Supporting Information

Nanoporous sulfur-bridged hexaazatrinaphthylene framework as organic cathode for lithium ion battery with well-balanced electrochemical performance

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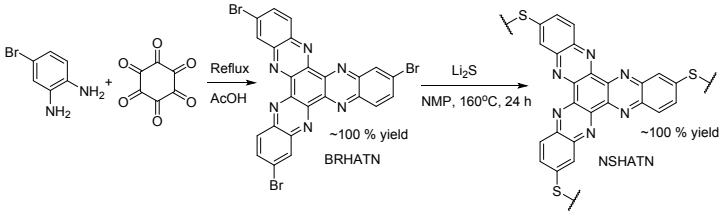
EXPERIMENTAL SECTION

General Considerations All reagents were purchased from Scientific Resources Pte Ltd. and used as received. Electrolytes were purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. Battery capacities and C-rates were calculated based on the mass of active material in the cathode.

Material synthesis



Synthesis of BrHATN Cyclohexaneketone octahydrate (0.193 g, 0.6 mmol) and 4-bromobenzene-1,2-diamine (0.336 g, 1.8 mmol) were charged in a 20 mL two-necked flask under argon. AcOH (10 mL) was slowly added. The reaction mixture was refluxed overnight. The solid precipitate was collected by centrifugation, and further washed with water, ethanol and acetone to give the BrHATN with near quantitative yield. BrHATN: ^{1}H NMR ($CDCl_3$): δ=8.87 (3H, Ar-H), 8.53 (3H, Ar-H), 8.13 (3H, Ar-H). ^{13}C NMR ($CDCl_3$): δ= 143.9, 142.3, 136.4, 132.8, 131.7, 127.5. MS^-(m/z): 617.

Synthesis of NSHATN BrHATN (0.103 g, 0.17 mmol) and Li_2S (18 mg 0.25 mmol) were added in a 20 mL two-necked flask with deoxygenated NMP (5 mL) under argon. The mixture was heated at 160 °C for 12 hours under stirring under nitrogen atmosphere. The flask was subsequently cooled to room temperature and water was added. The solid

precipitate was collected by centrifugation. The resultant dark solid underwent further Soxhlet extraction with methanol, and was dried at 60 ^{o}C under vacuum for 12 h to give NSHATN in quantitative yield.

Characterization Solid-^{13}C NMR experiments were conducted in a Bruker Advance 400 (DRX400) with CP/MAS. N_2 sorption analysis was performed on a Micromeritics ASAP 2020 (77 and 273 K, respectively). The SEM experiment was conducted using a field emission SEM (JEOL JSM-7400F) operated at an accelerating voltage of 5 keV. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris-1 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) experiments were conducted on a Bruker D8 advance. XPS data were taken on Kratos Axis Ultra DLD (Kratos Analytical Ltd., UK), the data were converted into VAMAS file format and imported into CasaXPS software package, calibrated by the C 1s signal (284.8 eV) and further processed. Cyclic voltammograms (CVs) were taken using a CHI 760C electrochemical workstation (CH Instruments, Inc.). The battery testing system (CT2001A, Wuhan LAND electronics Co., Ltd) was used to evaluate the electrochemical performance. The UV experiment was conducted in a SHIMADZU UV-3600, and the band gap was calculated using E_g=h c / λ.

Coin Cell Assembly The synthesized polymer materials were evaluated as cathode material for lithium batteries. Cathodes were prepared by mixing active material with graphene oxide (sheet, from Strem Chemicals, made by the Staudenmaier method) and polyvinylidene fluoride (PVDF) as a binder (ratio of 5:4:1 in weight). These materials were mixed with NMP (N-methyl-2-pyrrolidone) solvent, and the thus-obtained paste was coated on aluminum foil using a coater. NMP was then removed under vacuum at 80 °C for 12 h. Hermetically sealed two-electrode cells (CR2032) were used for electro-chemical experiments. The cathode was separated from the lithium anode by a polyethylene porous film (Celgard) wetted with an equimolar $LiCF_3SO_3$/G4 (tetraglyme) salt. The three layers were pressed between two current collectors, one in contact with the cathodic material and the other in contact with the lithium disk. All cells were assembled in an argon-filled glovebox. The cathode had a diameter of 12.7 mm and an active material loading of ~0.4 mg/cm^2. The capacity contributions of GO was around 25 mA h/g, as found from tests using a control under current conditions at 50 mA/g (Figure S9).

Density Functional Theory (DFT) calculation The DFT calculation was performed by using the B3PW91functional and the 6-31G (d) basis set as implemented in Gaussian 09 program package. Vibrational frequency calculations, from which the zero-point energies were derived, were performed for each optimized structure at the same level to identify the natures of all stationary points.

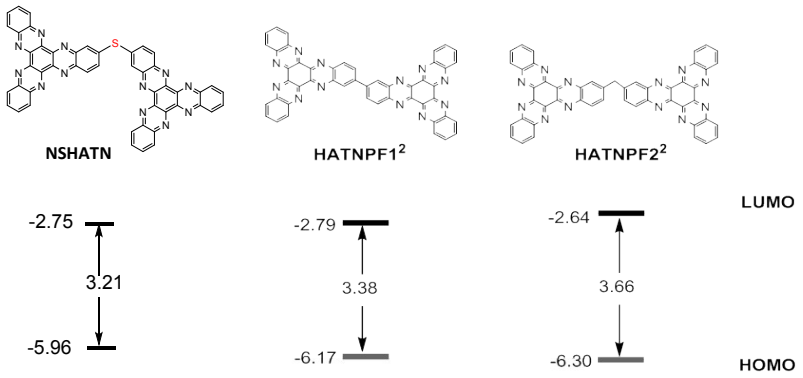


Fig. S1 The reduction potentials and the LUMO and HOMO energy levels and gaps of NSHATN, HATNPF1[21] and HATNPF1[21].

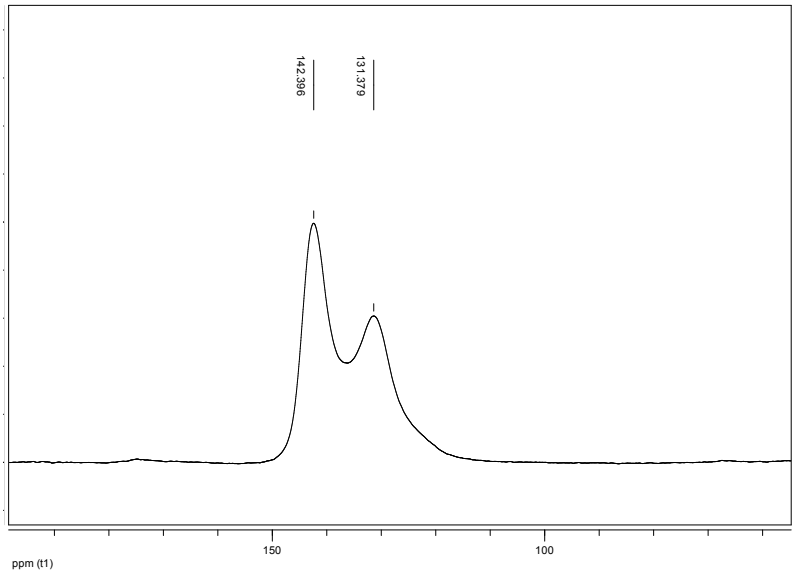


Fig. S2 Solid ^{13}C NMR spectrum of NSHATN.

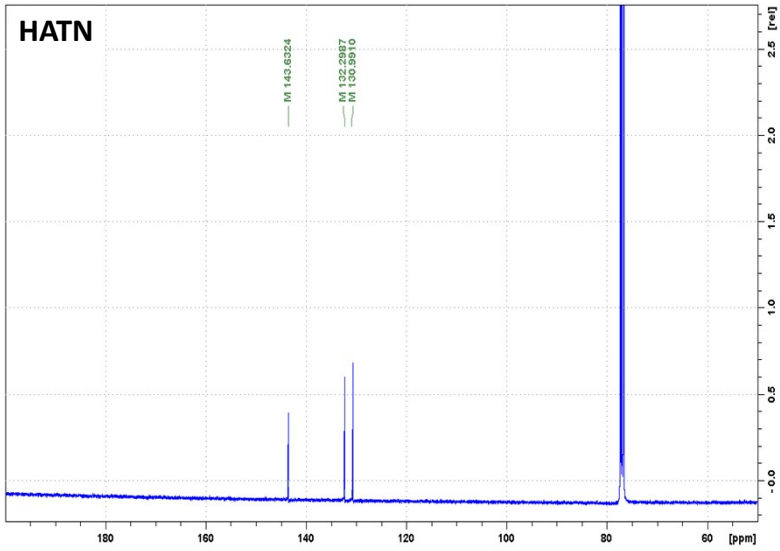


Fig. S3 ^{13}C NMR spectrum of HATN.

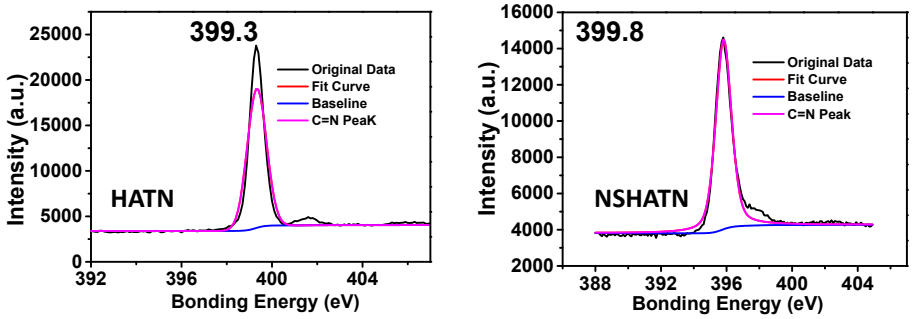


Fig. S4 XPS spectra (N 1s) of HATN and NSHATN.

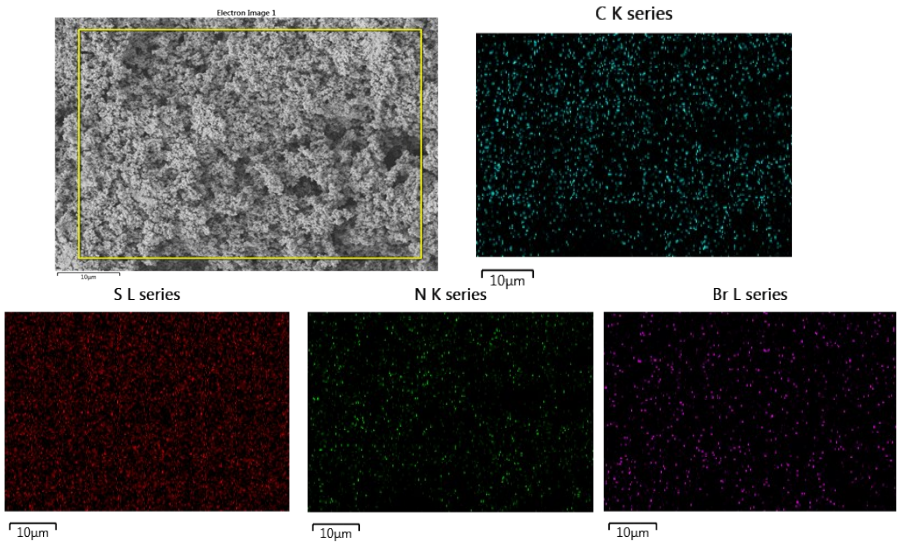


Fig. S5 SEM image and EDX mapping profile of C, S, N and Br elements of NSHATN.

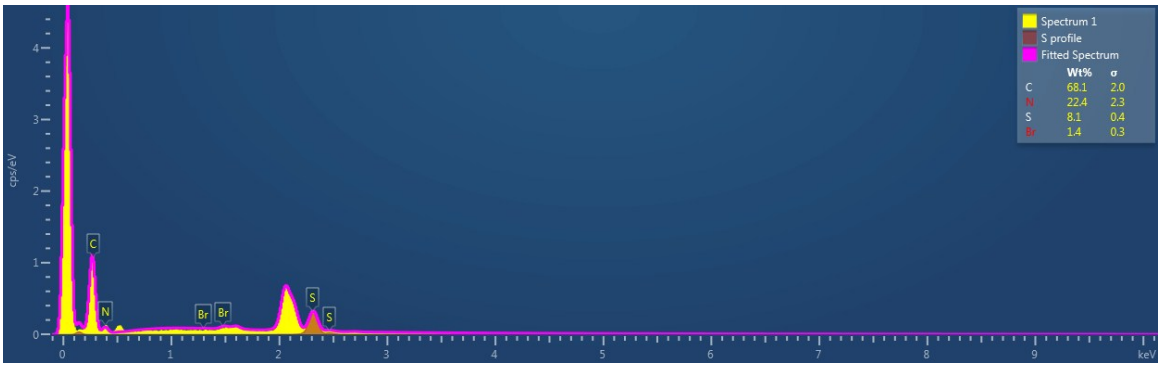


Fig. S6 SEM-EDX analyzer results of C, S, N and Br elements of NSHATN.

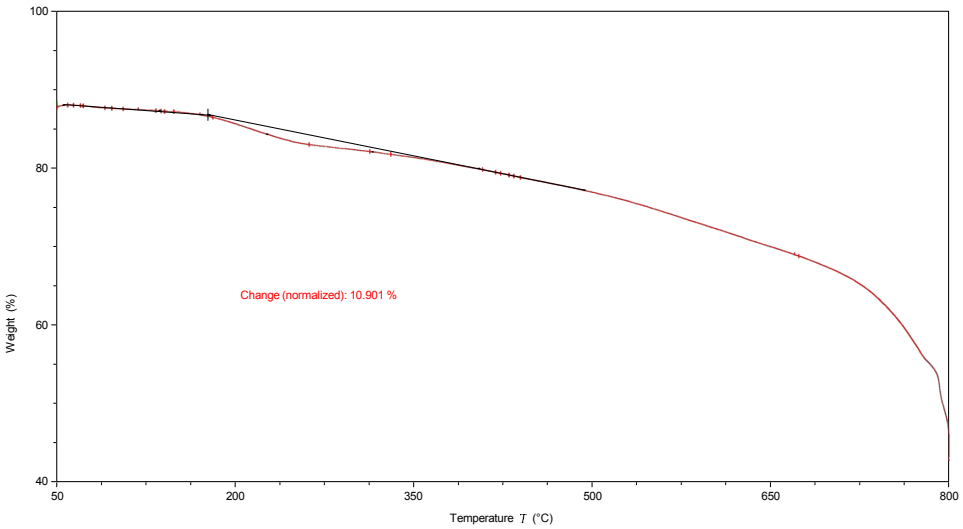


Fig. S7 Stability of NSHATN under N_2 gas by TGA

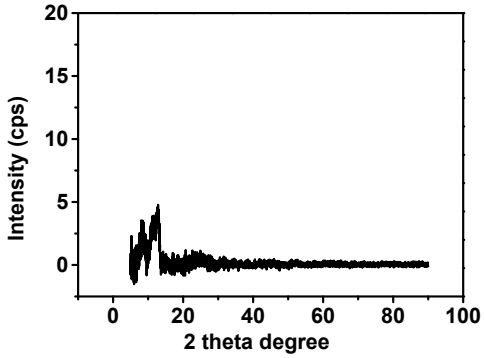


Fig. S8 XRD results of NSHATN.

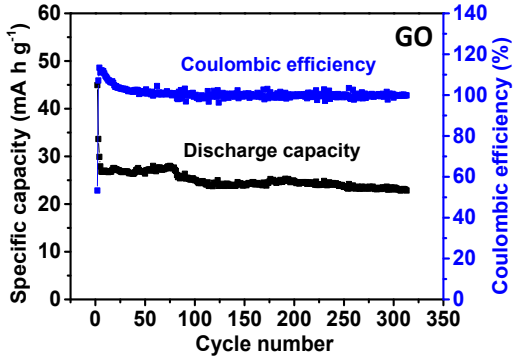


Fig. S9 The GO blank experiment (GO: PVDF = 5:1, current = 50 mA/g)

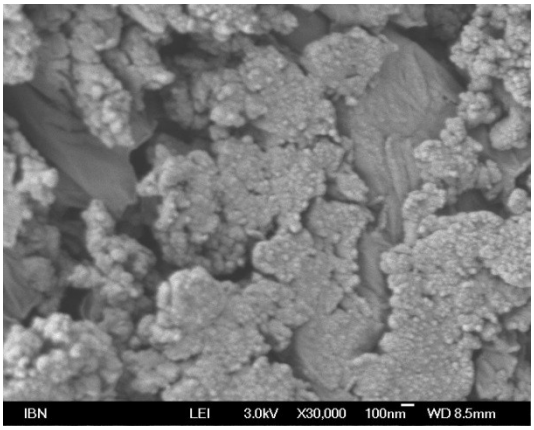


Fig. S10 SEM image of NSHATN and GO composite.

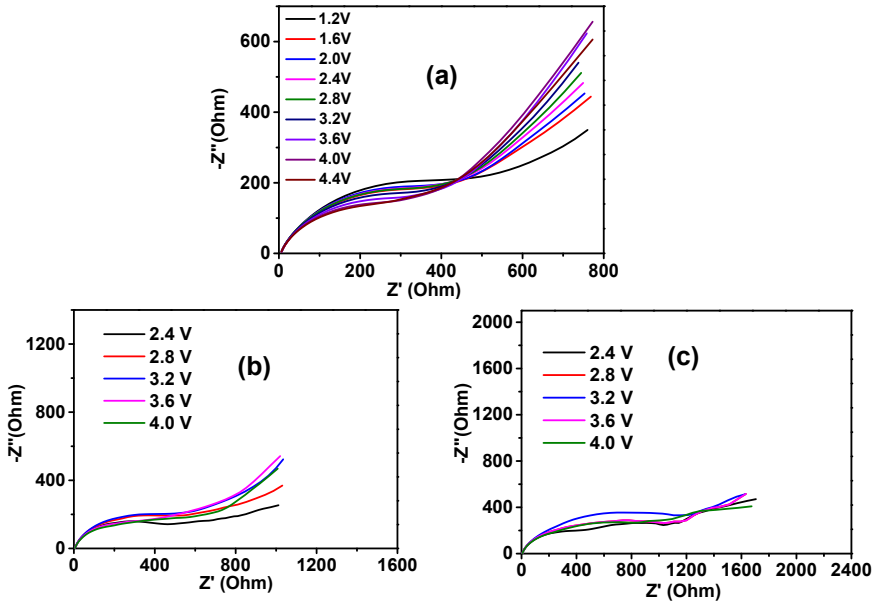


Fig. S11 the Nyquist plots,(a) NSHATN, (b) single bond-linked HATN porous materials, (c) methylene-linked HATN porous materials.

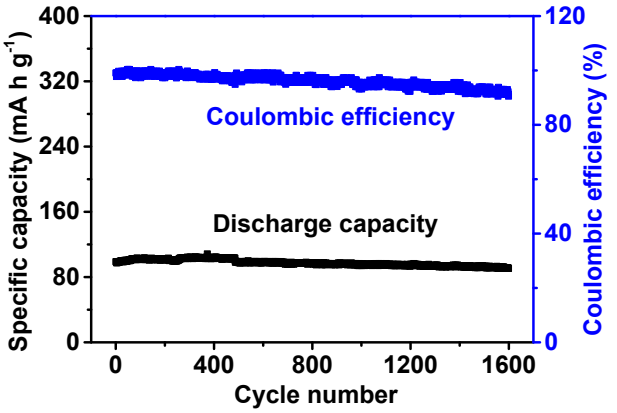


Fig. S12 Cycling performance at 8 A/g with NSHATN content of 50%.

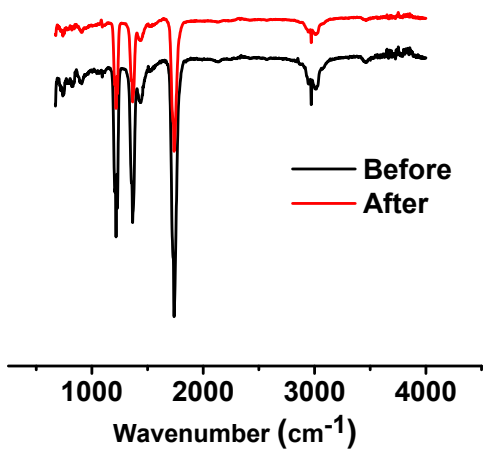


Fig. S13 The FT-IR spectra of the NSHATN materials before and after cycling.

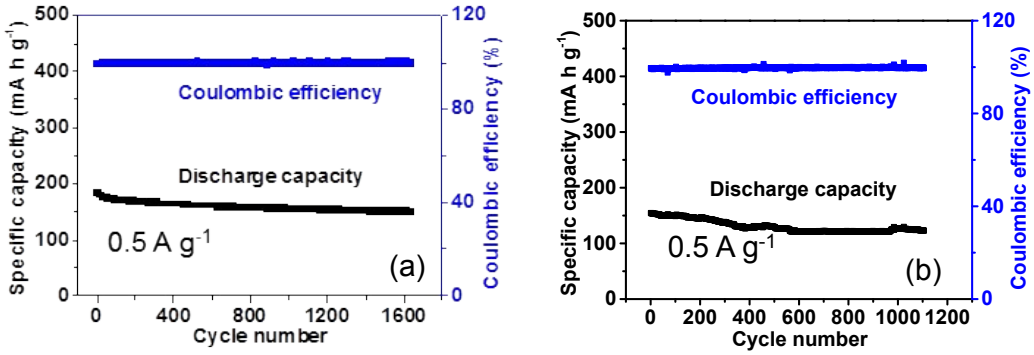


Fig. S14 Cycling performance of NSHATN/HATN at 0.5 A g-1: (a) NSHATN/GO; (b) HATN/GO.

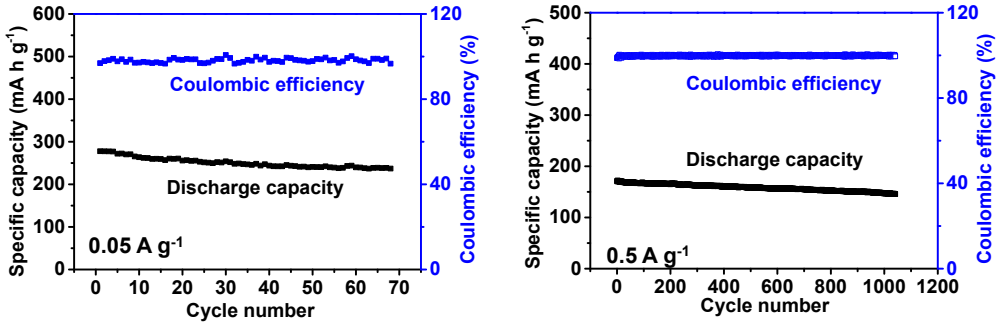


Fig. S15 Cycling performances at 0.05 A/g and 0.5 A/g with NSHATN content of 60%.

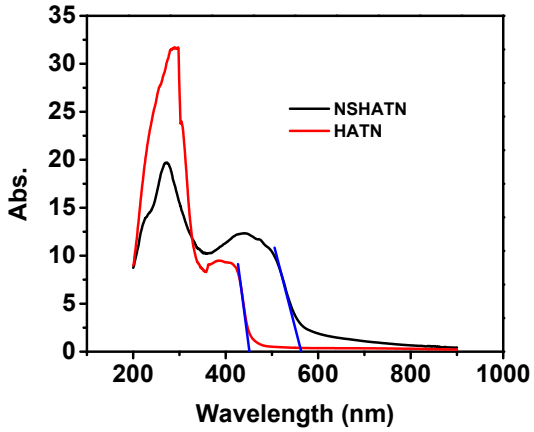


Figure S16 The UV-vis absorption spectra of the NSHATN and HATN.

Table S1 A comparison of HATN based electrodes.

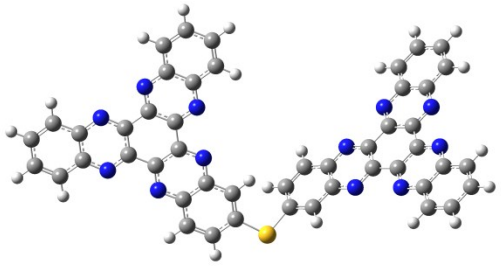
Materials	Ratio[a]	Electrolyte	Capacity (mAh/g) (cycles, ‰[b])	Ref
NSHATN	5:4:1	LiTFSI-DOL/DME	183-152 at 0.5 A/g (1500, 0.11) 122-106 at 4 A/g (1000, 0.13) 98-93 at 8 A/g (1500, 0.03)	This work
HATNPF1	4:5:1	LiTFSI-DOL/DME	180-105 at 0.5 A/g (1500, 0.28)	19
HATN/GO	5:4:1	$LiPF_6$/EC+DMC	152-122 at 0.5 A/g (1500, 0.13)	21
[c]HATN/RGO	3:6:1	LiTFSI-DOL/DME	318-263 at 0.8 A/g (1000, 0.17) 215-147 at 8 A/g (10000, 0.03)	18
Poly-HATN	6:3:2	$LiPF_6$/EC+DMC	147-95 at 0.1 A/g (50)	20
HATN	5:4:1	Solid electrolyte	250-190 at 0.2C and 323 K (30)	17

[a]Ratio = active material : conductive material : binder. [b] Capacity decrease rate. Voltage range: 1.5~4 V, [c]1.2~4.0V.

Computational Details

The calculations were carried out by performing DFT by use of the B3PW91functional with the 6-31G (d) basis set as implemented in Gaussian 09 program package. Vibrational frequency calculations, from which the zero-point energies were derived, have been performed for each optimized structure at the same level to identify the natures of all the stationary points.

Cartesian coordinates for the optimized geometry



NSHATN

C	-4.89298200	1.20823000	0.65189300
C	-6.22704900	1.72844900	0.78603900
C	-4.68314800	-0.17106900	0.16339000
C	-7.38850800	0.88166400	0.44211200
C	-7.18424500	-0.46386200	-0.02421300
C	-5.81377900	-0.99484300	-0.16776300
N	-8.60256500	1.39247800	0.57650600
N	-8.20191900	-1.25224700	-0.33529200
N	-6.45071800	2.96069800	1.21630300
N	-3.82987000	1.93695700	0.95514600
N	-3.44028500	-0.61269700	0.04129800
N	-5.66027200	-2.23662800	-0.60711200
C	-4.04359500	3.19683300	1.39760000
C	-2.93560900	4.01990000	1.73716200
C	-5.37390000	3.71679900	1.52874800
C	-3.14874000	5.30216700	2.18549000
H	-1.93969800	3.60197700	1.62917000
C	-5.56015100	5.04657600	1.99497200
C	-4.46789700	5.81818600	2.31476100
H	-2.30379600	5.93365500	2.44561600
H	-6.57678900	5.41599000	2.08526400
C	-9.65120600	0.59897100	0.26041400
C	-10.97505800	1.10046500	0.38668800
C	-9.44789100	-0.74395700	-0.20028400
C	-12.04415800	0.29633500	0.06852300
H	-11.10119100	2.12002100	0.73708100
C	-10.57419100	-1.54978200	-0.52018000
C	-11.84265600	-1.03592700	-0.38695600
H	-13.05722200	0.67703600	0.16439800
H	-10.39288700	-2.56255800	-0.86599200
C	-3.27067200	-1.87689900	-0.40938600
C	-4.39910600	-2.69855700	-0.73380400
C	-1.95560200	-2.39258700	-0.55087000
C	-4.17452100	-4.02311200	-1.20126200
C	-1.76909500	-3.67530900	-1.02271100
H	-1.12846600	-1.74738900	-0.27751800
C	-2.89526200	-4.49465400	-1.34813900
H	-5.03907000	-4.63190400	-1.44620200
H	-2.72501800	-5.49987500	-1.72363700
H	-4.60743200	6.83487700	2.67154800
H	-12.70533800	-1.64964000	-0.63102400

C	7.21276900	-0.02645300	0.64918000
C	6.22734300	-1.06125100	0.80939500
C	7.03462700	1.00854800	-0.39069700
C	5.03575000	-1.08841800	-0.06415900
C	4.86574800	-0.08511200	-1.08035500
C	5.87857100	0.97768200	-1.24575000
N	4.14508400	-2.05239500	0.11543400
N	3.81174700	-0.08311200	-1.88403400
N	6.35522300	-2.00609400	1.72815400
N	8.29164500	0.02790300	1.41505900
N	7.95900300	1.94925800	-0.50862400
N	5.68855900	1.88675400	-2.18978000
C	8.43530400	-0.93046700	2.35830600
C	9.57613400	-0.91703600	3.20592100
C	7.45272900	-1.96345700	2.51683400
C	9.72628700	-1.89041400	4.16546800
H	10.30470200	-0.12483300	3.06544900
C	7.63758500	-2.95527000	3.51804600
C	8.75208500	-2.91498100	4.32227500
H	10.59741600	-1.88269600	4.81465700
H	6.87932700	-3.72560200	3.61687200
C	3.06525900	-2.05884400	-0.69740900
C	2.07499700	-3.06548300	-0.53196800
C	2.89674900	-1.06095900	-1.71031100
C	0.97270000	-3.08701900	-1.35933700
H	2.21551700	-3.79805600	0.25564000
C	1.74505600	-1.10713800	-2.54514400
C	0.81283900	-2.10026100	-2.38136300
H	1.64097700	-0.34636600	-3.31223600
C	7.77722500	2.88517000	-1.46771300
C	6.62537100	2.85288100	-2.32187500
C	8.74030400	3.91709000	-1.63399500
C	6.46806900	3.85257000	-3.31998200
C	8.55945600	4.87024400	-2.60847600
H	9.60259800	3.91893300	-0.97477800
C	7.41754200	4.83779600	-3.45600400
H	5.58764300	3.80504100	-3.95300400
H	7.30004400	5.60356100	-4.21768900
H	9.29401500	5.66022900	-2.73789700
H	8.89620000	-3.67167300	5.08842800
H	-0.05849300	-2.14605400	-3.02646400
S	-0.17320700	-4.45383900	-1.22298500