

Electronic Supplementary Information for:

Cooperation behavior between heterogeneous cations in hybrid batteries

Hanping Zhang,* Xin Wu, Tao Yang, Shanshan Liang and Xiaojian Yang

Jiangsu Key Laboratory of Advanced Catalytic materials and technology, Changzhou University,

Changzhou, China. E-mail: jinhongshi0001@163.com

Experimental section

CV curves were traced with LiFePO_4 cathode being employed as the work electrode, and a piece of polished metal zinc as the counter and the reference. LiFePO_4 was prepared by solid-state reaction with a sugar-assisted ball milling method. 10 ml distilled water was washed with nitrogen for 30 min before 0.5 g sugar, 0.02 mol ferrous oxalate and 0.02 mol lithium dihydrogen phosphate was added in and followed with an extra nitrogen wash for another 30min. Then the mixture was ball milled for 8 hours before being dried at 60 °C in vacuum for 10 hours to form the precursor. The precursor was progressively heated to 700 °C at the rate of 10 °C min^{-1} and calcined at 700 °C in nitrogen for 6 h to form carbon-coated LiFePO_4 . The sample was mixed with acetylene black and poly(tetrafluoroethylene) (PTFE) in a weight ratio of 8:1:1 with the help of ethanol. The mixture was pressed into a film, and dried at 80 °C for 8 hours. Then the film was pressed onto a piece of Nickel grid to obtain the cathode. The cathode and anode were immersed into CH_3COOLi (15 wt%) and $\text{Zn}(\text{CH}_3\text{COO})_2$ (15 wt%) aqueous mixture to obtain $\text{Zn}|\text{CH}_3\text{COOLi}+\text{Zn}(\text{CH}_3\text{COO})_2|\text{LiFePO}_4$ battery.

An ICP-AES examination was performed to study the concentration of Zn^{2+} fluctuated with time. Four carbon $|\text{CH}_3\text{COOLi}+\text{Zn}(\text{CH}_3\text{COO})_2|\text{LiFePO}_4$ batteries that obtained almost the same

contents were fabricated and performed with half-charge, full-charge, half-discharge and full-discharge, respectively at a constant current rate of 1 C. Then the electrodes were taken out and the left electrolyte was performed by the ICP-AES.

The charge-discharge curves and cycle calendar life were traced on a cell tester (Neware) using the fabrication $\text{Zn}|\text{CH}_3\text{COOLi}+\text{Zn}(\text{CH}_3\text{COO})_2|\text{LiFePO}_4$. Rate performances were conducted at 0.5–1.7 V, the constant current rate shifted from 0.5 to 50 C progressively and turned back symmetrically. 5 charge-discharge cycles were performed at each rate. All of the cyclic behaviors were collected at room temperature.

Conventional powder XRD patterns were collected in the 10–80° 2θ range using a D/max 2500 PC with vertical goniometer and Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). Scanning electron microscope (SEM) images of the samples were collected on a JSM-6360LA at room temperature.

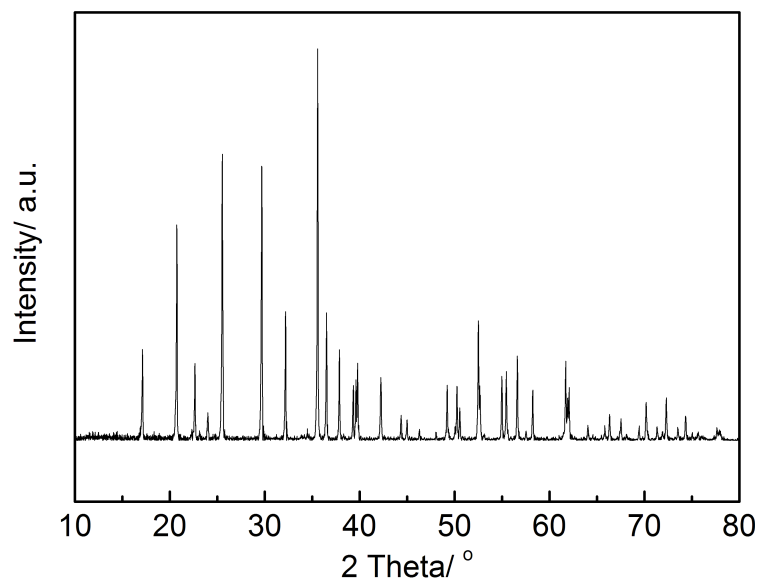


Figure S1. XRD pattern of the as-prepared LiFePO_4 by solid-state reaction with a sugar-assisted ball milling method.

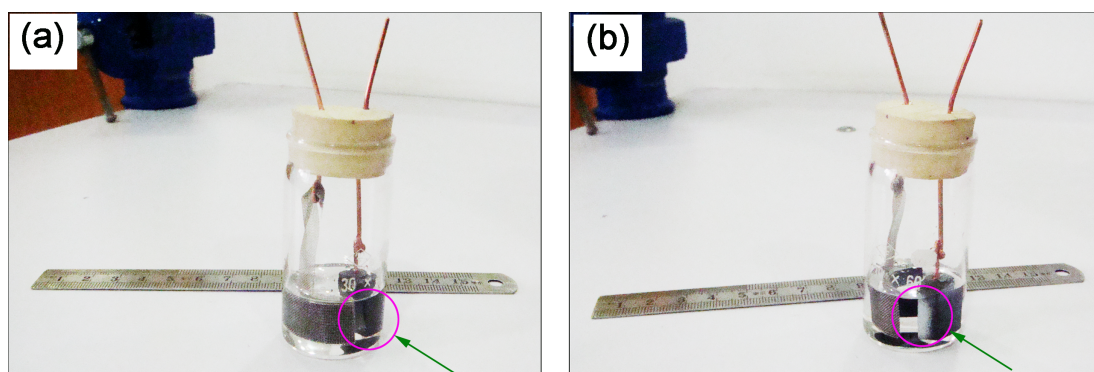


Figure S2. Fabrication of C|CH₃COOLi+Zn(CH₃COO)₂|LiFePO₄ battery: (a) before charging; (b) after charging. It is clear that before charging, there is no deposit on the surface of the carbon electrode, while after charging, deposits appear.

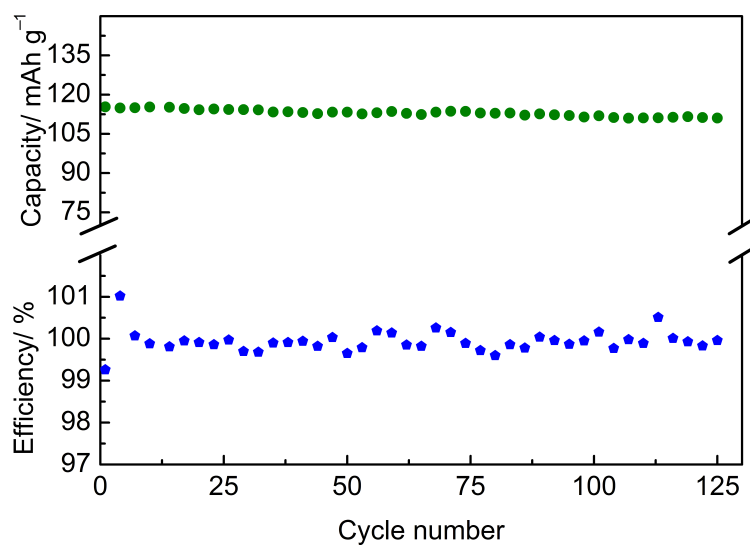


Figure S3. Cycling behavior of Zn|CH₃COOLi+Zn(CH₃COO)₂|LiFePO₄ battery at 1 C rate in the window range 0.5–1.7 V at room temperature.