

Electronic Supplementary Information (ESI)

A nonflammable phosphate-based localized high-concentration electrolyte for safe and high-voltage lithium metal batteries

Xiaofei Wang^a, Wenjun He^a, Haoliang Xue^a, Daoming Zhang^a, Jin Wang^b, Lina Wang^{b*}, Jun Li^{a*}.

a. State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, SINOPEC Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China

b. State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Innovation Center for Textile Science and Technology, Donghua University, Shanghai 201620, China

*Corresponding authors: Lina Wang (email: linawang@dhu.edu.cn) and Jun Li (email: lijun.sshy@sinopec.com).



Fig. S1 The Photograph of flammability testing of HFE.

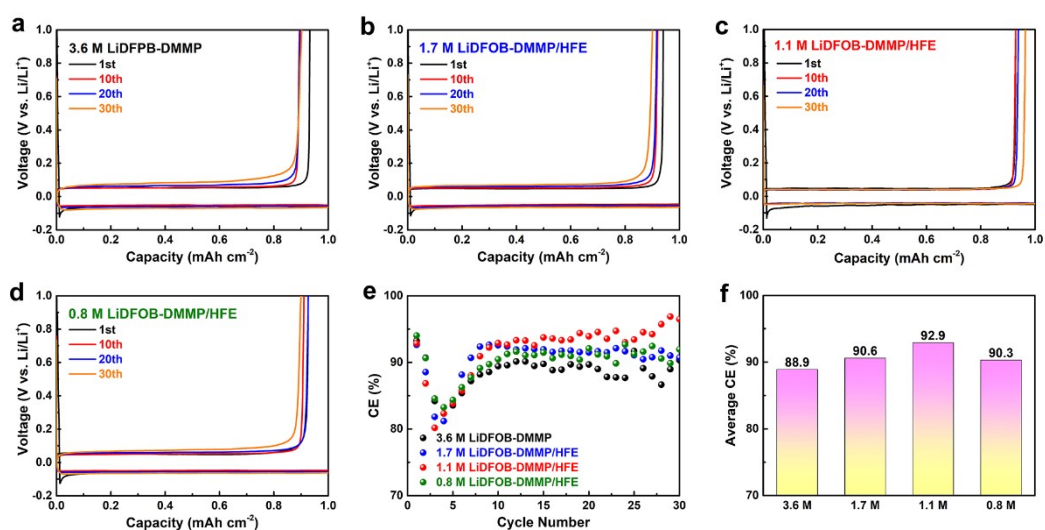


Fig. S2 Electrochemical performance of Li||Cu cells with different LiDFOB-DMMP/HFE electrolytes. Li plating/stripping profiles of Li||Cu cells with (a) 3.6 M LiDFOB-DMMP, (b) 1.7 M LiDFOB-DMMP/HFE, (c) 1.1 M LiDFOB-DMMP/HFE and (d) 0.8 M LiDFOB-DMMP/HFE electrolytes at a current density of 0.5 mA cm^{-2} and a deposition capacity of 1 mAh cm^{-2} . (e) The corresponding CEs of Li||Cu cells with different electrolytes. (f) The average CEs of Li||Cu cells with different electrolytes over 30 cycles.

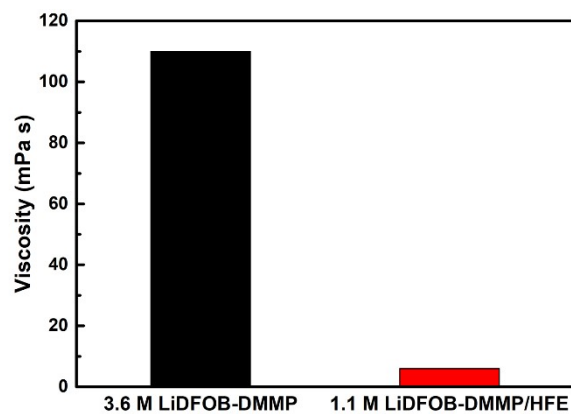


Fig. S3 The viscosity of 3.6 M LiDFOB-DMMP and 1.1 M LiDFOB-DMMP/HFE electrolytes.

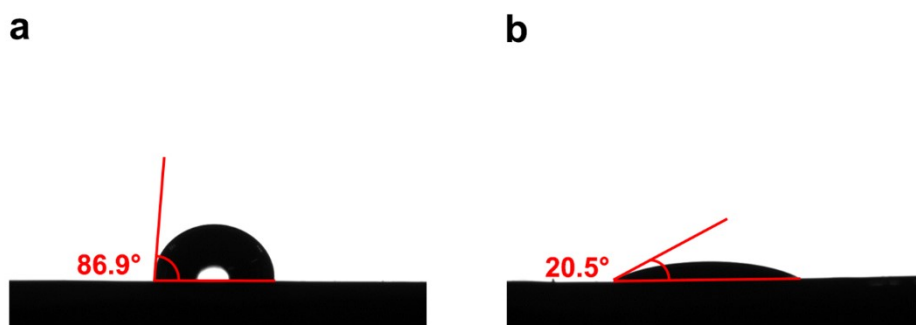


Fig. S4 The contact angles of (a) 3.6 M LiDFOB-DMMP and (b) 1.1 M LiDFOB-DMMP/HFE electrolytes over the surface of Celgard 2325 separator.

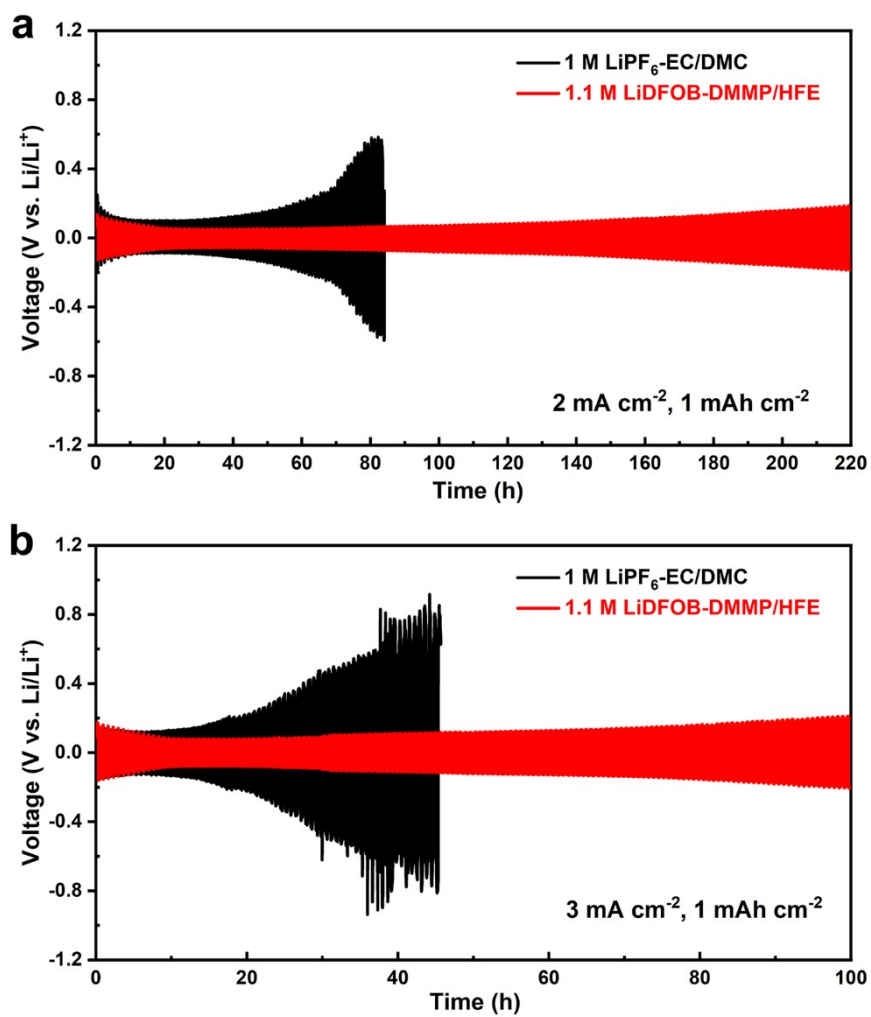


Fig. S5 The cyclic performance of Li||Li symmetrical cells with different electrolytes at (a) 2 mA cm⁻², 1 mAh cm⁻²; (b) 3 mA cm⁻², 1 mAh cm⁻².

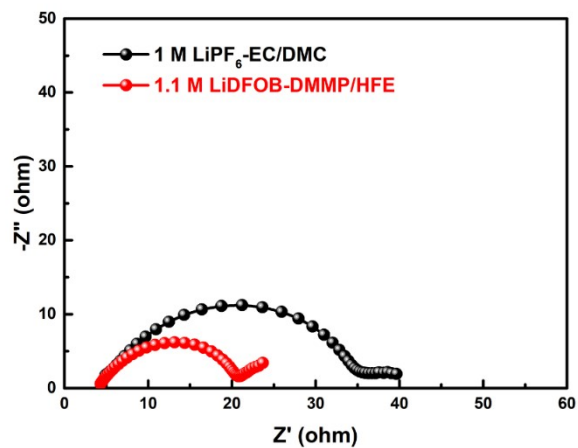


Fig. S6 Impedance spectra of the Li||Li cells cycled at 0.5 mA cm^{-2} after 10th cycle.

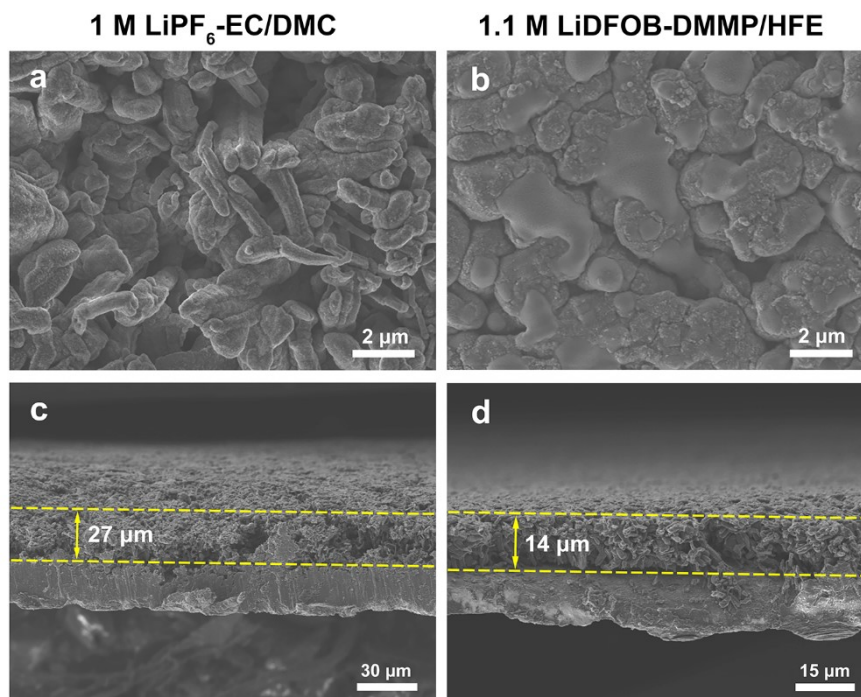


Fig. S7 Morphologies of the deposited Li in 1 M LiPF₆-EC/DMC and 1.1 M LiDFOB-DMMP/HFE electrolytes. (a, b) Top and (c, d) cross-sectional SEM images of the deposited Li obtained by plating 2 mAh cm^{-2} of Li on Cu substrate at a current density of 0.5 mA cm^{-2} .

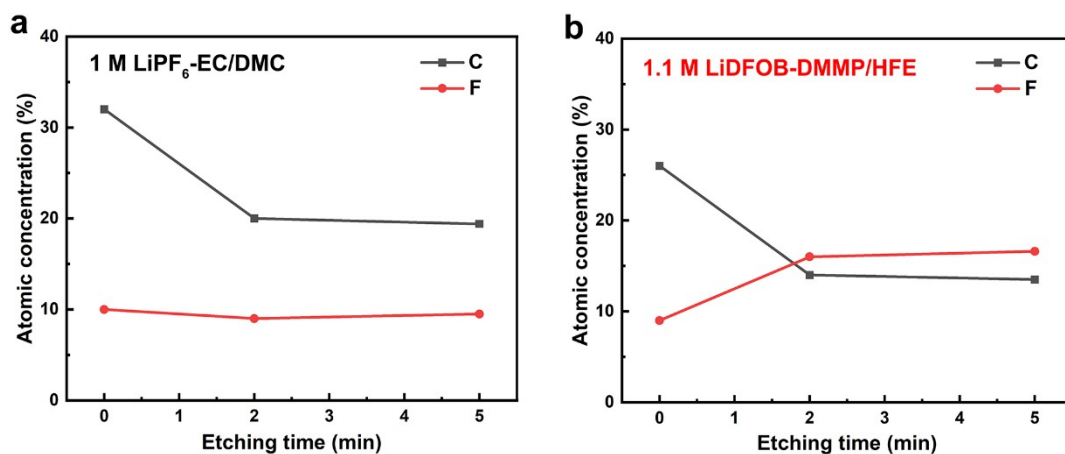


Fig. S8 The C and F atomic contents by XPS measurement of the SEI layer formed in (a) 1 M LiPF₆-EC/DMC and (b) 1.1 M LiDFOB-DMMP/HFE electrolytes.

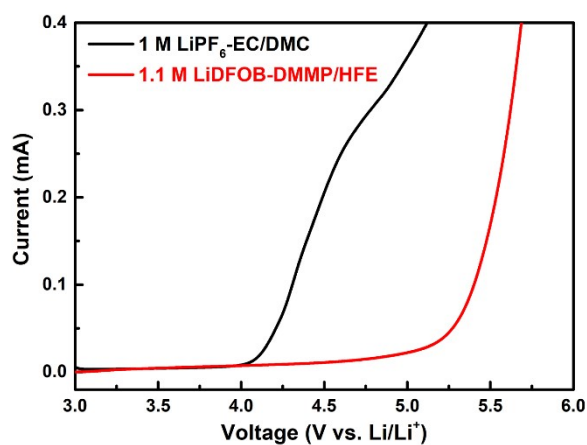


Fig. S9 Oxidative stabilities of 1 M LiPF₆-EC/DMC and 1.1 M LiDFOB-DMMP/HFE electrolytes in a two-electrode cell with a stainless steel as the working electrode and Li metal as the reference/counter electrode at a scan rate of 1 mV s⁻¹.

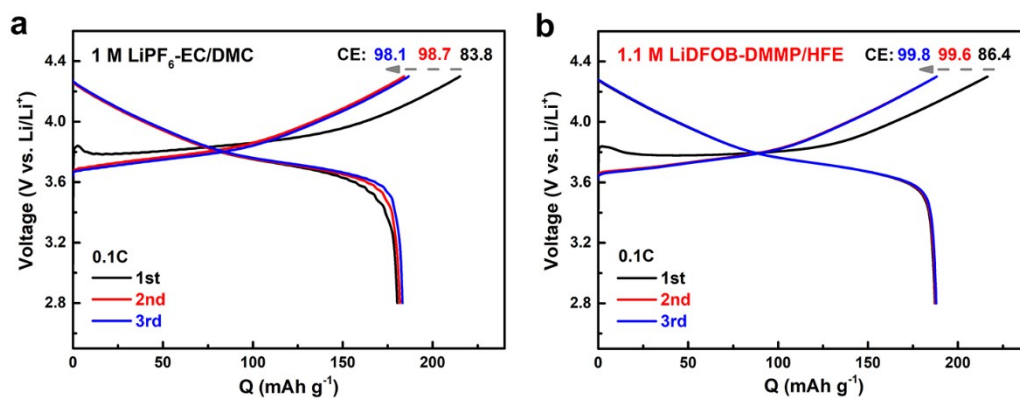


Fig. S10 The initial three charge-discharge profiles of Li||NMC622 cells with (a) 1 M LiPF₆-EC/DMC and (b) 1.1 M LiDFOB-DMMP/HFE electrolytes in the voltage range of 2.8–4.3 V at 0.1C.

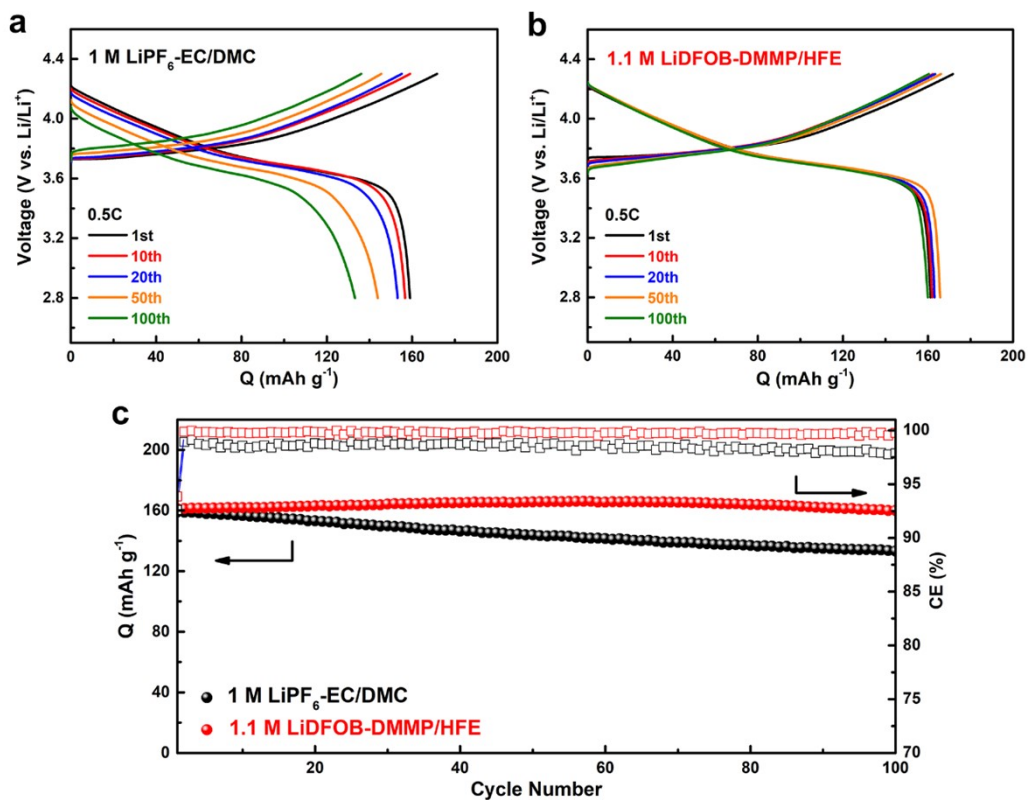


Fig. S11 Electrochemical performance of Li||NMC622 full cells with different electrolytes under the charging cutoff voltage of 4.3 V. Galvanostatic charge–discharge curves with (a) 1 M LiPF₆-EC/DMC and (b) 1.1 M LiDFOB-DMMP/HFE electrolytes at 0.5 C. (c) Cycling stability and CEs at 0.5 C.

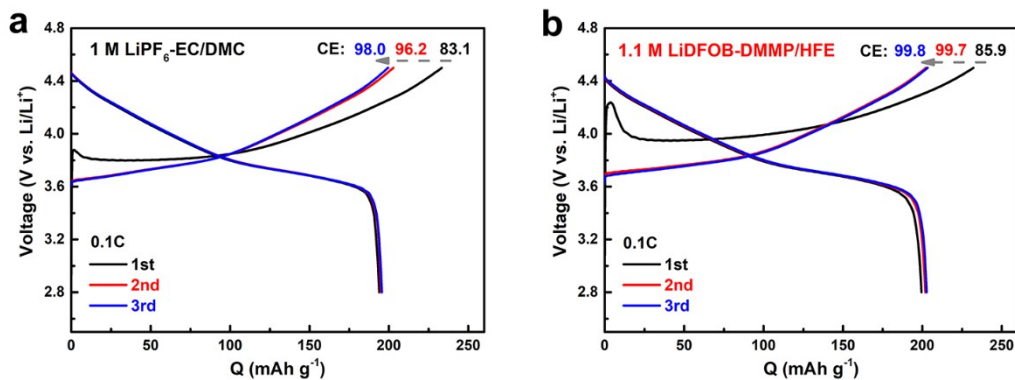


Fig. S12 The initial three charge-discharge profiles of Li||NMC622 cells with (a) 1 M LiPF₆-EC/DMC and (b) 1.1 M LiDFOB-DMMP/HFE electrolytes in the voltage range of 2.8–4.5 V at 0.1C.

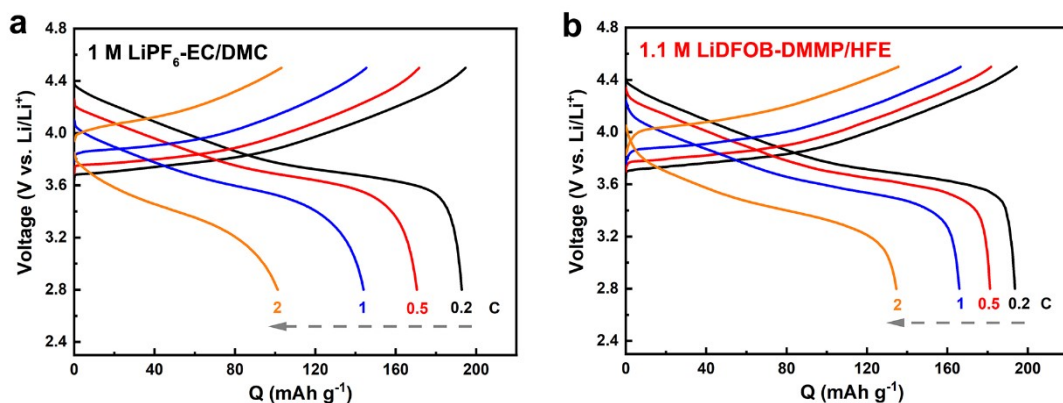


Fig. S13 The representative charge-discharge profiles of Li||NMC622 cells at different C-rates with (a) 1 M LiPF₆-EC/DMC and (b) 1.1 M LiDFOB-DMMP/HFE electrolytes.

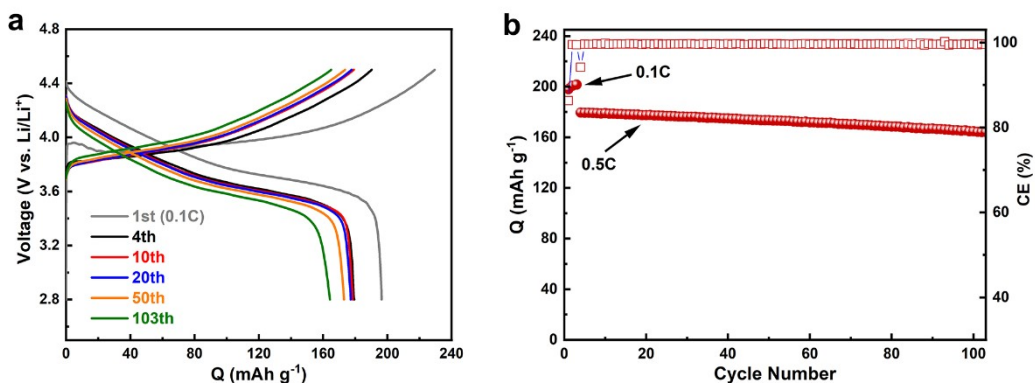


Fig. S14 Electrochemical performance of Li||NMC622 battery using 1.1 M LiDFOB-DMMP/HFE electrolyte with ultrathin Li (50 μm), high loading cathode (18 mg cm^{-2}) and medium electrolyte (50 μL) under the voltage window of 2.8–4.5 V. (a) Representative charge–discharge profiles and (b) corresponding cycling performance. The battery is firstly activated at 0.1 C for three cycles, and then tested at 0.5 C for 100 cycles.

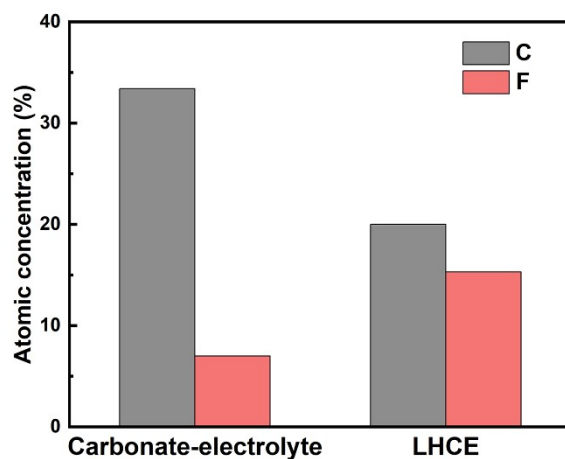


Fig. S15 The C and F atomic composition ratios by XPS measurement of the CEI film formed in 1 M LiPF₆-EC/DMC (Carbonate-electrolyte) and 1.1 M LiDFOB-DMMP/HFE electrolytes (LHCE).