Electronic Supplementary Information

Perylene Diimide-Diamine/Carbon Black Composites as High Performance Lithium/Sodium Ion Battery Cathodes

Experimental Section

Materials:

3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA) was purchased from Energy Chemical Inc. Ethylene diamine (EDA), trimethylene diamine (TDA), and 1,6-hexamethylenediamine (HDA) were purchased from Aladdin Chemical LLC. Carbon black (Super P) was provided by Shanghai Xiaoyuan Energy Technology Inc. All the reagents were of AR grade and used as received without further purification.

Preparation of PDI-DA/CB composites:

Typically, PTCDA (1.5 mmol) and the diamine (EDA, TDA, or HDA, 1.5 mmol) were first mixed in 1-methyl-2-pyrrolidinone (NMP, 30 mL) and the resulting suspension was continuously stirred for 12 h at room temperature. Meanwhile, carbon black (The mass ratio of carbon black to the total amount of PTCDA and diamine was 2 : 1) was dispersed in NMP (60 mL) by ultra-sonication and the resulting suspension was added to the aforementioned NMP dispersion. The mixture was heated at 180 ^{o}C for 9 h to allow the formation of PDI-DAs in the presence of carbon black. Finally, the suspension was cooled to room temperature, filtrated and washed with NMP and ethanol for several times. After vacuum drying at 80 ^{o}C for 6 h, the PDI-DA/CB composites were obtained as black powders with the yields over 95 % (according to the amount of PTCDA). According to the diamines used in the fabrication process, the composites were named as PDI-EDA/CB, PDI-TDA/CB, and PDI-HDA/CB, respectively. In controlled experiments, the aforementioned PDI-DAs were obtained under the same conditions without adding carbon black powder and the resultant samples were named as PDI-EDA, PDI-TDA, and PDI-HDA, respectively.

To optimize the mass ratios of PDI-DAs and carbon black in the composites, two reference samples were prepared via the following procedures:

PTCDA (1.5 mmol) and EDA (1.5 mmol) were first mixed in 1-methyl-2-pyrrolidinone (NMP, 30 mL) and the resulting suspension was continuously stirred for 12 h at room temperature. Meanwhile, carbon black (The mass ratio of carbon black to the total amount of PTCDA and diamine were 1 : 1 or 1 : 2) was dispersed in NMP (60 mL) by ultra-sonication and the resulting suspension was added to the aforementioned NMP dispersion. The mixture was heated at 180 ^{o}C for 9 h to allow the formation of PDI-DAs in the presence of carbon black. Finally, the suspension was cooled to room temperature, filtrated and washed with NMP and ethanol for several times. After vacuum drying at 80 ^{o}C for 6 h, the PDI-EDA/CB composites were obtained as black powders with the yields over 95 % (according to the amount of PTCDA). According to the ratios of PDI-EDA and carbon black, the composites were named as PDI-EDA/CB-11, and PDI-EDA/CB-21, respectively.

Structural characterization:

The weight contents of PDI-DAs in the composites were calculated by the results from element analysis (EA, Vario EL Cube). The Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 6700 spectrometer by homogeneously mixing the samples with anhydrous KBr. The crystallization degree of the samples was investigated by powder X-Ray diffraction (XRD, Rigaku D/Max 2500) with Cu-Kα radiation (λ=1.54 Å) at a generator voltage of 40 kV and generator current of 40 mA at a speed of 5 ^{o} min^{-1} from 5 ^{o} to 60 ^{o}. Thermogravimetric analysis (TGA) curves were monitored on a Q5000IR apparatus (TA Instruments, USA). The surface morphologies of the PDI-DAs and PDI-DA/CB composites were observed by scanning electron microscope (SEM, JEOL JSM-7800F Prime, 5kV) and transmission electron microscopy (TEM) measurements (JEM-2010F, JEOL, Japan) with an accelerating voltage of 200 kV. Samples were dispersed in ethanol and transferred onto a Cu grid for TEM measurements. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a AXIS Ultra DLD system from Kratos with Al Kα radiation as X-ray source for radiation.

Electrochemical measurements:

Electrochemical performances of the PDI-DA/CB composites in lithium ion batteries (LIBs) were measured in CR2016 coin-type battery. As the controlled samples, PDI-DAs were firstly mechanically mixed with carbon black in a mass ratio of 1 : 2. The working electrodes of the LIBs were fabricated by mixing the PDI-DA/CB composites or the mechanical mixtures of PDI-DAs/carbon black and polyvinylidene fluoride (PVDF) as the binder with a mass ratio of 90 : 10 in NMP. The resulting slurries were uniformly spread onto an aluminum foil current collector. The obtained electrodes were vacuum dried at 80 ^{o}C for 12 h and subsequently punched into small discs with the diameter of 1 cm and the mass loading of 0.8 mg cm^{-2}. Using lithium foil as the counter electrode, Celgard 2400 membrane as the separator and the ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 vol. %) solution of $LiPF_6$ (1 M) as the electrolyte, the manufacture of coin-cell type LIBs were finished in an argon-filled glove box with the moisture and oxygen/water concentrations below 1 ppm.

The electrochemical performances of the PDI-DA/CB composites as the cathode materials in sodium-ion batteries (SIBs) were also evaluated in a similar way as the aforementioned LIB tests except that the counter electrode, separator and electrolyte were sodium foil, glass fiber and the EC/DMC (1:1 w/w) solution of $NaPF_6$ (1 M), respectively. For the characterization of the PDI-DA/CB cathodes after cycling tests, the coin-type cells were disassembled in the argon-filled glove box with the moisture and oxygen concentrations below 1 ppm. And the corresponding cathodes were repeatedly washed with pure dimethyl ether (DME) for several times and then vacuum dried at 60 °C for 2h. The obtained samples were then sent for SEM and XPS characterization.

The galvanostatic charge-discharge tests were performed by Land CT2001A testing system in the potential range from 1.50 to 3.50 V. The current densities were calculated according to the content of active materials (PDI-DAs) in the cathodes. The specific capacities of the samples were calculated by the amount of PDI-DAs in the electrodes. The CV curves were measured on a CHI760e electrochemical workstation at a scan rate of 0.5 mV s^{-1} in a voltage range of 1.50 – 3.50 V (vs. Li/Li+). And the electrochemical impedance spectroscopy (EIS) was also recorded on the CHI760e electrochemical workstation with an amplitude of 5 mV over the frequency range from 0.01 to 100000 Hz.

The theoretical capacity of PDI-DAs as the LIB/SIB cathodes can be calculated by following the reported procedure:[1]

The formula for theoretical capacity calculation is

$$\text{Theoretical capacity} = (26800 \times n/M)$$

Where n = number of electrons involved;

M = molecular weight of the active substance.

Therefore, the theoretical capacity for PDI-EDA ≈ (26800 x 2/418) = 128 mAh g^{-1}; for PDI-TDA ≈ (26800 x 2/432) = 125 mAh g^{-1}; for PDI-HDA ≈ (26800 x 2/474) = 113 mAh g^{-1}.

Table S1. The elemental analysis results of the PDI-DAs and PDI-DA/CB composites

Name	**N (wt%)**	**C (wt%)**	**PDI-DA (wt%)**[a]	**Carbon black (wt%)**[b]
PDI-EDA	6.92	70.72	100.00	-
PDI-EDA/CB	2.24	91.60	32.37	67.63
PDI-EDA/CB-11	3.36	86.38	48.55	51.45
PDI-EDA/CB-21	4.43	82.06	64.02	35.98
PDI-TDA	6.99	69.56	100.00	-
PDI-TDA/CB	2.10	91.76	30.04	69.96
PDI-HDA	5.26	71.71	100.00	-
PDI-HDA/CB	1.94	89.83	36.88	63.12

[a] The contents of PDI-DAs in the PDI-DA/CB composites are determined by the weight contents of N element from the EA results. The N contents in pure PDI-DAs are derived from the EA results of the corresponding samples. And the N contents in carbon black is 0.00 wt%.

[b] The contents of CB in the composites are calculated according to the contents of PDI-DAs.

To optimize the mass ratio of PDI-DAs and carbon black in the composites, the electrochemical performances of PDI-EDA/CB, PDI-EDA/CB-11 and PDI-EDA/CB-21 as the cathode materials in lithium ion batteries were evaluated by galvanostatic charge-discharge tests in coin-type cells using lithium foils as the counter electrode with the voltage between 1.50 – 3.50 V (vs. Li/Li^+). The rate capabilities of the three samples with the current densities in the range of 0.1 to 5.0 A g^{-1} are compared in Figure S1. At 0.1 A g^{-1}, the specific capacities of PDI-EDA/CB, PDI-EDA/CB-11 and PDI-EDA/CB-21 are ~128, 104 and 100 mAh g^{-1}, respectively. With the current densities varying from 0.1 to 5.0 A g^{-1}, the capacities of PDI-EDA/CB are higher than those of PDI-EDA/CB-11 and PDI-EDA/CB-21. PDI-EDA/CB still delivers a high capacity of ~100 mAh g^{-1} even at an ultrahigh current density of 5.0 A g^{-1}, much better than PDI-EDA/CB-11 and PDI-EDA/CB-21. Compared with PDI-EDA/CB, the inferior electrochemical performances of PDI-EDA/CB-11 and PDI-EDA/CB-21 should be because the high ratio of PDI-EDA in the composites cannot grantee the sufficient contact between PDI-EDA and carbon black, thus leading to the utilization of PDI-EDA with a low efficiency. According to the above results, PDI-EDA/CB has the optimized ratio of PDI-EDA and carbon black, resulting in the best electrochemical performances among the three composites. Therefore, the mass ratio of 1 : 2 for PDI-DA and carbon black is selected for the fabrication of the PDI-DA/CB composites in this work.

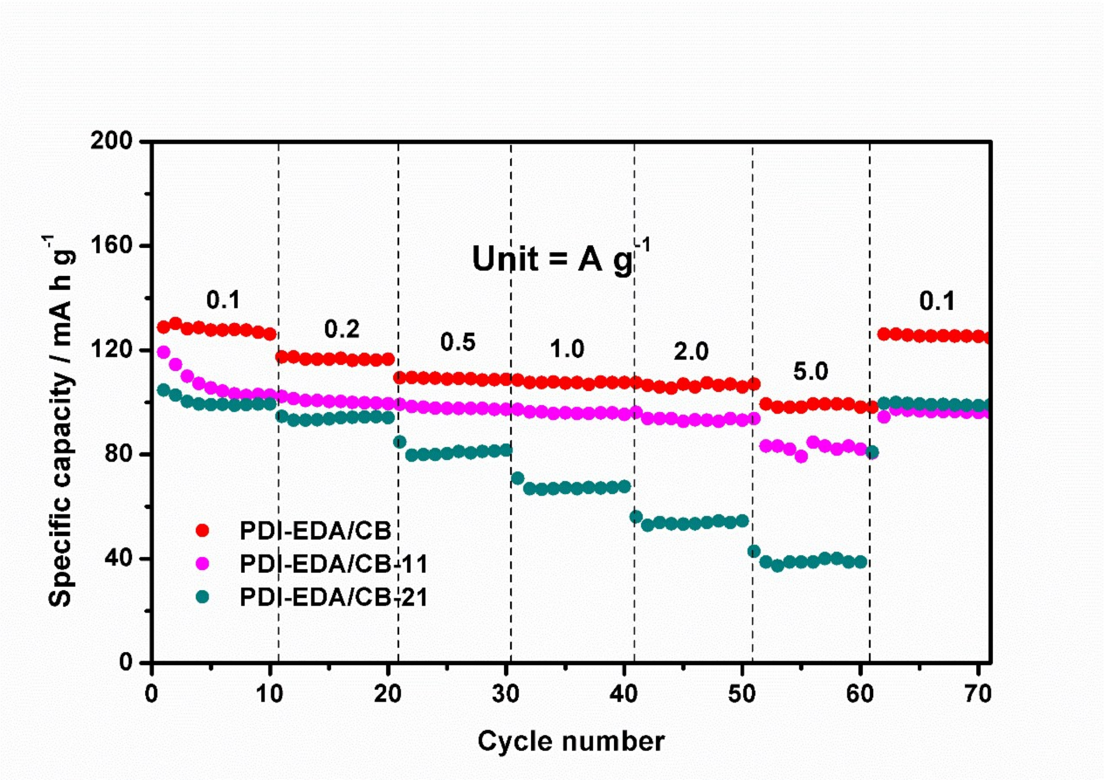


Figure S1. The rate capabilities of PDI-EDA/CB, PDI-EDA/CB-11 and PDI-EDA/CB-21 as the cathode in lithium ion battery with the charge-discharge current density varying from 0.1 – 5.0 A g^{-1}.

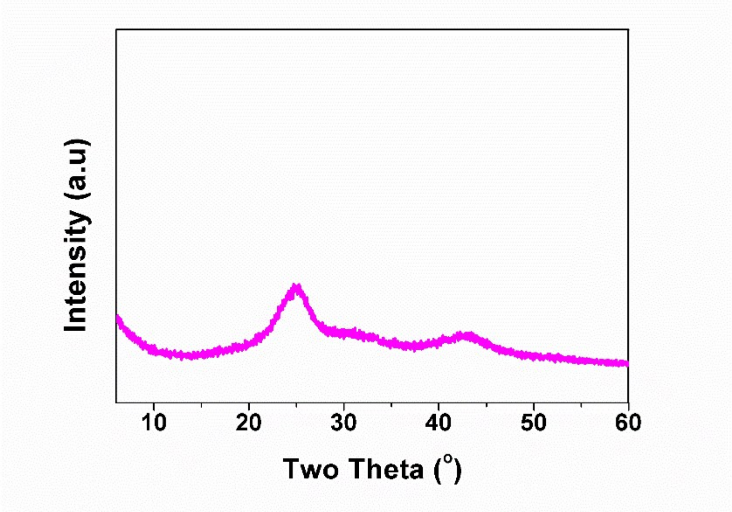


Figure S2. XRD patterns of carbon black.

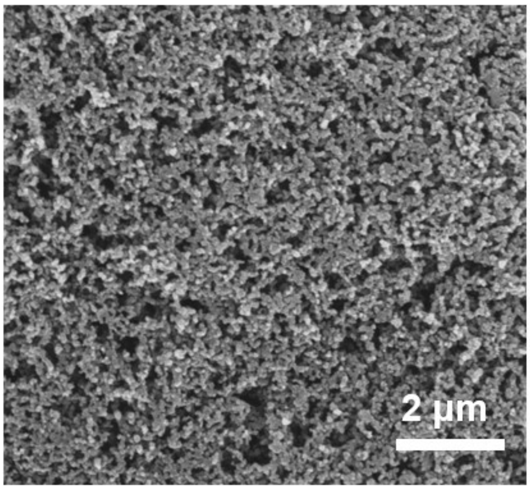


Figure S3. SEM image of carbon black powder.

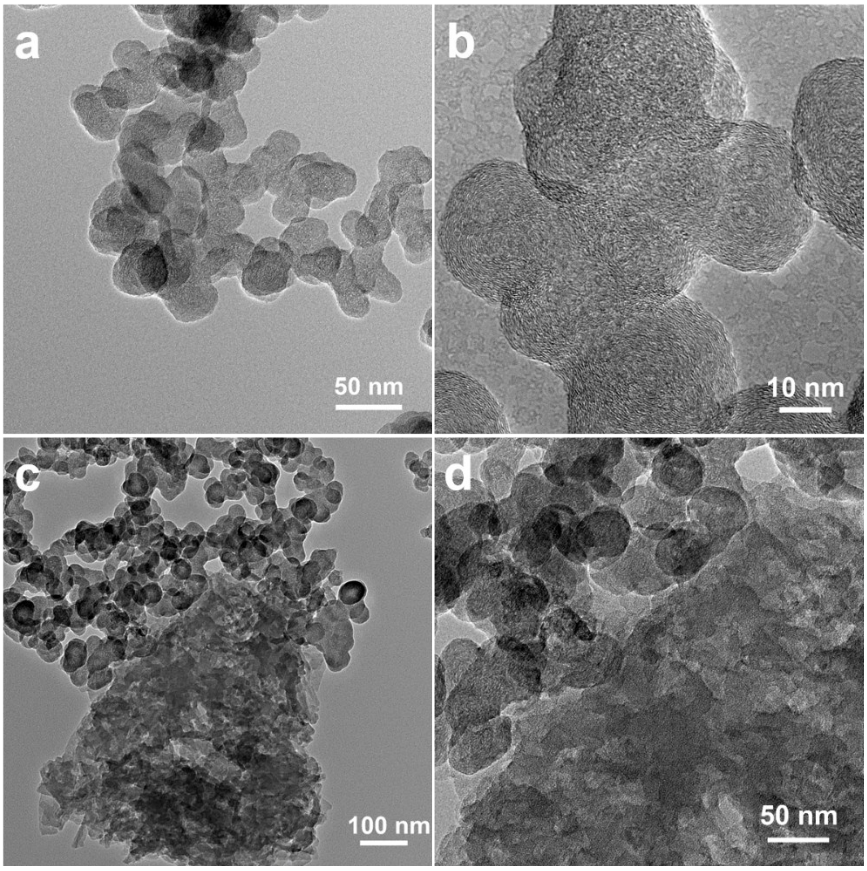


Figure S4. TEM images of a) and b) carbon black; c) and d) the mechanically mixed PDI-EDA and carbon black.

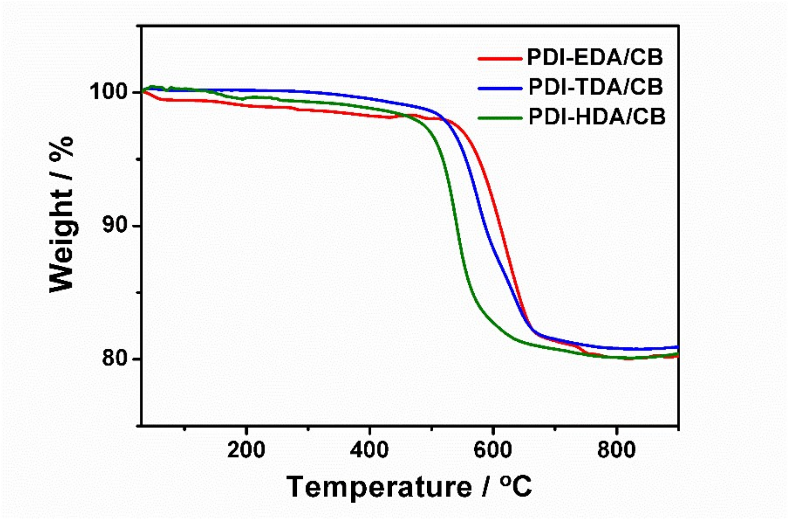


Figure S5. TGA curves of the PDI-DA/CB composites obtained at nitrogen atmosphere.

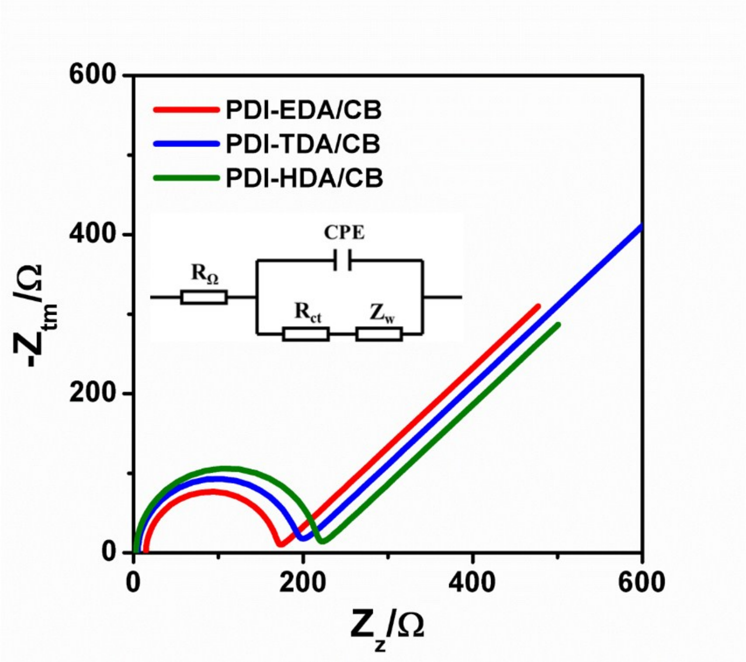


Figure S6. The fitted EIS spectra of the PDI-DA/CB composites.

Table S2. The impedance parameters of the PDI-DA/CB composites.

Sample name	R_{Ω}(Ω)	R_{ct} (Ω)
PDI-EDA/CB	14.68	152.8
PDI-TDA/CB	5.12	184.2

PDI-HDA/CB	3.04	210.9

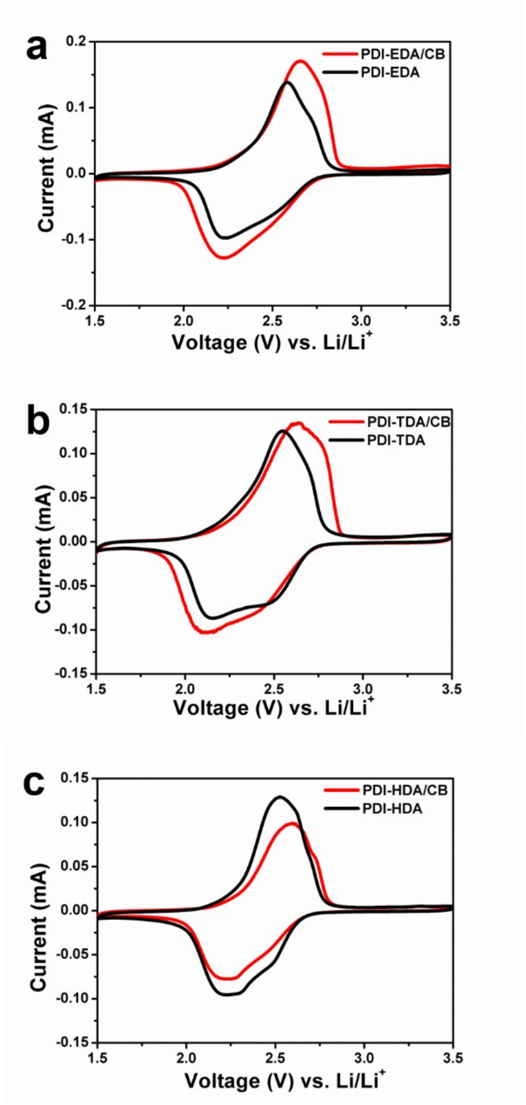
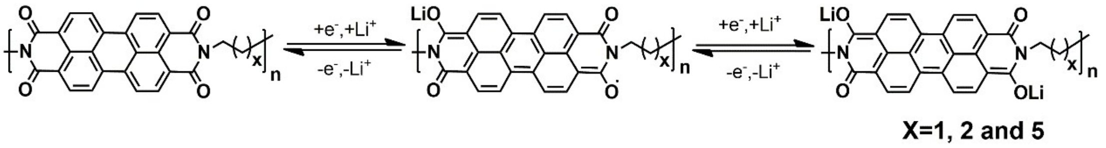


Figure S7. a) The CV curves of PDI-EDA and PDI-EDA/CB at 0.5 mV s^{-1}; b) the CV curves of PDI-TDA and PDI-TDA/CB at 0.5 mV s^{-1}; c) the CV curves of PDI-HDA and PDI-HDA/CB at 0.5 mV s^{-1}.



Scheme S1. The electrochemical redox reactions of PDI-DAs with Li ions in the voltage range of 1.50 - 3.50 V.

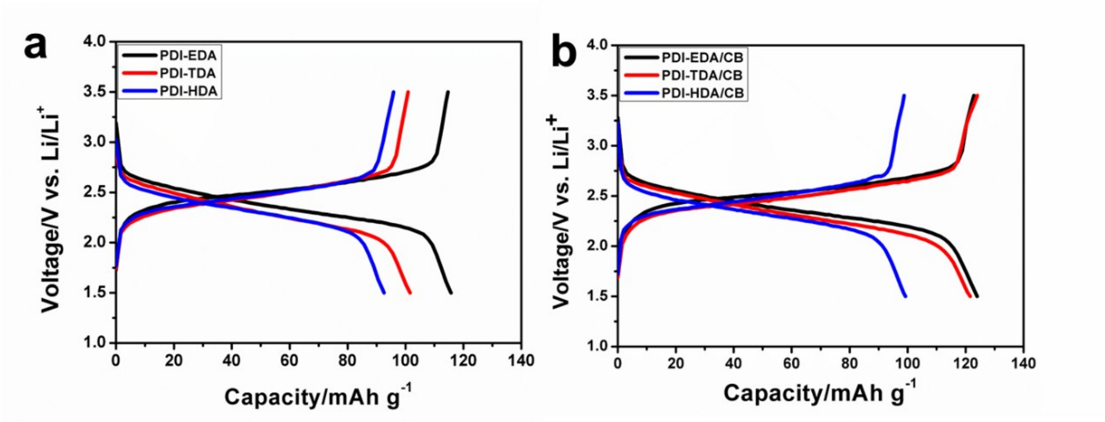


Figure S8. a) The galvanostatic discharge-charge profiles of PDI-DAs as the cathode materials in LIBs at 0.1 A g^{-1}; b) The galvanostatic discharge-charge profiles of PDI-DA/CBs as the cathode materials in LIBs at 0.1 A g^{-1}.

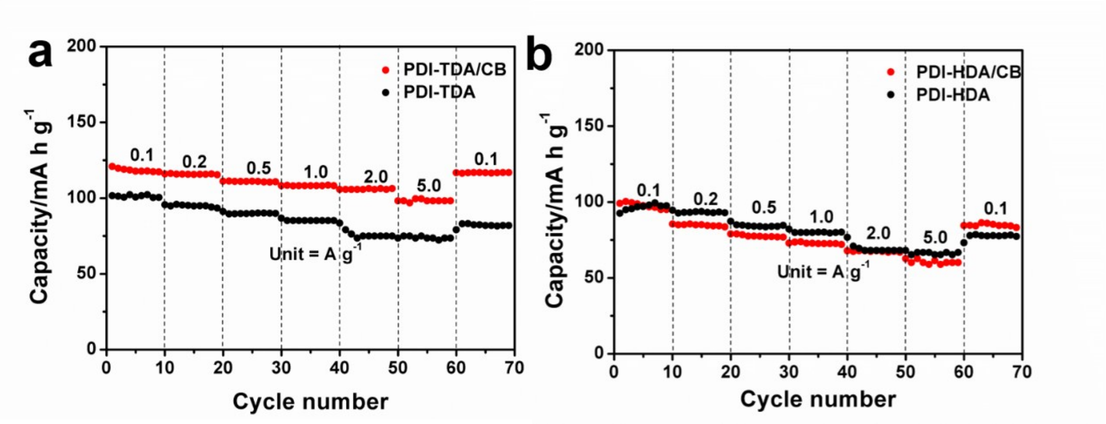


Figure S9. a) The rate capabilities of PDI-TDA and PDI-TDA/CB as LIB cathodes with the current densities ranging from 0.1 – 5.0 A g^{-1}; b) the rate capabilities of PDI-HDA and PDI-HDA/CB as LIB cathodes with the current densities ranging from 0.1 – 5.0 A g^{-1}.

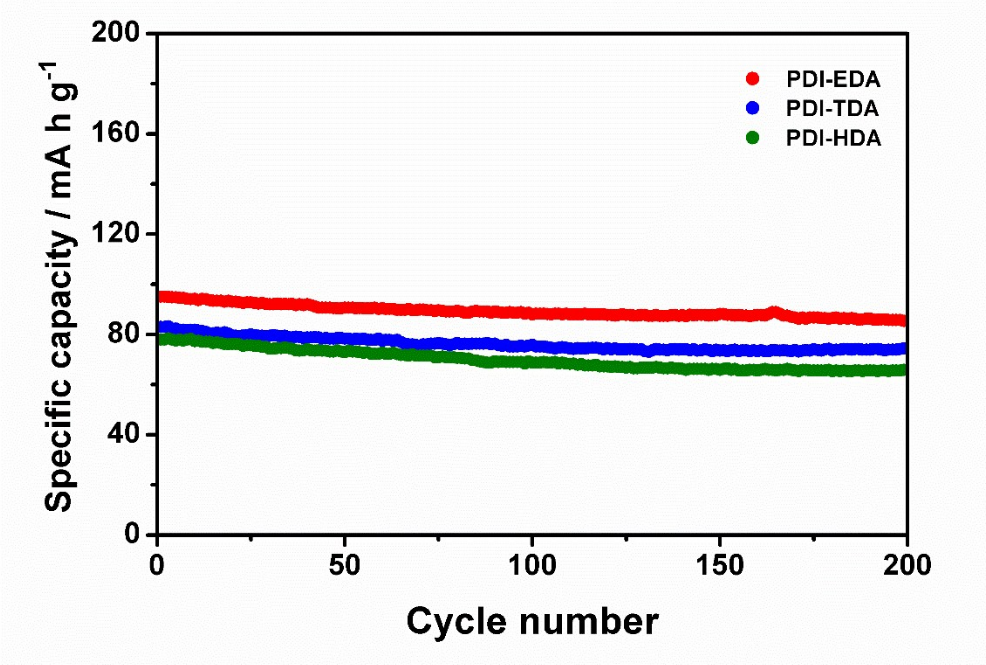


Figure S10. The cycling stabilities of PDI-EDA, PDI-TDA and PDI-HDA as LIB cathodes at the current densities of 1.0 A g^{-1}.

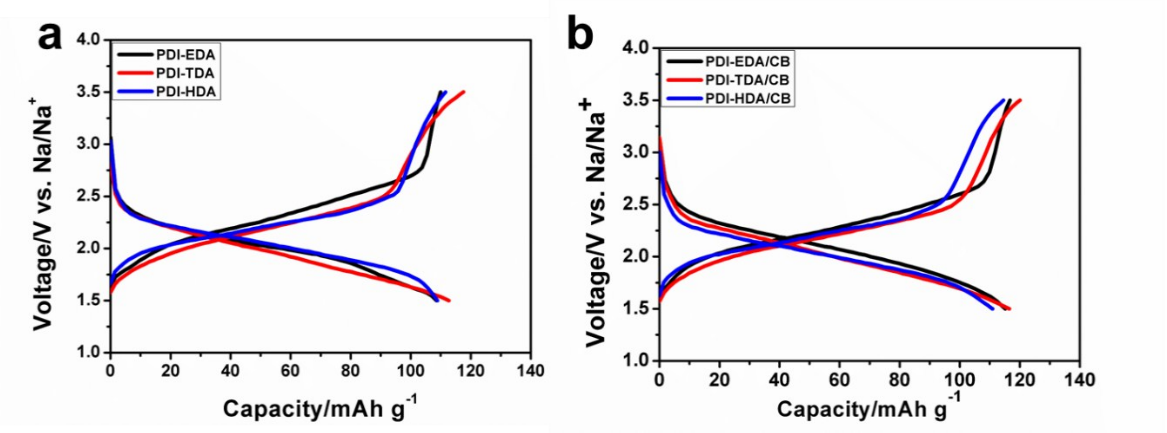


Figure S11. a) The galvanostatic discharge-charge profiles of PDI-DAs as the cathode materials in SIBs at 0.1 A g^{-1}; b) The galvanostatic discharge-charge profiles of PDI-DA/CBs as the cathode materials in SIBs at 0.1 A g^{-1}.

Scheme S2. The electrochemical redox reactions of PDI-DAs with Na ions in the voltage range of 1.50 - 3.50 V.

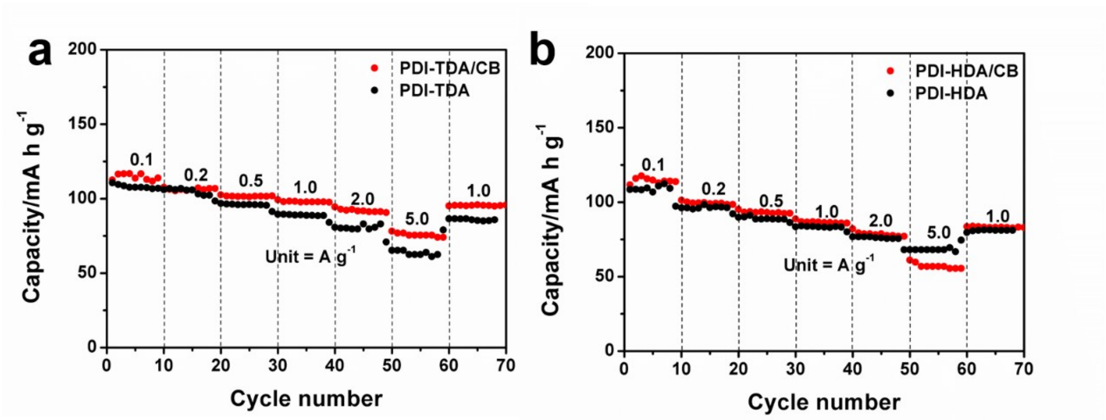


Figure S12. a) The rate capabilities of PDI-TDA and PDI-TDA/CB as SIB cathodes with the current density ranging from 0.1 – 5.0 A g^{-1}; b) the rate capabilities of PDI-HDA and PDI-HDA/CB as SIB cathodes with the current density ranging from 0.1 – 5.0 A g^{-1}.

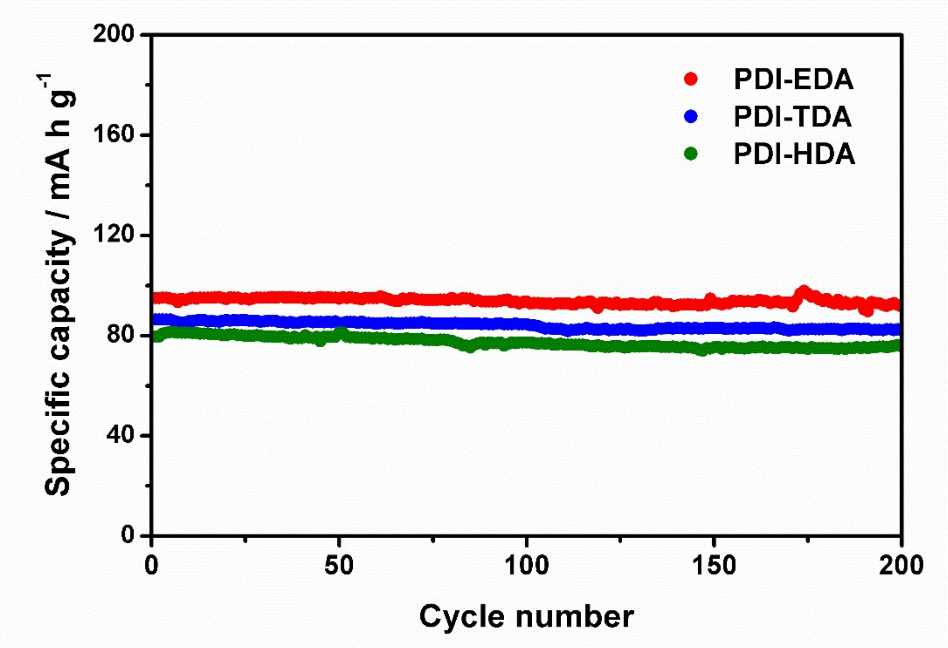


Figure S13. The cycling stabilities of PDI-EDA, PDI-TDA and PDI-HDA as SIB cathodes at the current densities of 1.0 A g^{-1}. The initial capacities of PDI-EDA, PDI-TDA and PDI-HDA are 95, 86 and 79 mA h g^{-1}, which decay to 92, 82 and 76 mA h g^{-1}, respectively after 200 charge-discharge cycles.

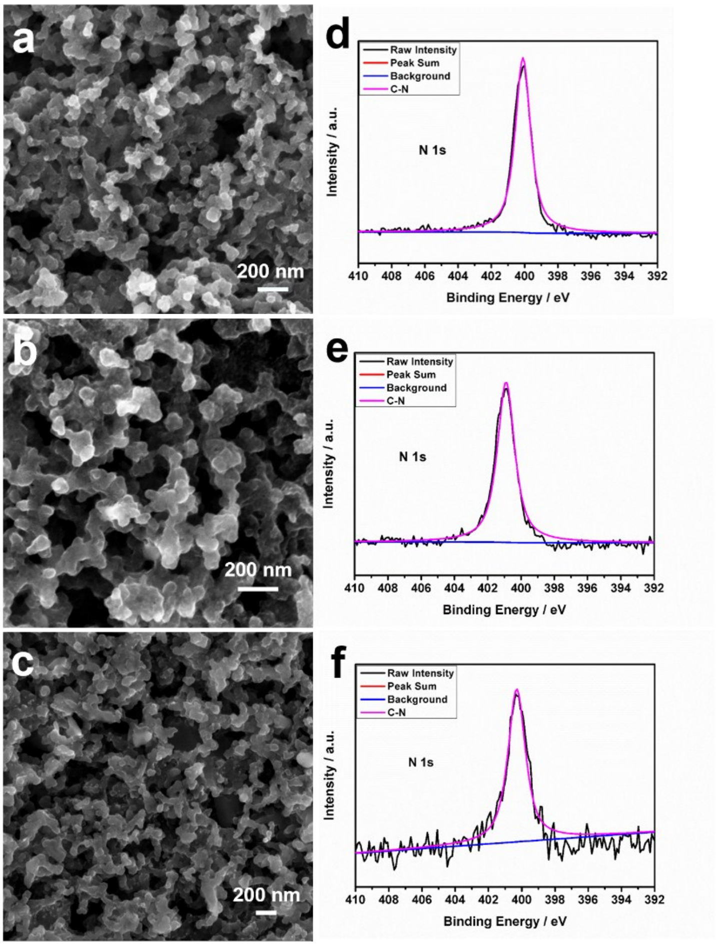


Figure S14. SEM images of a) as made PDI-EDA/CB cathode, b) PDI-EDA/CB cathode after 1000 cycling in LIB, and c) PDI-EDA/CB cathode after 1000 cycling in SIB; High resolution N1s XPS spectra of d) as made PDI-EDA/CB cathode, e) PDI-EDA/CB cathode after 1000 cycling in LIB, and f) PDI-EDA/CB cathode after 1000 cycling in SIB. It should be noted that the N1s spectra of the three samples have almost the same shape with minor shifts. The shifts of the peak positons may be due to the influence of the electrolytes and the unchanged peak shape indicates the stable structure of PDI-EDA after the cycling tests.

References:

[1] Han, C.; Li, Z.; Li, W.-J.; Chou, S.-L.; Dou, S.-X. *J. Mater. Chem. A*, **2014**, 2,

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