

Supporting Information

Boosting the Performance of Organic Cathodes through Structure Tuning

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Experimental Section

1. Synthesis of compound 2

2,7-dibromo-pyrene-4,5,9,10-tetraone (compound 1, 630 mg, 1.5 mmol) and TsOH.H₂O (570 mg, 3.0 mmol) were added into a flask with a mixed solution of ethylene glycol (15 mL) and toluene (15 ml). The resulted mixture was refluxed at 140 °C under argon protection for 36 hrs. After the solution cooled down to room temperature, the precipitate was filtrated, washed in success of H₂O and small amount of MeOH, dried to obtain light yellow solid (compound 2, 560 mg, 63%). ¹H NMR (CDCl₃, 300 MHz): δ 7.89 (s, 4H), 4.19 (s, 8H), 3.66 (s, 8H); ¹³C NMR (CDCl₃, 75 MHz): δ 135.0, 130.3, 127.4, 123.8, 91.9; HRMS: Calculated for C₂₄H₂₀Br₂O₈ + H⁺: 598.9562; Found: 598.9551 (M+ H⁺); Elemental Analysis for C₂₄H₂₀Br₂O₈: Calculated: C, 48.35%; H, 3.38%. Found: C, 48.11%; H, 1.91%.

2. Synthesis of PPTO

In a dried 50 mL Schlenk tube was added subsequently of bis(1,5-cyclooctadiene) nickel(0) (390 mg, 1.42 mmol), 1,5-cyclooctadiene (154 mg, 1.42 mmol) and 2,2'-bipyridine (220 mg, 1.42 mmol) and anhydrous DMF (4 ml). The solution was heated at 85 °C for 30 mins under argon protection. Compound 1 (480 mg, 0.8 mmol) in 8 mL toluene was added into the tube and the mixture solution was heated at 85 °C for 36 hrs and cooled down to room temperature. The precipitated solid was filtrated, washed in success with H₂O, MeOH and THF, dried to obtain the white solid, which was used directly in next step. The obtained solid was dissolved in a mixture of TFA-H₂O (9:1, 20 ml) and refluxed in a sealed tube under argon protection for 24 hrs. After the solution cooled down to room temperature, the mixture solution was dropped on the ice slowly. The precipitate was filtrated, washed with H₂O and methanol, dried to give the rough deep red product PPTO. The PPTO was further purified through soxhlet extraction installation

using acetone, THF and CHCl_3 respectively to obtain the PPTO (80 mg, 38%). FTIR: 1678 cm^{-1} , 1602 cm^{-1} ; Elemental Analysis: Calculated for $\text{Br(PPTO)}_3\text{H}$ (considering that Br atom could hardly be completely eradicated): C, 66.92%; H, 1.52%. Found: C, 66.42%; H, 2.65%.

3. Synthesis of PEPTO

In a dried 100 mL two-neck flask was added subsequently of compound **2** (480 mg, 0.8 mmol), bis(trimethylstannyl)acetylene (282 mg, 0.8 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (56 mg, 0.08 mmol) and finally anhydrous toluene (50 ml). Then the solution was refluxed at $120\text{ }^\circ\text{C}$ under argon protection for 24 hrs and cooled down to room temperature. The precipitated solid was filtrated, washed in success of H_2O , MeOH and THF, dried to obtain the green solid, which was used directly in next step. The obtained solid was dissolved in a mixture of TFA- H_2O (9:1, 20 ml) and refluxed in a sealed tube under argon protection for 24 hrs. After the solution cooled down to room temperature, the mixture solution was dropped on the ice slowly. The precipitate was filtrated, washed with H_2O and MeOH, dried to give the rough black product PEPTO. The PEPTO was further purified through soxhlet extraction installation using acetone, THF and CHCl_3 respectively to obtain the PEPTO (142 mg, 67%). FTIR: 1683 cm^{-1} ; Elemental Analysis: Calculated for $\text{Br(EPTO)}_3\text{Sn}(\text{CH}_3)_3$ (considering that Br and $\text{Sn}(\text{CH}_3)_3$ groups could hardly be completely eradicated): C, 62.44%; H, 1.93%. Found: C, 61.42%; H: 2.01%.

4. Electrode Preparation and Coin-Type Cell Fabrication

The as-prepared PPTO and PEPTO samples (each 9 mg) were mixed with carbon additives (multi-wall carbon nanotubes) (15 mg) and polymer binders (polyvinylidene fluoride) (6 mg) with a weight ratio of 3:5:2, separately. The mixture powders were ground with a pestle for 50 mins with the addition of a few droplets of N-methyl-2-pyrrolidone solvent. Homogeneous PPTO and PEPTO electrode slurries were separately obtained and uniformly pasted onto the

battery grade aluminum foils. The as-prepared electrode films were dried at 60 °C overnight in a vacuum atmosphere and then taken out. Finally, PPTO and PEPTO electrodes with diameters of 12 mm were separately punched and to be used. The electrode mass loadings are typically 1.5-2.5 mg per electrode. To investigate the electrochemical performance of PPTO and PEPTO, lithium foils were used as the counter electrodes. The electrolyte system consists of 1 mol/L (M) lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) in 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME) solvent (1/1, v/v). Celgard 2400 membrane was applied as the separator and CR2032 coin-type electrochemical cell construction was applied. The cells were prepared in a glovebox filled with pure argon gas wherein the oxygen and moisture levels were both maintained below 1 ppm. The cells were finally assembled and placed for an equilibration time of 12 h to be separately tested.

5. Characterization and Electrochemical Measurement

NMR spectra were recorded with a Bruker AV 300 Spectrometer at 300 MHz (¹H NMR) and 75 MHz (¹³C NMR). HRMS results were recorded on Waters ACQUITY UPLC® System. EA was conducted on a PerkinElmer 2400Series II CHNS/O elemental analyzer. FTIR spectra were recorded on a PerkinElmer Spectrum Frontier FTIR spectrometer. TGA profiles were obtained from a TA Instruments TGA Q500 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. SEM images were obtained by JEOL/JSM-6340F performed at an accelerating voltage of 5 kV. The cells were tested on a NEWARE multichannel battery test system (at room temperature) with the galvanostatic charge and discharge in the ranges of 3.5-1.5. CV was performed on an electrochemical analyzer (CH Instrument CHI604e) at a scan rate of 0.1 mV s⁻¹. EIS analysis was conducted by the same instrument between 100 kHz and 10mHz.

6. Computational Methodology.

The geometry structure of the trimers was optimized by using DFT calculations (B3LYP/6-31G*),^{1,2} and the frequency analysis was followed to assure that the optimized structures were stable states.

All calculations were carried out using *Gaussian 09*.³

References:

(1) Becke, A. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *Journal of Chemical Physics* **1993**, *98*, 5648.

(2) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785-789.

(3) Gaussian 09, Revision A.1,

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

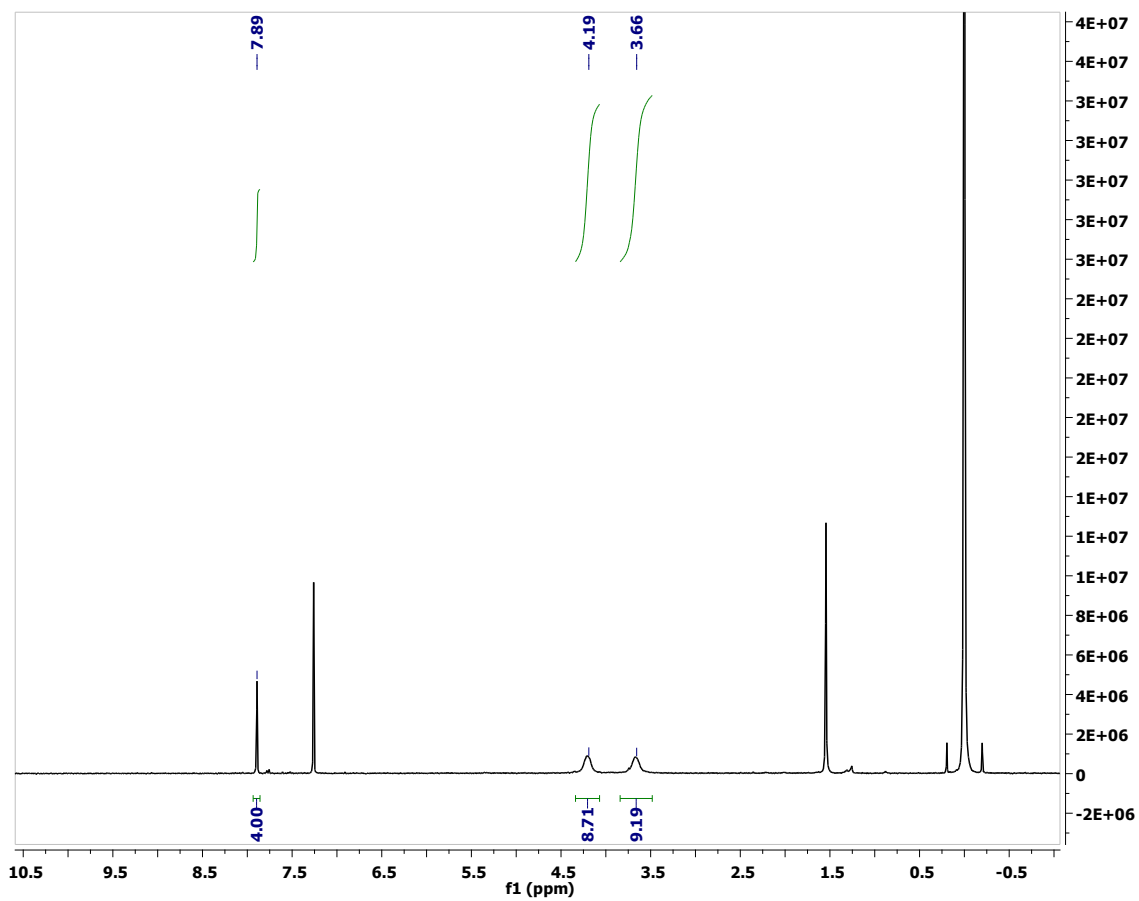


Figure S1. ^1H NMR of compound 2.

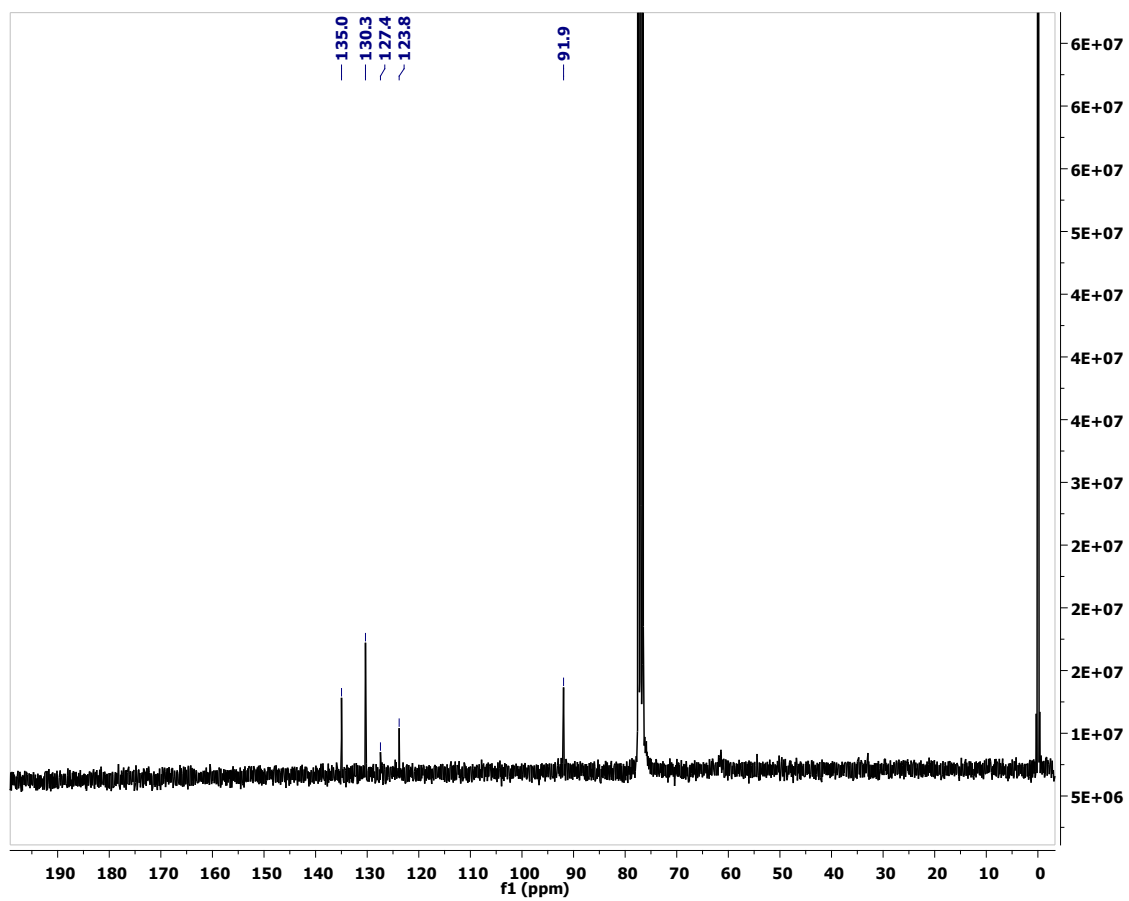


Figure S2. ^{13}C NMR of compound 2.

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

53 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

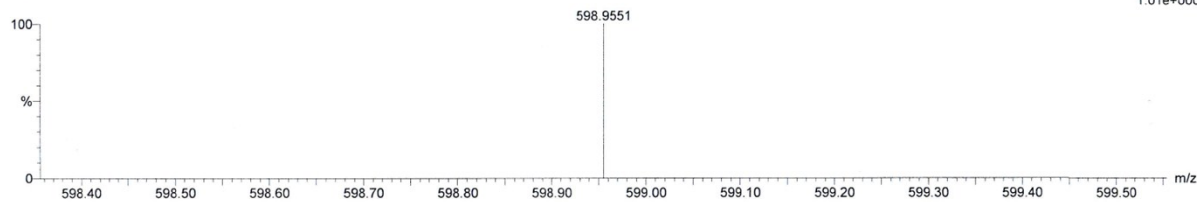
Elements Used:

C: 20-24 H: 18-21 O: 0-8 79Br: 0-2 81Br: 0-2

C24H20Br2O8

cwq-2B 51 (1.134)

1: TOF MS ES+
1.01e+000



Minimum:				-1.5					
Maximum:		5.0	20.0	50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
598.9551	598.9562	-1.1	-1.8	13.5	12.6	0.0	C24	H21	O8 81Br2

Figure S3. HRMS of compound **2**.

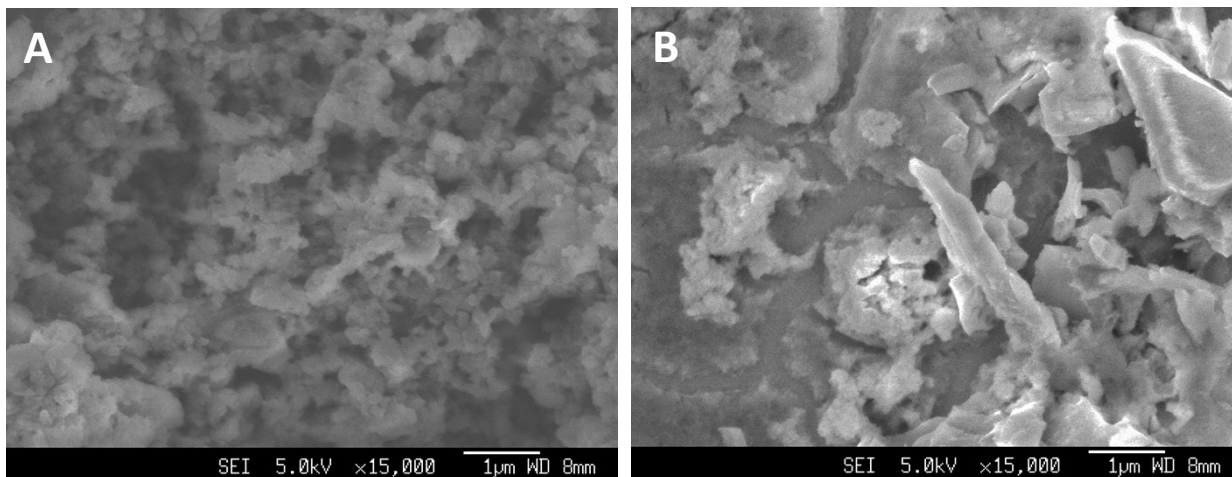


Figure S4. HRSEM images of as-prepared (A) PPTO and (B) PEPTO.

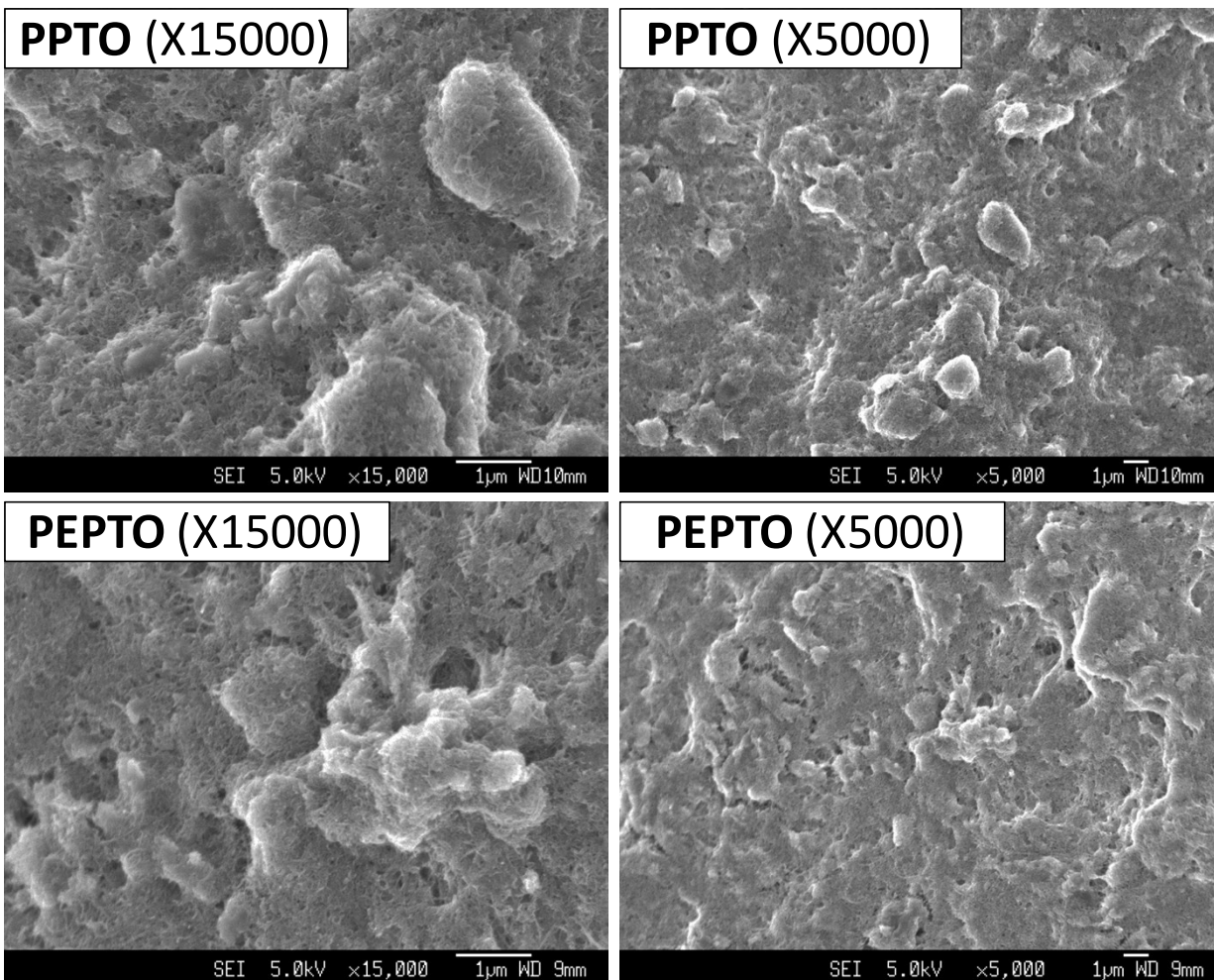


Figure S5. HRSEM images of PPTO and PEPTO electrodes with different magnifications (after mixing with CNTs and binders).

Table S1. Average operating voltage calculations of PPTO and PEPTO cathodes between 3.5 and 1.5 V.

Compound	Practical Energy Density (Wh kg⁻¹)	Specific Capacity (the 2nd discharge) (mAh g⁻¹)	Average Operating Voltage (V)
PPTO	530	217	2.44
PEPTO	507	205	2.47

The energy density values are obtained from the galvanostatic charge-discharge profiles of PPTO and PEPTO at 20 mA g⁻¹. The average operating voltages are calculated by energy density/specific capacity.

Table S2. A comparison table includes several polymer electrodes for rechargeable batteries.

Polymer electrode materials ^{[reference]a)}	Shuttling ions	Initial, final reversible capacity (mAh g ⁻¹) (at the current density or C rate)	Cycle numbers (at the current density or C rate)	Average output potential (V)
PEPTO (This work)	Li ⁺	244, 155 (at 20 mA g⁻¹); 139, 110 (at 800 mA g⁻¹)	100 cycles (at 20 mA g⁻¹); 953 cycles (at 800 mA g⁻¹)	2.47
PPTO (This work)	Li ⁺	234, 161 (at 20 mA g⁻¹); 131, 97 (at 800 mA g⁻¹)	100 cycles (at 20 mA g⁻¹); 953 cycles (at 100 mA g⁻¹)	2.44
3D-RGO/PI composite ^[42]	Li ⁺	123, 101 (at 0.5 C)	150 cycles	2.07
EDP ^[43]	Li ⁺	85, 75 (at 50 mA g ⁻¹)	50 cycles	~2.50
HP ^[43]	Li ⁺	130, 110 (at 50 mA g ⁻¹)	50 cycles	~2.50
UP ^[43]	Li ⁺	65, 130 (at 50 mA g ⁻¹)	50 cycles	~2.50
PAQI ^[44]	Na ⁺	213, 190 (at 50 mA g ⁻¹)	150 cycles	~1.90
PI-1 ^[45]	Li ⁺	~61, ~10 (at 25 mA g ⁻¹)	65 cycles	~2.30
PI-2 ^[45]	Li ⁺	104, 68.5 (at 25 mA g ⁻¹)	65 cycles	~2.40
PI-3 ^[45]	Li ⁺	~78, ~57.9 (at 25 mA g ⁻¹)	65 cycles	~2.40
PI/CNT nanocomposite ^[46]	Li ⁺	~102, 95 (at 100 mA g ⁻¹)	300 cycles	~2.50
PENDI ^[47]	Li ⁺	113, ~50 (at 20.2 mA g ⁻¹)	100 cycles	~2.25

a) The reference numbers are according to those cited in the paper.