# *Supporting information*

## A Pretreatment Method to Form High-quality LiF-enriched Solid-electrolyte-interface for Li Anode Protection in Li-$O_2$ Battery

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**Supplementary Figures:**

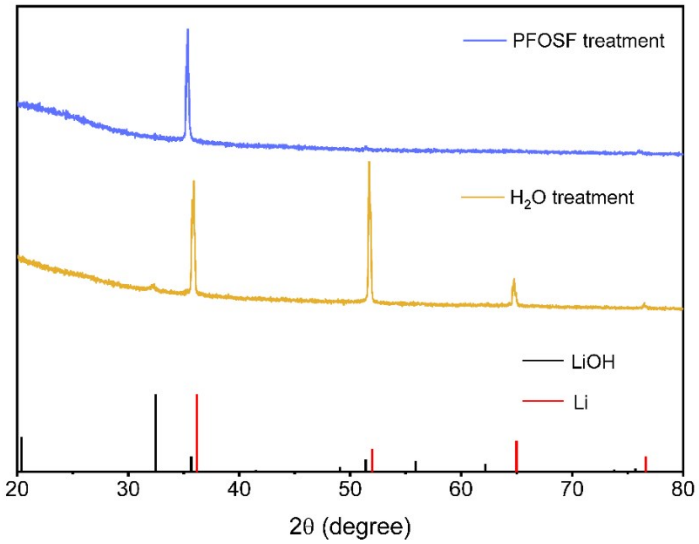


**Fig. S1**. XRD analysis of Li foils after trace of $H_2O$ (yellow line) and PFOSF solvent treatment (blue line).

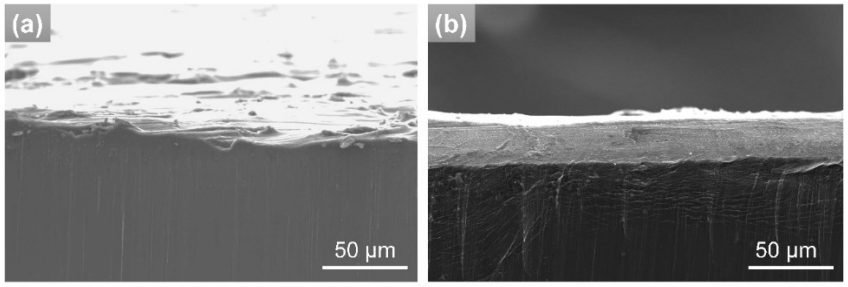


**Fig. S2**. High magnification cross-sectional images of (a) pristine Li and (b) PFOSF-Li with PFOSF treatment for 60 mins.

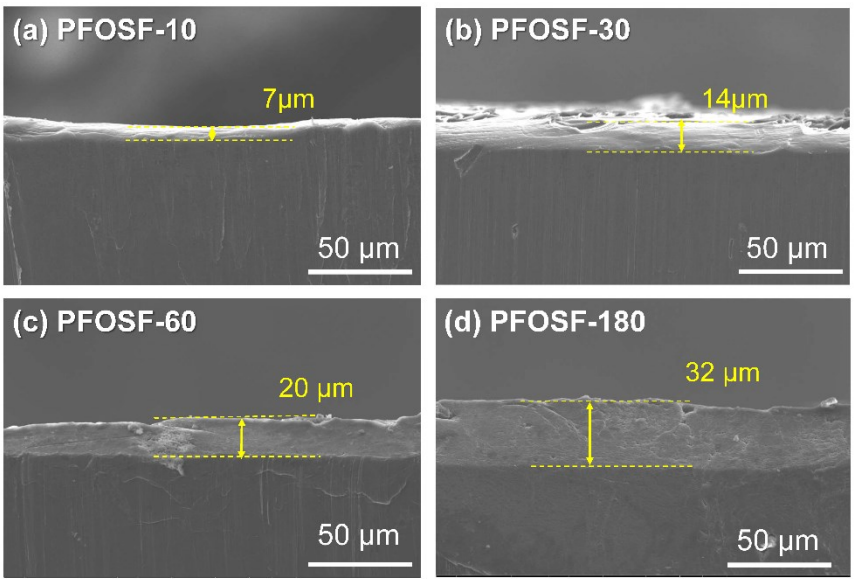


**Fig. S3**. Cross-sectional SEM images of the PFOSF-Li of PFOSF treatment for (a) 10 min; (b) 30 min; (c) 60 min; (d) 180 min.

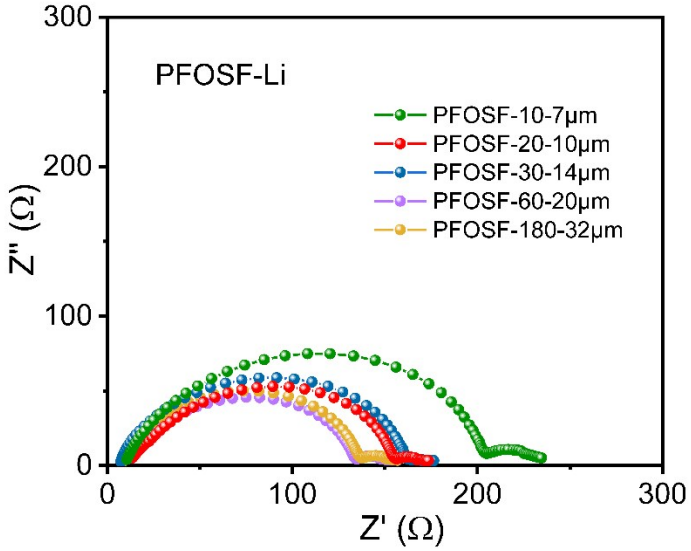


**Fig. S4**. Nyquist plots of the symmetric cells with PFOSF-Li anodes obtained from different PFOSF treatment times.

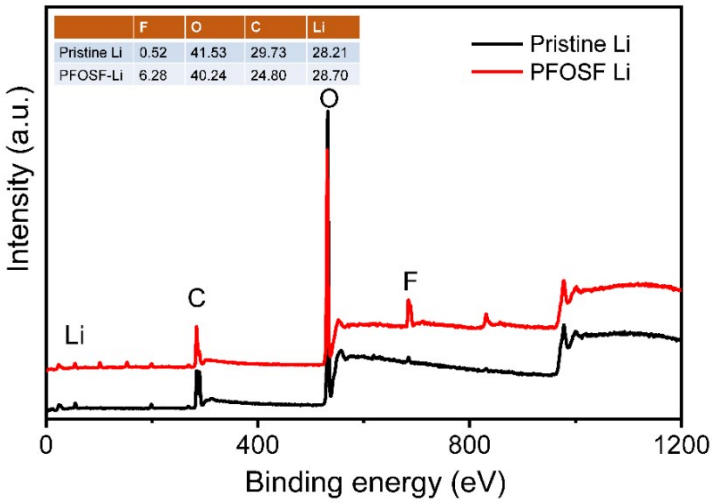


**Fig. S5**. XPS full spectra of pristine Li (black line) and PFOSF Li metal (red line). The inset form shows the F, O, C and Li element contents of the Li surface.

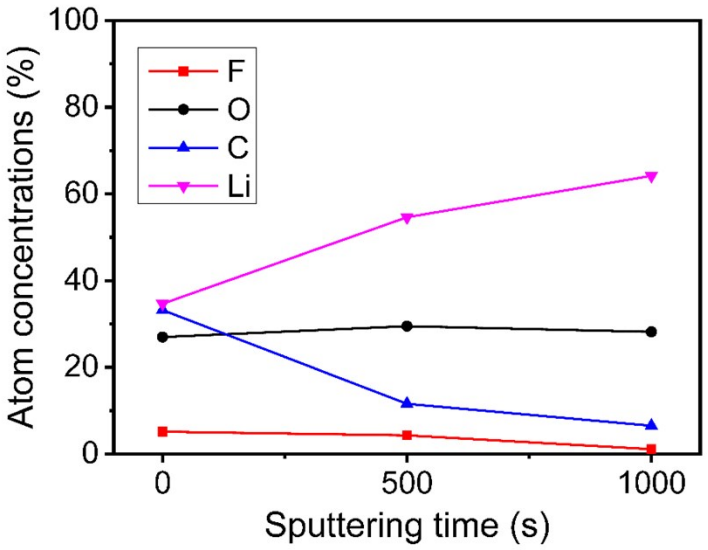


**Fig. S6.** F, O, C and Li atom concentrations of the SEI film as the Ar sputtering time extented to 500 and 1000s.

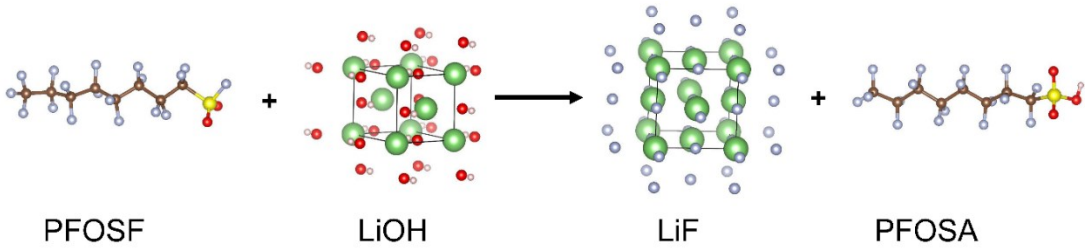


**Fig. S7.** The schematic diagram of the reaction of PFOSF and LiOH. Note: The formation energy corresponding to the reaction is calculated to 1.07 eV that derived from the subtraction of total energy of reactants to resultants.

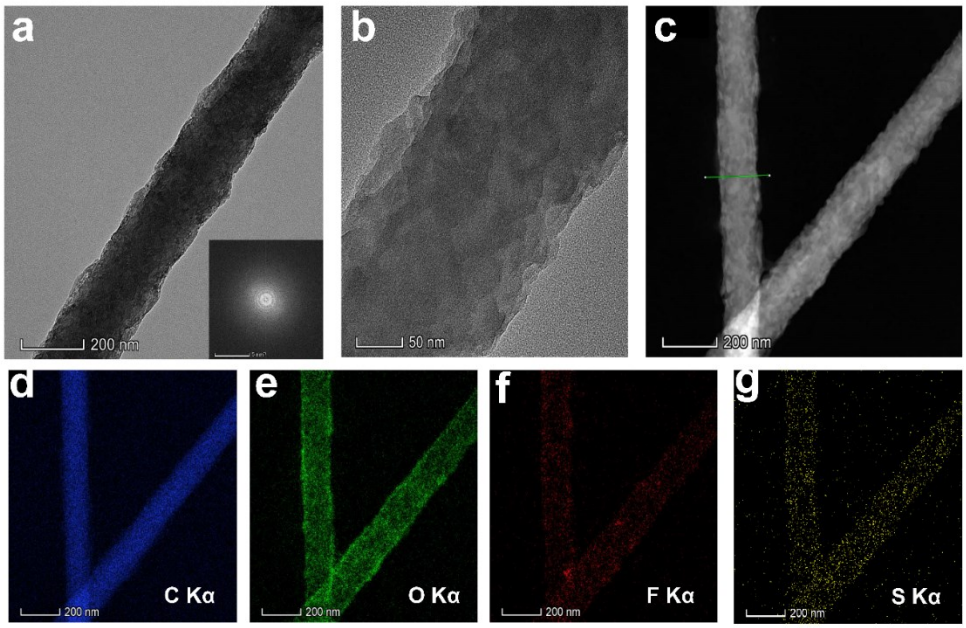


**Fig. S8**. (a) TEM image of the carbon fiber after Li plating and stripping in TEGDME electrolyte. (b) High resolution TEM image of the selected area for the carbon fibers. (c) HADDE analysis of the carbon fiber and (d-g) corresponding elements mapping analysis

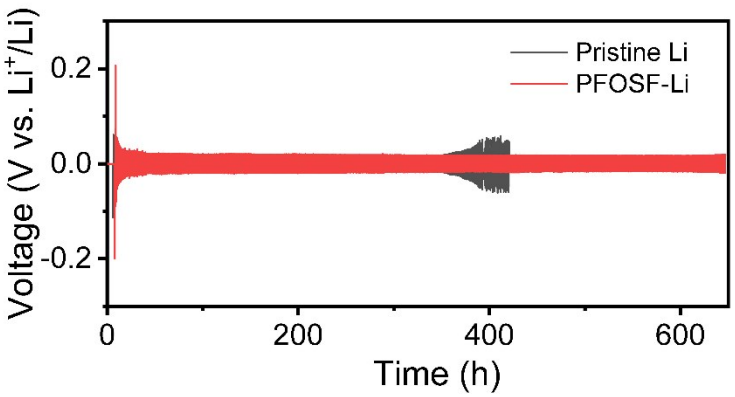


**Fig. S9**. Cycling performance of the symmetric Li||Li cells under Ar atmosphere at current density of 2 mA $cm^{-2}$ with capacity of 1mAh $cm^{-2}$.

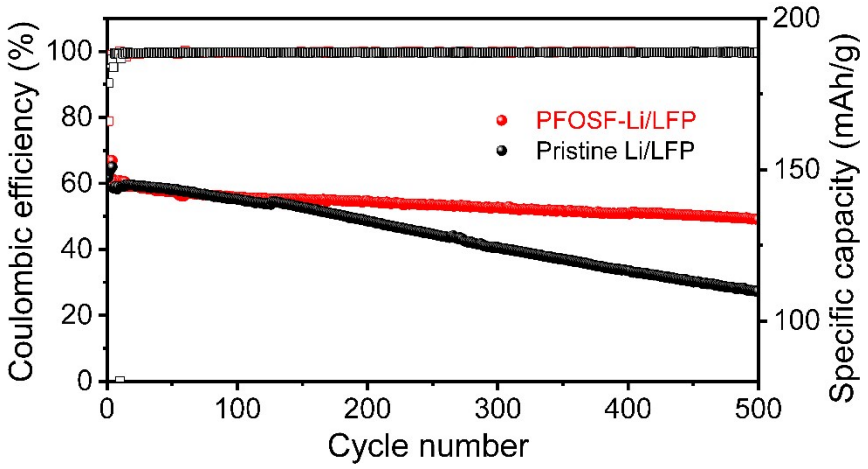


**Fig S10.** Comparison of the cycling performance of Li||LFP batteries with pristine Li and PFOSF Li anodes.

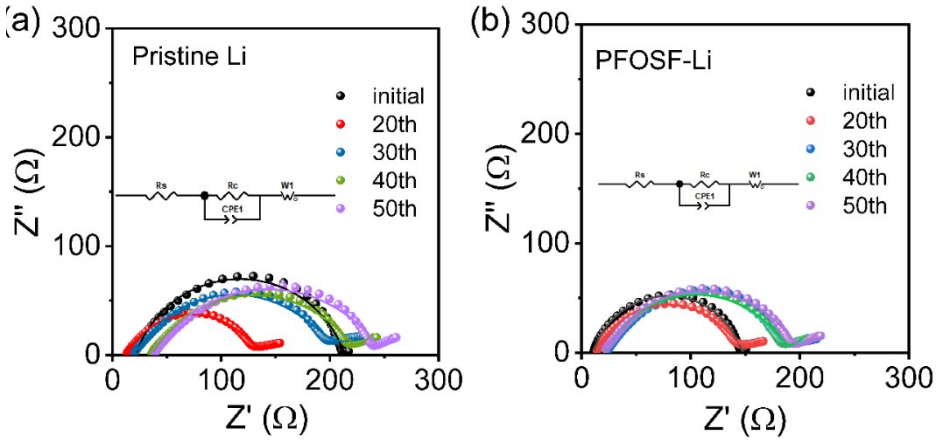


**Fig. S11**. Electrochemical impedance spectra (EIS) of the symmetrical Li||Li cells with (a) pristine Li and (b) PFOSF treated Li anode after different cycles under $O_2$ atmosphere.

**Table S1**. $R_s$ and $R_c$ values in the equivalent circuit.

| Cycles numbers | $R_s$/Pristine-Li | $R_s$/PFOSF-Li | $R_c$/Pristine-Li | $R_c$/PFOSF-Li |
|---|---|---|---|---|
| 0 | 21.5 | 192.8 | 10.8 | 135.7 |
| 20 | 10.94 | 113.1 | 12.8 | 127.5 |
| 30 | 14.51 | 166.4 | 21.3 | 153.6 |
| 40 | 35.7 | 187.9 | 15.3 | 162.6 |
| 50 | 38.7 | 208.1 | 21.3 | 165.3 |

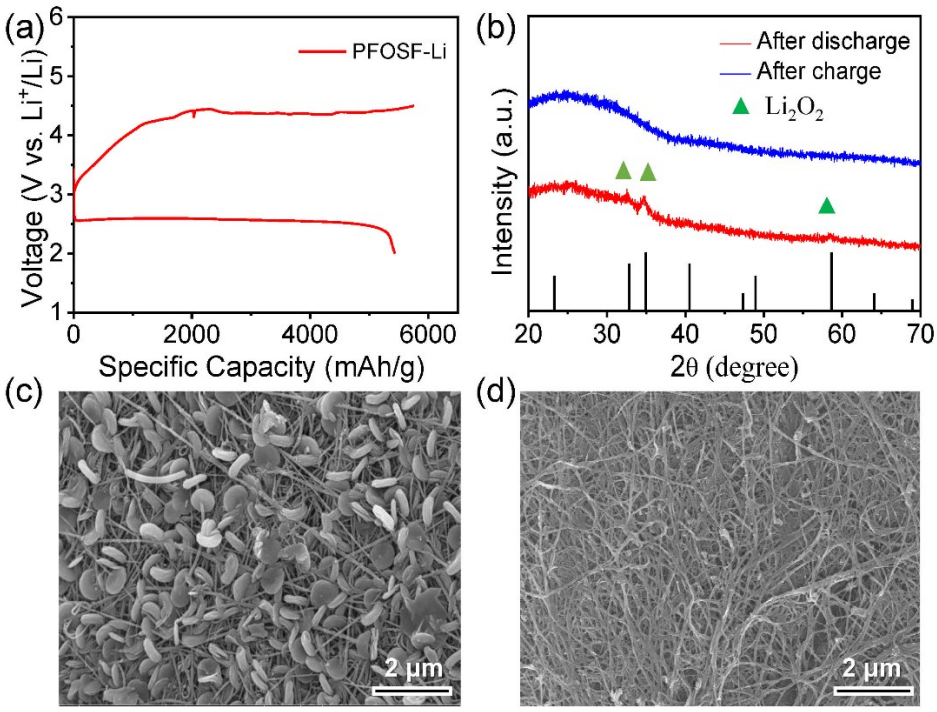


**Fig. S12.** (a) Charge and discharge curves of the LOBs with PFOSF-Li anodes. (b) XRD data after discharge and charge of the oxygen cathodes. SEM images of the cathode after (c) discharge and (d) charge.

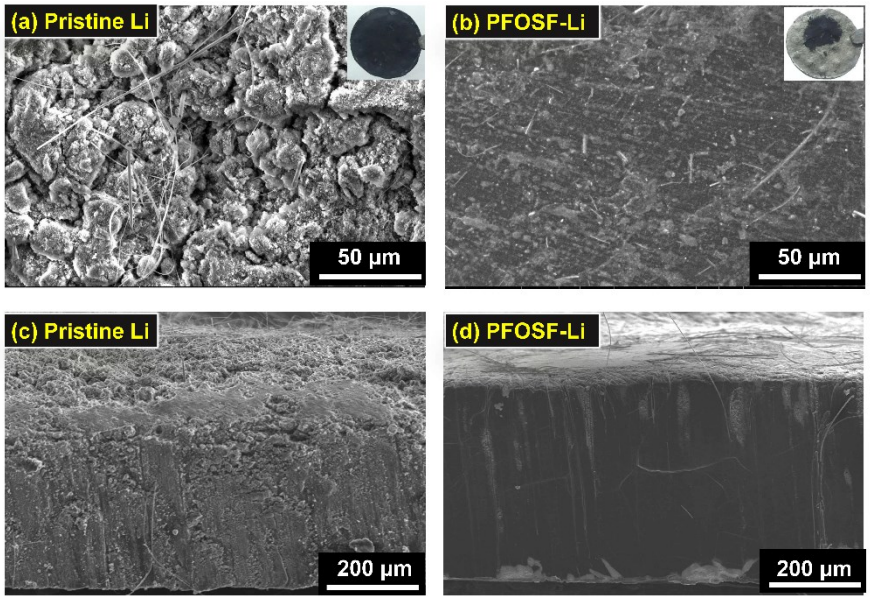


**Fig. S13.** Top views images of the (a) pristine Li anode and (b) PFOSF treated Li anode; Cross-sectional views of (c) pristine Li anode and (d) PFOSF treated Li anode after cycling for 10 cycles.

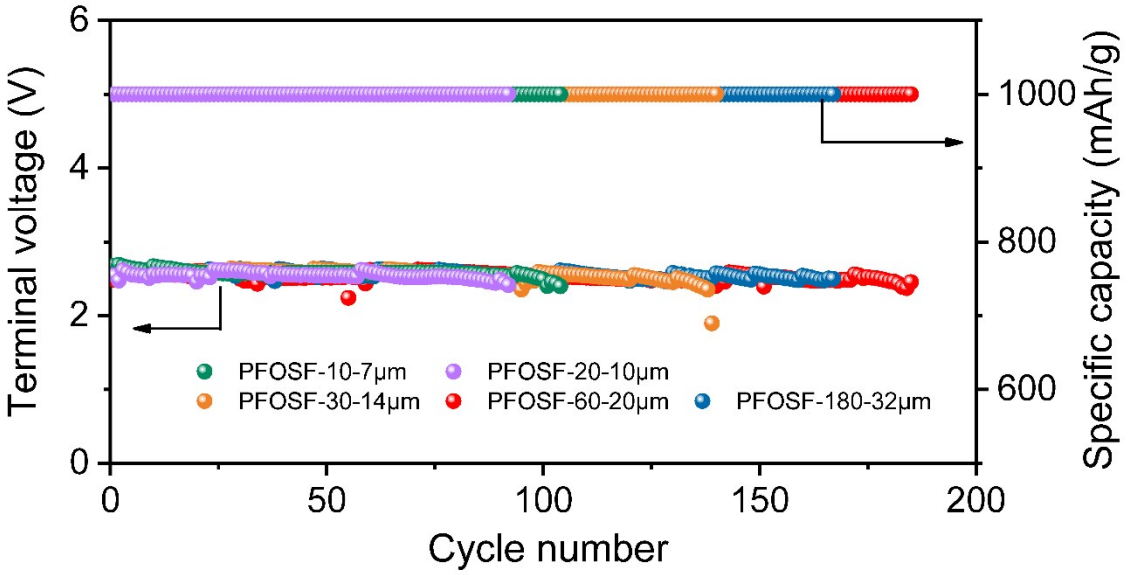


**Fig. S14**. Cycling performance of the LOBs with PFOSF-Li anodes obtained from different PFOSF treatment times.

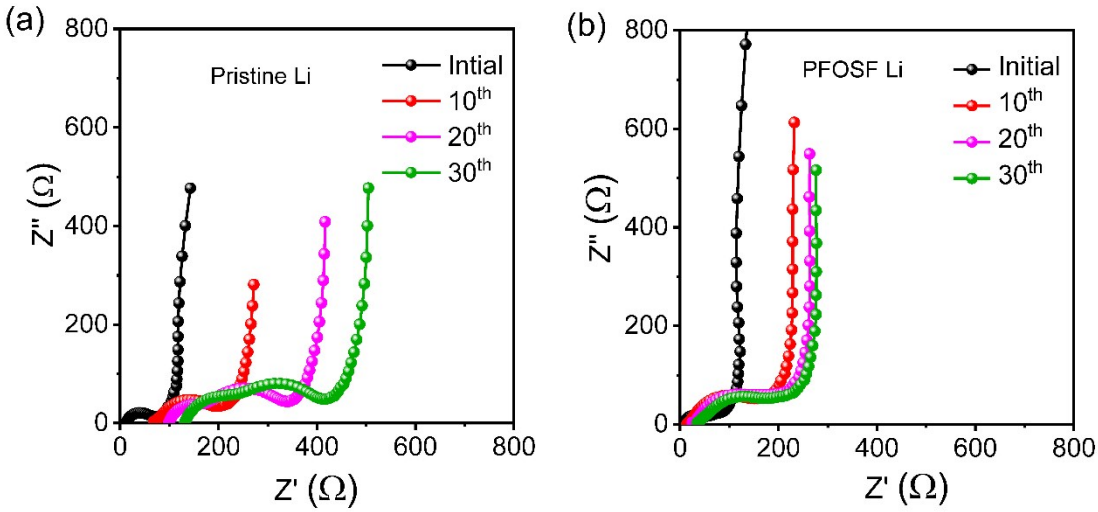


**Fig. S15.** EIS of LOBs with (a) pristine Li and (b) PFOSF-Li after different cycles.