Supporting Information

Nanostructured potassium-organic framework as an effective anode for potassium-ion battery with a long cycle life

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Experimental Section

General information: Pyridine-2,6-dicarboxylic acid (H₂PDA) and potassium hydroxide (KOH) were commercially obtained from Aladdin Inc. and used directly. The single-crystal X-ray diffraction data were obtained from a Bruker Xcalibur Eos CCD diffractometer using a graphite-monochromated MoKa (λ =0.71073Å) radiation at room temperature. The Fourier transform infrared spectra (FT-IR) was operated on Nicolet iS50 spectrometer (Nicolet Co.) with the wavenumber range of 400-3200 cm⁻¹. The thermogravimetric analysis (TGA, TA-Q50) was tested from room temperature to 800 °C under the N₂ atmosphere at a heating rate of 10 °C min⁻¹. The morphology image was collected by the filed-emission scanning electron microscope (FE-SEM, Hitachi, S3400N). The X-ray diffraction measurement was conducted on X'Pert Pro MPD (XRD, λ =1.54056Å) using Cu K α radiation with the scanning rate of 0.06° s⁻¹ in the 2 θ range of 10-50°. CCDC No. 1962863.

Synthesis of $[C_7H_3KNO_4]_n$: $[C_7H_3KNO_4]_n$ was feasibly synthesized with the neutralization reaction. Briefly, 1.671 g pyridine-2,6-dicarboxylic acid (H₂PDA, 10 mmol) and 1.178 g potassium hydroxide (KOH, 21 mmol) was mixed into an enclosed tube with the 40 ml deionized H₂O and stirred for 1 h at 60 °C. Then, the solution refluxed for another 12 h at 110 °C and got a clarified solution. Finally, with the addition of absolute ethanol into the above solution, the as-obtained precipitate was obtained after filtered and vacuum-dried at 110 °C overnight with a satisfactory yield of 85% (1.736 g). The single crystals of $[C_7H_3KNO_4]_n$ were gained by the recrystallization from ethanol and DI water. And the nanoparticles of $[C_7H_3KNO_4]_n$ were obtained by the clarified aqueous solution of $[C_7H_3KNO_4]_n$ dropwise added into the stirring ethanol.

Synthesis of $[C_7H_3KNO_4]n@CNTs$: The $[C_7H_3KNO_4]_n@CNTs$ composite was simply *in-situ* synthesized with the following process. 100 mg CNTs (13.33 wt.% vs. $[C_7H_3KNO_4]_n$) was uniformly dispersed in the absolute ethanol. And then 30 mg ml⁻¹ aqueous solution of $[C_7H_3KNO_4]_n$ (20 ml) was added dropwise with stirring. Finally, the as-obtained composite was filtered and vacuum-dried at 110 °C.

K-ion half cells fabrication and test: Electrochemical measurements were carried out by using CR2032 two-electrode half cells. The working electrodes were prepared by casting the slurry (contains activity materials (60 wt.%), carbon additive (super P, 30 wt.%; or CNTs 10 wt.% and super P 20 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%)) onto a clean copper foil and vacuum-dried at 110 °C for 12 h. The neat material loadings of $[C_7H_3KNO_4]_n$ on copper foil was ~2.5 mg cm⁻². The counter electrode was potassium foil. The electrolyte is 1 M potassium bis(fluorosulfonyl)amide (KFSI, Ark Pharm Inc.) in the mixed solvents of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio of 1:1. The separator was glass microfibre filters (GF/F) of Whatman. These cells were assembled in the Ar-filled glove box with a high purity of 99.999%. The cyclic voltammetry (CV) test was operated by the Arbin instrument electrochemical workstation (Arbin 2000). The

galvanostatic charge-discharge curves were collected by a CT2001A cell test instrument (LAND Electronic Co.) during the voltage window of 0.1-2.0 V at room temperature. The electrochemical impedance spectroscopy (EIS) test was measured by Solartron Analytical instrument in the frequency range of 10^{-2} - 10^5 Hz. The theoretical specific capacity of $[C_7H_3KNO_4]_n$ is calculated to be 131 mAh g⁻¹. *The K-ion half cells with only Super P and CNTs showed very similar capacity values to the ones with Super P only* (Fig. S4).

Quantum calculations: The crystal structure calculation was performed using the Cambridge Serial Total Energy Package (CASTEP) ^{1, 2}, utilizing the plane-wave pseudopotential (PWPP) method based on Density Functional Theory (DFT) in conjunction with the Perdew-Burke-Ernzerhof (PBE) ^{3, 4} form of the generalized gradient approximation (GGA). The calculation structure of $[C_7H_3K_2NO_4]_n$ was achieved by adding additional K ions and electrons based on the $[C_7H_3KNO_4]_n$ cell.

[CCDC No. 1962863 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Atom	x	V	Z
C1	3246(2)	-459.9(15)	1232.7(17)
C2	3963(3)	206(15)	2658.6(19)
C3	3322(3)	-1652.4(17)	1264.2(18)
Н3	3922	-2036	2130
C4	2500	-2261(2)	0
H4	2500	-3060	0
N1	2500	140.6(17)	0
01	3768(2)	1250.6(11)	2690.1(15)
02	4718(2)	-433.6(12)	3775.5(14)
K1	2500	2619.3(5)	0
Monoclinic 103.046(7) ^c	, space group $I2/a$, , and $\Omega = 739.7(1)$	a = 7.0581(5), b = 11.6424 Å ³ .	$4(7), c = 9.2407(6), \beta =$

Tab. S1 The fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for $[C_7H_3KNO_4]_n$.

Tab. S2 The experimental and calculated lattice parameters for the conventional cell of $[C_7H_3KNO_4]_n$ and $[C_7H_3K_2NO_4]_n$, respectively.

	$[C_7H_3KNO_4]_n$	$[C_7H_3K_2NO_4]_n$
	experimental	calculated
a (Å)	7.0581	10.4123
b (Å)	11.6424	10.5578
c (Å)	9.2407	16.9440
β (°)	103.046	137.8395
Ω (Å ³)	739.7	1250.248



Fig. S1 (a) The FT-IR spectra of $[C_7H_3KNO_4]_n$ and H_2PDA . (b) The thermogravimetric analysis of $[C_7H_3KNO_4]_n$ and H_2PDA .



Fig. S2 The powder XRD pattern of $[C_7H_3KNO_4]_n$ and the calculated XRD peaks.



Fig. S3 The selected discharge-charge curves of neat conductive carbon additive of super P (SP:PVDF=3:1) in PIBs. (a) At 10 mA g^{-1} ; (b) under different current rates.



Fig. S4 (a) The selected charge-discharge curves for the $[C_7H_3KNO_4]_n$ @CNTs anode. The current density was 10 mA g⁻¹ and voltage window was 0.1-2.0 V. (b) The EIS plots of $[C_7H_3KNO_4]_n$ and $[C_7H_3KNO_4]_n$ @CNTs in K-ion batteries at open-circuit voltage.

References:

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