

An Inorganic-rich SEI Induced by LiNO_3 Additive for Stable Lithium Metal

Anode in Carbonate Electrolyte

Experiments

Materials and Electrolytes Preparation.

The electrolyte of 1 M LiPF₆ EC/EMC/DMC (1:1:1 by volume) was purchased from DodoChem. Pyridine (99.5%, with molecular sieves, water ≤ 50 ppm) was purchased from Shanghai Macklin and lithium nitrate (LiNO₃, ≥ 99.9%) was purchased from Shanghai Aladdin. All the solvents were stored in the glovebox (H₂O and O₂ content below 0.1 ppm). The Li foil with diameter of 16 mm was purchased from China Energy Lithium Co., LTD. To prepare the electrolyte with 1.0 wt% LiNO₃, 0.64 g LiNO₃ was first dissolved in 2 ml pyridine and stirred for 3 h to obtain a saturated LiNO₃-pyridine solution. Then, adding 4.7 wt% above solution into 3 ml blank electrolyte.

Characterizations.

The morphologies of anodes surface were observed by SEM (Hitachi SU8010) at 5 kV. The morphology evolution was observed by in suit optical microscope (1000X digital microscope). The ¹³C, ⁷Li NMR spectra were obtained by Bruker Avance NEO 600. The compositions of SEI were characterized by X-ray photoelectron spectroscopy (PHI X-tool). Fourier transform infrared spectroscopy (FTIR) was analyzed with Thermo Scientific Nicolet iS5 at attenuated total reflection (ATR) pattern. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested on CHI600E electrochemical workstation.

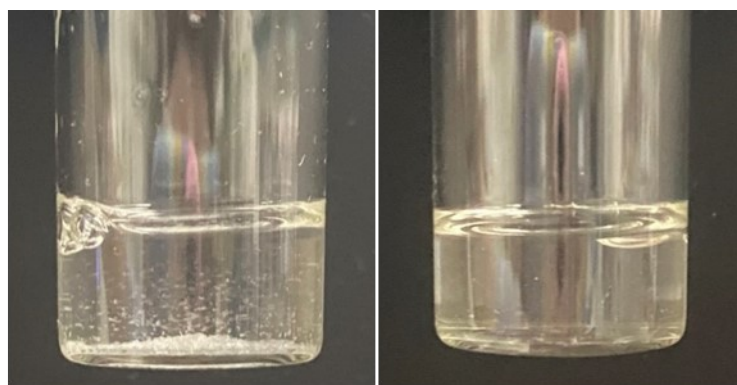
Electrochemical Measurements.

CR2032 coin cells with Celgard 2320 (20 μm) separator and 50 μL electrolyte

were applied in all the electrochemical performances and assembled/disassembled in an Ar-filled glovebox with H₂O and O₂ content below 0.1 ppm. The batteries measurements were used on the LAND battery testing system at 25 °C. The Li||Li symmetrical cells were tested at various current densities of 1 mA cm⁻² or 2 mA cm⁻² under deposition capacity of 1 mAh cm⁻². The CE was calculated in Li||Cu half cells with the similar procedure reported by Wang et al.¹ In short, Q_T represents the initial Li plating capacity (3 mAh cm⁻²) at a current density of 1 mA cm⁻². Then, the cell galvanostatic cycles at a fixed capacity (Q_C=1 mAh cm⁻²) for n cycles. Finally, a capacity retention (Q_R) was obtained by Li recharged to cut-off voltage of 0.5 V. The CE value can be calculated according to the following equation: $CE = (nQ_C + Q_R) / (nQ_C + Q_T)$. EIS measurements of symmetrical cells were carried out in the frequency ranging from 10⁵ to 10⁻² Hz. CV tests of Li||Cu half cells were performed in the voltage ranging from 2.5~0.0 V under a scanning rate of 0.1 mV s⁻¹.

Reference

- 1 N. Piao, S. Liu, B. Zhang, X. Ji, X. Fan, L. Wang, P.-F. Wang, T. Jin, S. Liou, H. Yang, J. Jiang, K. Xu, M. A. Schroeder, X. He and C. Wang, *ACS Energy Lett.*, 2021, 1839–1848.



BE with 1.0 wt% LiNO₃

BE-Py/LiNO₃

Fig. S1 Optical images of BE with 1.0 wt% and BE-Py/LiNO₃

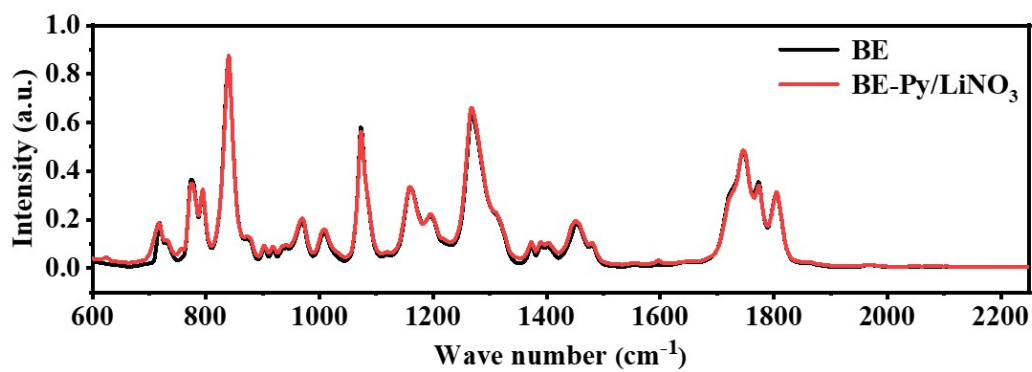


Fig. S2 Fourier transformed infrared (FTIR) spectra of BE and BE-Py/LiNO₃.

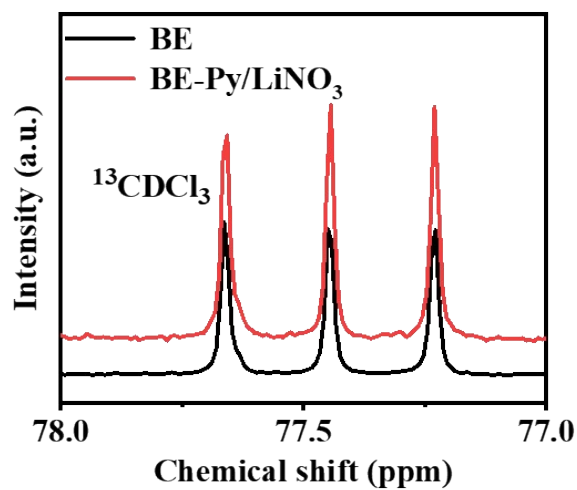


Fig. S3 CDCl₃ spectra of BE and BE-Py/LiNO₃.

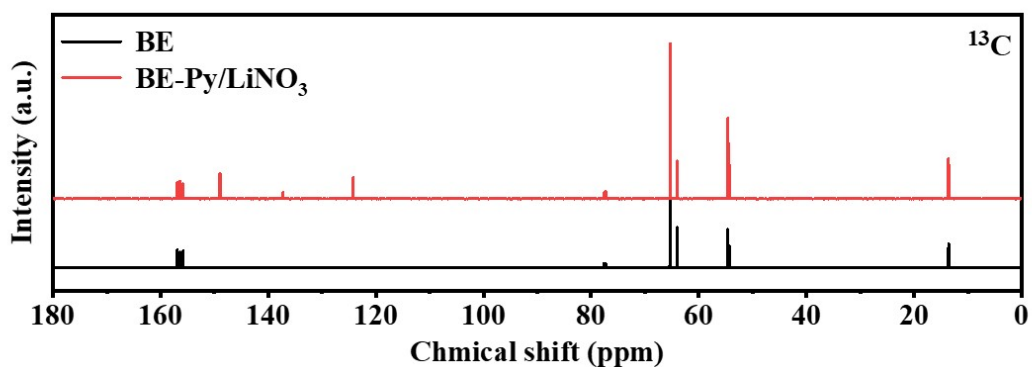


Fig. S4 Overall ^{13}C NMR spectra of BE and BE-Py/LiNO₃.

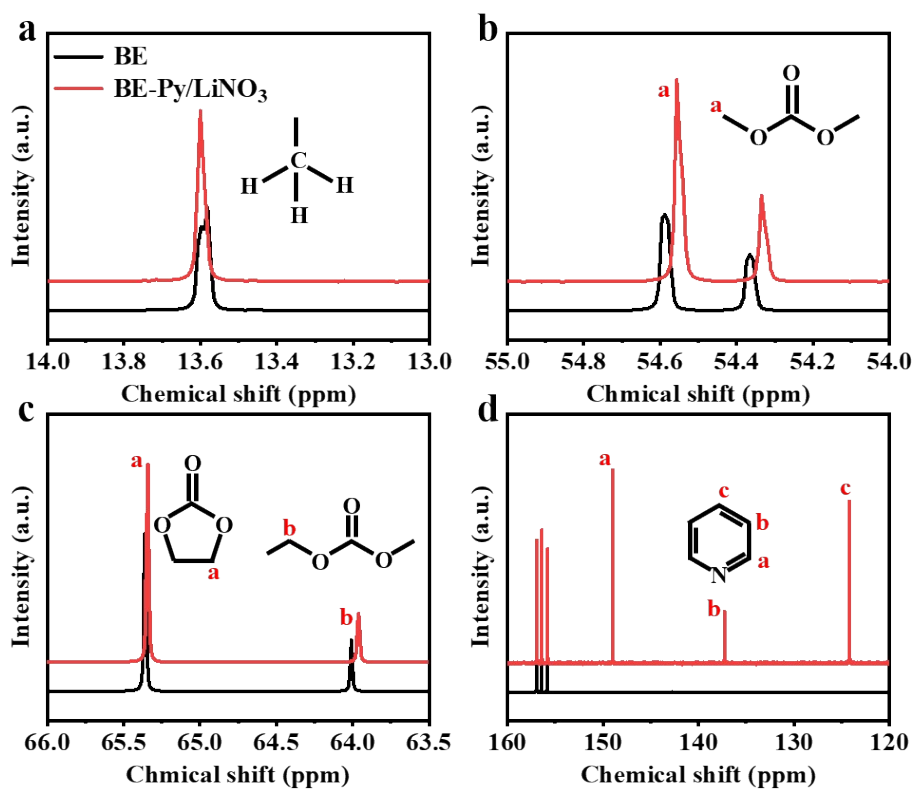


Fig. S5 Enlarged view of ^{13}C peak in Figure S4.

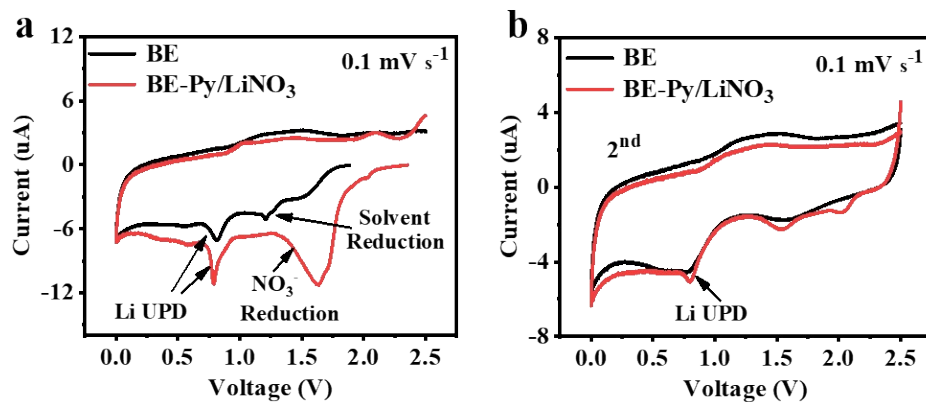


Fig. S6 CV curves of BE and BE-Py/LiNO₃ in Li|Cu half cells scanned at 2.5~0 V, The BE shows a small peak at 1.18 V and a sharp peak at 0.81 V in the first cathodic scan, which can be attributed to the decomposition of the LiPF₆ and the underpotential deposition of Li metal, respectively. For BE-Py/LiNO₃ electrolyte, the obvious and broad reduction at 1.68 V is ascribed to the reduction of LiNO₃, and the decomposition of solvent and Li salt is prevented.

Table S1. CE comparison of our designed electrolyte with previously reported works

Electrolyte	Li CE performance	Reference
1.0 M LiPF ₆ in EC/DMC/EMC=1:1:1 Vol% with 1 wt% LiNO ₃	95.86% (1 mA cm ⁻² , 1 mAh cm ⁻²)	This work
1.2 M LiDFOB in EC/EMC=3:7 Vol%	95%	Energy Environ. Sci., 2018 , 11, 2600- 2608
1.0 M LiPF ₆ in EC/DMC=1:1 Vol% with 2 wt% SO ₂ Cl ₂	95% (0.5 mA cm ⁻² , 0.5 mAh cm ⁻²)	J. Mater. Chem. A. 2019 , 7, 25003- 25009
1.0 M LiPF ₆ in EC/DEC=1:1 Vol% with 0.5 wt% Sn(OTf) ₂ and 5 wt% LiNO ₃	98.4% (1 mA cm ⁻² , 1 mAh cm ⁻²)	Adv. Mater. 2020 , 32, 2001740
1.0 M LiPF ₆ in FEC/EC/DEC=2:9:9 Vol% with 0.1 M RbCE	97.1% (0.5 mA cm ⁻² , 1 mAh cm ⁻²)	Adv. Funct. Mater. 2021 , 2102128
1.0 M LiPF ₆ in EC/DMC=1:1 Vol% with 5 wt% FEC	94.1% (0.5 mA cm ⁻² , 0.5 mAh cm ⁻²)	ACS Energy Lett. 2021 , 6, 1839-1848
1.0 M LiPF ₆ in EC/DEC=1:1 Vol% with 2 wt% 2-FP	90.61% (0.5 mA cm ⁻² , 1 mAh cm ⁻²)	Chem. Eng. J. 2020 , 393, 124789
1.0 M LiPF ₆ in EC/DEC=1:1 Vol% with 10 wt% VEC	93.2% (0.25 mA cm ⁻² , 1 mAh cm ⁻²)	ACS Appl. Mater. Interfaces. 2019 , 11, 6118-6125
1.0 M LiPF ₆ in EC/DEC=1:1 Vol% with 0.2 wt% CuF ₂ and 1 wt% LiNO ₃	98.1% (0.25 mA cm ⁻² , 1 mAh cm ⁻²)	Angew. Chem. Int. Ed. 2018 , 57, 14055-14059
1.0 M LiPF ₆ in FEC/DMC=1:4 Vol%	98.5% (0.5 mA cm ⁻² , 1 mAh cm ⁻²)	ACS Energy Lett. 2017 , 2, 1321-1326
1.0 M LiPF ₆ in PC with 2 wt% LiAsF ₆ and 2 wt% VC	96.7%	ACS Energy Lett. 2018 , 3, 14-19
3.7 M LiFSI in DMC	97.5% (0.5 mA cm ⁻² , 1 mAh cm ⁻²)	Adv. Mater. 2018 , 30, 1706102
1.2 M LiFSI in EC/EMC=2:8 Vol% with BTFE and 0.15 M LiDFOB	98.5% (0.5 mA cm ⁻² , 1 mAh cm ⁻²)	ACS Energy Lett. 2018 , 3, 2059-2067
5 M LiFSI in EC/DEC=1:1 Vol% with 0.5 wt% AN	98.4% (0.5 mA cm ⁻² , 1 mAh cm ⁻²)	Nano Energy. 2021 , 88, 106298

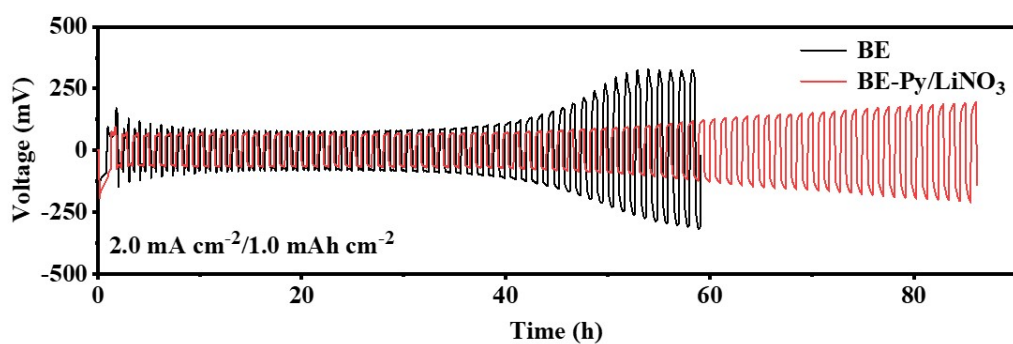


Fig. S7 Cycling stability of Li plating/stripping in BE and BE-Py/LiNO₃ at 2 mA cm⁻² and 1 mAh cm⁻².

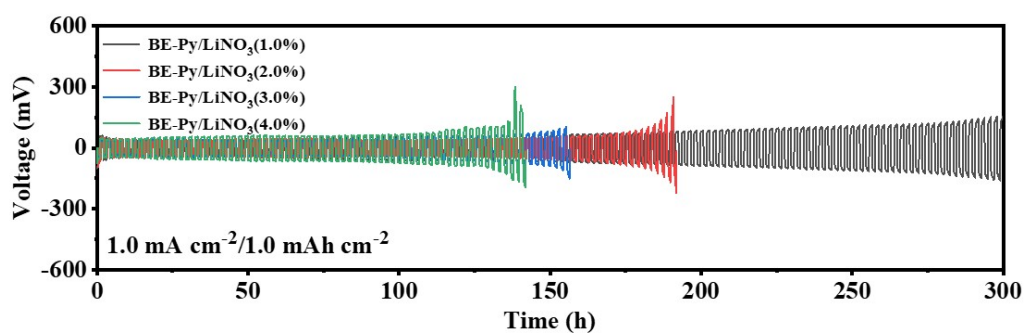


Fig. S8 Cycling stability of Li plating/stripping in BE-Py/LiNO₃ with different amounts of Py/LiNO₃ at 1 mA cm⁻² and 1 mAh cm⁻².

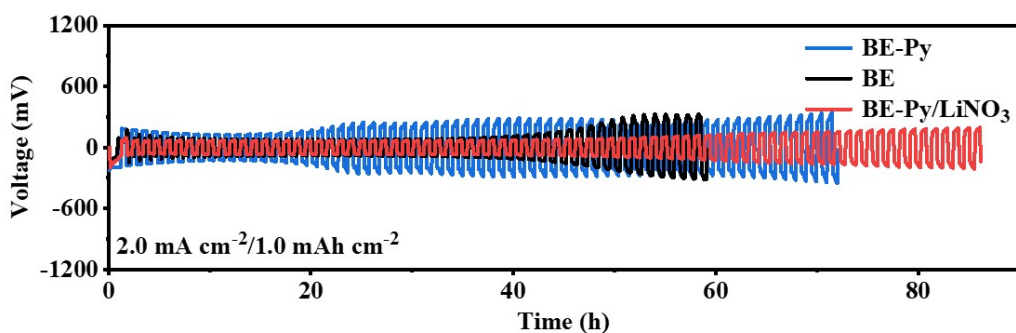


Fig. S9 Cycling stability of Li plating/stripping in BE-Py, BE and BE-Py/LiNO₃ at 2 mA cm⁻².

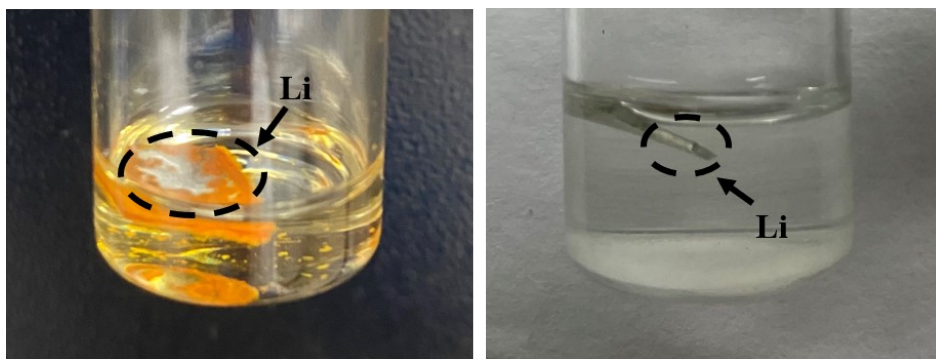


Fig. S10 Optical images of Li metal placed in Pyridine for 5 min and BE-Py/LiNO₃ for 15 days respectively.

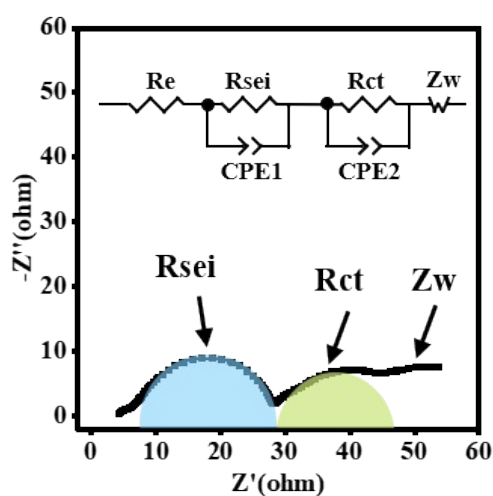


Fig. S11 Equivalent circuit of Nyquist plots of EIS for symmetric cells.

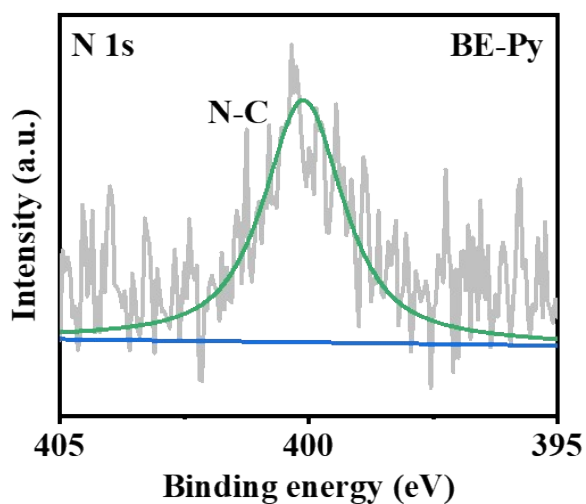


Fig. S12 XPS spectra of the SEI films in Li||Li symmetric cells after 10 cycles at 1 mA cm⁻² and 1 mAh cm⁻². The peak at 400.2 eV in N 1s spectrum can be indexed to be N-C bond because of the use of Py.

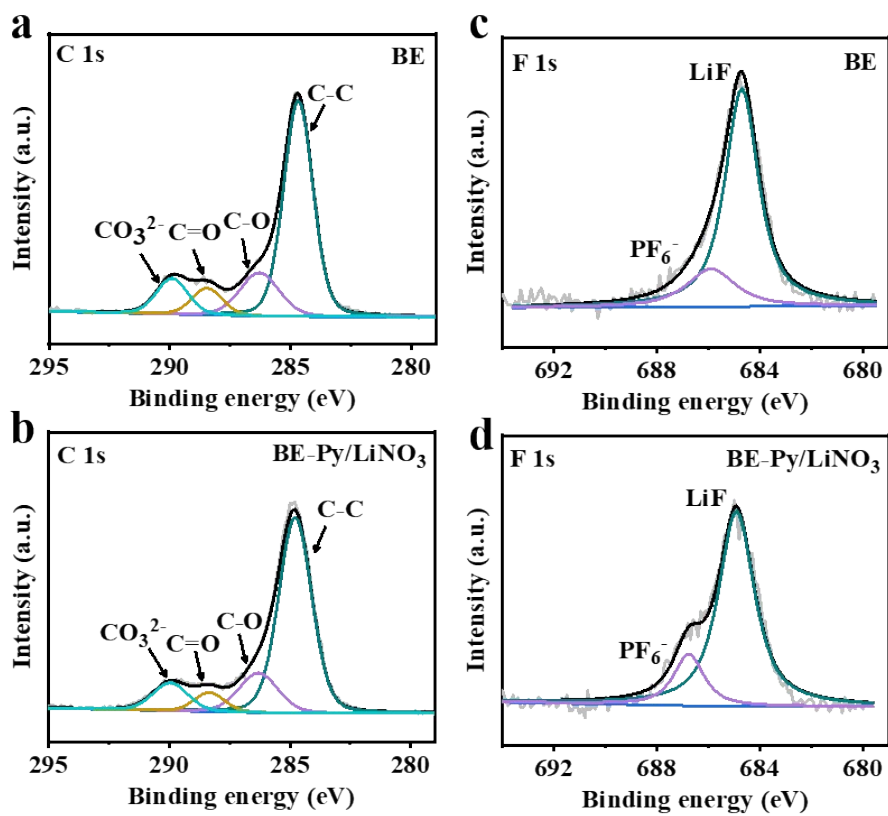


Fig. S13 XPS spectra of the SEI films in Li||Li symmetric cells after 10 cycles at 1 mA cm⁻² and 1 mAh cm⁻². (a and b) C 1s spectra. (c and d) F 1s spectra.