Atomically dispersed metal sites anchored in the N-doped carbon nanosheets to

boost the Li storage performance

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Experimental Section

Material Synthesis

The atomically dispersed metal sites anchored on N-doping carbon nanosheets were prepared through the facile method. First, the 0.4 mmol metal salts $(Mn(CH_3COO)_2 \cdot 4H_2O, Ni(CH_3COO)_2 \cdot 4H_2O)$ or Fe(NO₃)₃·9H₂O), 2 mmol sucrose and 0.4 mol urea were solved deionized water followed by constant stirring to form homogeneous solution. The obtained solution was transferred to a beaker and treated with the vacuum freeze-drying. Then, mixture was annealed at 550 °C for 2 h, with a slow speed and then annealed at 800 °C for 2 h. All of the heat treatments were located in an argon atmosphere. The products after annealing was treated with the acid liquor to remove the metal-based clusters. The Mn, Ni and Fe-based composite were soaked in concentrated HCl for 12 h, and then they are washed with deionized water several times to remove the residual. Finally, the residuals were also removed via the water. Finally, the composites were treated with the vacuum freeze-drying again to remove the water. The obtained samples were signed as Mn-N-C, Ni-N-C, and Fe-N-C. The N-doping carbon nanosheet was also prepared as a comparison without the additive metal-salts.

Material Characterization

An X-ray diffraction (XRD) machine (Phillips X'pert ProMPD diffractometer with $Cu_{K\alpha}$, $\lambda = 1.54056$ Å) was used to investigate the structure of as-prepared samples. Raman spectra were collected using a microscopic confocal Raman spectrometer (LabRAMAramis, Horiba Jobin Yivon) with a laser wavelength of 532 nm. The surface analysis was carried out by X-ray photoelectron spectroscopy (XPS) using ESCALAB 250Xi spectrometer (Thermo Fisher). The morphologies were obtained by field emission scanning electron microscopy (FESEM, SU-8010, Hitachi) and transmission electron microscopy (TEM, an acceleration voltage of 200 kV, JEM-2010, JEOL). The Brunauer-Emmett-Teller surface area was measured by N₂ adsorption at 77 K on a surface area and the Barrett-Joyner-Halenda (BJH) method was used to simulate the pore size.

Li-ion Battery Assembly

The preparation of working electrode was similar to that of in Li-O_2 battery. The composition of the electrode was 70 % sample, 20 % acetylene black and 10 % PVDF. The mixture was pasted on copper foil (15 µm) and dried overnight at 110 °C overnight. The mass loading of the electrode

material was 1.5 mg. The Li-ion battery was fabricated with a working electrode and lithium foil counter electrode, separated by a Celgard membrane. The electrolyte was a solution of 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC)-dimethyl carbonate (DMC) (v/v = 1 : 1). All the processes of the battery fabrication were carried out in an Argon filled glove box (H₂O, O₂<0.5 ppm).

Electrochemical Measurements

The electrochemical impedance spectra were measured on an electrochemical workstation (IM6, German) by AC impedance over the frequency range from 10 mHz to 100 kHz with an amplitude of 5 mV. The cyclic voltammetry (CV) curve was collected on an electrochemical workstation (CHI660e). Galvanostatic discharge-charge data were collected on a NEWWARE multichannel battery testing system. Cycling performance was conducted in the voltage range between 0.01-3.0 V.

The Contribution of Capacitive Effects

The capacitive effects can be determined by the calculation 1 and 2. As for the capacitance and the diffusion contribution, the CV measurements were carried out in different scanning rate, 0.1, 0.2, 0.4, 0.8 and 1.0 mV s⁻¹. The contribution of the capacitance and the diffusion of the materials were determined: $i = av^b$, where *i* was the current, *v* was the scan rate, *a and b* were constant. The quantitatively distinguish the capacitive contribution from the total Li⁺ storage was based on the relationship between current response at a fixed voltage, i(V), capacitive contribution (k_1v), and diffusion contribution ($k_2v^{1/2}$), which was determined by $i(V) = k_1 v + k_2 v^{1/2}$.^{S1}

Computational Details

Based on the spin polarized density functional theory (DFT) and the projector augmented wave (PAW) method^{S2} as implemented in the Vienna Ab-initio Simulation Package (VASP), the density of states were calculated by the strongly constrained and appropriately normed (SCAN) functional^{S3, S4} within the meta-generalized-gradient approximation (meta-GGA).^{S5} A plane-wave basis set^{S6} was used with kinetic energy cutoff of 500 eV with a K-point grid of $2\times 2\times 2$ for Mn-N-C and N doped graphene, respectively, using the Gamma centered method. A vacuum layer of 10 Å was applied to decouple adjacent atomic slabs. The convergence criterion for force and energy were 0.01 eV Å ⁻¹ and 10⁻⁵ eV.

Sample	I(sp ²)	I(sp ³)	I(sp ²)/I(sp ³)
Mn-NC	12867	23334	0.62
Ni-NC	43561	65826	0.66
Fe-NC	24309	39328	0.62
NC	12576	27098	0.44

Table S1 details of the C 1s spectra for as-prepared samples

Table S2 The element content in different materials

Sample	Atom %		
	С	Ν	М
Mn-N-C	78.53	19.87	1.60
Ni-N-C 0.1327	81.40	16.50	2.10
Fe-N-C 0.043	84.61	14.80	0.59
NC	81.19	18.81	

Li storage materials	Current density (mA g ⁻¹)	Capacity (after x cycles) (mA g ⁻¹)	Reference
Mn-N-C	1000	644 (600 cycles)	This work
	2000	500 (400 cycles)	This work
	5000	400 (400 cycles)	This work
Ni-N-C	5000	400 (300 cycles)	This work
Fe-N-C	2000	720 (100 cycles)	This work
PG ^a	100	~450 (80 cycles)	<i>Adv. Mater.</i> 2013 ⁸⁷
atc. PNC-750 ^b	1000	~ 600 (400 cycles)	ACS Nano 2018 ^{S8}
g-C ₃ N ₄ fibre	5240	< 150 (100 cycles)	Adv. Funct. Mater. 2018 ⁸⁹
NCH ^c	1000	600 (500 cycles)	J. Mater. Chem. A 2018 ^{S10}
OHC ^d	1000	600 (100 cycles)	J. Mater. Chem. A 2015 ^{S11}
pHC ^e	400	< 300 (500 cycles)	Small 2020 ^{S12}
GeCH ₃ /RGO ^f	1000	~ 300 (500 cycles)	<i>Carbon</i> 2020 ^{S13}
CSC-np ^g	5000	469 (100 cycles)	J. Power Sources 2020 ^{S14}
HNCNBs ^h	1000	~ 500 (500 cycles)	Nanoscale 2019 ^{S15}
	5000	< 400 (100 cycles)	

Table S3 Comparison of the Li storage performance with carbon-based materials

^{*a*}Phosphorus-doped graphene, ^{*b*}N-doped hierarchical porous carbon with uniaxially packed carbon nanotubes, ^{*c*}Nitrogen-doped carbon honeycomb-like structures, ^{*d*}Ox horn derived carbon, ^{*e*}Chemically prelithiated hard-carbon, *f* Few-layer methyl-terminated germanene-graphene nanocomposite, ^{*g*}Candle soot carbon nanoparticles, ^{*h*}Hollow nitrogen doped carbon nano boxes



Fig. S1 (a) SEM, (b) TEM, and (c) HRTEM for NC.



Fig. S2 (a) SEM, (b) HRTEM, (c) STEM images and (d) elemental mapping for Ni-N-C.



Fig. S3 (a) STEM, (TEM) (c) HRTEM, (d) elemental mapping for Fe-N-C based on (a).



Fig. S4 (a) Survey spectra, (b) Mn 2p, (c) Mn 3s, (d) Ni 2p, (e) Fe 2p for as-prepared materials.



Fig. S5 EIS spectra for different electrode based on Mn-N-C, Ni-N-C, Fe-N-C, NC.



Fig. S6 The relation between real resistance and frequency of Mn-N-C and NC before cycle.



Fig. S7 TDOS of Ni-N-C and Fe-N-C.



Fig. S8 Discharge-charge profiles for Ni-N-C and NC in different cycles at (a) 2 A g⁻¹ and (b) 5 A g⁻¹. (c) Rate performance of Ni-N-C and (d) the average specific capacity at different current density.



Fig. S9 Discharge-charge profiles for Fe-N-C and NC in different cycles at 2 A g⁻¹.



Fig. S10 Optimized structure of (a) fresh Mn-N-C, (b) Mn-N-C after Li-adsorption and (c) continuous Li-desorption.



Fig. S11 Optimized structure of Li-adsorption with (a) weak and (b) strong M-N in Mn-N-C.

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