Coordination induced electron redistribution to achieve highly

reversible Li-ion insertion chemistry in metal-organic framework

Electronic Supplementary Information (ESI)

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I. Materials and methods

Raw Materials. Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, aladin, 98%), lithium hydroxide (LiOH, 98%), potassium hydroxide (KOH, 98%), zinc acetate (Zn(CH3COO)₂, 98%), deionized water.

Synthesis of K-PTCA/Li-PTCA/Zn-PTCA. K-PTCA/Li-PTCA were synthesized by refluxing PTCDA and KOH/LiOH in 50 ml deionized water with mole ratio of ~1:10. Zn-PTCA was prepared by adding Zn(CH3COO)₂ (0.4 mmol, 50 ml) dropwise to the solution of K-PTCA (0.2 mmol, 50 ml) and an orange precipitate was immediately obtained. The mixture was then transferred into a Teflon-lined stainless-steel vessel (100 ml) and heated at 100°C in oven for 12 h. The precipitate was collected by

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filtration after cooling down to room temperature and washed with deionized water several times, then dried in vacuum at 80 °C overnights.

Characterization. The phase was checked by XRD (Panalytical X'pert PRO MRD, Holland) with Cu K α radiation. The morphology and particle size of the samples were observed by field-emission scanning electron microscopy (JSM 7600F, JEOL, Japan). The chemical structure of powders was determined by Raman (inVia, Renishaw) in the range of 100 to 3200 cm⁻¹ and FTIR (Nicolet iS50, Thermofisher) in the range of 400 to 4000 cm⁻¹.

NMR. Experiments were carried out on a Bruker 500M (11.7T) Advance III spectrometer containing a Bruker 1.3 mm solid-NMR probe assembly and operating at 500.66 MHz and 125.9 MHz for ¹H and ¹³C, respectively. ¹H and ¹³C chemical shift were both externally referenced to TMS (0 ppm). ¹H NMR data was acquired using a zg pulse sequence at a spin rate of 40kHz with all samples packed into 1.3 mm rotor. 1H MAS spectra were acquired with a 90° pulse length of 0.9 μ s and recycle delay of 30 ms with 64 scans, and the relaxation delay is 2s. ¹H–¹³C CP NMR spectra were acquired with a CP contact time of 2 ms, a recycle delay of 3s, and 2000 scans at a spin rate of 12 kHz with all samples packed into a 4 mm rotor.

Electrochemical Measurements. The electrochemical performance was obtained by testing CR2302 coin cells assembled in argon atmosphere in a glove box with metallic Li as counter electrode. The working electrode was prepared by applying a slurry of 60 wt% active material (PTCDA/Li-PTCA/Zn-PTCA), 30 wt% Super P and 10 wt% Poly(vinylidene fluoride) (PVDF) onto copper coil then dried in vacuum at 80 °C overnights. The average loading of active material is about 0.4~0.6 mg cm⁻². Finally, the cells were assembled by using LB-315 commercial electrolyte (main composition: 1mol L⁻¹ LiPF₆ solution in ethylene carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC)). The galvanostatic charge-discharge profiles were tested on a Land battery measurement system (Land, China). CV measurements were carried out on Solartron Analytical between 0.01 V and 2 V at a scan rate of 0.2 mV s⁻¹. For

XRD, SEM, PDF and ex situ Raman and FTIR measurements, samples at different charge and discharge states were collected by dismantling cells in an argon-filled glove box with water/oxygen content lower than 0.1 ppm. The electrodes extracted from the cells were washed with propylene carbonate (PC) several times and dried in glove box for several days.



I. Supporting Figures

Fig. S1. Raman spectroscopy of PTCDA/Li-PTCA/Zn-PTCA powder.



Fig. S2. (A) charge and discharge curve and (B) cycle performance of Super P electrode at current density of 50 mA g⁻¹. The Super P electrode was prepared in the same way with Zn-PTCA but in the proportion of 90 wt% Super P, 10 wt% PVDF.



Fig. S3. Enlarged curves of CV plots of Zn-PTCA at scan rate of 0.2 mV s⁻¹.



Fig. S4. CV curves of PTCDA electrode at scan rate of 0.1 mV s⁻¹.



Fig. S5. CV curves of Li-PTCA electrode at scan rate of 0.1 mV s⁻¹.



Fig. S6. (A) charge and discharge curves and (B) cycle performance of Zn-PTCA/Li-PTCA/PTCDA at current density of 1 A g⁻¹.

states	Raman				FT-IR
	In-plane C- H bending (cm ⁻¹)	Perylene plane deformation (cm ⁻¹)	Benzene deformation (cm ⁻¹)	C=C stretches (cm ⁻¹)	Out-of-plane C-H bending (cm ⁻¹)
pristine	1297	1351		1568	876,810,771
dis 1V	1293	1359		1567	
dis 0.45V	1293	1356	1453	1572,1607	868,833
dis 0.01V	1291	1385	1456	1576,1602	833
ch 1.1V	1293	1380	1448	1573,1604	868,833
ch 2V	1291	1353, 1374	1453	1573,1605	868,835

Table S1. Characteristic Raman and FTIR: main peaks for ZnPTCA electrode at different charge and discharge states under a current density of 50 mA g⁻¹.



Fig. S7. XRD patterns of Zn-PTCA electrodes before and after discharge.



Fig. S8. (A) Fit of experimental and calculation curves. (B) peak assignment. (C) and (D) comparison of Zn...Zn in Zn metal, Zn...O in ZnO of different space groups and those in Zn-PTCA.