

Supporting Information

Potassium Perylene-tetracarboxylate with Two-electron Redox Behaviors as a Highly Stable Organic Anode for K-ion Batteries

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Experimental Section

Synthesis of potassium perylene-3,4,9,10-tetracarboxylate (K₄PTC): Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) (3.92 g, 10 mmol, Aladdin Incorporation) was added into the deionized water (5 ml) with KOH (2.805 g, 50 mmol) at 55 °C. After stirring the mixture for 5 min, 35 ml deionized water was gradually added and sequentially stirred for another 12 h. Then, the solution was added to 300 ml EtOH and the yellow precipitate of K₄PTC was formed with the yield above 80%. ¹H-NMR spectra were recorded on AC Bruker spectrometer (400 MHz) at room temperature by using D₂O as the solvent, and the chemical shifts were expressed in part per million (ppm) relative to the residual H₂O. And the theoretical specific capacity of K₄PTC is calculated to be 93 mAh g⁻¹.

Preparation of K₄PTC@CNT and K₄PTC@SP compositions: The K₄PTC@CNT composite was simply *in-situ* prepared as follows: 30 mg (5:60 weight relative to K₄PTC) multi-walled carbon nanotubes (CNT) was uniformly dispersed in 100 ml *N*-methyl pyrrolidone (NMP)

under ultrasound for 30 min. And then 10 ml aqueous solution of K_4PTC (36 mg ml^{-1}) was added dropwise into the CNT solution under stirring. Finally the as-obtained precipitate was filtered and vacuum-dried at $110 \text{ }^\circ\text{C}$ overnight. The ball-milled sample of $K_4PTC@SP$ was prepared in a planetary ball mill running at 400 rpm for 6 h by mixing K_4PTC with Super P (SP) with weight rate of 2:1 using 10 ml EtOH. The as-obtained sample was vacuum-dried at $110 \text{ }^\circ\text{C}$ overnight. The morphology images of the samples were collected by the field-emission scanning electron microscope (FE-SEM, Hitachi, S3400N).

K-ion half cells fabrication and test: The electrochemical measurements were carried out by using half cells of CR2023 type. The working electrode was prepared by casting the slurry onto a clear copper round disk ($d=12 \text{ mm}$), where the slurry contains $K_4PTC@CNT$ (65 wt%), carbon additive (acetylene black, 25 wt%) and poly(vinylidene fluoride) (PVDF, 10 wt%) or $K_4PTC@SP$ (90 wt%) and PVDF (10 wt%). The loading of neat K_4PTC on copper foil was above 2 mg cm^{-2} . The as-prepared electrodes were dried in a vacuum oven at $110 \text{ }^\circ\text{C}$ for 12 h. The counter electrode was potassium foil and self-cut from potassium-metal block (Chengdu Kelong Inc.). The electrolyte was 1 M potassium bis(fluorosulfonyl)amide (KFSI, Ark Pharm Inc.) in the mixture solvents of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume rate of 1:1 (Suzhou Fosai New Materials Co. Ltd.) and the water content was $\sim 1 \text{ ppm}$ in these solvents. The separate was glass microfiber filters (GF/F) of Whatman. These cells were assembled in the Ar-filled glove box with high purity of 99.9999%. The cyclic voltammetry (CV) test was operated by the BioLogic science instrument electrochemical workstation (VMP3-128). The galvanostatic charge-discharge curves were collected by a CT2001A cell test instrument (LAND Electronic Co.) during the voltage window of 0.1-2 V at room temperature. And the electrochemical impedance

spectroscopy (EIS) test was measured by a CHI instrument electrochemical workstation in the frequency range of 10^{-2} - 10^5 Hz.

Quantum calculations: All the calculations were performed by Gaussian09 package at the level of density functional theory (DFT).¹ K_4 PTC and K_6 PTC were optimized by the B3LYP functional,²⁻⁴ with the 6-31G* basis set.^{5, 6} The solvent effect was with self consistent reactions field (SCRF) based on the SMD model,⁷ where the dielectric constant (ϵ) was set as 7.3 to mimic the experimental solvent condition. Frequency calculations at the same level were carried out to corroborate all of the stationary points as minima (no imaginary frequency) and to compute free energies at 298.15 K.

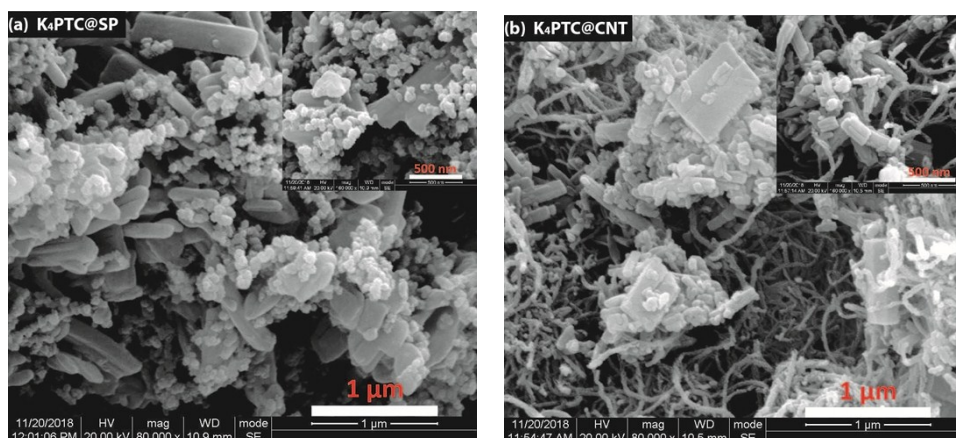
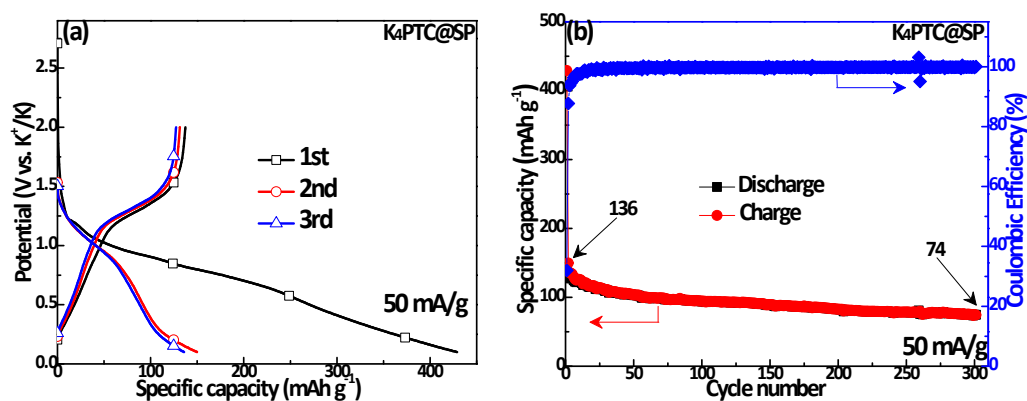


Fig. S1 The SEM images for (a) K_4 PTC@SP and (b) K_4 PTC@CNT composites.



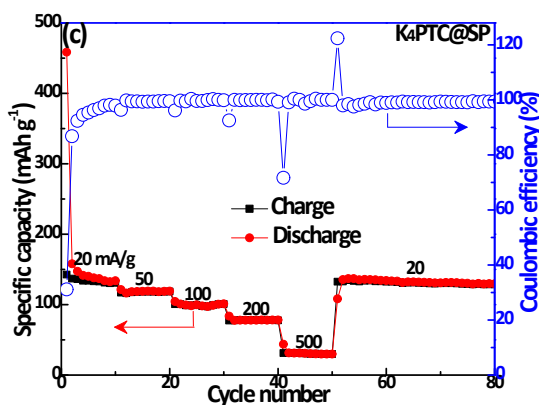


Fig. S2 (a) The charge-discharge curves of K₄PTC@SP during the initial 3 cycles; (b) The long-cycle profile of K₄PTC@SP for 300 cycles at a current density of 50 mA g⁻¹; (c) The rate performance for K₄PTC@SP.

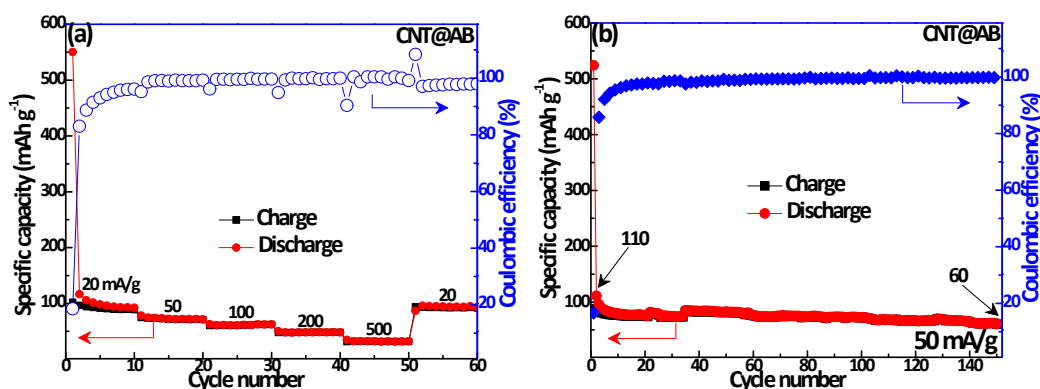


Fig. S3 (a) The rate performance for CNT@AB control cell; (b) The long-cycle profile of CNT@AB control cell during 150 cycles at a current density of 50 mA g⁻¹.

Table S1: The performance summary for the currently-reported organic anodes of KIBs.

Organic Anodes	Theoretical Capacity	Cyclability (capacity retention to the 2nd cycle)	Ref.
K ₄ PTC@CNT	93 mAh g ⁻¹	132 mAh g ⁻¹ at 50 mA g ⁻¹ , 500 cycles (73.5%) 73 mAh g ⁻¹ at 500 mA g ⁻¹ , 2500 cycles (68.5%)	This work
K ₄ C ₆ O ₆	76.5 mAh g ⁻¹	65 mAh g ⁻¹ at 25 mA g ⁻¹ , 10 cycles (84.6%)	8
K ₂ TP	221 mAh g ⁻¹	249 mAh g ⁻¹ at 200 mA g ⁻¹ , 100 cycles (92%) 194 mAh g ⁻¹ at 1000 mA g ⁻¹ , 500 cycles (94.6%)	9
K ₂ BPDC@GR	168 mAh g ⁻¹	170 mAh g ⁻¹ at 50 mA g ⁻¹ , 100 cycles (72.9%) 143 mAh g ⁻¹ at 1000 mA g ⁻¹ , 3000 cycles (41.9%)	10
VK@GNT	313.5 mAh g ⁻¹	300 mAh g ⁻¹ at 100 mA g ⁻¹ , 100 cycles (74.1%)	11

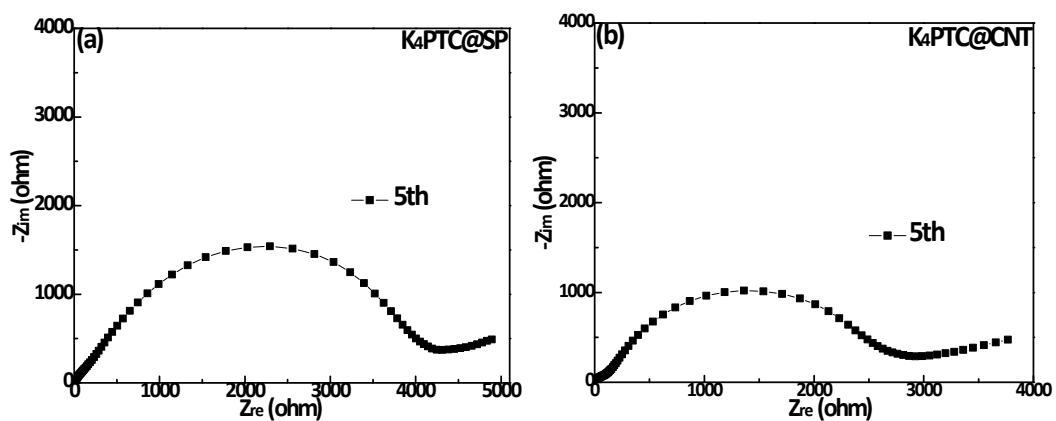


Fig. S4 The EIS plots of (a) K₄PTC@SP and (b) K₄PTC@CNT after 5 cycles.

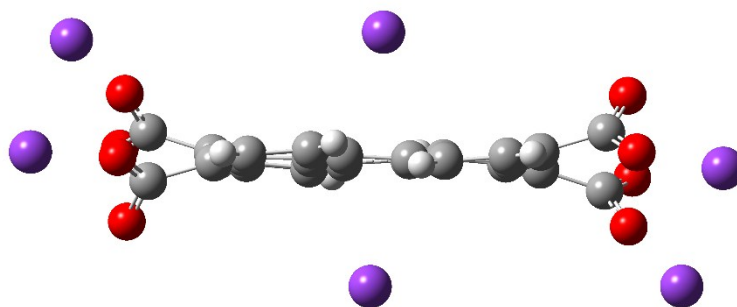


Fig. S5 One of the possible configurations for K₆PTC with the inserted two K⁺ ions suspending on and below the center of perylene plane.

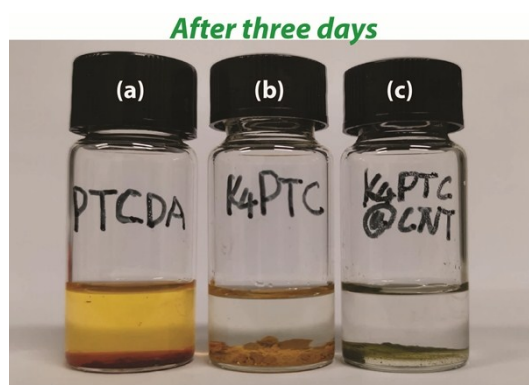


Fig. S6 The dissolution test for (a) PTCDA (5 mg/ml), (b) K₄PTC (5 mg/ml) and (c) K₄PTC@CNT (neat K₄PTC is 5 mg/ml) into 1 M KFSI in EC/DMC. The samples stood for 3 days.

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