Supporting Information

Reversible interaction of 1-butyl-1-methylpyrrolidinium cations with 5, 7, 12, 14-pentacenetetrone from pure ionic liquid electrolyte for dual-ion batteries

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Section SI. Experimental Section

Electrodes preparation:

The cathode was prepared by blending 90 wt% of natural graphite flake (Aladdin, 1200 mesh, purity >99.9%), 2 wt% acetylene black (Cell Grade, Zhengzhou Jinghong New-Energy Technology Co. Ltd.), and 8 wt% PVDF (Arkema) in NMP, which was then coated on aluminum foil (thickness: 30 μm, purity >99.9%), dried at 100°C for 12 h under vacuum. The anode was prepared by blending 70 wt% 5, 7, 12, 14-pentacenetetrone (Aladdin, >95.0% (HPLC)), 20 wt% acetylene black (Cell Grade, Zhengzhou Jinghong New-Energy Technology Co. Ltd.), and 10 wt% PVDF (Arkema) in NMP, which was coated on aluminum foil (thickness: 30 μm, purity >99.9%), dried at 100°C for 12 h under vacuum. The average mass loading of the graphite cathodes and 5, 7, 12, 14-pentacenetetrone anodes were 4.8 and 0.97 mg cm^{-1}, respectively. According to the work of Schmuelling[7], the maximum capacity of the insertion of $TFSI^-$ into graphite is 115 mA h g^{-1}. In this work, to better understand the behavior of PCT, the graphite cathodes are excess. The ionic liquid 1-butyl-1-methylpyrrolidiniumbis (trifluoromethylsulfonyl)imide ($Pyr_{14}TFSI$, purity 99%), $PP_{14}TFSI$ and EmimTFSI were purchased from Lanzhou Institute of Chemical Physics (China).

Electrochemical measurement:

Electrochemical tests were measured using CR2025 coin-type cells with ~100 μL electrolyte. Coin cells were assembled in glove box ([O_2] <0.01ppm, [H_2O] <0.01ppm) with argon. Galvanostatic charge-discharge tests were carried out on a Neware CT-4008 battery test system (China) at room temperature. Cyclic voltammetry (CV) tests were characterized on a Gamry electrochemical workstation (US) at a scan rate of 0.5 mV s^{-1}, and the electrochemical impedance spectroscopy (EIS) tests were characterized on a Gamry electrochemical workstation (US).

Characterization:

The Ex-situ XRD measurements were performed on a Bruker D8 ADVANCE diffractometer (Germany). The morphologies and structure of the graphite cathode and 5, 7, 12, 14-pentacenetetrone anode were characterized by Hitachi SU8220 field emission electron microscope.

Section SII. Supporting Figure and Table

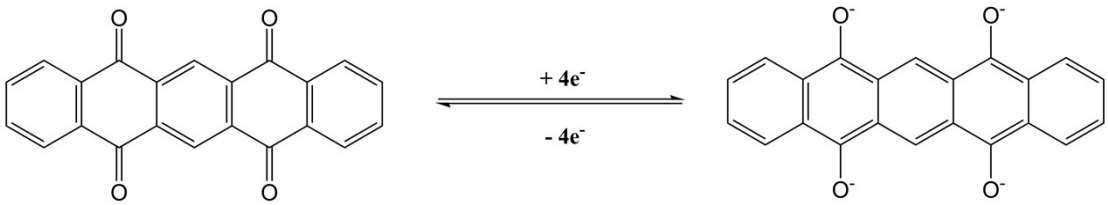

Fig. S1 Full four electron redox reactions of 5, 7, 12, 14-pentacenetetrone

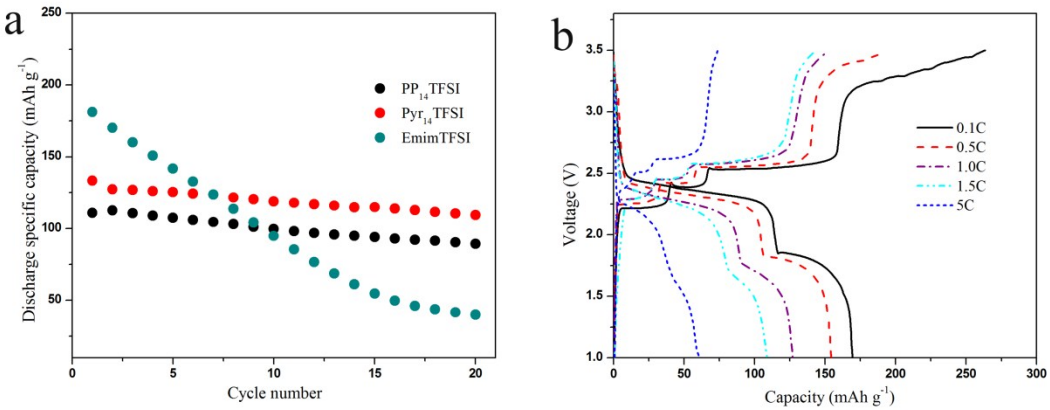

Fig. S2 a) Cycling performance of the graphite//PCT DIBs with of different pure ionic liquid electrolyte ($PP_{14}TFSI$, $Pyr_{14}TFSI$， EmimTFSI). b) Charge-discharge curves of the graphite//PCT DIBs at 0.1, 0.5, 1.0, 1.5, 5 C.

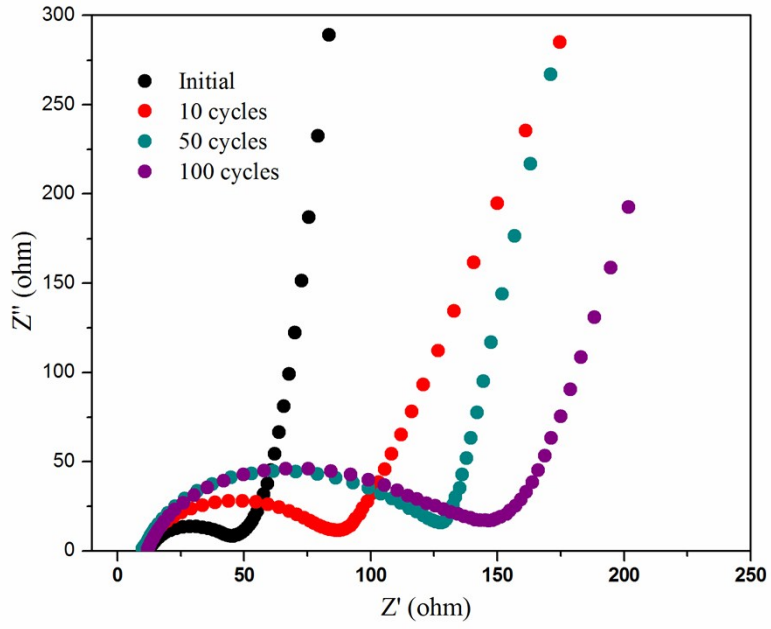

Fig.S3 Electrochemical impedance curves of graphite//PCT DIBs for different cycles.

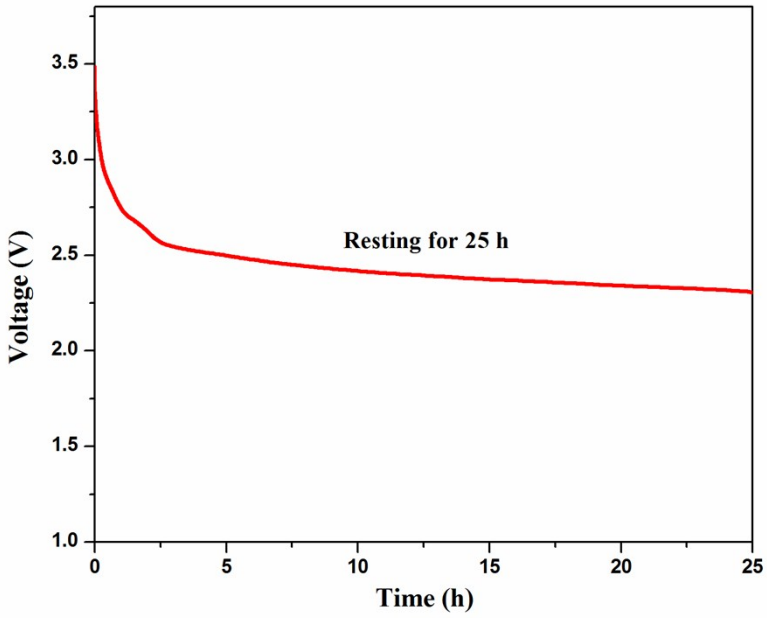

Fig. S4 Open circuit voltage–time curve of the PCT//graphite cell (charged to 3.5 V)

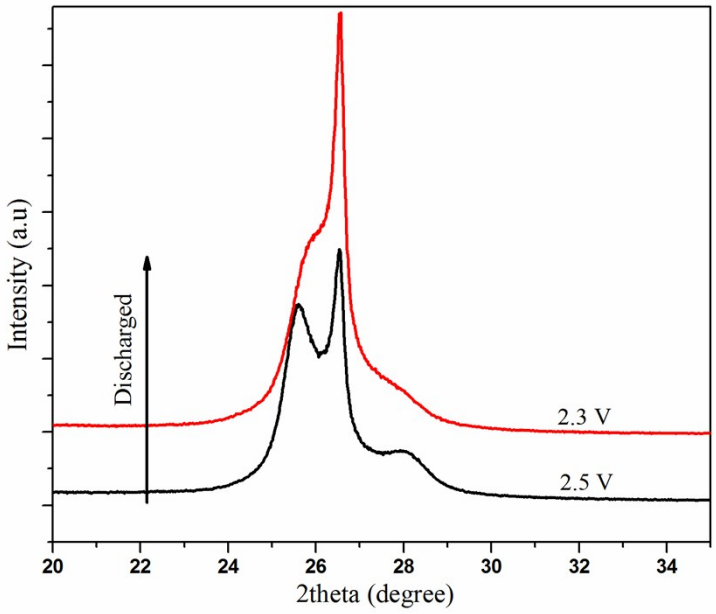

Fig. S5 Ex-situ X-ray diffraction (XRD) spectra of graphite cathode when discharged from 2.5 V to 2.3 V.

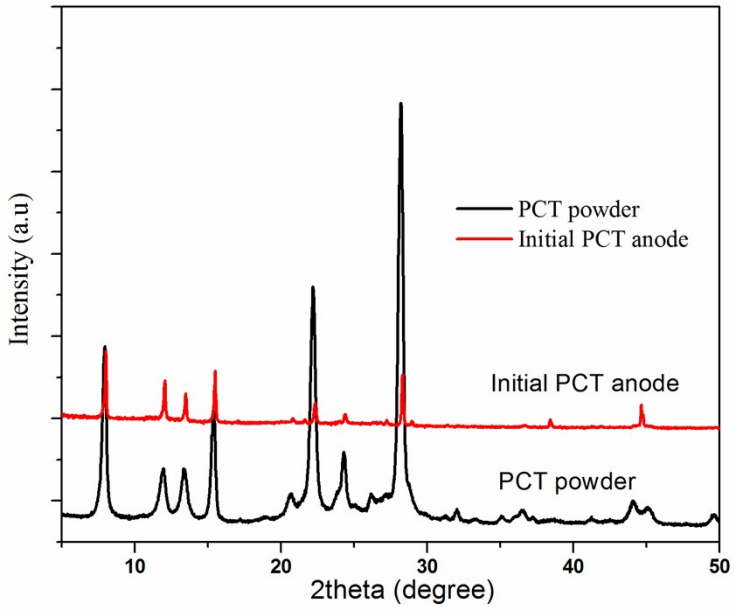

Fig. S6 Ex-situ X-ray diffraction (XRD) spectra of PCT powder and initial PCT anode

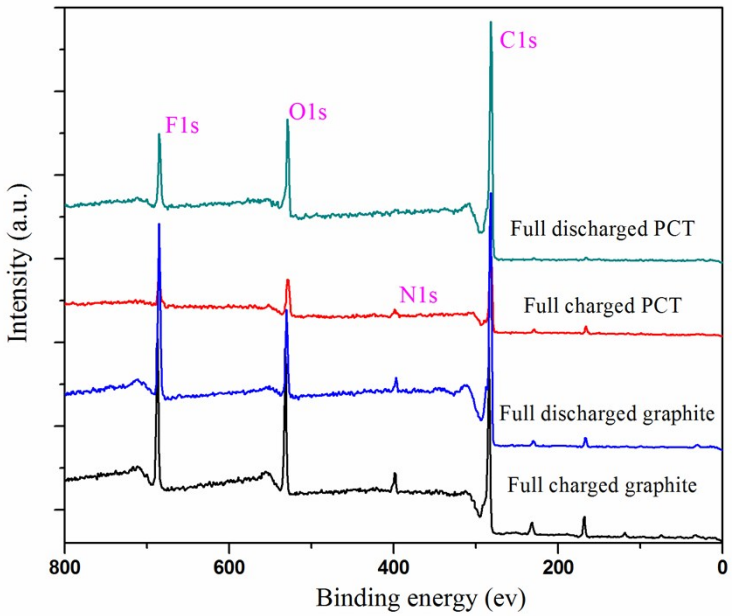

Fig. S7 XPS spectra of electrodes at different states

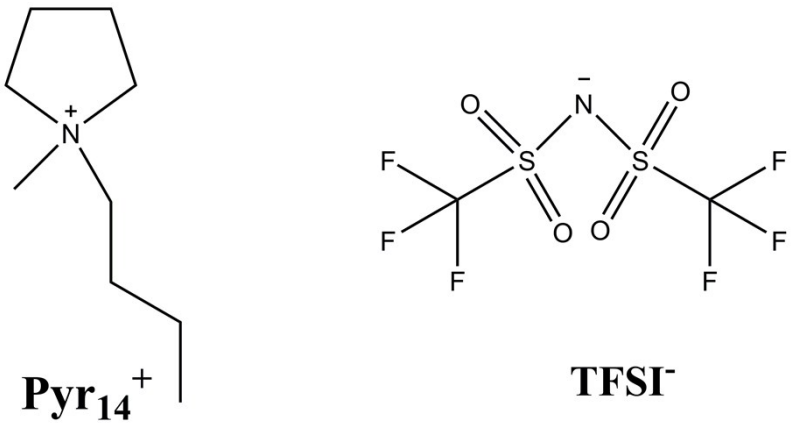

Fig. S8 The structure diagram of $Pyr_{14}TFSI$

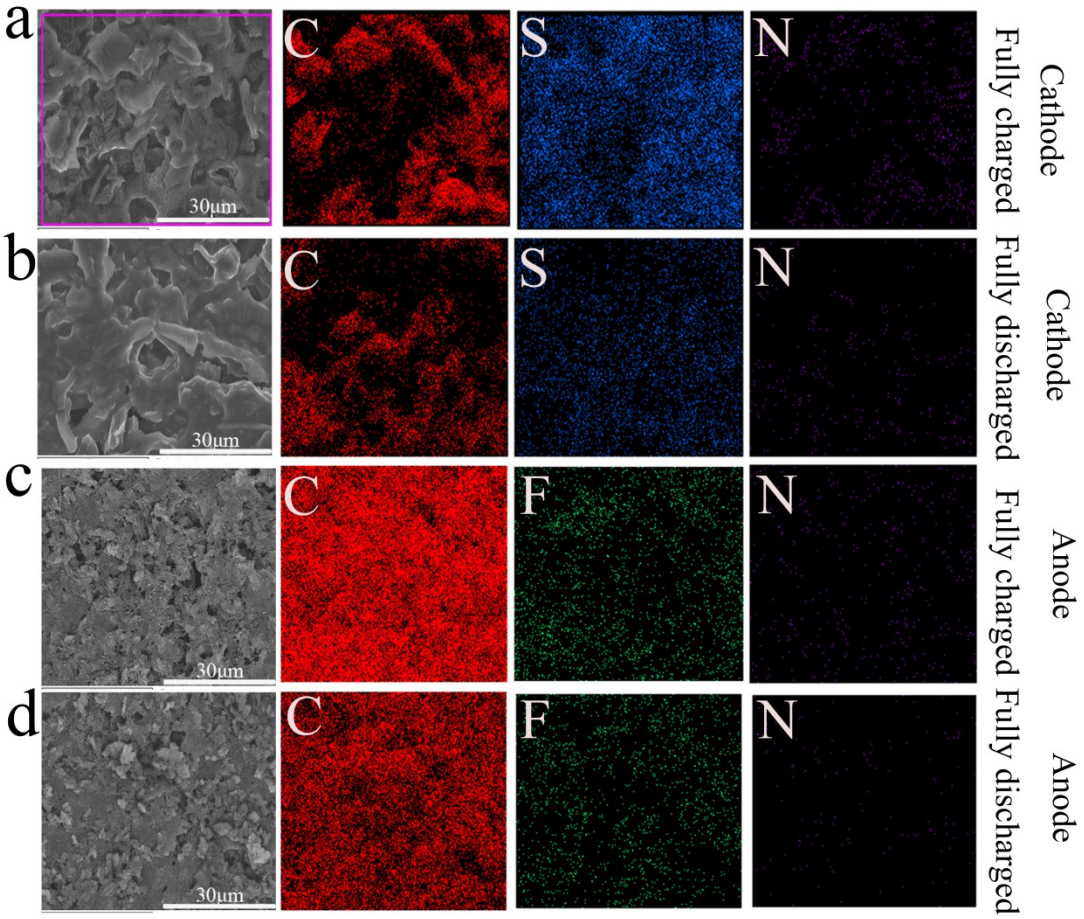

Fig. S9 Elemental mapping of C, S, F, and N in the fully charged and discharged: a, b) cathode and c, d) anode.

Table S1: The XPS results of graphite electrodes at different states

element	Full charged graphite cathode			Full discharged graphite cathode		
	Position BE (ev)	Atomic Conc%	Mass Conc %	Position BE (ev)	Atomic Conc%	Mass Conc %
F	688.100	14.56	20.15	685.300	15.79	22.34
O	532.100	16.08	18.75	529.900	6.66	7.94
N	399.300	2.92	2.98	397.500	2.43	2.53
C	284.500	66.43	58.12	282.400	75.12	67.19

Table S2: The XPS result PCT electrodes at different states

element	Full charged PCT anode			Full discharged PCT anode		
	Position BE (ev)	Atomic Conc%	Mass Conc %	Position BE (ev)	Atomic Conc%	Mass Conc %
F	686.200	9.57	13.73	684.900	6.54	9.66
O	529.300	12.04	14.55	528.900	9.62	11.97
N	399.500	4.13	4.37	396.500	0.46	0.51
C	282.200	74.26	67.35	282.200	83.38	77.87