Low-Temperature and Fast-Charge Lithium Metal Batteries Enabled by Robust Interphase via Dual-Additive Synergistic Strategy

Jiaxin Liu[a], Yuzhen Zeng[a], Xiaofei Gong[b], Guowei Yu[a]， Ruiqi LI[a]，Lei Zheng[a,b]*

[a]*Hubei Three Gorges Laboratory, Yichang, Hubei, 443007, P. R. China*

[b]*Hubei Xingfa Chemicals Group Co., Ltd., Yichang 443000, China*

*Corresponding Authors

Email:lzheng@xingfagroup.com (L Zheng)

Experimental Details

Electrolytes and electrodes

Ethylene carbonate (EC, 99%), ethyl methyl carbonate (EMC, 99%), and diethyl carbonate (DEC, 99%) were purchased from DoDoChem Co. Ltd. LiFSI is a product that was personally developed by the Hubei Xingfa Chemicals Group Co. Ltd. The solvents were dried by 4 Å molecular sieves before utilization. All of the electrolytes were prepared in an argon filled glove box with water and oxygen content below 0.1ppm. 1 M $LiPF_6$ was dissolved into mixtures of EC, EMC, and DEC with volume ratio of 3:5:2 is referred as LPF. For a comparison, 1 M LiFSI dissolved in an identical solvent was termed as FSI. Furthermore, the 1w% $LiPF_6$ and 0.5w% TMSB was dissolved into mixtures of FSI electrolytes which called FPB. The humidity content of above electrolytes was controlled to be less than 10 ppm.

The LFP cathode was prepared to assess the influence of dual additives in LMBs. Generally, the LFP electrodes were prepared by uniformly mixing N-methyl 2-pyrrolidone (NMP), poly(vinylidene fluoride)(PVDF), and carbon black (super-P) with a weight ratio of 90:5:5 and it was casted onto current collector of Al foil. The electrode was dried at 100 °C for 12 h to remove any remaining water in a vacuum oven and subsequently cut into 16.0 mm (diameter) disks. The half cells were assembled in an argon-filled glove box.

Electrochemical measurements

The constant-currents charge and discharge cycling performances of Li||LFP half cells were tested with a LAND test system (CT2001A, China) with a working voltage of 2.5-4.2 V. The rate test of charge-discharge current was set at the ones corresponding to C/5, 0.5C, 1 C,

3 C, 5 C, 10 C, 15 C and 18 C without using a constant-voltage mode at both ends of charge and discharge. The Li||Li symmetric cells were fabricated with 16 mm Li metal foil, and the tests were operated by Land setting for galvanostatic cycling with a current density of 0.5 and 1.0 mA cm^{-2}. Floating test was conducted by the LAND test system (CT2001A, China) preserved at constant voltages for 14400 s from 4.2 V, relying on the half-cell. Linear scanning voltammetry (LSV) and cyclic voltammetry (CV) were performed using three-electrode cells (Al electrode as the working electrode, Li foil as the counter electrode and reference electrode) in the Chenhua electrochemical workstation (CHI660E, Chenhua Instrument Co.) at a scanning rate of 1 mV s-1. The LSV and CV were collected in 2~6 V and 2.5~4.2 V, respectively. Electrochemical impedance spectroscopy (EIS) was carried out in the CHI660E under an open circuit voltage, with a frequency range of 10^5-10^{-2} Hz and an amplitude of 5 mV. All the above tests were carried out at 25 °C.

The tafel plot was obtained from linear sweep voltammetry measurement using Li||Li symmetrical cells at 0.5 mV s–1. Then the values of exchange current density were calculated by the Tafel equation: η=a+blog(I) when the η equaled to 0. I, η represent the current and potential, respectively; a, b refer to the constant which are able to be aquired after fitting the data.The transference number of Li^+ (t_{Li^+}) in the electrolyte was assessed by EIS and the polarization with an agitation voltage of 10 mV for 1 h at room temperature, and t_{Li^+} was calculated by the formulation[3].

$$t_{Li^+} = \frac{I_s(\triangle V - I_0 R_0)}{I_0(\triangle V - I_s R_s)}$$

Where I_0 and I_s are the initial current and the stable-state current, R_0 and R_s denotes the resistances of the initialization and steady-state, and ΔV is the perturbation voltage.

In GITT measurement, a short negative current pulse was applied and then withdrew, followed by a dramatic increase and gradual rise to reach the thermodynamic equilibrium potential. The cells were set to relax for 4 h after every 8 min at discharging/charging rates of 0.5 C.

Li||Cu asymmetric cells were manufactured with 16 mm Li metal foil and Cu foil, respectively, according to the Aurbach CE test[1]. A standard protocol was followed: 1) performing one initial formation cycle with Li deposition of 5 mAh cm^{-2} on Cu under 0.5 mA cm^{-2} and stripping to 1V; 2) deposited 5 mAh cm^{-2} Li on Cu under 0.5 mA cm^{-2} as a Li reservoir; 3) repeatedly stripped/deposited Li of 1 mAh cm^{-2} under 0.5 mA cm^{-2} for 10 cycles; 4) stripped all Li to 1V.

Material characterizations

The cells were disassembled after 100 cycles in an argon-filled glove box. The cycled LFP cathode and lithium disc were rinsed with DMC more than five times to remove remained electrolyte, and then vacuum dried for 10 h at room temperature. The surface morphology of LFP cathode before and after cycle was observed by scanning electron microscope (SEM, Hitachi SU8020 Japan). The chemical composition of LFP cathode surface before and after cycle was analyzed by using Al Ka line as X-ray source by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, USA).

Supplementary tables

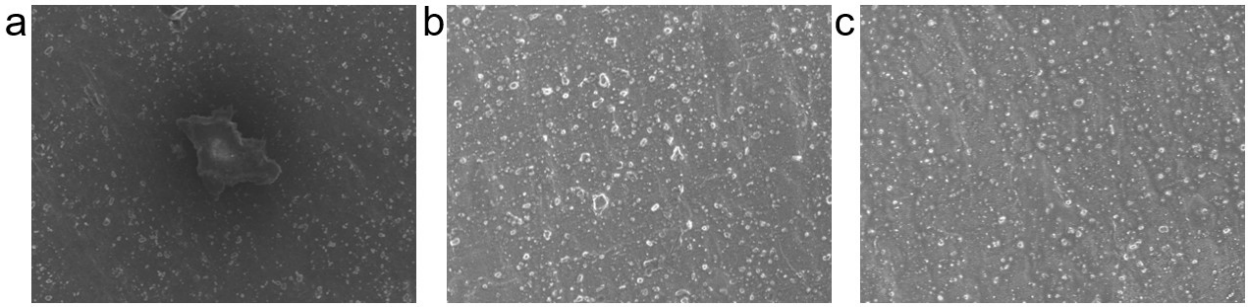

Figure S1. Ex-SEM images of cycled Al foils in (a) FSI, (b) LPF (c) FPB, respectively.

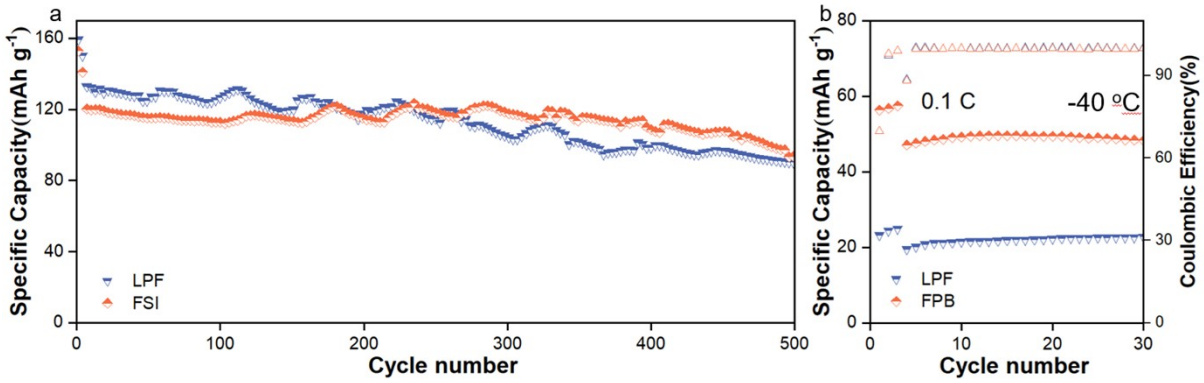

Figure S2. (a) Cycling performance of the Li||LFP half batteries comparing LPF and FSI; (b) Cycling performance of Li||LFP half cells using LPF and FPB electrolytes at -40 °C at 0.1 C.

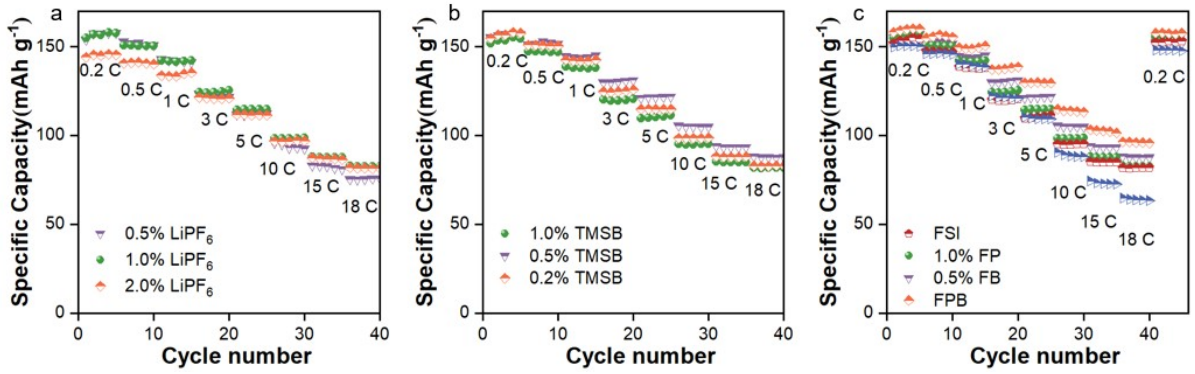

Figure S3. Rate performance of Li||LFP batteries using FSI electrolytes with different amounts of $LiPF_6$ (a) and TMSB (b); (c) Rate performance of the Li||LFP half batteries at different rates from FSI, single-additive (1.0% FP, 0.5% FB) and dual-additive (FPB).

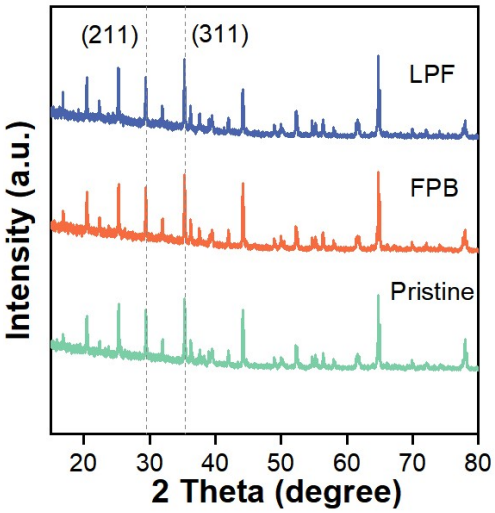

Figure S4. XRD pattern comparing LPF, FPB and pristine electrode.

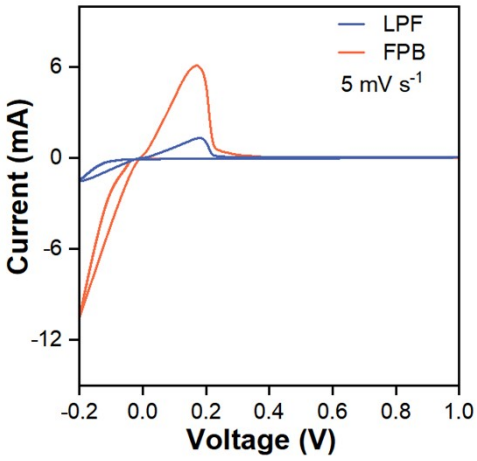

Figure S5. Cyclic voltammetry in Li‖Cu cells in LPF and FPB electrolytes at 5 mV s^{-1}.

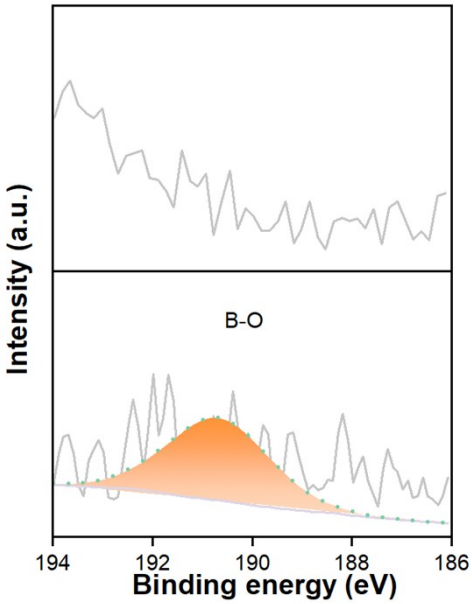

Figure S6. B 1s of the Li anode after 10 cycles in FPB (below) and LPF (above).

References

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