# Self-sacrificial organic lithium salt enhanced initial columbic

## efficiency for safer and greener lithium-ion batteries

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## **Experimental Section**

### Synthesis of the L<sub>i2</sub>DHBA material

First, 0.01-mol 3,4-dihydroxybenzoic (Aladdin, AR) acid was added into 20 mL of a DMF solvent (Aladdin) in air and stirred for 10 min; then, 0.02-mol lithium hydride (Aladdin, AR) was slowly added into the solvent in a glove box full of argon gas. The mixture was stirred overnight to obtain a white suspension. After filtration, the filtrate was dried under vacuum for 2 h to obtain pure Li<sub>2</sub>DHBA.

#### **Material characterization**

X-ray diffraction (XRD) patterns of the power samples were collected on RigakuMiniFlex 600, with Cu K $\alpha$  radiation ( $\lambda = 0.154056$  nm). Next, the experiments were carried out at a scan rate of 5° min<sup>-1</sup> from 10° to 80°. The morphology of the samples was represented by QUANTA 250 (FEI, US) field-emission scanning electron microscopy (FE-SEM). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) using Al K $\alpha$  (hv = 1486.6 eV) radiation was conducted next. Further, for Fourier transform infrared spectrometry (FTIR), a Bruker Vertex 70 device was used in the wavenumber range from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. KBr pellets were prepared to record the KBr spectra. Next, nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AVANCE 500-MHz spectrometer. Deuterated methanol (CD<sub>3</sub>OD) was used as the solvent and as the internal standard for the chemical shifts.

### **Electrochemical measurements**

The positive electrodes were made by mixing 75 wt% of the active materials, 15 wt% of super P, and 10 wt% of polyvinylidene fluoride (PVDF). 1-Methyl-2-

pyrrolidinone (NMP) was used as the solvent to make the slurry, which was then coated on an Al foil and dried in a vacuum oven at 80°C. The anode was made by mixing 75 wt% of the active materials, 15 wt% of super P, and 10 wt% of PVDF. NMP was used as the solvent to make the slurry, which was then coated on a Cu foil and dried in a vacuum oven at 80°C. Next, 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v) was used as the electrolyte, and a Celgard 2300 membrane was used as the separator. All of them were assembled into CR2025 coin cells in a pure-argon-filled glove box for various electrochemical measurements. The loading mass of the active materials of the electrodes was limited in the range of  $2.1 \pm 0.1$  mg cm<sup>-2</sup>. The galvanostatic charge–discharge measurements of the cells were conducted on a land battery testing system (CT2001A). The lithium metal half cells of the Li<sub>2</sub>DHBA electrode, the LiFePO<sub>4</sub> electrode, and the mixed electrode were charged/discharged from 2.0 to 4.2 V at a current density of 0.1 C. The LiFePO<sub>4</sub>/graphite, mixed electrode/graphite full cells were charged/discharged from 2.0 to 4.2 V at a current density of 0.1 C. The ratio of active materials between cathode and anode is 1:1~1.1. The diameter of the anode is 10 mm while the diameter of the cathode is 13 mm. The specific capacities were calculated on the basis of the mass of the cathode active materials.



Figure S1. SEM images of 3,4-dihydroxybenzoic acid a), b) and Li<sub>2</sub>DHBA c), d)



Figure S2.<sup>13</sup>C Nuclear magnetic resonance spectrum of Li2DHBA after filtration



Figure S3. First cycle profiles of a) hard carbon and b) full cells with and without Li2DHBA



Figure S4. XRD patterns of pure Li<sub>2</sub>DHBA electrode before and after cycled: a) 5° - 90°; b) 10° -30°



Figure S5. Infra-red spectra of the electrolyte of LFP and LFP-Li<sub>2</sub>DHBA half cells after cycles



**Figure S6**. Photographs of the separators of LFP and LFP-Li<sub>2</sub>DHBA half cells after cycles.





**Figure S8**. Z'- $\omega^{-1/2}$  curves of LFP and LFP- Li<sub>2</sub>DHBA half cells and full cells.

The pristine LFP- Li<sub>2</sub>DHBA half cell possessed a much larger value of Rf + Rct (65.277  $\Omega$ ) than that of LFP half cell (40.14  $\Omega$ ). After 50 cycles, the values of Rf + Rct for the LFP- Li<sub>2</sub>DHBA half cell were 59.621  $\Omega$ , with that of LFP half cell were 60.854  $\Omega$ , which indicate that the additive has no adverse effect on resistance after cycles. Similar result occurred in the full cells, the values of Rf + Rct for the LFP and LFP- Li<sub>2</sub>DHBA full cells were 70.549  $\Omega$  / 104.043  $\Omega$  (before cycle) and 80.341  $\Omega$  / 81.66  $\Omega$  (after 50 cycles). Besides, the conductivity of LFP and LFP- Li<sub>2</sub>DHBA cells is similar after 50 cycles. Warburg diffusion parameters can be easily found in Z'- $\omega$ <sup>-1/2</sup> curves. After cycles, the warburg diffusion parameters " $\sigma$ " of LFP- Li<sub>2</sub>DHBA half and full cells is smaller than LFP cells which indicate that the additives help to increase the diffusion after cycles. This may be due to the fact that the pores left after the dissolution of the additive enhance the contact of the electrode with the electrolyte.



Figure S9. First cycle profiles of the graphite cathodes.



Figure S10. 390-cycles of the LFP- Li<sub>2</sub>DHBA half cell.

Sample	1	2	3	4	5	Average
Weight of cathode material before cycled/mg	2.13	2.11	2.13	2.08	2.09	2.108
Weight of cathode material after cycled/mg	0.58	0.56	0.59	0.50	0.50	0.546
Weight loss/mg	1.55	1.55	1.57	1.58	1.59	1.562
Weight loss rate	72.7%	73.4%	73.7%	75.9%	76.0%	74.1%

Table S1. Weight loss of cathode material before and after cycled

\*The cathode material include super P, polyvinylidene fluoride (PVDF) and active material