

## **Dendrite Inhibited and Dead Lithium Activated Dual-Function Additive for Lithium Metal Batteries**

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## EXPERIMENTAL METHODS

### *Electrolytes and electrodes*

LiFePO<sub>4</sub> powder, poly (vinyl difluoride) (PVDF) and Super P were mixed in N-methyl pyrrolidone (NMP) at a weight ratio of 8:1:1, stirred for a few hours and evenly coated on aluminium foil, then baked in a vacuum oven at 80°C for 12 h. The laminate was cut into discs (diameter 12 mm). Areal mass loading of LiFePO<sub>4</sub> on discs was ~1.3 mg cm<sup>-2</sup>. 1.0M bistrifluoromethanesulfonimide lithium salt (LiTFSI) and 0.2M lithium nitrate (LiNO<sub>3</sub>) in 1,3-Dioxolane (DOL) and 1,2- Dimethoxyethane (DME) (v/v = 1/1) without other additives was applied as the base electrolyte, added 2-F-5-IPy to base electrolyte to form modified electrolyte. Polypropylene (PP) was applied as the separator.

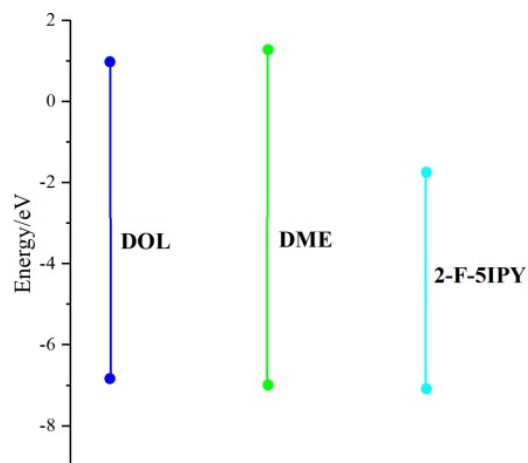
### *Electrochemical tests*

Symmetric cells (both Li-Li foils were applied as working and counter electrodes), the Li||Cu cells and Li||LiFePO<sub>4</sub> cells were assembled as CR2032 or CR2025 coin cells in a glove box filled argon (both H<sub>2</sub>O and O<sub>2</sub> concentrations below 0.1 ppm), the amount of electrolyte added to each cell is controlled at 40-50μL. All cell tests were carried out on NEWARE battery testers inside temperature chambers with the temperature held at 25 °C. The voltage windows for Li||LiFePO<sub>4</sub> cells cycling were 2.5-4.2 V. Li plating/stripping measurements were performed on NEWARE multichannel battery testing system at 25 °C. EIS (Electrochemical Impedance Spectroscopy) tests were carried out on the CHI660D electrochemical workstation in the frequency range of 0.1-10<sup>6</sup> Hz. LiFePO<sub>4</sub> was used as cathode material for

Li||LiFePO<sub>4</sub> cells (CR2025). The Li||LiFePO<sub>4</sub> cells were tested in a voltage range of 2.8-4.2 V on NEWARE multichannel battery testing system.

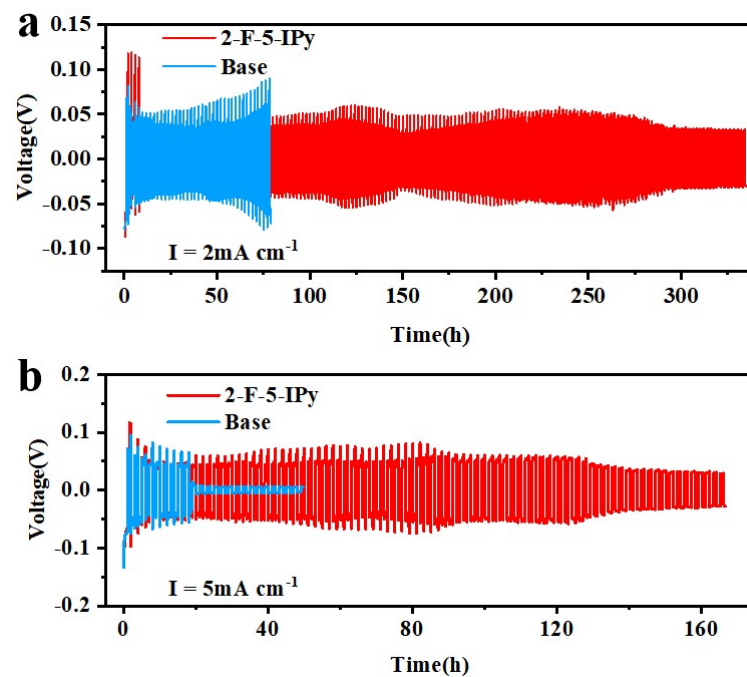
### ***Characterizations***

The morphology of the electrodes was examined by a field emission scanning electron microscope (SU8010, Hitachi) equipped with an energy dispersive X-ray spectroscopy detector (INCA Energy, Oxford Instruments). In addition, the surface film characterization was analyzed by X-ray photoelectron spectroscopy (XPS, PHI VersaProbe 4). The binding energy was corrected based on the C1s peak of hydrocarbon at 284.8 eV. Prior to measurements, the cells are disassembled in an argon-filled glove box to retrieve electrode samples. And all the samples were rinsed with an ethylene carbonate (EC) solvent to remove the residual electrolyte salt and by-products.

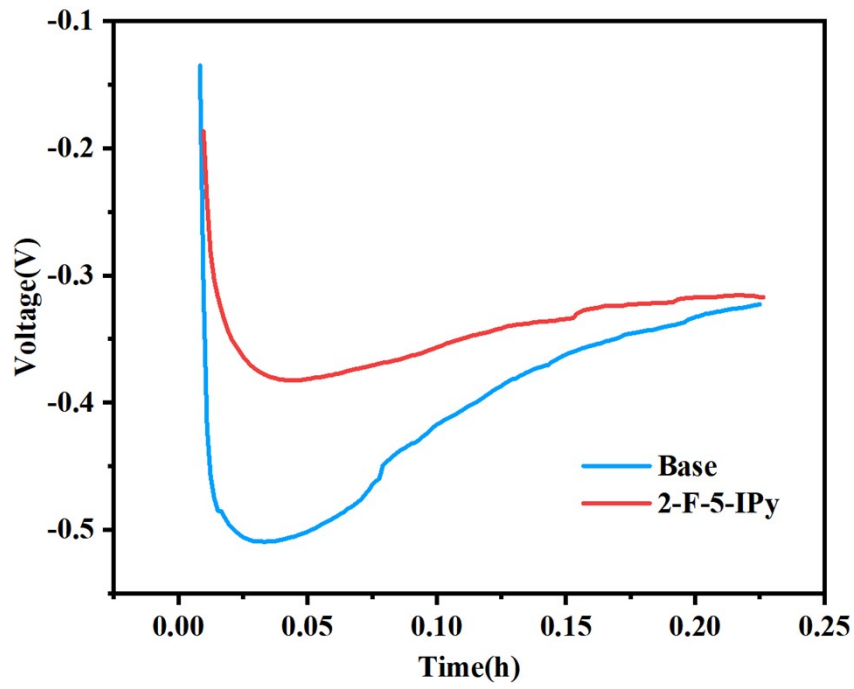


**Figure S1.** HOMO and LUMO of 2-F-5-IPy, DOL and DME.

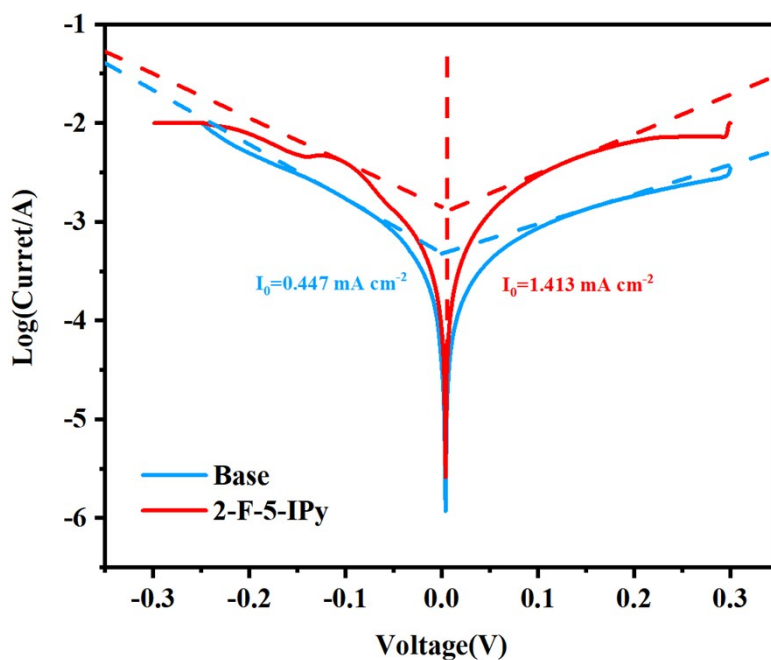
Based on the frontier (molecular) orbital theory, the electrochemical oxidation/reduction potentials of organic molecules are closely related to the highest occupied molecular orbital energy (HOMO) and lowest unoccupied molecular orbital energy (LUMO). Generally speaking, the higher the HOMO of a molecule, the easier it is to oxidized. At the same time, the lower the LUMO energy of the molecule, the easier it is to reduced.<sup>1</sup>



**Figure S2.** Symmetrical cell cycle curves at different current densities. (a)  $2 \text{ mA cm}^{-2}$  and  $2 \text{ mAh cm}^{-2}$ . (b)  $5 \text{ mA cm}^{-2}$  and  $5 \text{ mAh cm}^{-2}$ .

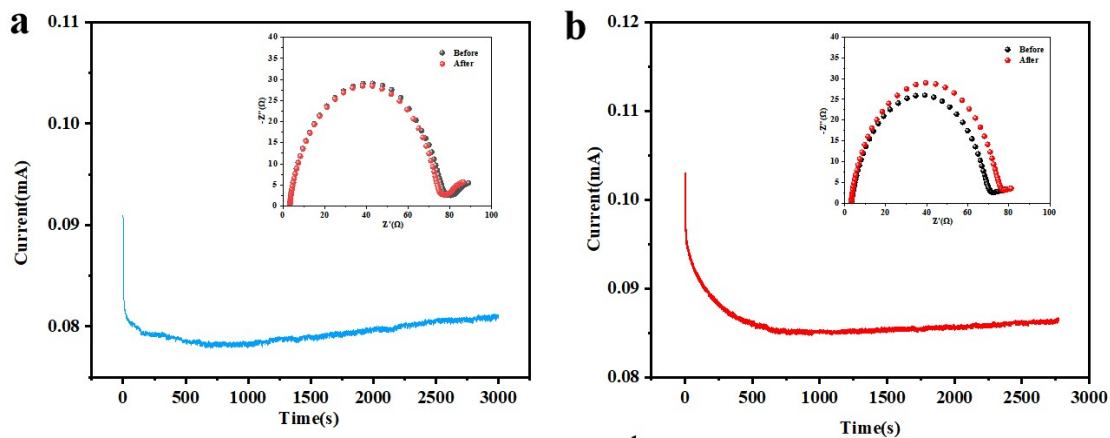


**Figure S3.** Over-potentials of lithium-ion deposited in the first cycle on Li||Cu cells.



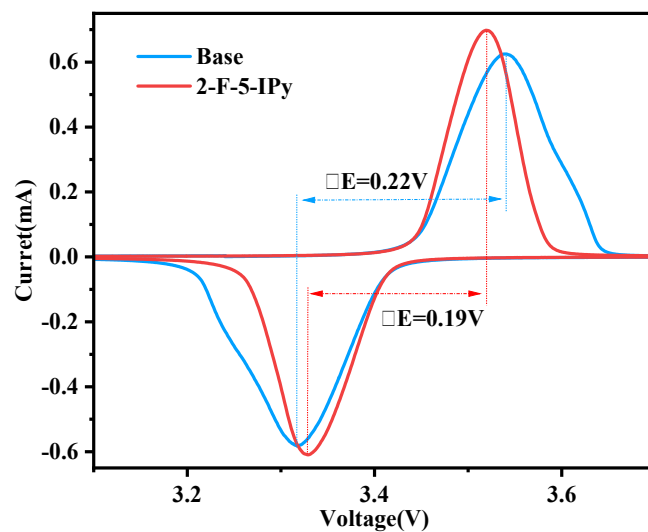
**Figure S4.** The Tafel curves of Li||Li symmetrical cells.

In the Tafel curves, the exchange current density ‘*i*’ can be obtained by cutting the curve parts on both sides of the  $\eta$  axis and intersecting the  $\eta$  axis. As can be seen from Fig. S4, the exchange current density of the symmetrical cell without 2-F-5-IPy is  $0.45 \text{ mA cm}^{-2}$ , which significantly increased to  $1.41 \text{ mA cm}^{-2}$  after the addition of 2-F-5-IPy. The observed increase in the *i* indicates an improvement in the net reaction speed and a reduction in the electrode polarization, leading to easier electrode reactions.



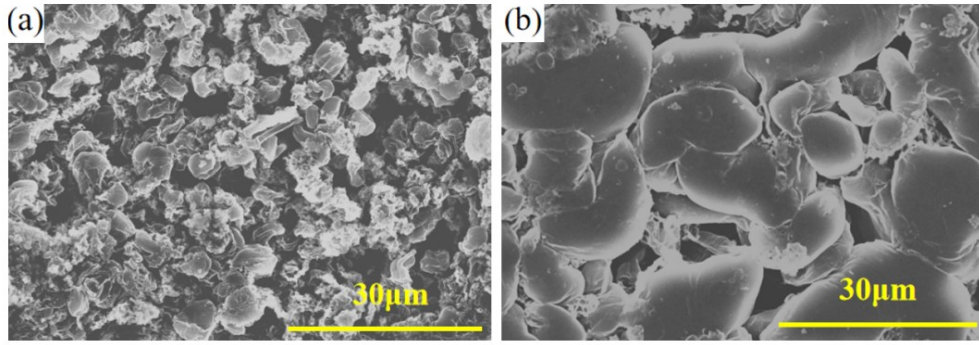
**Figure S5.** The Current-Time (i-t) curves of Li||Li symmetrical cells.



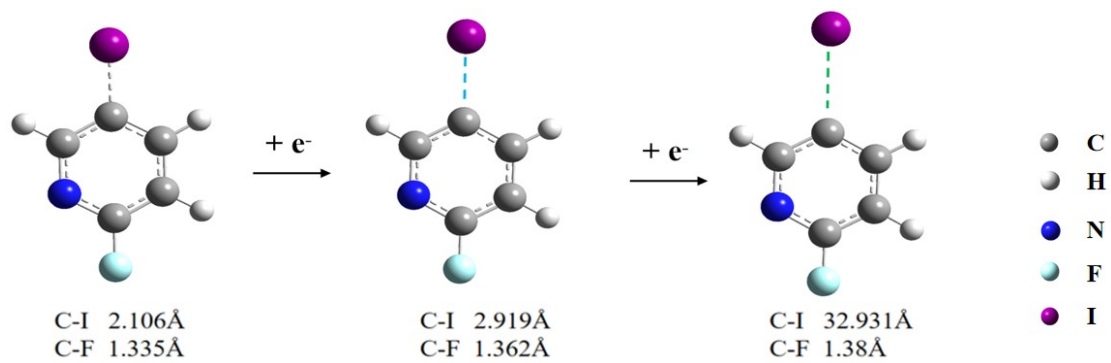


**Figure S6.** The cyclic voltammetry (CV) results of Li||LiFePO<sub>4</sub> cells.

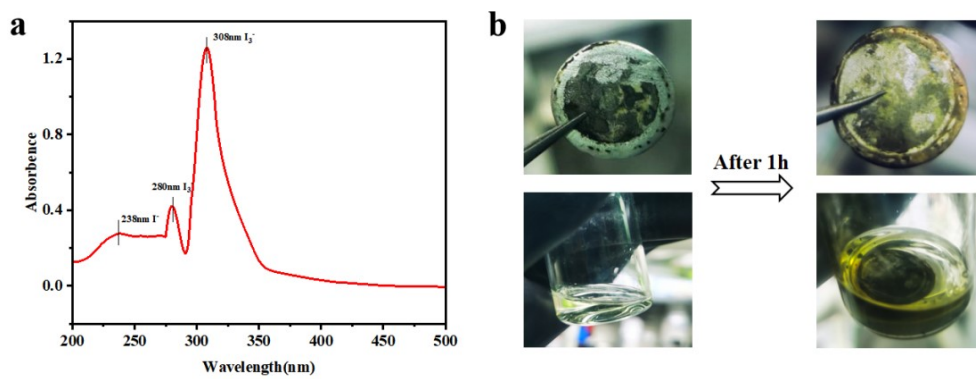
Compared with the base electrolyte, the redox peak currents of the cell increased significantly when 2-F-5-IPy was added. The voltage difference between the two peaks is 0.22V, and after adding 2-F-5-IPy, the voltage difference between the two peaks is decreased to 0.19V. These data show that 2-F-5-IPy can not only increase the oxidation and reduction current but also decrease the polarization of the cells. This is a good demonstration of 2-F-5-IPy can improve the kinetic performance of the cells.



**Figure S7.** SEM images of lithium anode surface. (a) Without 2-F-5-IPy. (b) With 2-F-5-IPy.



**Figure S8.** Calculation of bond length changes when 2-F-5-IPy obtains electrons.



**Figure S9.** Verify the behavior and function of iodine in 2-F-5-IPy. (a) UV-visible spectrum of the electrolyte with 2-F-5-IPy. (b) Reaction phenomenon of dead lithium with electrolyte with 2-F-5-IPy.

$$CE_{avg} = \frac{nQ_C + Q_S}{nQ_C + Q_T}$$

Formula

S1

where  $Q_S$  stands for dissolution capacity;  $Q_T$  stands for deposition capacity;  $Q_C$  stands for cyclic capacity;  $n$  stands for the number of cycles

$$t_{Li}^+ = \frac{I_S(V - R_0I_0)}{I_0(V - R_S I_S)}$$

Formula S2

Where  $I_S$  stands for current of the cell after test;  $I_0$  stands for current of the cell before the test;  $R_S$  stands for impedance of the cell after test;  $R_0$  stands for impedance of the cell before the test.

## References

1 Yang. T, Fan. W, Wang. C, Lei. Q, Ma. Z, Yu. L, Zou. X and Nan. J, *ACS Appl. Mater. Interfaces*, 2018, **10**, 31735–31744.