Supporting Information

Nitrogen-Doped Multi-Channel Carbon Nanofibers Incorporated with Nickel Nanoparticles as Multifunctional Modification of Separator for Ultra Stable Li-S Batteries

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Contents

Experimental

Chemicals

Nickel(II) acetylacetonate ($Ni(acac)_2$) was obtained from J&K; Poly(styene) (PS) was obtained from Acros; Polyacrylonitrile (PAN, Fw=230000) was obtained from Goodfellow Cambridge; Methyl-2-pyrrolidone (NMP, 99.9%) was from Aladdin; N,N-dimethylformamide (DMF) was obtained from Sinopharm Chemical Reagent Co. Ltd; Poly(vinylidene fluoride) (PVDF, 99.5%) and sulfur (99.5%) were obtained from Sigma-Aldrich; Lithium sulfide (Li_2S, 99.9%) was obtained from Alfa Aesar; 1,3-Dioxolane (DOL, 99.95%) and 1,2-dimethoxyethane (DME, 99.95%) were obtained from DoDo Chem.

Synthesis of nitrogen-doped multi-channel carbon nanofibers incorporated with nickel nanoparticles (Ni-NMCCF) and nitrogen-doped multi-channel carbon nanofibers (NMCCF)

Polyacrylonitrile (PAN) 0.6 g, Poly(styene) (PS) 0.6 g and nickel acetylacetonate ($Ni(acac)_2$) 0.2 g were dissolved in 10 mL N, N-dimethyformamide. Then the mixture solution was stirred at room temperature overnight to get fully dissolved. Electrospinning was conducted with the condition of 10 kV voltage between the aluminum foil and the injector, 15 cm between the receiving plate and the needle, injector pushing speed of 0.6 mm/min. Then, the polymer fiber film was taken into the vacuum drying oven and dried at 60 ℃ for all night to remove the redundant DMF. Finally, the fiber film was taken into the quartz boat and stabilized at 250 ℃ (heating rate: 2 ℃/min) for 1 h in the air, and then heated to 800 ℃ for 2h under Ar float (heating rate: 2 ℃/min). The production was named as “Ni-NMCCF”. For the comparison sample, NMCCF was synthesized under the same procedure without adding nickel acetylacetonate.

Synthesis of the Ni-NMCCF/PP and NMCCF/PP separators

The separator was prepared by traditional coating technology, Ni-NMCCF/PP was consisted by 90 wt.% Ni-NMCCF and 10 wt.% PVDF. After grinding for 30 min, the mixing was coated on PP (Celgard 2500) separator and vacuum dried at 60℃ for 12 h. In the end, the Ni-NMCCF/PP separators were cut into coin-shape by the infant with diameter of 19 mm and dried at 60℃ for 1 h. The NMCCF/PP separators were prepared under the same procedure.

Synthesis of the cathode

The cathode material was synthesized as follows: 3 g Iron (III) citrate tribasic hydrate were heated to 800 ℃ for 2h under Ar float (heating rate: 5 ℃/min). Then, the product was etched by hydrochloric acid (1 M) for 12 h and washed with deionized water by vacuum filtration. Finally, the product was transferred to the vacuum drying oven at 60 ℃ for 12 h to gain the carbon cathode S host.

The C/S cathode of Li-S battery was prepared by the traditional melt-diffusion method (the loading of S reached 65%). Specifically, the above product and sulfur were mixed by mortar for 30 min. Then transferred the mixture to the vacuum sealed container and heated at 155℃ for 12 h. The cathode materials were consisted by 70 wt.% S/C, 20 wt.% Super P and 10 wt.% PVDF. Beside these materials were coated on Al foil, which were dried at 60℃ for 12 h under vacuum. In the end, the electrodes were cut into coin-shape by the infant with diameter of 12 mm (S loading: 1.0 mg/cm^2) and dried at 60℃ for 1 h. Meanwhile, the electrolyte/S ratio is around 14 μL/mg.

Electrochemical Measurement

CR2016-Type Coin cells were assembled in the glove box under Ar-filled environment. As-prepared cathode, as-prepared Ni-N-MCCF separator and the metal lithium anode were

accompanied with electrolyte (dissolving 1.0 M bis(trifuloromethane) sulfonamide lithium salt (LiTFSI) and 1.0 wt.% of lithium nitrate ($LiNO_3$) in mixed solvent of dimethoxymethane and 1,3-dioxolane (DME/DOL, 1:1 volume ratio)). Constant current charge-discharge test was performed on LAND electrochemical equipment under the voltage range of 1.7 V-2.8 V. Cyclic voltammetry (CV) was tested with the scan rate of 0.1, 0.2, 0.5, 1.0 mV s^{-1}. Electrochemical impedance spectra (EIS) tests were performed with amplitude of 5 mV from 0.01 to 100000 Hz.

Materials Characterization

The morphologies of the materials were measured by scanning electron microscopy (SEM) (Hitachi S-4800) and high-resolution TEM (HRTEM, Philips Tecnai G2). X-ray photoelectron spectroscopy (XPS) was tested by Kratos AXIS Ultra spectrometer with a source gun of Al Kα. The composition of the material was characterized by X-ray diffraction (XRD, ULTRA-55 D5000, Cu Kα).

Figure Captions in Supporting Information

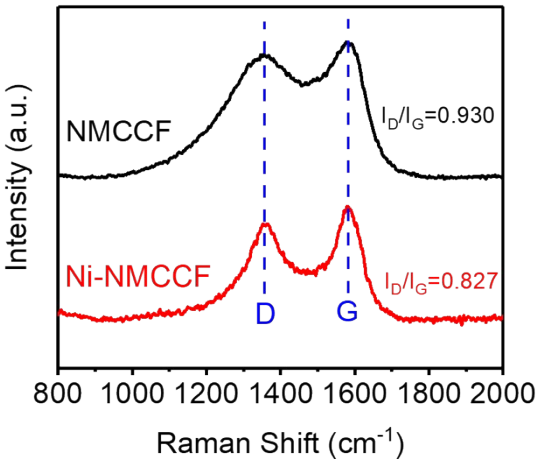

Figure S1. Raman spectra of Ni-NMCCF and NMCCF.

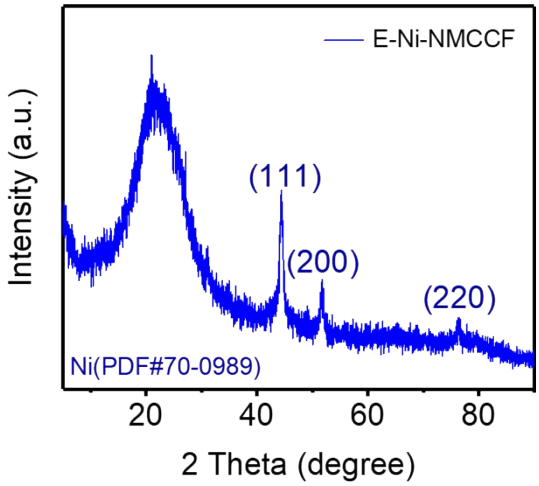

Figure S2. XRD pattern of E-Ni-NMCCF.

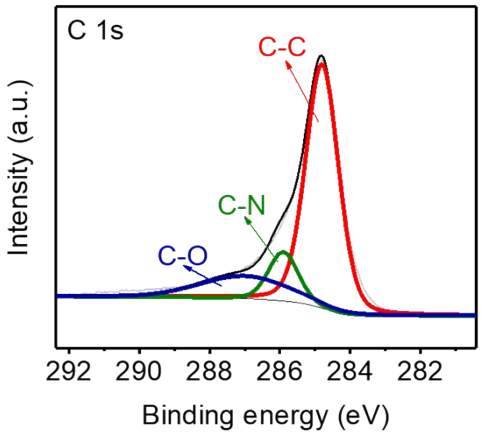

Figure S3. C 1s patterns of Ni-NMCCF.

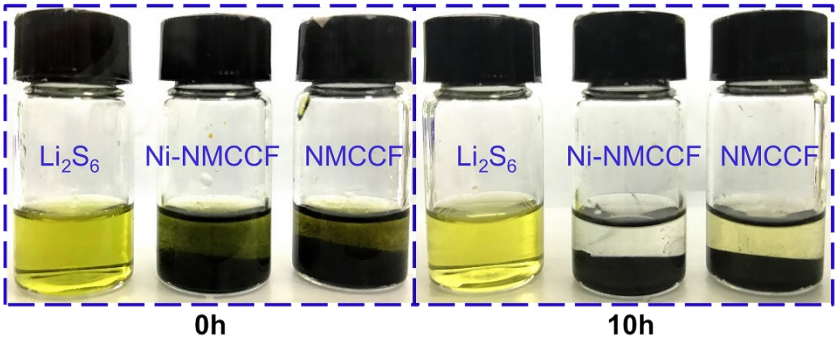

Figure S4. Li_2S_6 adsorption experiments of Ni-NMCCF and NMCCF.

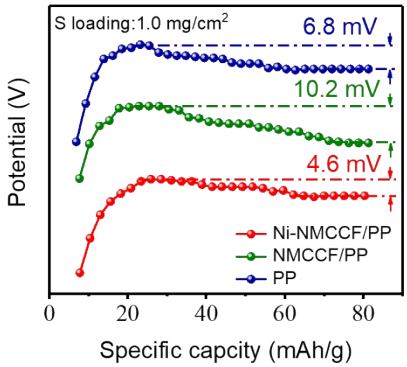

Figure S5. Charge profiles of Li-S batteries based on the PP, NMCCF/PP and Ni-NMCCF/PP separators showing the overpotentials for conversion from insoluble Li_2S_2/Li_2S to soluble LiPS at the current density of 0.2 C.

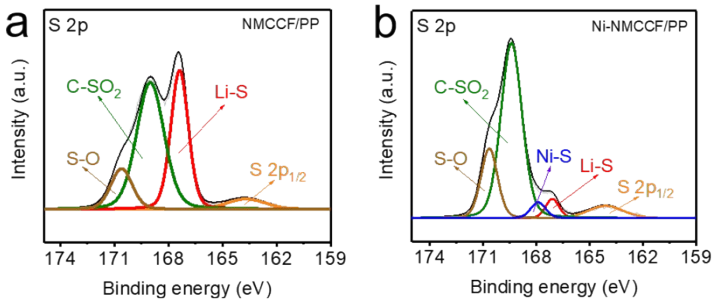

Figure S6. a, b) S 2p patterns of Ni-NMCCF/PP and NMCCF/PP at 0.2 C after 100 cycles.

Table S1. The composition of S atom of Ni-NMCCF and NMCCF (%).

	S-O	C-SO_2	Ni-S	Li-S	S
N-MCCF	**12.15**	**48.5**	**0**	**33.9**	**5.45**
Ni-N-MCCF	**20**	**63.9**	**4.12**	**4.53**	**7.45**