Electronic Supplementary Information for:

Cooperation behavior between heterogeneous cations in hybrid batteries

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Experimental section

CV curves were traced with LiFePO4 cathode being employed as the work electrode, and a piece of polished metal zinc as the counter and the reference. LiFePO4 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 30 min. 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 LiFePO4. 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 CH₃COOLi (15 wt%) and Zn(CH₃COO)₂ (15 wt%) aqueous mixture to obtain Zn|CH₃COOLi+Zn(CH₃COO)₂|LiFePO4 battery.

An ICP-AES examination was performed to study the concentration of Zn²⁺ fluctuated with time. Four carbon|CH₃COOLi+Zn(CH₃COO)₂|LiFePO4 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 Zn|CH$_3$COOLi+Zn(CH$_3$COO)$_2$|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 Kα radiation (λ=1.5406 Å). 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|CH$_3$COOLi+Zn(CH$_3$COO)$_2$|LiFePO$_4$ 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(CH$_3$COO)$\text{Li}+\text{Zn(CH$_3$COO)$_2$}$|LiFePO$_4$ battery at 1 C rate in the window range 0.5–1.7 V at room temperature.