

Supporting Information

Self-Healing Interface on Lithium Metal with Lithium Difluoro(bisoxalato) Phosphate for Enhanced Lithium Electrochemistry

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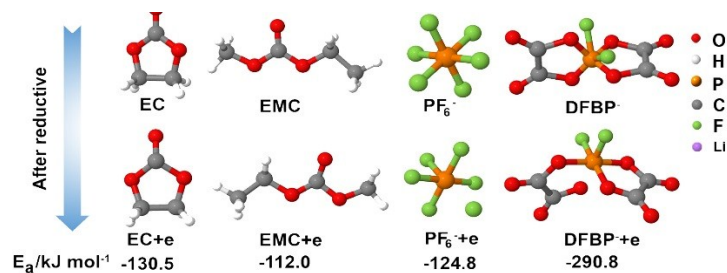


Figure S1. The restore structure of EC, EMC, PF_6^- and DFBP $^-$.

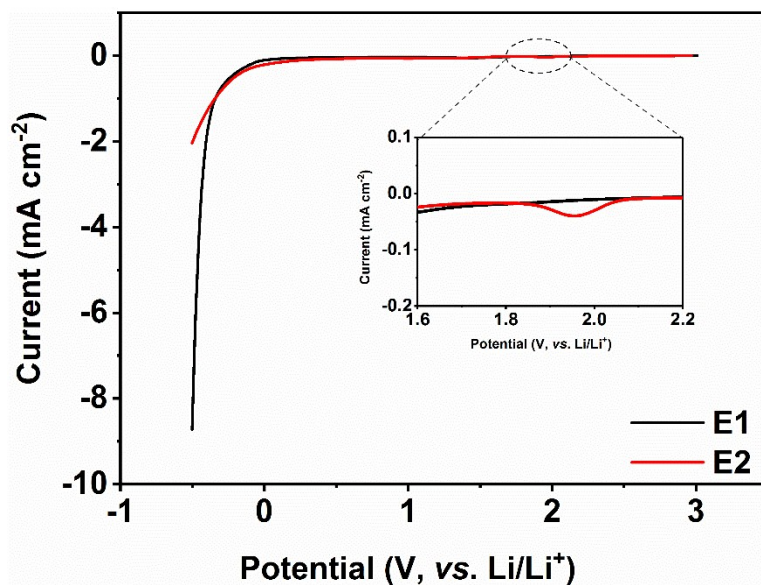


Figure S2. The LSV curves of Pt electrodes in Li-Pt cells cycled with E1 and E2 electrolyte.

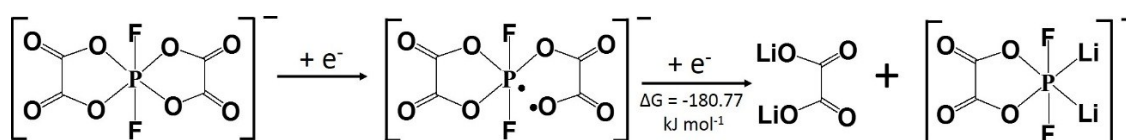


Figure S3. The possible reaction path about evolution of DFBP $^-$.

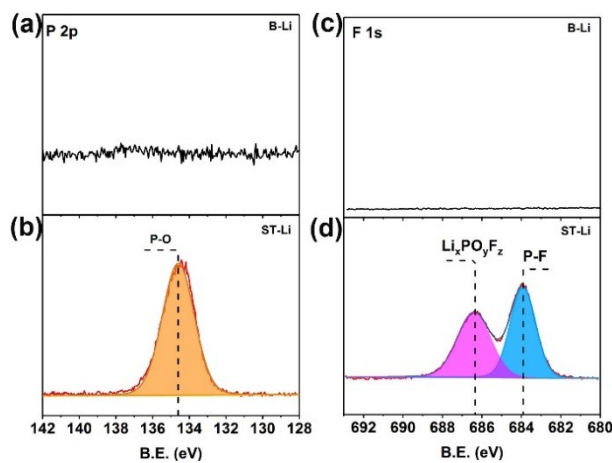


Figure S4. XPS spectrums (a, b) P 2p and (c, d) F 1s of bare lithium electrode before and after

surface treatment.

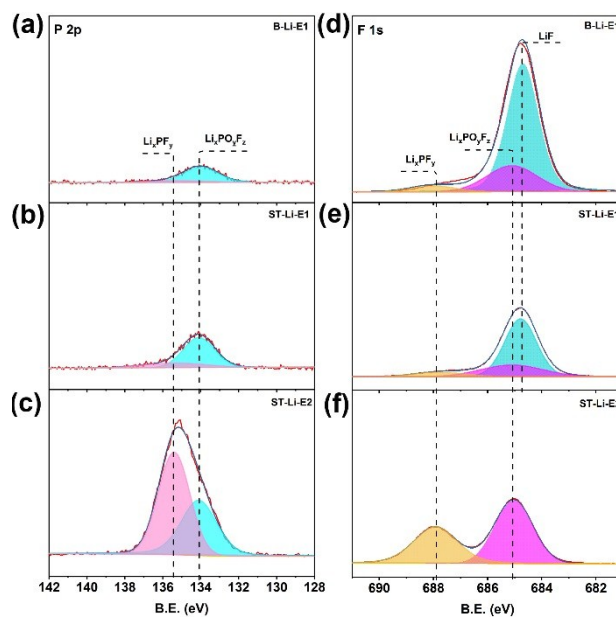


Figure S5. XPS spectrums of (a, b, c) P 2p and (d, e, f) F 1s of (a, d) B-Li cycled in E1, (b, e) ST-Li cycled in E1 and (c, f) ST-Li cycled in E2 electrolyte.

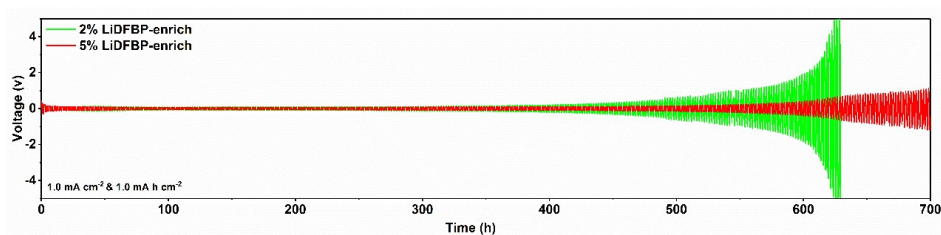


Figure S6. The comparison of cyclic stability of Li symmetric cell cycled in the 2% and 5% LiDFBP-riched E2 electrolyte. The cycleability improvement increases with the enhanced concentration of LiDFBP, indicative of LiDFBP belonging to the consumables.

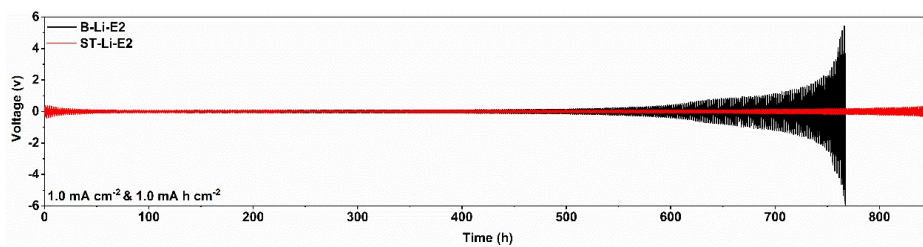


Figure S7. The cycle performances of cells using B-Li (black line) or ST-Li (red line) cycled in E2. The latter obtains a lower overpotential and longer lifetime than that of former the pre-forms.

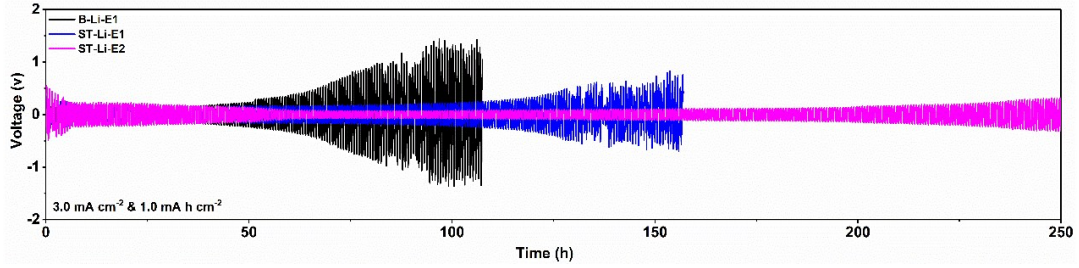


Figure S8. Cyclic stability of Li-Li symmetric cells with a lithium capacity of 3.0 mA h cm^{-2} at a current density of 1.0 mA cm^{-2} .

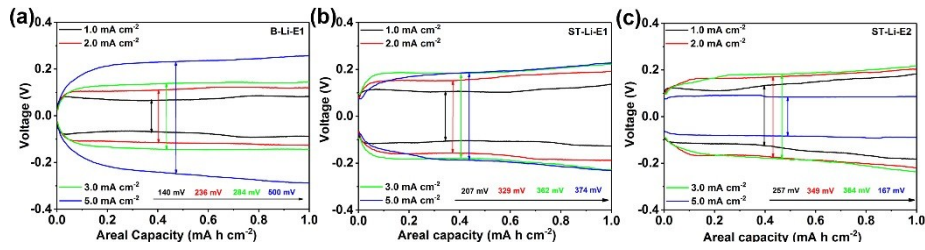


Figure S9. Rate performances of (a) B-Li cycled in E1, (b) ST-Li cycled in E1, and (c) ST-Li cycled in E2 at different current densities of 1, 2, 3 and 5 mA cm^{-2} , respectively.

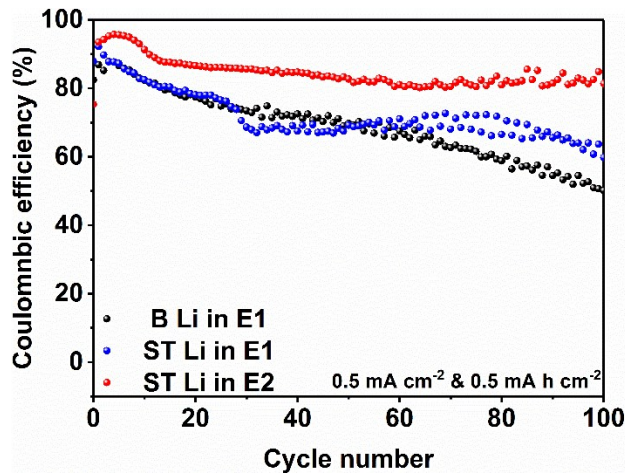


Figure S10. The coulombic efficiency of Li||Cu cells of B-Li cycled in E1, ST-Li cycled in E1, and ST-Li cycled in E2 at current densities of 0.5 mA cm^{-2} with a capacity of 0.5 mA h cm^{-2} .

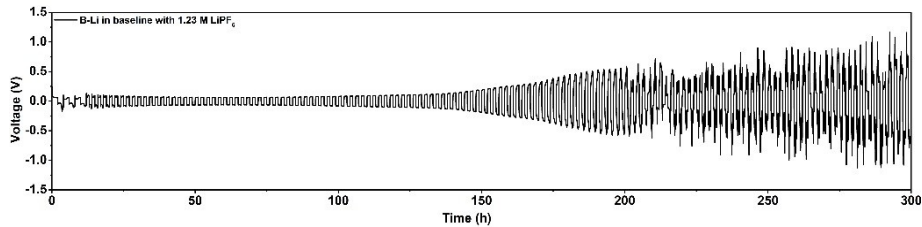


Figure S11. Cyclic stability of Li-Li symmetric cell with a Li capacity of 1.0 mA h cm^{-2} at a current density of 1.0 mA cm^{-2} in LiDFBP-free with 1.23 M LiPF_6 .

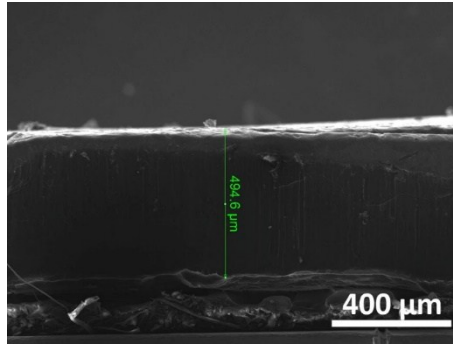


Figure S12. The cross-section SEM image of the pristine Li metal electrode.

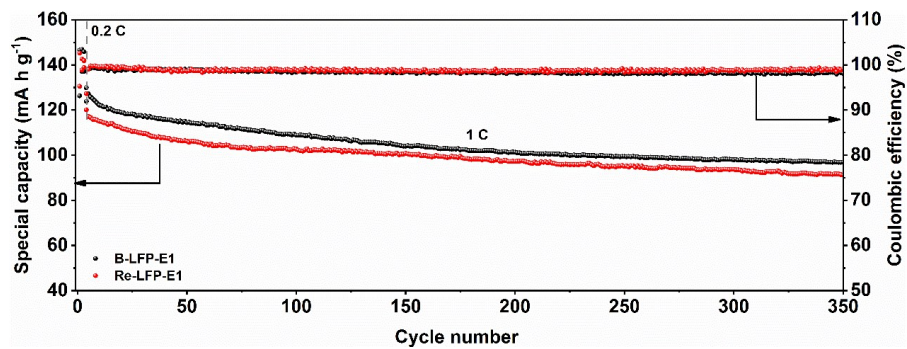


Figure S13. The comparison of cyclic stability of B-Li||Bare LiFePO₄ (B-LFP) and B-Li||recycled LiFePO₄ cell (Re-LFP). The recycled LiFePO₄ electrode is performed by pre-cycling in E2 electrolyte at 0.2 C for 3 cycles, and then reassembled with fresh lithium foil as counter electrode and cycled in E1.

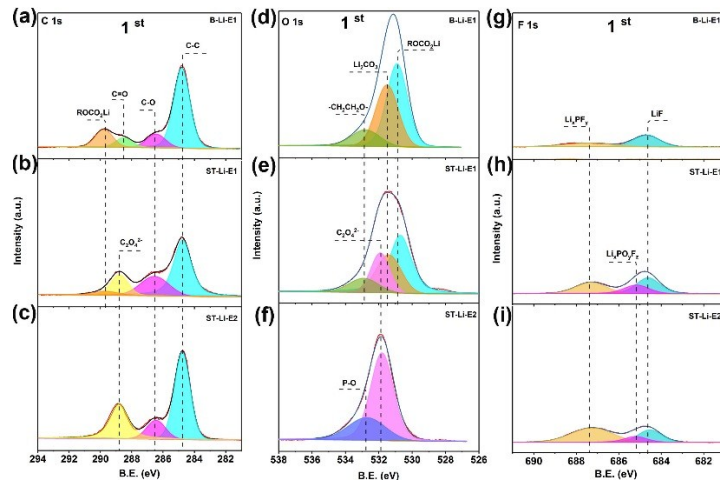


Figure S14. XPS spectra of (a, b, c) C 1s, (d, e, f) O 1s and (g, h, i) F 1s of (a, d, g) B-Li cycled in E1, (b, e, h) ST-Li cycled in E1 and (c, f, i) ST-Li cycled in E2 electrolyte after 1st cycle..

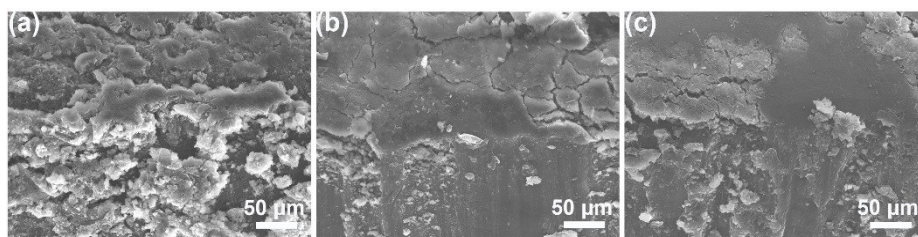


Figure S15. SEM images of (a) B-Li-E1, (b) ST-Li-E1, and (c) ST-Li-E2 of Li-LiFePO₄ (Li-LFP) cells at a rate of 1C after 100 cycles from side view.

Experimental Section

Electrolyte preparation: Carbonate solvents (EC and EMC) and Lithium salt (lithium hexafluorophosphate) were obtained from Guangzhou Tinci Materials Technology Co., Ltd., China. The LiDFBP (>99%) was purchased from Chemtros Co., Ltd., Korea. The baseline electrolyte marked as E1 of 1.0 M LiPF₆ in a mixed solvent of EC and EMC (1:1, in weight) was prepared in the argon-filled glove box (MBraun Germany), which oxygen and water were controlled below 0.1 ppm. The 5% LiDFBP (weight ratio) was added into baseline electrolyte as the LiDFBP-enrich electrolyte marked as E2.

Electrode preparation and cell assembly: The Li metal (12 mm, diameter) signed as ST-Li was removed the surface and then soaked in 15% (in weight) LiDFBP-enrich electrolyte. The LiFePO₄ electrode was prepared by mixing 80 wt. % LiFePO₄, 10 wt. % polyvinylidene fluoride (PVDF) and 10 wt. % acetylene black in N-methyl-2-pyrrolidinone (NMP) on Al current collector, which was dried at 120°C for 12 h in a vacuum oven. The average loading of the LiFePO₄ on prepared cathode is about 7.5 mg cm⁻². The 2025-type Li-Li symmetric cell was assembled in the glove box with Li metal anode (B-Li or ST-Li) and the Celgard 2400 polypropylene porous membrane was employed as separators. The Li-LiFePO₄ (Li-LFP) cell was fabricated with Li metal electrode as anode and LiFePO₄ electrode as cathode.

Electrochemical Measurements: Linear sweep voltammetry (LSV) of E1 and E2 electrolyte was tested by Li-Pt cells using Pt as cathode electrode and Li metal as anode electrode on Solartrio-1480 instrument (England). The charge/discharge performance of Li-Li symmetric cell and Li-LFP cell were tested by LAND system (CT2001A, Wuhan, China). The Li-Li symmetric cell was cycled at different current densities of 1.0 and 3.0 mA cm⁻² with various capacities of 1.0, and 3.0 mAh cm⁻², respectively. Rate performance of Li symmetric cell was exhibited at 1, 2, 3 and 5 mA cm⁻², respectively. The cycle of Li-LFP cell was tested at 0.2 C for initial three formation cycles and cycled at 1 C between 2.1 V to 4.2 V at room temperature. Electrochemical impedance spectroscopy (EIS) of Li symmetric cell and Li-LiFePO₄ cell were measured by PGSTAT-30 electrochemical station (Autolab, Metrohm, Netherlands) at a frequency range from 10⁵ to 10⁻² Hz.

Physical characterization: the morphology of cycled Li metal anodes in Li-Li and Li-LFP cells were observed with Scanning Electron Microscope (SEM, FEI-quanta-FEG-250, USA). In order to remove the residuary electrolyte on the Li metal anode, all the cycled Li anode was rinsed with EMC solvent for three times and then left overnight in glove box. And then, the surface compositions of Li metal anode were analyzed by X-ray photoelectron spectroscope (XPS, Thermo Fisher Scientific, UK) under extreme vacuum.

Theoretical calculations: The density functional theory (DFT) calculations were performed on Gaussian 09 package. The structures of carbonate solvents (EC and EMC), Hexafluorophosphate anion (PF₆⁻) and Difluorobisoxalic acid phosphate (DFBP⁻) were optimized at B3LYP/6-311++G(d) level. Electron affinity energy (E_a) corresponding to the reductive property of all the anionic and neutral molecules were calculated from the energy (E, RB3LYP)

before and after reduction of various species, for example, $E_a(\text{EC}) = E(\text{EC}+e^-) - E(\text{EC})$. Binding energy (E_b) was converted from the energy of various species, for example, $E_b(\text{Li-LiF}) = [E(\text{Li-LiF}) - E(\text{Li}) - E(\text{LiF})]$.