

Supporting Information

Anion Dependent Potential Pre-Cycling Effects on Lithium Deposition/Dissolution Reaction Studied by Electrochemical Quartz Crystal Microbalance

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SUPPLEMENTAL MATERIALS AND METHODS

Materials. Commercially available QCM electrodes, with a mirror like polished copper film (apparent area: 0.196 cm^2), prepared on the surface of the AT-cut quartz crystal (fundamental frequency; 9.0 MHz), were used. The QCM electrode (working electrode) was rinsed with 10 wt% H_2SO_4 solution, sonicated with ultrapure water which is purified by a Milli-Q system (Sartorius, Arium H_2O Pro-UV) for 3 min, and thoroughly dried by a nitrogen flow prior to the experiments¹. Lithium ribbon (Sigma Aldrich, 99%) were used as reference and counter electrodes. Battery grade "Chameleon reagents" of tetraglyme (G4) solutions containing 1 M LiPF_6 (LiPF_6 -G4), 1 M LiTFSI (LiTFSI -G4), and 1 M LiFSI (LiFSI -G4) were purchased from Kishida chemicals and used as received. A custom-made Teflon cell was used for the EQCM measurements. The water content of all the electrolyte solutions was less than 30 ppm as certified by the supplier. All the experiments including the cell assembly were performed inside the glove box (Glovebox Japan, BGJF080) under argon atmosphere at room temperature, with the water content less than 0.1 ppm (dew point $\sim -90^\circ\text{C}$).

Electrochemical Measurements. EQCM analyzer (Seiko EG&G, QCM922A) was used in conjunction with a potentiostat (Hokuto Denko, HZ-7000) for the electrochemical studies. Two different typed samples were prepared as following;

A) After linear potential scan from 3.0 V (vs. Li/Li^+), where is close to the open circuit potential (ca. 3.2 V), to 0.35 V, cyclic voltammograms (CVs) between 0.35 V and -0.1 V were measured for 5 cycles. This sample was labeled as "without pre-SEI".

B) After linear potential scan from 3.0 V to 0.35 V and potential cycling between 0.35 V and 0 V for 2 cycles, CVs between 0.35 V and -0.1 V were measured for 5 cycles. This sample was labeled as "with pre-SEI".

Before the sample preparation as above, we wait for more than 30 minutes to stabilize OCP, Δm , and ΔR . In all the electrochemical experiments, a scan rate was 1 mV s^{-1} and the apparent electrode area was 0.2 cm^2 .

Spectroscopic Measurements. X-ray photoelectron (XP) spectra were measured with the XPS system (Thermo Fisher Scientific, K-Alpha) under ambient pressure less than 10^{-4} Pa . Infrared reflection absorption (IRRA) spectra were measured with the IRRAS system (JASCO, PM-IRRAS-FV with FT/IR-6100) under nitrogen atmosphere. After the samples were washed with dimethyl carbonate (DMC) and G4, the samples were transferred from the glove box to each system in the transfer vessel to avoid exposure to the air as much as possible.

SUPPLEMENTAL RESULTS

As examples, XP and IRRA spectra with and without the pre-SEI prepared in the TFSI-G4 are shown in Figs. S1 and S2.

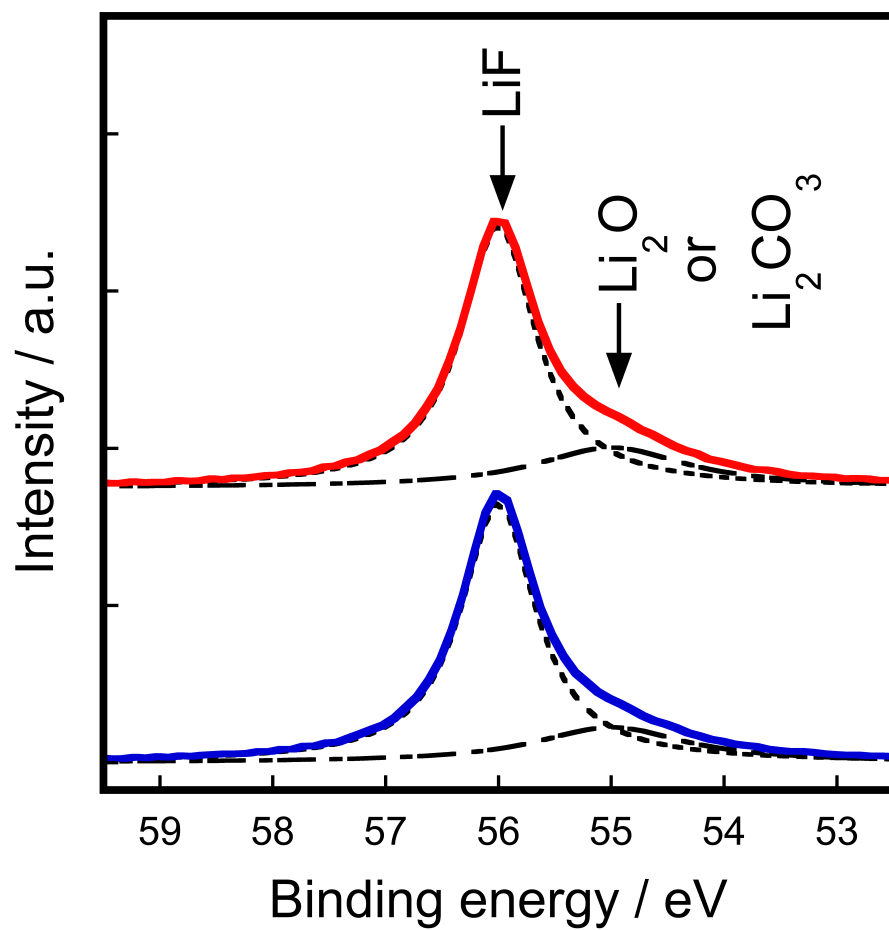


Figure S1. XP spectra in Li1s region with (red) and without (blue) the pre-SEI, which were prepared in the TFSI-G4.

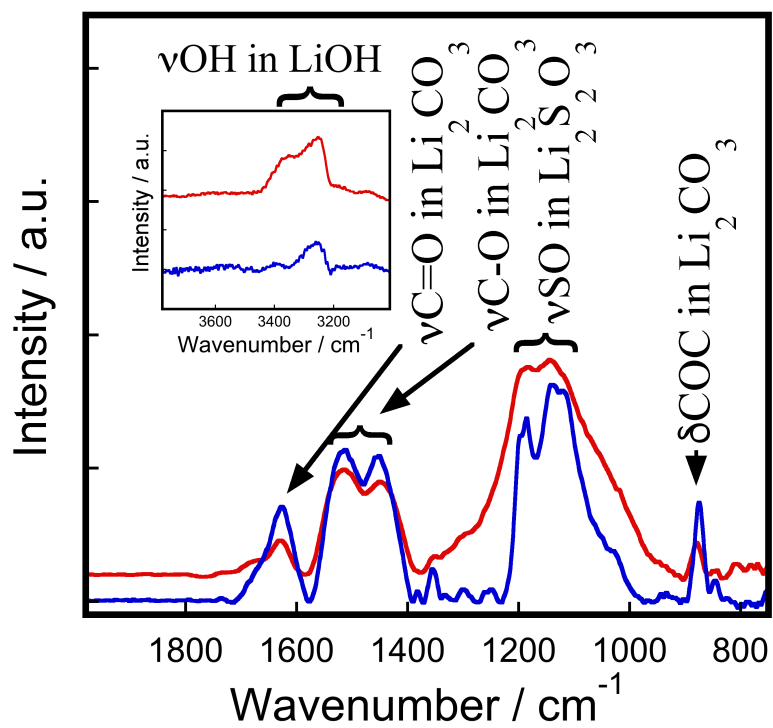


Figure S2. IRRA spectra with (red) and without (blue) the pre-SEI, which were prepared in the TFSI-G4.

SUPPLEMENTAL REFERENCES

- (1) Sharma, A.; Das, K.; Fecht, H.-J.; Das, S. Effect of Various Additives on Morphological and Structural Characteristics of Pulse Electrodeposited Tin Coatings from Stannous Sulfate Electrolyte. *Appl. Surf. Sci.* **2014**, *314*, 516-522.