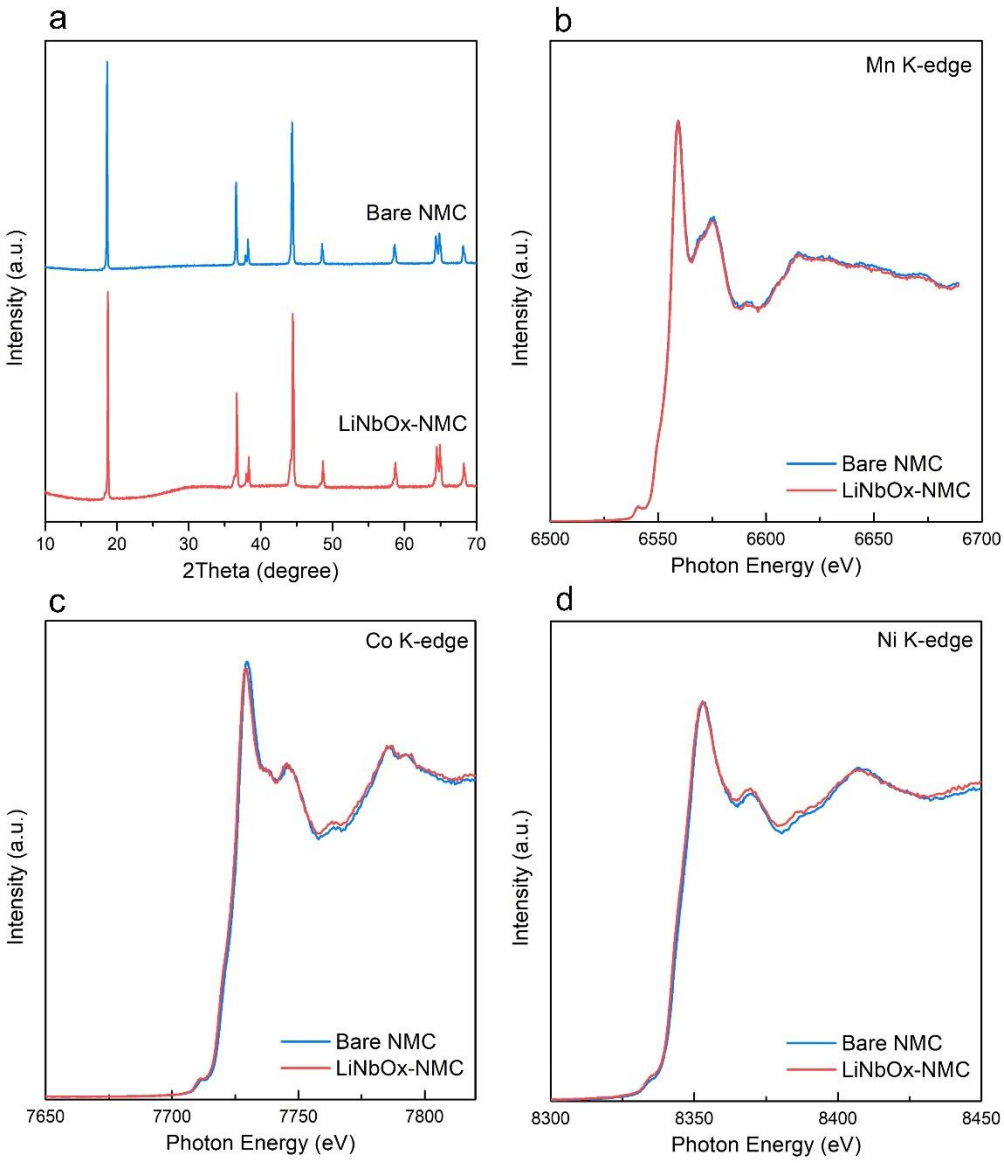

Figure S1. Physical characterizations of bare and LNO coated NMC811 composites. (a) XRD patterns; (b-d) Mn, Co, and Ni K-edge spectra.

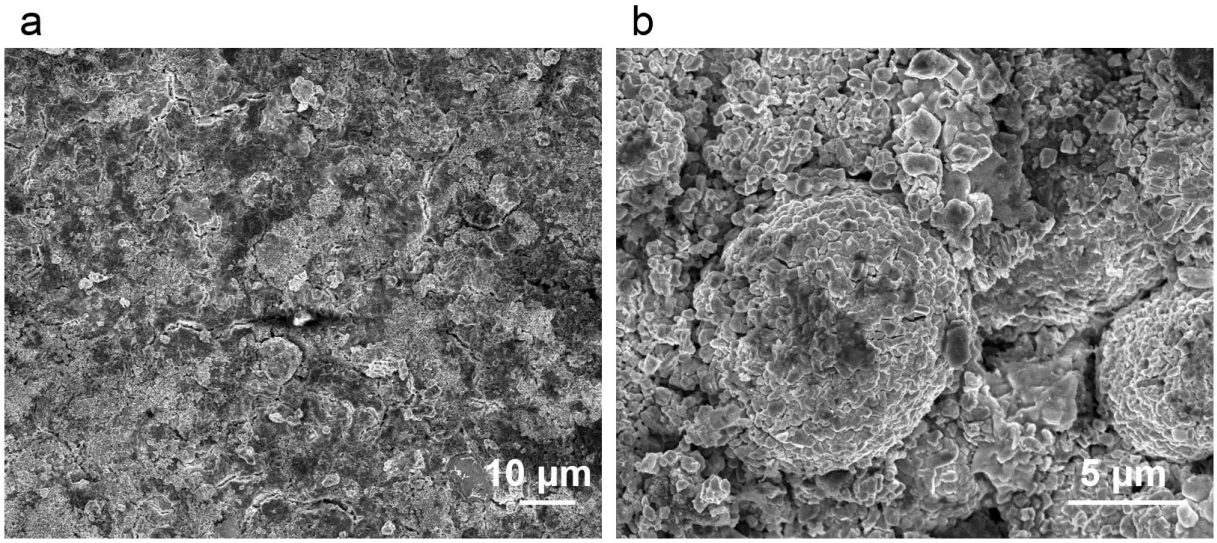

Figure S2. SEM images of the top view of the pressed NMC811-LGPS pellet.

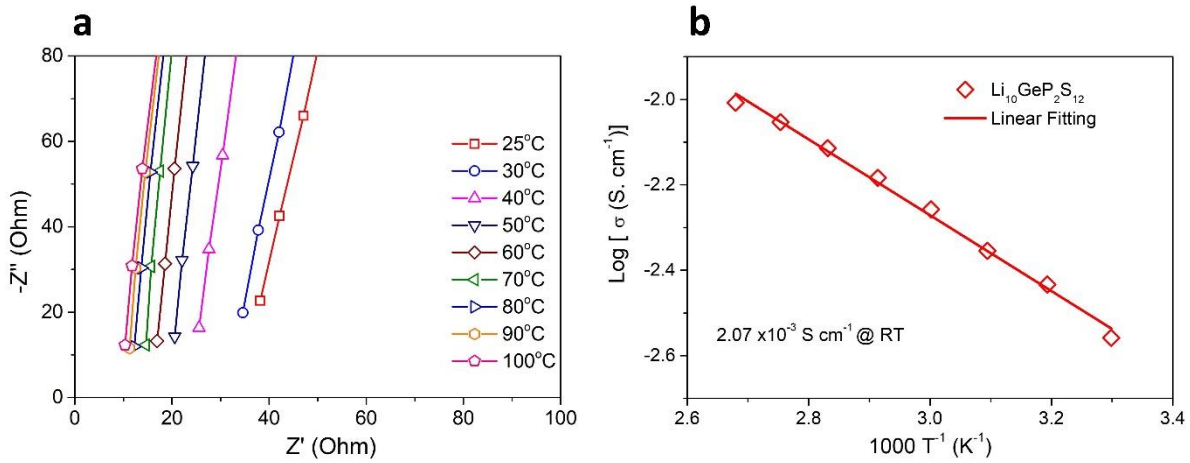

Figure S3. (a) EIS plots of LGPS measured at different temperature and (b) the calculated ionic conductivity.

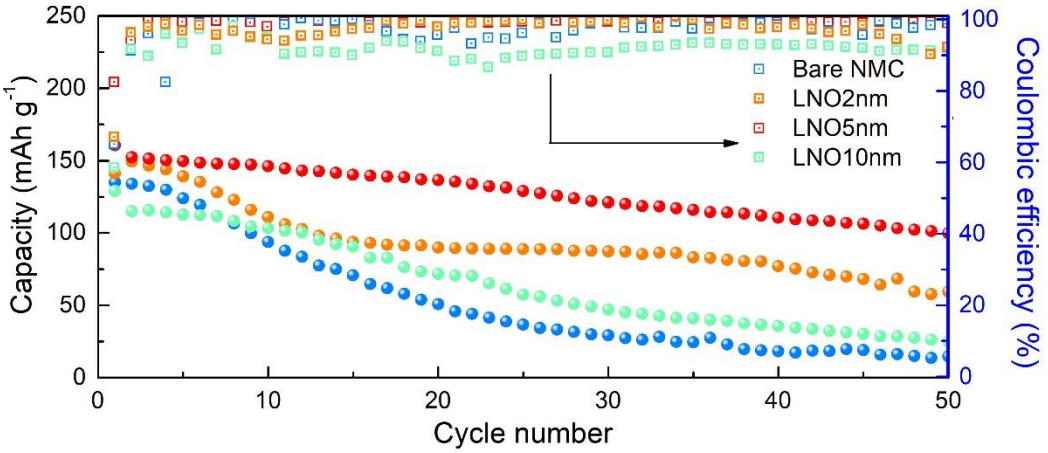

Figure S4. Electrochemical characterizations of LNO coated NMC811 cathodes with various coating thickness.

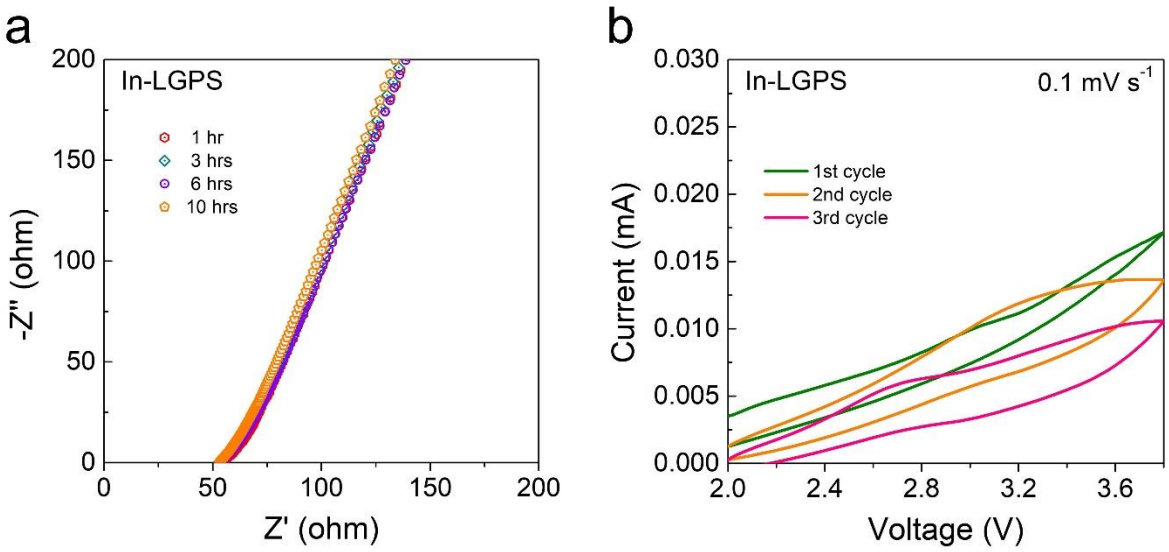

Figure S5. (a) EIS plots of In-LGPS-In battery measured at a various resting time and (b) the CV curves of In-LGPS-In battery at 0.1 mV s^{-1}.

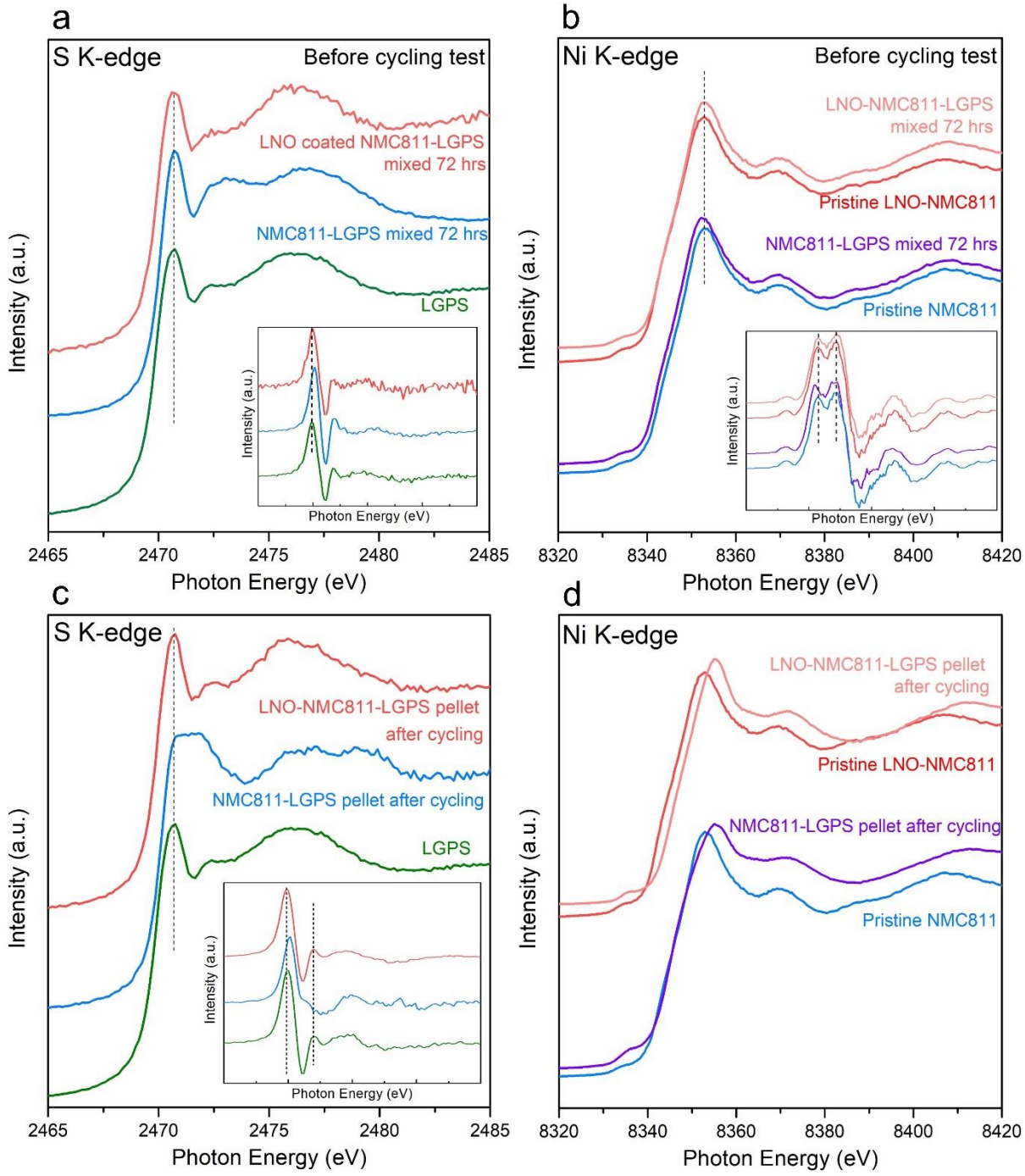

Figure S6. Ex-situ XANES spectra of NMC 811 cathode materials and LGPS sulfide electrolytes. (a, b) Before and (c, d) after cycling.

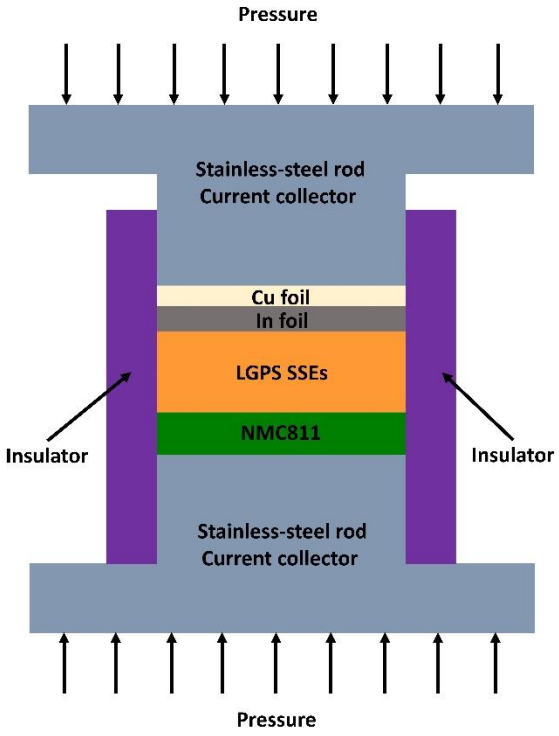

Figure S7. Schematic figure of model cell for electrochemical test.

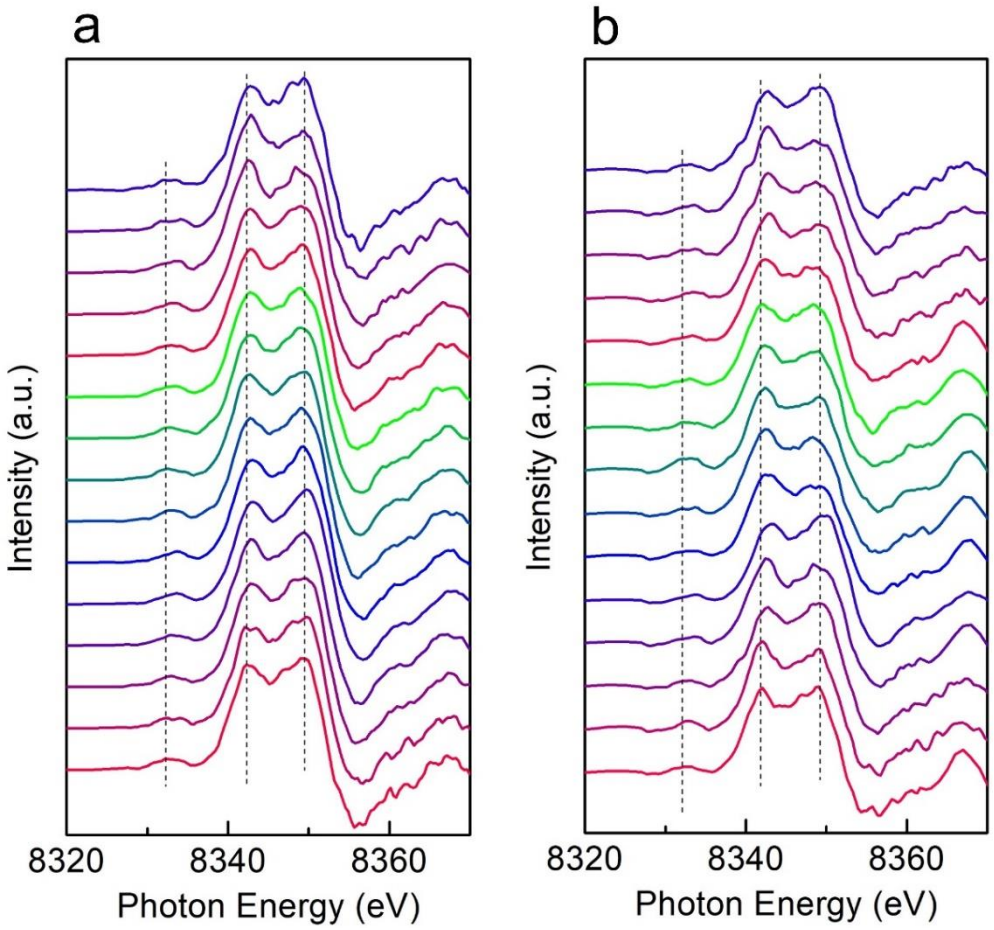

Figure S8. The corresponding first derivation of operando Ni K-edge spectra in Figure 3c and 3f: (a) bare NMC811-LGPS and (b) LNO NMC811-LGPS SSLIBs.

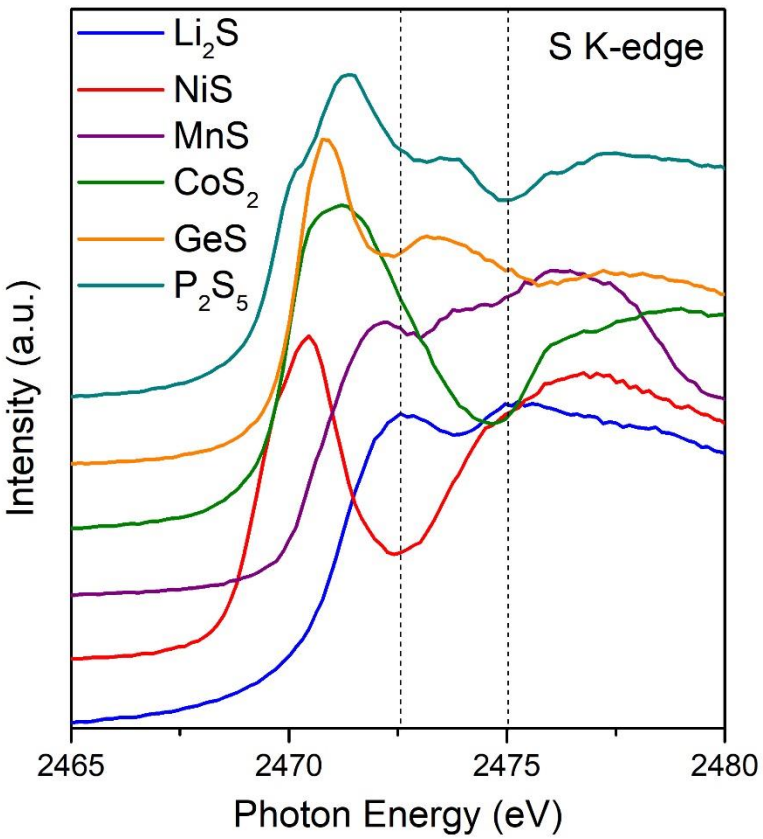

Figure S9. S K-edge XANES spectra of standard reference samples.

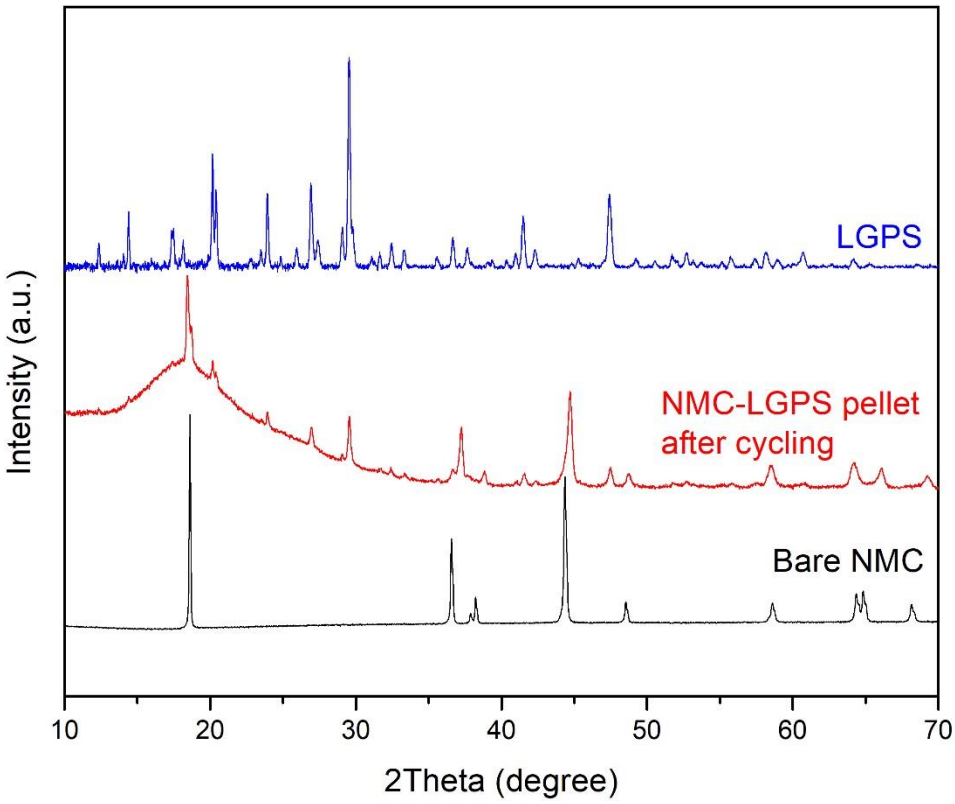

Figure S10. XRD patterns of bare NMC811-LGPS pellet after cycling with reference samples.

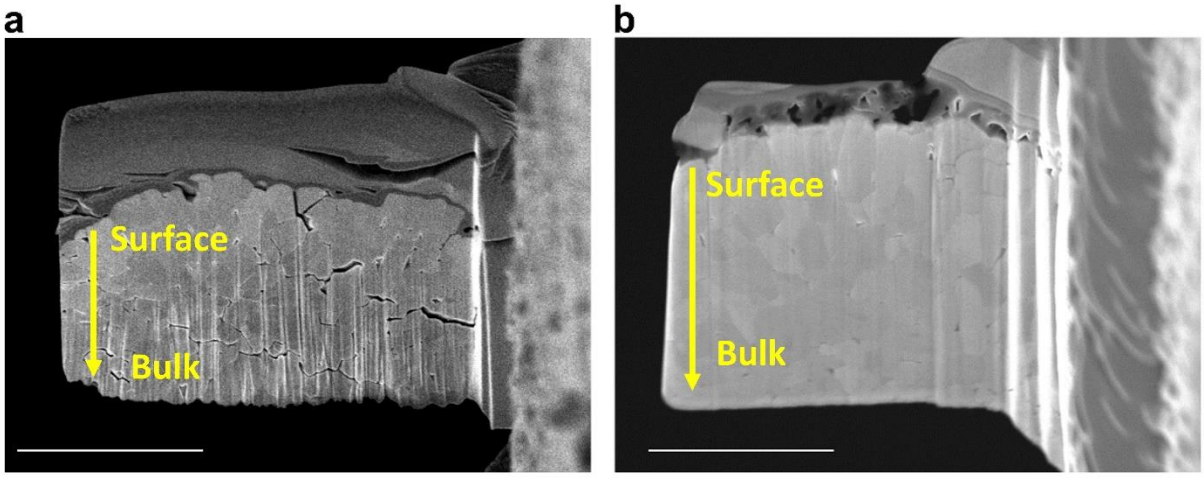

Figure S11. SEM images of the thinning FIB films of NMC811 cathodes after cycling. (a) Bare NMC811 and (b) LNO coated NMC811. The scale bars in the figures are 3 μm (a) and 2 μm (b).

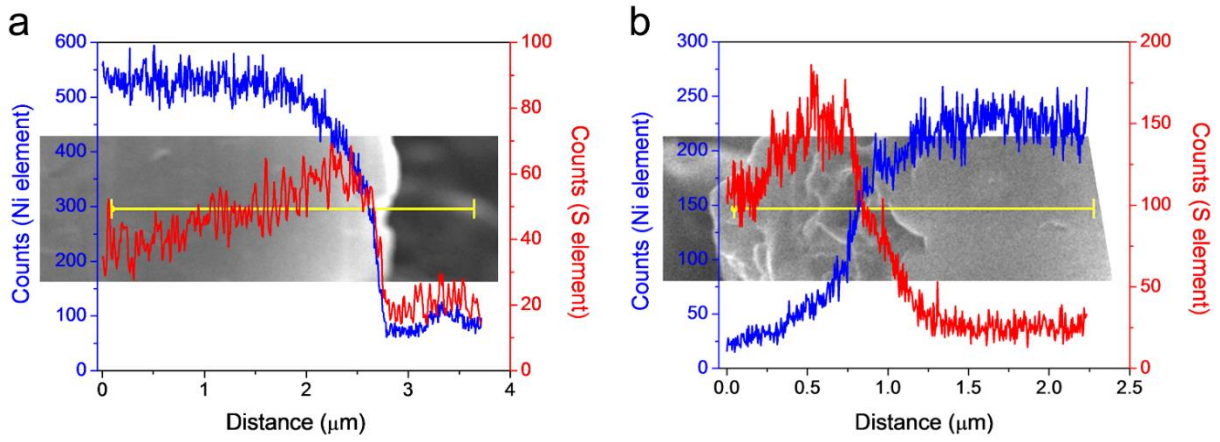

Figure S12. SEM-EDX linear scan of NMC811 cathode after cycling. (a) Bare NMC811 and (b) LNO coated NMC811.

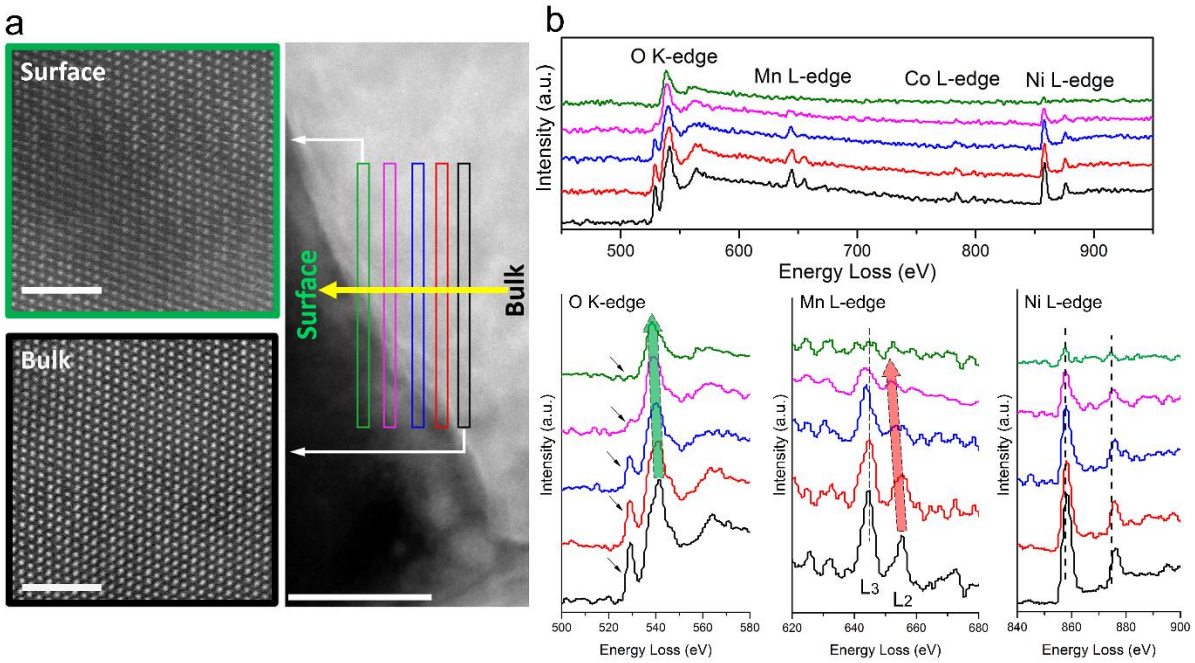

Figure S13. (a) STEM-HAADF images and (b) the corresponding EELS spectra of LNO coated NMC811 after cycling. Scale bars in the figures (a, left top and left bottom) 2 nm, and (a, right) 20 nm.