Electronic Supplementary Information

Breathing and oscillating growth of solid-electrolyte-interphase upon electrochemical cycling

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Sample preparation:

A model SEI is formed and cycled on the surface of a well polished Cu electrode. Our electrochemical cell consists of Li metal as the reference electrode and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) as the counter electrode with 1M $LiClO_4$, EC:DEC (1:1 by wt) as the electrolyte. The experimental setup has been reported in a previous work, and more details on the electrochemical cell is provided in the **Figure S1**.[1] The cell is assembled and tested in a high purity Ar glove box with oxygen and water concentrations both less than 1 ppm. Electrochemical cycling is performed at room temperature between 3.0V and 0.005V vs Li^+/Li under a constant current rate of 15μA/cm^2. 3V is close to the initial "floating" potential of the copper electrode, so we stop the voltage at 3 V to avoid direct reaction with Cu material. Capacities are calculated with respect to the surface area of the Cu electrode. A VMP electrochemical station with EC-Lab software (Biologic) is used for all the electrochemical tests. After holding at the ending potential for 2 hours to allow the SEI to reach equilibrium, the samples are taken out from the electrolyte, immediately rinsed in DMC for 30-60 seconds. It has been found before that electrode surfaces need to be raised properly for obtaining intrinsic SEI signal.[2-3] The clear contrast of the electrodes processed in exactly the same way indicates the validity of our sample preparation procedure for revealing the intrinsic SEI signals. The electrode samples are mounted onto experimental holder inside the glove box, and the holder was loaded into the experimental chamber through a home-made sample transfer kit to avoid any air exposure. We note that we have noticed obvious change of the SEI composition if the samples are exposed even briefly to trace amounts of water or air.

Soft x-ray absorption spectroscopy:

sXAS measurements of C and O *K*-edges of SEI samples formed at different voltages are performed at beamline 8.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory.[4] The experimental energy resolution is better than 0.15eV. All the sXAS experiments are performed at 90K with liquid N_2 cooling to avoid radiation damage effect on the samples. Additionally, X-ray beam has been defocused to reduce the area exposure while maintaining good statistics through our specially designed tunable mirrors. Samples in comparison were always processed and loaded together onto one sample holder, with data

collected in one batch of continuous experiments for reliable comparison. The spectra are collected in the both surface sensitive total electron yield (TEY) and bulk sensitive total fluorescence (TFY) mode. The probing depth is about 10 nm and 100 nm for TEY and TFY, respectively. All the spectra are normalized to the photon flux measured by the photocurrent of an upstream clean gold mesh.

Time-of-flight secondary ion mass spectrometry:

TOF-SIMS analyses are conducted on a PHI TRIFT V nanoTOF spectrometer (Physical Electronics, Chanhassen, MN). Samples are kept in sealed vessels filled with Ar during transfer from the Ar filled glove box to the SIMS. The analysis chamber of the instrument was maintained at a pressure of less than 5×10^{-7} Pa during analysis. A 30kV Au^+ ion source is used for both sputtering and analysis. The analysis area is 50 μm × 50 μm, which is in the center of a sputter area of 200 μm × 200 μm. The sputtering rate maintains at ~2 nm/min (calibrated with a 100 nm standard SiO_2 wafer). For SEI thickness calculation, a uniform sputter rate is assumed regardless of the SEI composition and porosity.[5-7]

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7. Lu, P.; Li, C.; Schneider, E. W.; Harris, S. J., Chemistry, Impedance, and Morphology Evolution in Solid Electrolyte Interphase Films during Formation in Lithium Ion Batteries. *The Journal of Physical Chemistry C* **2014,** *118* (2), 896-903.

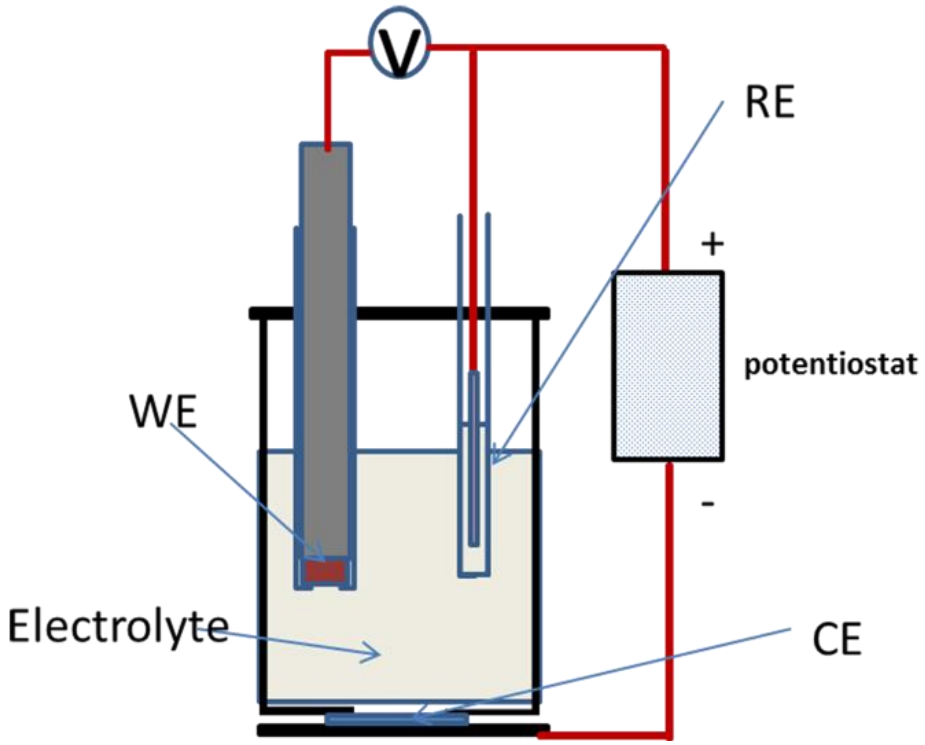

Figure S1 three electrode model cells used for the electrochemical cycling.

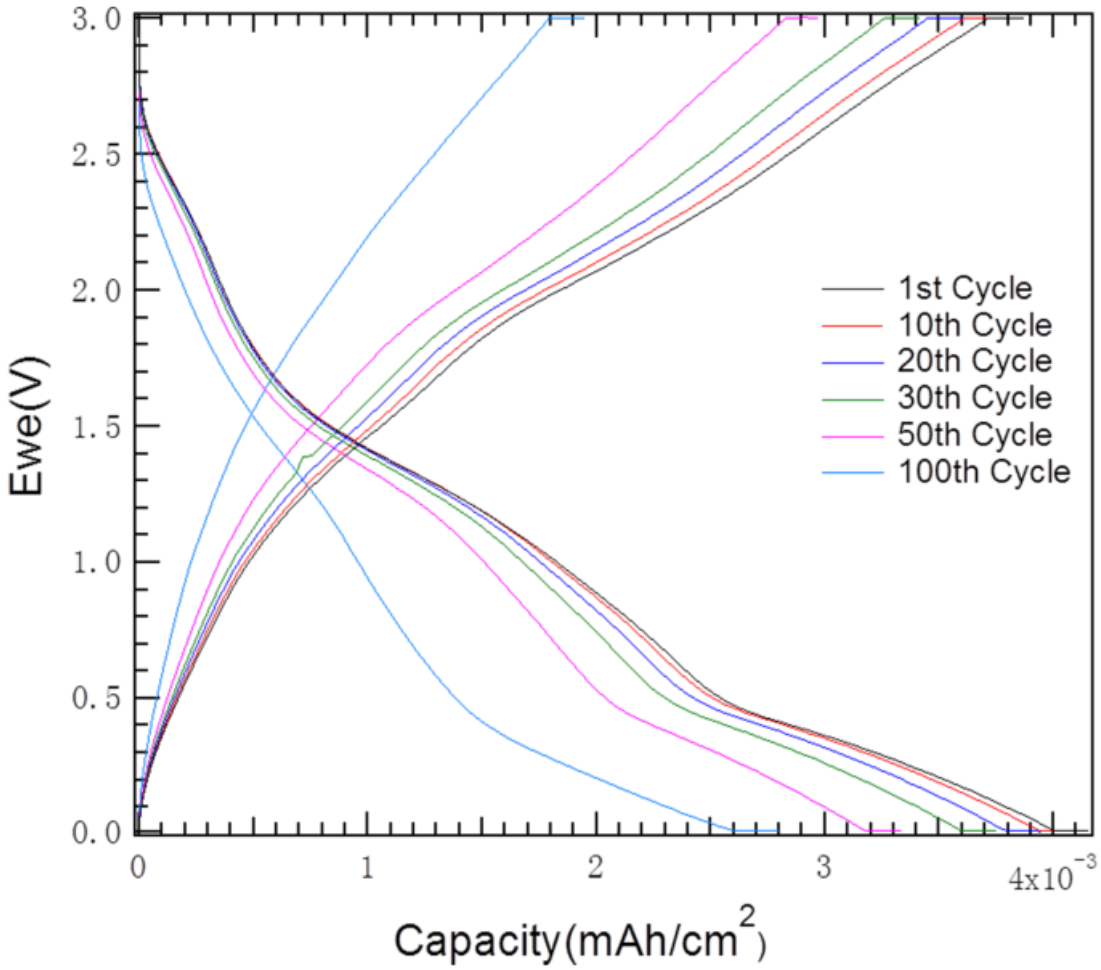

Figure S2 the selected cycles (1, 10, 20, 30, 50, and 100) capacity voltage curves of SEI, which are cycled in the same electrolyte with formation process

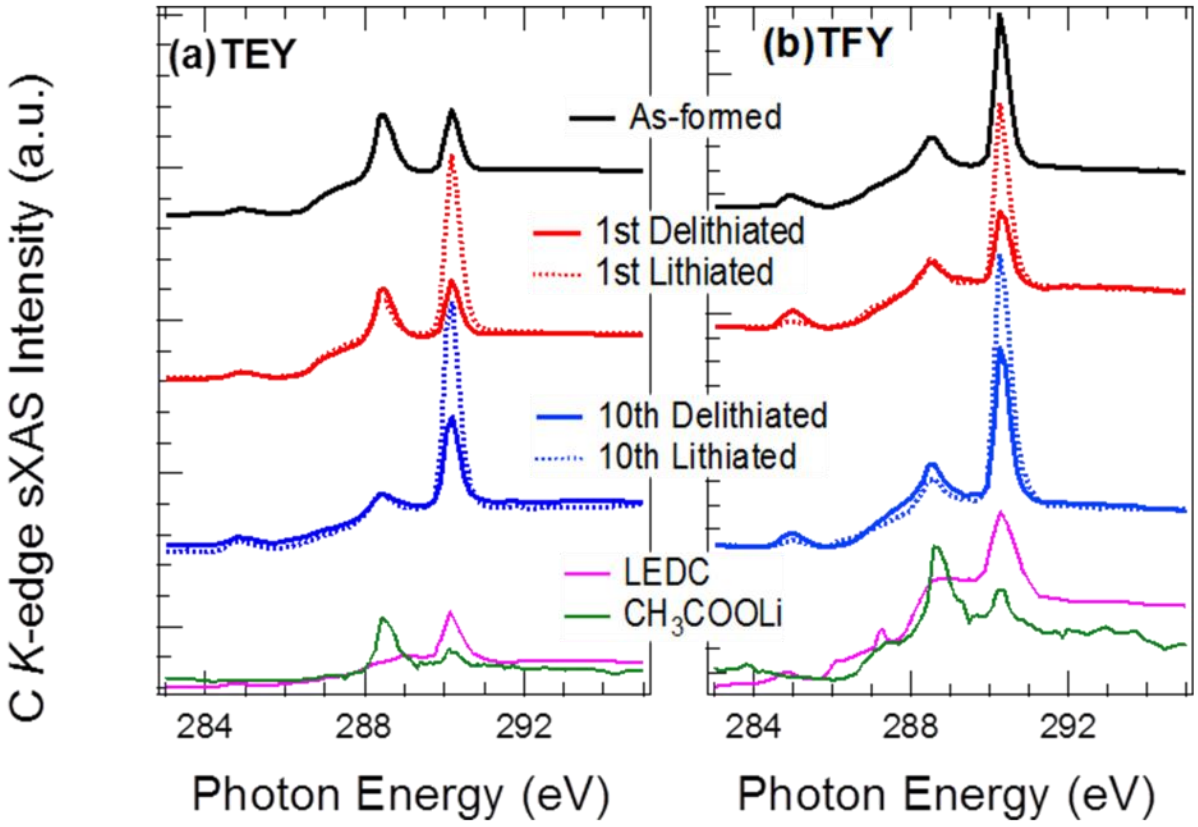

Figure S3 (a) C K-edge TEY spectra of the as-formed SEI (black), and the SEIs at delithiated (solid lines) and lithiated (dotted lines) states at the 1st (red) and 10th (blue) cycles. (b) C K-edge TFY spectra of the same series of SEIs.

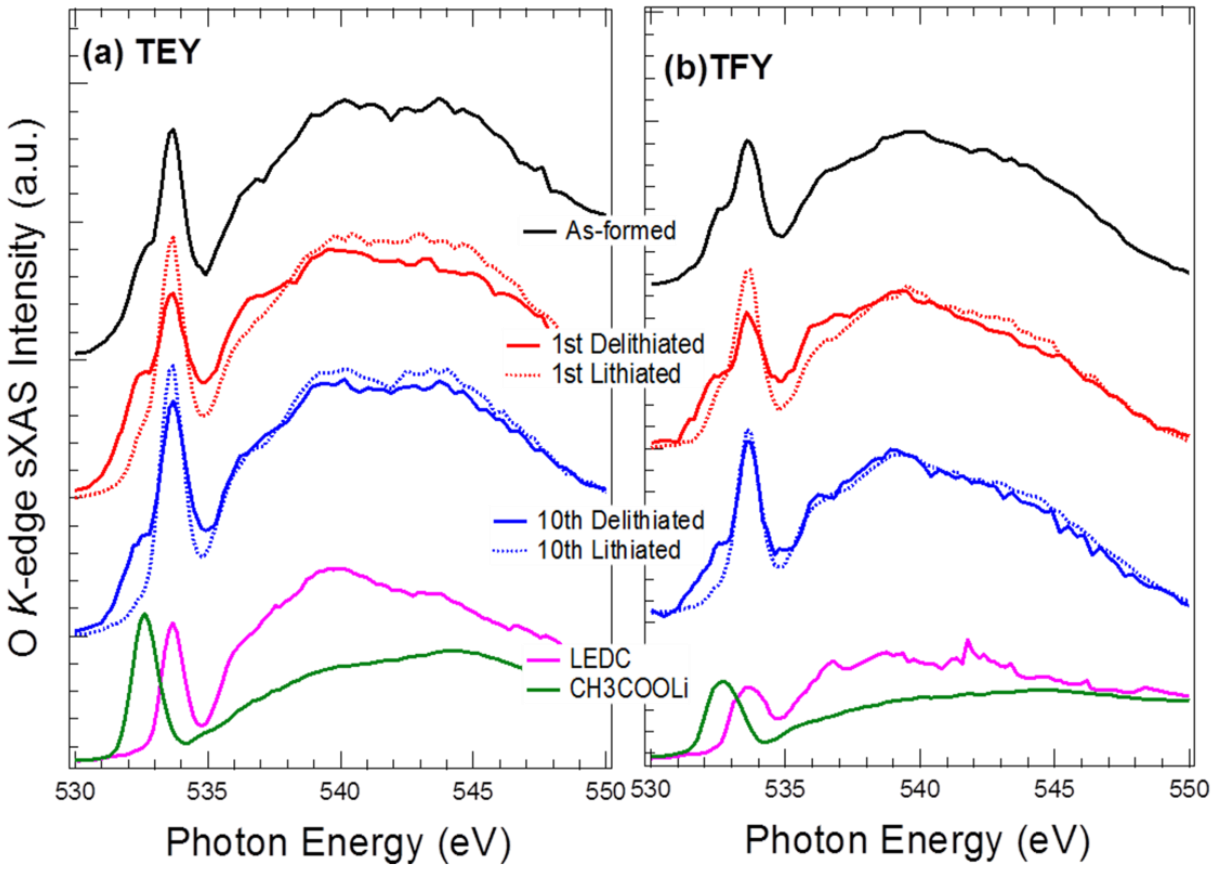

Figure S4 (a) O K-edge TEY spectra of the as-formed SEI (black), and the SEIs at delithiated (solid lines) and lithiated (dotted lines) states at the 1st (red) and 10th (blue) cycles. (b) O K-edge TFY spectra of the same series of SEIs.