Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Bipolar Nitrogen-Doped Graphene Frameworks as High-Performance Cathodes for Lithium Ion Batteries

Table S1. Comparison of the electrochemical performance of N-GF-450 and previously reported organic and non-inorganic cathodes.

Sample	Current density (mA g-1)	Specific capacity (mAh g-1) (cycle)	Ref.
PI/SWNT	221.5	175 (200)	*Adv. Mater.* 2014,26,3338
PMTA/SWNT	191	127 (200)	*Adv. Mater.* 2015, 27, 6504
Fe5(PO4)4(OH)3 2H2O	50	155 (300)	*J. Mater.Chem. A* 2014, *2*, 6174
PMAQ–SWNT	221	150 (300)	*J. Mater. Chem. A*, 2016, 4, 2115
LFP–SG	17	130 (100)	*Adv. Energy Mater.* 2013, 3, 113
amorphized FeF3	23.7	200 (85)	*Adv. Mater.,* 2014, 26, 2558.
PI-FLEG	221	108 (200)	*RSC Adv.,* 2016, 6, 33287
(AQ)/CMK-3	514	174(200)	*Adv. Sci.*, 2015, *2*, DOI: 10.1002/advs.201500018.
Cu(2,7-AQDC)	1	105(50)	*J. Am. Chem. Soc.*, 2014, *136*, 16112.47
PBQS	500	158(1000)	*Adv. Sci.*, 2015, *2*, DOI: 10.1002/advs.201500018.
N-GF-450	500	370 (2500)	This work

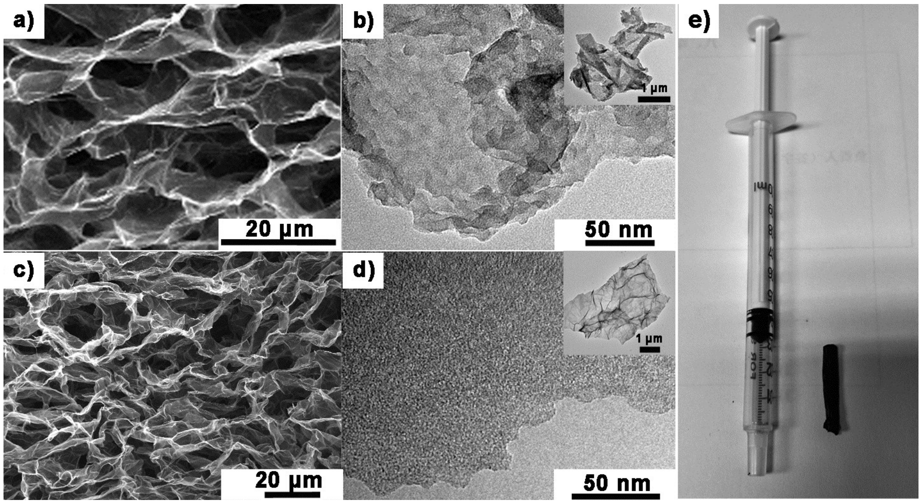

Fig. S1 SEM and HR-TEM of N-GF-300 (a and b) and N-GF-600 (c and d). Insets b and d TEM images of N-GF-300 and N-GF-600.e) Photograph of N-GFs monoliths after removal from the syringe and thermal treatment.

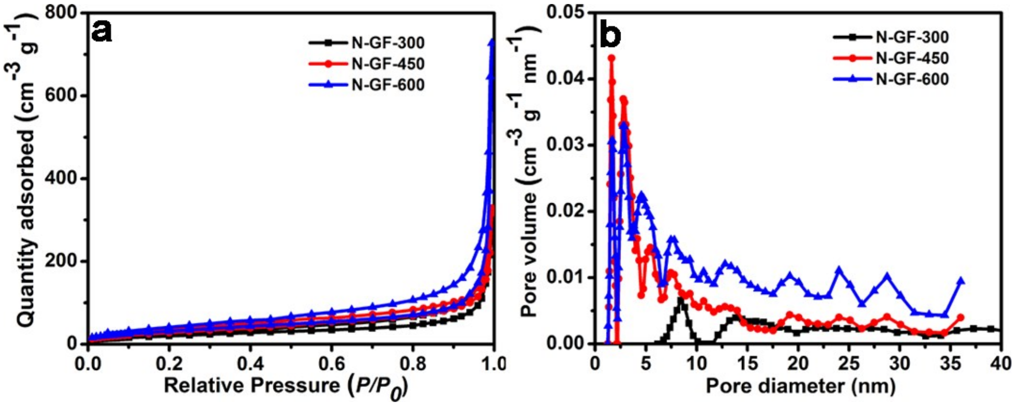

Fig. S2 a) Nitrogen adsorption and desorption isotherms and b) pore size distributions of N-GFs

Table S2. Nitrogen and oxgen contents of the N-GFs in the work

Sample	N-GF-300	N-GF-450	N-GF-600
N (wt.% by EA)	4.51	6.36	5.48
N (wt.% by XPS)	4.68	6.63	4.88
N(at.% by XPS)	4.16	5.14	4.26
O(wt.% by XPS)	11.43	9.39	8.97
O(at.% by XPS)	8.89	7.28	6.94

From the XPS result showed that the content of O atom in the N-GF-300, N-GF-450 and N-GF-600 are 8.89, 7.28 and 6.94 at.%, respectively. The content is reduced with the increased of carbonization temperature because of the oxygen functional groups on the graphene surface are descomposed during 300-600 °C.

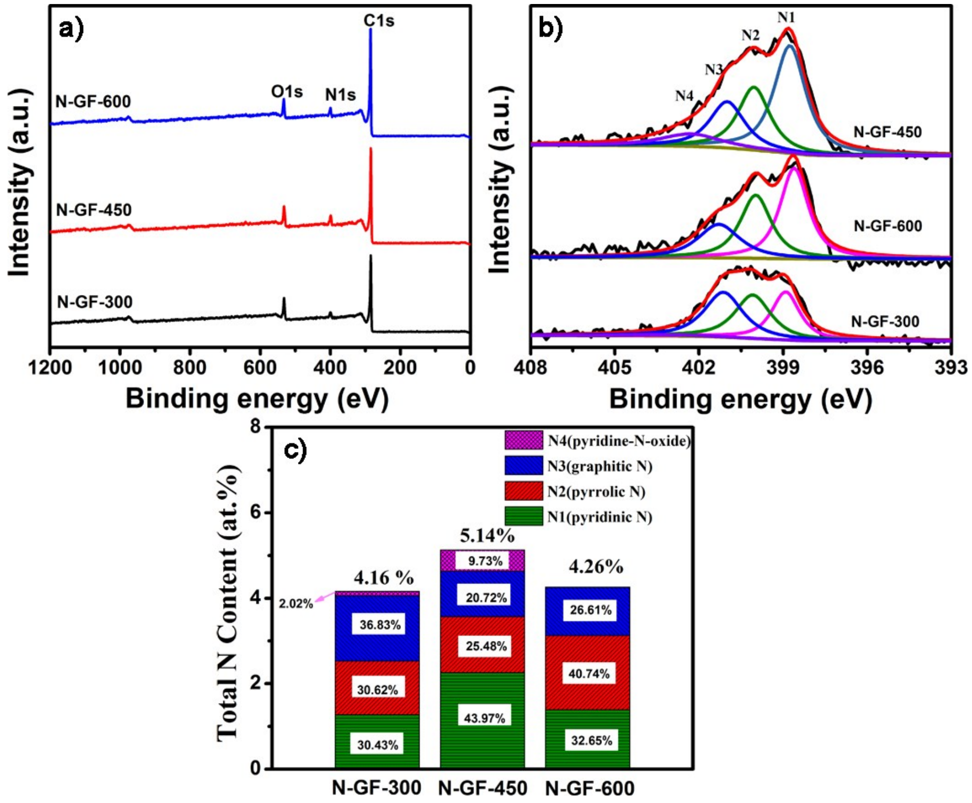

Fig. S3 a) XPS spectra of N-GF-300, N-GF-450, N-GF-600, b) the corresponding high-resolution N1s peak and c) Atomic percentages of four nitrogen species for N-GF-300, N-GF-450, N-GF-600 derived from XPS analysis.

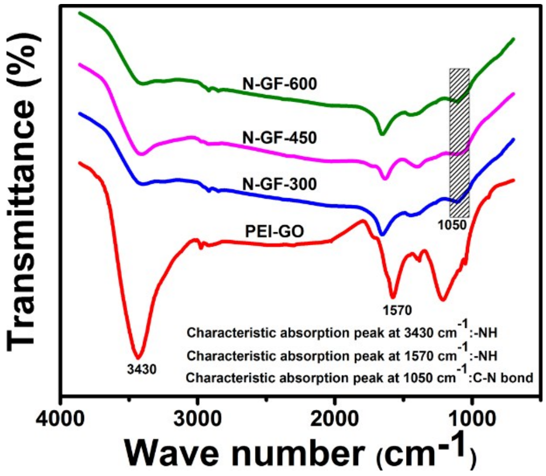

Fig. S4 FTIR spectra of PEI-GO, N-GF-300, N-GF-450 and N-GF-600

The successful build-up of N-doped in graphene framework was also confirmed by Fourier transform infrared (FTIR) spectroscopy (Fig. S4). The strong absorption peaks at 3430 and 1570 cm^{-1} in PEI-GO are assigned to the stretching vibration of –NH. After being thermally treated, the absorption peak 1050 cm^{-1} is apeared in N-GFs, which can be attributed to the stretch vibration of the C-N bond, thus indicating the successful N doped on graphene framework.

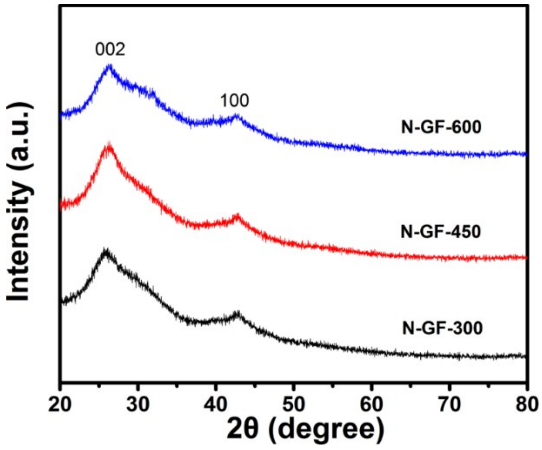

Fig. S5 XRD patterns of N-GF-300, N-GF-450 and N-GF-600

Additionally, the three N-GFs show very closed X-ray diffraction (XRD) patterns with broad peaks at 25 and 43^o, corresponding to (002) and (100) diffractions of graphitic carbon (Fig. S5), which indicates the carbon frameworks of these samples have similar crystalline degrees.

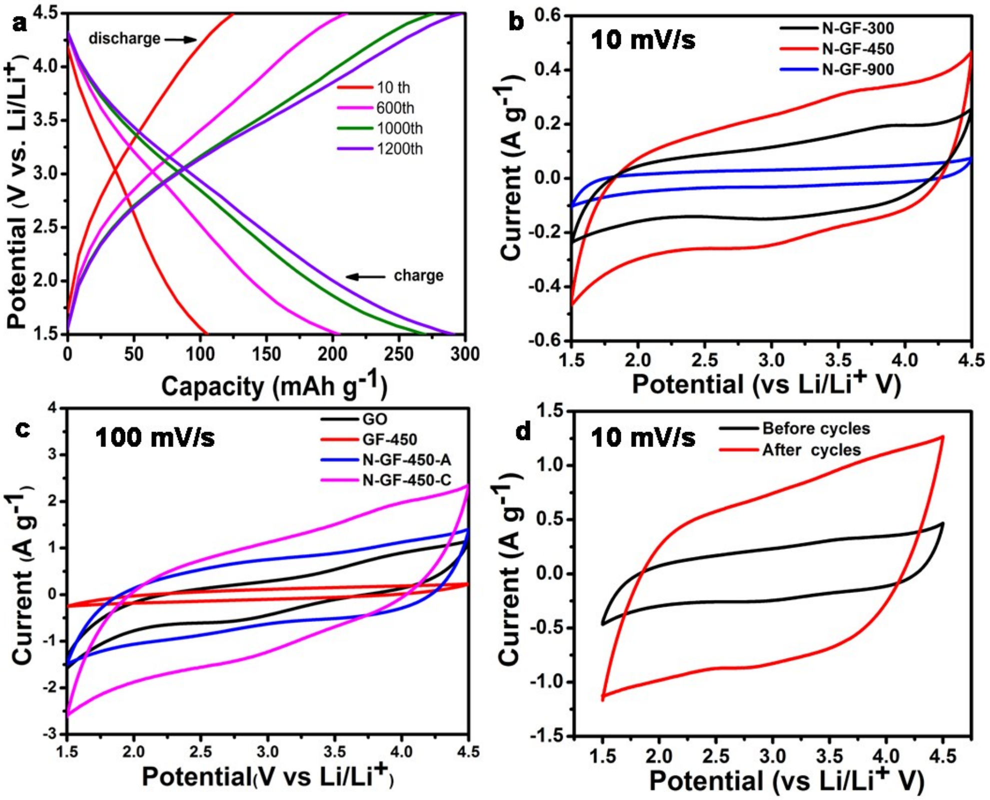

Fig. S6 a) charge-discharge profile of N-GF-450 at the current density of 0.5 A g^{-1}.b) Cyclic voltammetry (CV) curves of N-GF-300, N-GF-450 and N-GF-600 at the scan rate of 10 mv s^{-1}. c) CV curves of GF-450, GO, N-GF-450-A and N-GF-450-C at the scan rate of 100 mv s^{-1}. d) CV curves of N-GF-450 before and after 2500 cycles at the scan rate of 10 mv s^{-1}.

GF-450 without the doping of N atoms shows no peaks in the CV curve, suggesting that the electrochemical reaction is negligible in the potential range of 1.5 -4.5 V (Fig. 2a and Fig. S6). For

GO, a couple of redox peaks is observed at about 2.8/4.2 V, due to the association/disassociation of Li ion process between Li^+ and the carbonyl, hydroxyl and epoxy groups on the electrode materials. All N-GFs show higher peak current than GO and GF-450, indicating that the N-GFs have more electrochemical active species and higher capacity.

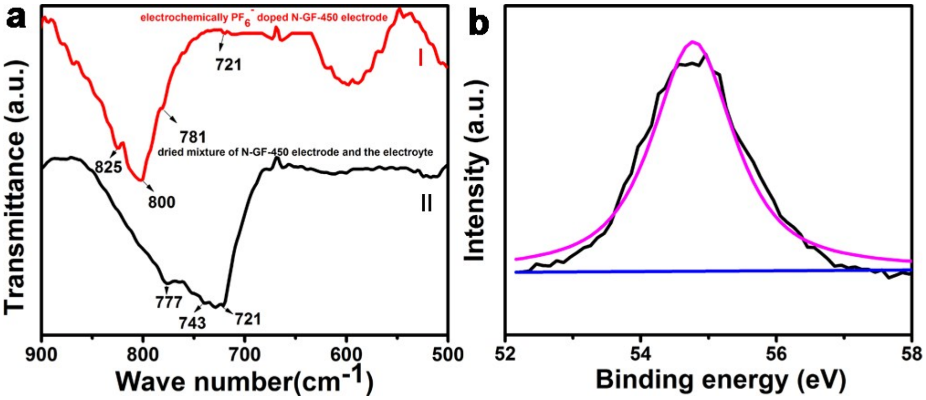

Fig. S7 a) FTIR spectra of N-GF-450 in the full charged state and b) Core-level XPS spectra of Li 1s spectrum of N-GF-450 in the full discharged state.

The FTIR spectra of N-GF-450 also confirm that the PF_6^- is electrochemically doped in N-GF-450 at full charge state (4.5 V, p-doped region, Fig. S6a, red), compared with the dried mixture of N-GF-450 and the electrolyte (1M $LiPF_6$ in EC:DMC, Fig. S6a, black). The PF_6^-doped in N-GF-450 is indicated as I, the mixture of N-GF-450 and electrolyte is indicated as II. The peak at 775 and 717 cm^{-1} in II is attributed to EC. The peak at 830 cm^{-1} in both I and II can be assigned to the infrared-active ν_3 mode for compounds consisting of PF_6^-. The peak at 743 cm^{-1} in I which is infrared-inactive ν_1 mode for free PF_6^-, which becomes active due to the coordination to N-GF-450. The coordination interaction between Li and N lone-pair electrons can be further confirmed by XPS after full discharge to 1.5 V (Fig. S6b). The Li 1s spectrum can be fitted with the peak at 54.7 eV, which can be attributed to Li-N bond.

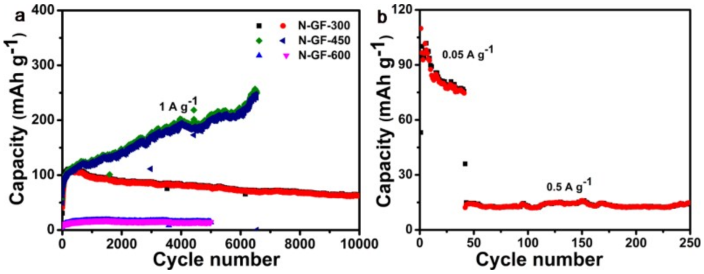

Fig. S8 Cycling performance of a) N-GFs at a current density of 1 A g^{-1} and b) GF-450 at 0.05 and 0.5 A g^{-1}. Without the doping of N atoms, GF-450 only delivers a low capacity of 15 mAh g^{-1} at 0.5 A g^{-1}.

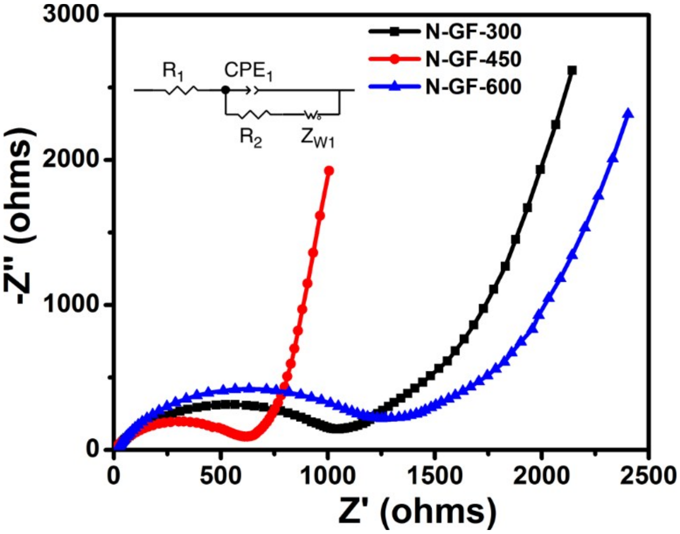

Fig. S9 Nyquist plots of N-GF electrodes obtained by applying a sine wave amplitude of 5.0 mV over the frequency range 100 kHz–0.01 Hz.(inset: the Randles equivalent circuit).

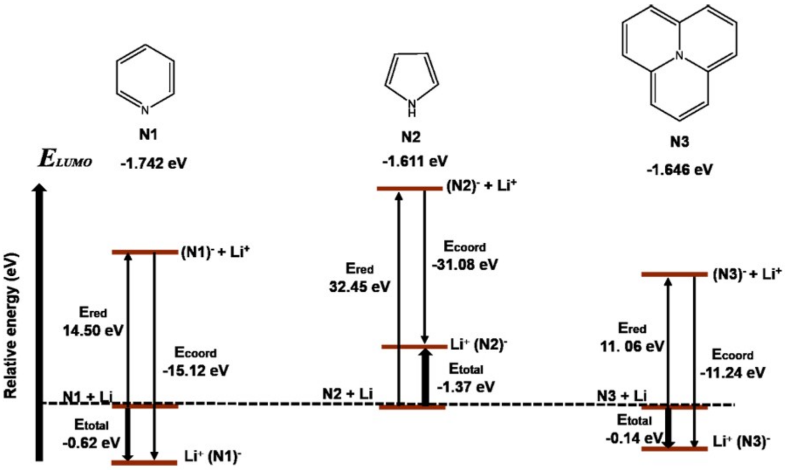

Fig. S10 Redox properties of cyclic 1,2-diketones obtained by DFT calculations (B3LYP/6-31G(d)). Relative energies (eV) of the reduced forms without and with Li coordination based on the neutral form.

The capacity is calculated via C=Q/M. Q charge = Number of Li atoms in cathode *e M=mass of Li-N-doped graphene. The capacity is calculated at certain voltage (3V) which is found by Exp. The specific capacity of the N-doped graphene (N content of approximately 5 at.%) with a Li concentration of 5 at.% was estimated to be 121 mAh g^{-1}.