

Article

Ni-NiS Heterojunction Composite-Coated Separator for High-Performance Lithium Sulfur Battery

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Abstract: The shuttle effect and slow REDOX kinetics of lithium polysulfides (LiPSs) lead to low sulfur utilization rate, short cycle life, poor rate performance, which hinder the application of Li-S batteries. Herein, the Ni-NiS/NCF heterojunction composite was prepared with multistage pore structure and a large specific surface area, which can effectively capture LiPSs, provide more active sites for catalyzing LiPSs. Moreover, due to the heterojunction structure of Ni-NiS, in which NiS can effectively capture and catalyze lithium polysulfide, and Ni can effectively accelerate the diffusion and charge transfer of lithium ions, the Ni-NiS/NCF heterojunction composite establishes a high ion and electron conduction network, so as to achieve efficient mass and charge transfer capacity. The mutual coordination of uniformly distributed Ni-NiS heterojunctions inhibits the shuttle effect of LiPSs. When the sulfur load is 1.8 mg/cm², the initial capacity of the cell with Ni-NiS/NCF-coated separator at 1 C is 1109.6 mAh/g, and the final discharge capacity is maintained at 618.0 mAh/g after 300 cycles. At the same time, the reversible specific capacity was maintained at 674.0 mAh/g after 50 cycles even under high sulfur load.

Keywords: shuttle effect; Li-S battery; Ni-NiS; heterojunction; lithium polysulfides



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1. Introduction

With the continuous consumption of fossil energy and other non-renewable energy, problems such as environmental pollution and energy crisis are becoming more and more prominent. Lithium-sulfur batteries have attracted great attention in the next generation of electrochemical energy storage systems due to their high theoretical specific capacity (1675 mAh/g) and high theoretical energy density (2600 Wh/kg), low cost, and environmental friendliness [1–3]. However, the shuttle effect and slow REDOX kinetics of lithium polysulfides (LiPSs) lead to low sulfur utilization rate, short cycle life, poor rate performance, which hinder the application of Li-sulfur batteries [4–8]. It is found that transition metals and metal compounds can effectively promote the conversion of soluble long-chain polythionine sulfide to short-chain lithium sulfide, improve their reaction kinetics, and effectively inhibit the shuttle effect, so as to achieve good long-cycle performance and rate performance more effectively [9–17].

In recent years, many metal compounds, such as metal nitrides, sulfide, oxide, phosphide, etc., have been used in the efficient catalysis of lithium polysulfide because of their good catalytic performance. However, many materials with heterostructures have also been used to catalyze lithium polysulfide in consideration of its advantage in mass transfer, electrical conductivity, and adsorption effects. For example, MoS₂/MoO₃, Ni@Ni₃N, Ti_xO_y-Ti₃C₂ene, NiS₂-ZnS, etc. Compared with single metal compounds, these heterostructures show more efficient catalytic effect on polysulfide lithium [18–21].

On the other hand, due to the high dispersion of metal nodes and rich diversity in metal organic frameworks (MOFs), derivatives with MOFs as the precursor have the

advantages of flexible and adjustable metal element types, large specific surface area, and highly dispersed catalytic centers, which make them have great application potential in catalysis and energy storage fields [22–24].

Based on the discussion above, herein we prepared Ni-HDCOF/CNT composites by solvothermal method, and further prepared Ni-NiS/NCF heterojunction composites by vulcanization, which was used as the separator coating in Li-S battery. On the one hand, Ni-NiS/NCF composites have large specific surface area and multi-pore structure, which provide more active sites for the adsorption and catalysis of LiPSs. On the other hand, the strong catalysis of NiS on lithium polysulfide and the charge migration ability of Ni are combined to form Ni-NiS heterojunction to promote the conversion ability of LiPSs, inhibiting the shuttle effect of lithium polysulfide, so as to improve the sulfur utilization rate and the cycle life of Li-S battery. As a result, when the sulfur load is 1.8 mg/cm², the Li-S cell with Ni-NiS/NCF-coated separator has the initial capacity of 1109.6 mAh/g at 1 C, and maintained the final discharge capacity of 618.0 mAh/g after 300 cycles. Moreover, the reversible specific capacity was maintained at 674.0 mAh/g after 50 cycles even under high sulfur load. Compared with the reported literature, our work shows the synergetic catalytic effect of nickel based heterojunction in lithium polysulfide, which provides a research idea for the subsequent research and development of separator coatings that can effectively inhibit the shuttle effect.

2. Materials and Methods

2.1. Synthesis of Ni-HDCOF/CNT

A total of 20 mg of activated carbon nanotubes (HWRK CHEM, Beijing, China) were dispersed in 2 mL methanol for ultrasonic use, 100 mg HATP-6HCl (2, 3, 6, 7, 10, 11-hexamino-triphenylhexaplenate, HWRK CHEM, Beijing, China) and 2 mL triethylamine (HWRK CHEM, Beijing, China) were added to the above solution and heated at 80 °C, then stirred in argon for 20 min for use. About 290 mg of DFP (2-hydroxybenzaldehyde, HWRK CHEM, Beijing, China) was sonicated and dispersed in 4 mL methanol for later use. The above two solutions were mixed and sonicated evenly, and the reaction time was 24 h at 75 °C in an oven. After the reaction was stopped, it was cooled, filtered, and washed once with DMF and twice with methanol. After drying in an oven at 60 °C, the reddish-brown powder HDCOF/CNT was obtained. About 0.1 g HDCOF/CNT and 0.5 g nickel acetate were sonically dispersed in 25 mL methanol, stirred for 72 h, filtered and washed three times with methanol, and dried in an oven at 60 °C to obtain dark brown powder Ni-COF/CNT.

2.2. Synthesis of Ni-NiS/CNT, Ni/NCF, and NiS/NCF

The porcelain boat with 0.02 g sulfur powder was placed upstream of the tube furnace, and the porcelain boat with 0.2 g Ni-COF/CNT was placed downstream of the tube furnace and calcined under argon atmosphere at 700 °C for 3 h. The calcined product was named Ni-NiS/NCF. Under the same conditions, Ni/NCF and NiS/NCF were obtained when no sulfur powder was added or excess sulfur powder was added.

2.3. Preparation of Ni-NiS/CNT, Ni/NCF, and Ni/NCF-Coated Separators

Ni-NiS/CNT, Ni/NCF, or Ni/NCF, super-P and LA132 adhesives were dispersed and prepared into slurry with n-propanol solution in the ratio of 6:2:2. The slurry was then coated on a Celgard-2400 separator and dried in a vacuum drying oven at 60 °C for 24 h. It was cut into a wafer size with a diameter of 19 mm using a microtome to obtain Ni-NiS/CNT-, Ni/NCF-, and Ni/NCF-coated separators.

2.4. Preparation of S Cathode

The MWNTs were heated in a vacuum drying oven at 100 °C for 12 h. CNT/S complex was prepared by reaction of S and MWNTs in a 155 °C reactor with a mass ratio of 1:3 for 12 h. CNT/S complex, super-P, and LA132 binder were prepared by a mass ratio of 8:1:

The proportion of was prepared by dispersing n-propanol solution into slurry, which was coated on aluminum foil and dried in a vacuum drying oven at 55 °C for 12 h. It was cut into 12 mm diameter electrode discs with a microtome, and the electrodes with a sulfur load of 1.8 mg/cm² and 5 mg/cm² were prepared with scrapers of different thickness.

2.5. Characterization

Powder X-ray diffraction patterns (Bruker D8 Advance, Cu K α radiation) were used at 40 kV. Scanning electron microscopy (SEM, TESCAN, Brno, Czech Republic) image and energy-dispersive X-ray spectrometry (EDX, Carl Zeiss AG, Oberkochen, Germany) elemental mapping analysis were recorded on Tescan Maia3. Bel sorp Max surface area size analyzer (MicrotracBEL, Leverkusen, Germany) was used to measure the pore size and surface area at 77 K.

2.6. Electrochemical Measurements

The Li-S cells with different separator are assembled in CR2032 in the glove box with the atmosphere of Ar. The diameter of coated separator is 19 mm, and the coating material faces the sulfur cathode. The electrolyte is the conventional electrolyte of lithium sulfur battery (1 M LiTFSI, the solvent is the mixed solvent of DOL and DME with 1:1 volume ratio, adding 1% LiNO₃).

Li₂S deposition: discharge the Li-S cell to a voltage of 2.06 V at a constant current of 0.15 mA, and keep at a constant potential of 2.05 V until the current drops below 10^{−5} A for deposition and growth of Li₂S on various substrate surfaces.

The electrochemical impedance test was measured with CHI660C electrochemical workstation, frequency range: 0.01–100,000 Hz.

3. Results

As shown in Figure 1, HDCOF/CNT composites were prepared by HATP·6HCl, DFP and CNT ligands, and Ni-HDCOF/CNT composites were prepared by mixing HD-COF/CNT composites with nickel acetate. The XRD results showed (Figure 2a) that HDCOF/CNT had clear HDCOF and CNT components. The diffraction peaks of 3.77°, 7.90°, 11.36°, and 25.82° are attributed to the (100), (200), (300), and (001) crystal planes of HDCOF, respectively. The SEM images of HDCOF/CNT are displayed in Figure 2b,c. It is shown that HDCOF grow uniformly on CNTs. Ni-HDCOF /CNT was prepared by reacting the HDCOF/CNT with nickel acetate. According to Figure 2a, Ni-HDCOF/CNT has better crystallinity. As shown in Figure 2d, 1606 cm^{−1} is an obvious C=N stretching vibration band. When Ni²⁺ is coordinated with HDCOF, the C=N stretching vibration band is significantly weakened, and the stretching vibration band of C-O is from 1250 cm^{−1} to 1224 cm^{−1}, which indicates the coordination of Ni²⁺ with imine and hydroxyl group. The SEM results showed that the morphology of Ni-HDCOF/CNT did not change significantly after metal coordination (Figure 2e,f).

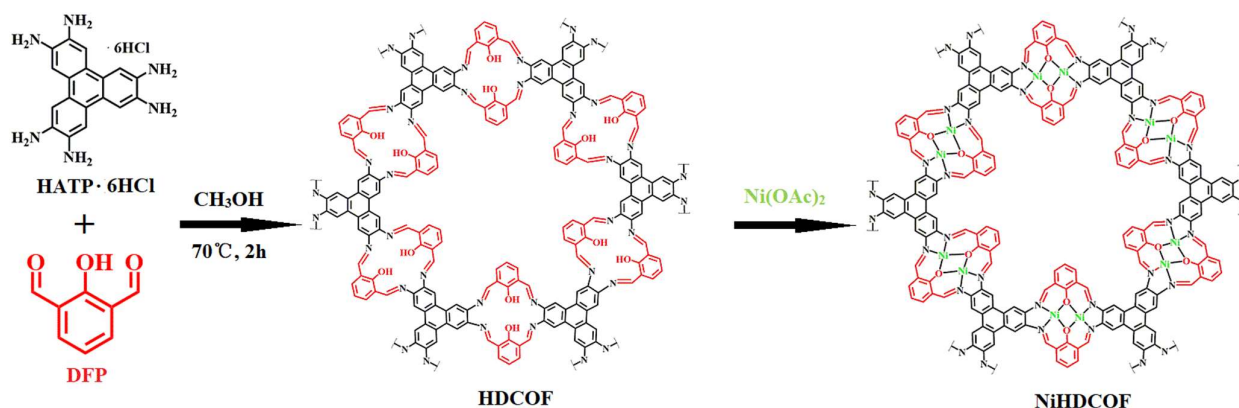


Figure 1. Scheme of the synthesis process of NiHDCOF.

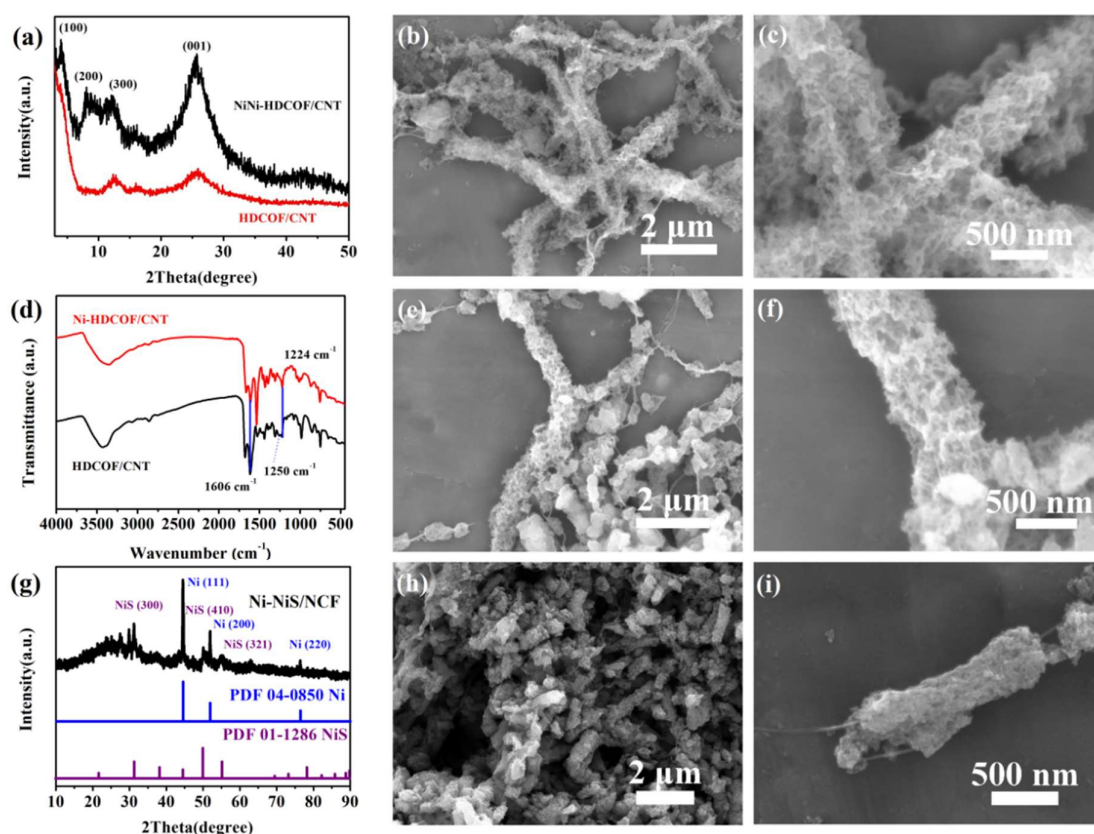


Figure 2. (a) XRD pattern of HDCOF and Ni-HDCOF/CNT. (b,c) SEM images of HDCOF/CNT. (d) IR spectrum of Ni-HDCOF/CNT. (e,f) SEM images of Ni-HDCOF/CNT. (g) XRD pattern of Ni-NiS/CNF. (h,i) SEM images of Ni-NiS/CNF.

Then, the prepared Ni-HDCOF/CNT composites were carbonized at 700 °C under sulfur atmosphere to obtain Ni-NiS/NCF composites. As shown in Figure 2g, the diffraction peak at 26.5° is attributed to the (002) crystal plane of graphitic carbon. The three diffraction peaks at 44.50°, 51.84°, and 76.37° can be attributed to the (111), (200), and (220) crystal planes of Ni, while the three diffraction peaks at 31.36°, 50.07°, and 55.29° are attributed to the (300), (410), and (321) crystal planes of NiS. XRD results showed that metal and metal sulfide complexes were formed after vulcanization in Ni-NiS/NCF. It can be observed from SEM images that Ni-NiS-doped porous carbon materials uniformly grow on carbon nanotubes, which are further connected to each other to form a three-dimensional network structure (Figure 2h,i).

The TEM images in Figure S1a (Supplementary Materials) further show that Ni-NiS particles are doped in porous carbon in series with CNT. High resolution transmission electron microscopy (HRTEM) images (Figure S1b) display the lattice plane of graphitic carbon (002). As shown in Figure S1c, the spacing of NiS plane lattice is 0.52 nm, and that of Ni plane lattice is 0.176 nm. The EDS mapping in Figure S1d shows that elements C, Ni, S, and N are uniformly distributed in Ni-NiS/NCF composites, which further confirms the doping of Ni-NiS heterojunctions in derived carbon materials.

The nitrogen adsorption and desorption curves and porosity of Ni-NiS/NCF at 77 K are shown in Figure 3a. The specific surface area of Ni-NiS/NCF is 230.36 m²/g, and the pore size is mainly mesoporous and distributed at 9.13, 23.72, and 21.36 nm. The large specific surface area and porous structure of Ni-NiS/NCF can effectively adsorb LiPSs and provide more electrochemical active sites, which is beneficial to improve the electrochemical performance. The XPS results of Ni-NiS/NCF are shown in Figure 3b. The presence of C, Ni, S, and N elements can be observed from the full spectrum. The N 1s pattern can be divided into three peaks, which are pyridine (398.4 eV), pyrrole (399.8 eV), and graphite-

N (401.1 eV). In the Ni-NiS/NCF complex, graphite N can improve the conductivity by increasing electron transport in the carbon plane, while the redox-active pyridine-N and pyrrole-N can act as active sites to trap LiPSs. The C 1S map shown in Figure 3c shows a peak at 284.6 eV, indicating the existence of sp^2 hybrid carbon atom C=C in Ni-NiS/NCF. In addition, there are two peaks at 286.1 eV and 287.7 eV, corresponding to C-C and C-O bonds, respectively. In the Ni 2P map (Figure 3d), the two main peaks were around 856.47 and 873.60 eV, respectively, and the two salt peaks were around 861.48 eV and 879.60 eV, respectively, which confirmed the existence of Ni^{2+} in Ni-NiS/NCF composite. In addition, the peaks at 856.4 and 873.6 eV indicate the presence of metal Ni (Figure 4e). The S 2P pattern has two peaks at 161.8 eV and 163.0 eV, the characteristic peaks of $S 2p^{3/2}$ and $S 2p^{1/2}$ states in NiS (Figure 4f).

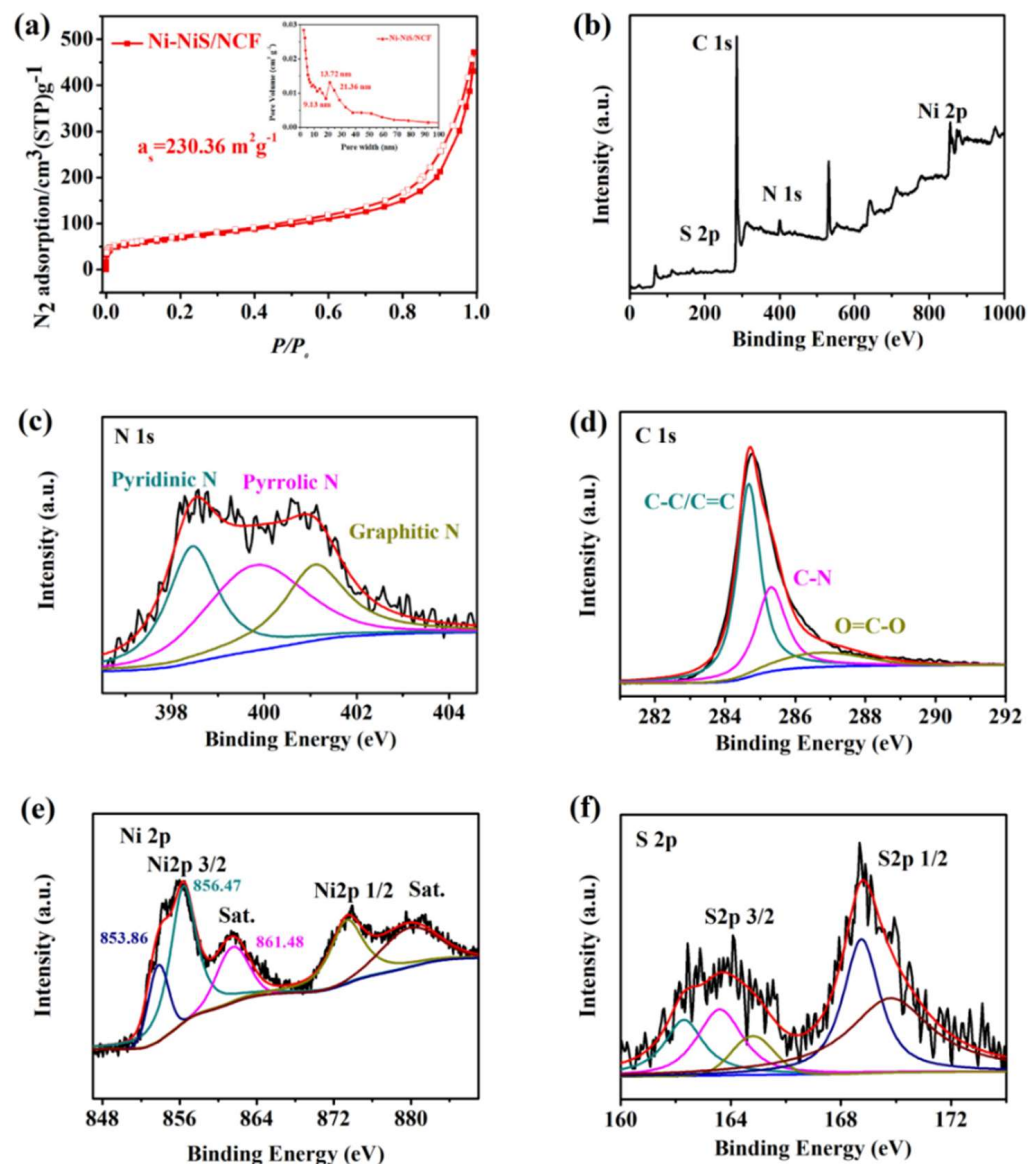


Figure 3. (a) Nitrogen adsorption and desorption isotherms of Ni-NiS/NCF; (b) total spectra of Ni-NiS/NCF; High resolution (c) N 1s XPS spectrum; (d) C 1s XPS spectrum; (e) Ni 2p XPS spectrum; (f) S 2p XPS spectrum.

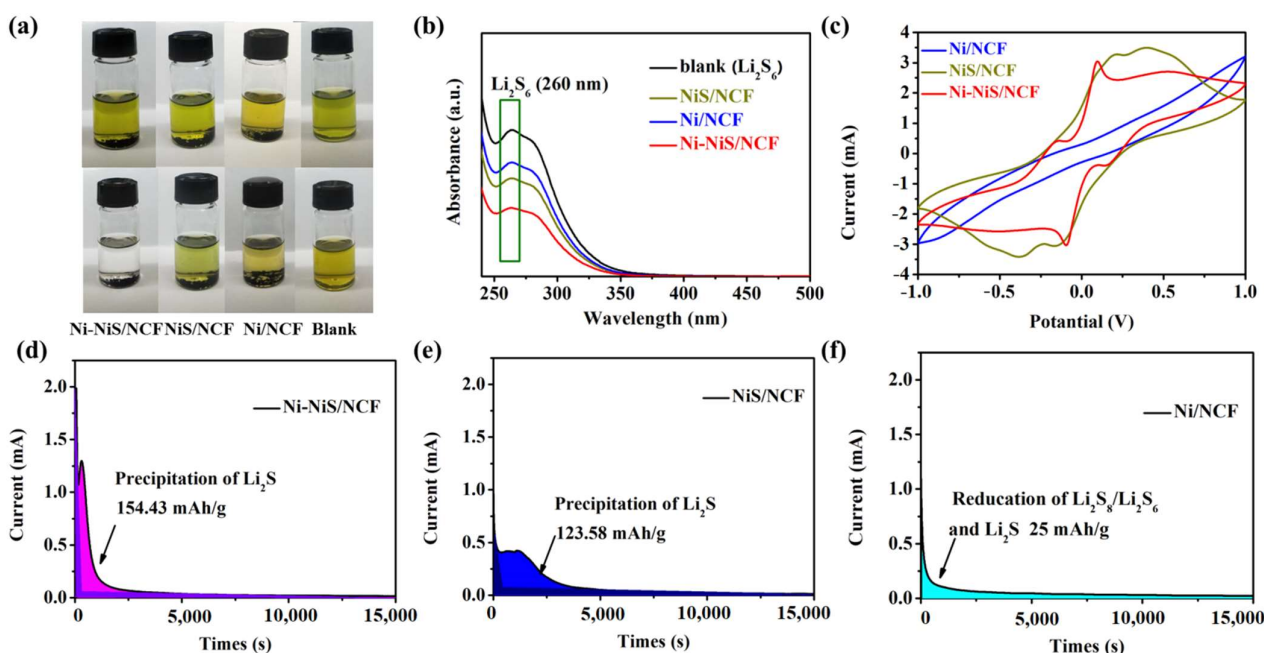


Figure 4. (a) Visual adsorption of Li_2S_6 with different materials; (b) UV absorption profile after adsorption of Li_2S_6 ; (c) the CV curves of symmetric cells with Ni-NiS /NCF, NiS/NCF, and Ni/NCF using Li_2S_6 as electrolyte. Time–current–time curve of 2.05 V constant voltage discharge on Ni/NCF. (d) Ni-NiS /NCF; (e) NiS/NCF; (f) Ni/NCF.

In conclusion, the large specific surface area and porous structure of Ni-NiS/NCF, rich nitrogen doping sites, Ni and NiS heterojunctions can effectively adsorb lithium polysulfides and provide more electrochemical active sites, so as to efficiently catalyze lithium polysulfide. In order to verify the adsorption effect of Ni-NiS/NCF on lithium polysulfide, we tested and compared the adsorption properties of Ni/NCF, NiS/NCF, and Ni-NiS/NCF for Li_2S_6 . As shown in Figure 4a, Ni-NiS/NCF can adsorb LiPSs more effectively than NiS/NCF and Ni/NCF. The UV test results showed that NiS played a more important role than Ni in the adsorption of Li_2S_6 (Figure 4b). In order to further explore the effect of Li_2S_6 and Ni-NiS/NCF composites, XPS analysis was performed on Ni-NiS/NCF after adsorption (Figure S2). After the adsorption of lithium polysulfide, the peaks of Ni 2p in Ni-NiS/NCF move to a higher binding energy, indicating that Ni^{2+} in Ni-NiS/NCF has a strong interaction with Li_2S_6 .

In order to prove the catalytic ability of Ni-NiS/NCF to LiPSs, Ni-NiS/NCF, NiS/NCF, and Ni/NCF were coated on aluminum foil as working electrodes, and series-symmetric cells were assembled with Li_2S_6 as electrolyte. The catalytic intensity of the material to LiPSs can be judged by the strength of the REDOX peak produced in the process of lithium polysulfide oxidation. As shown in Figure 4c, the REDOX peak of the symmetric cell of Ni/NCF is small, indicating that the catalytic effect of Ni on LiPSs is small. However, the REDOX peak of the symmetric cell of NiS/NCF is higher, with obvious reversible peak, indicating that the catalysis of NiS is stronger than that of simple Ni. In the symmetric cell of NiS/NCF, the oxidation peaks at 0.2 V and 0.4 V represent the oxidation behavior of Li_2S to Li_2S_4 and Li_2S_4 to S_8 , respectively. The reduction peaks at -0.14 V and -0.38 V represent the reduction behavior of S_8 to Li_2S_4 and Li_2S_4 to Li_2S , respectively. For the cell with Ni-NiS/NCF, the oxidation peaks are present at -0.17 V and 0.1 V, while the reduction peaks are present at 0.17 V and -0.1 V, which proves that Ni-NiS/NCF can catalyze the conversion of Li_2S_6 more effectively.

When the CV scanning rate was increased from 2.5 mV/s to 20 mV/s, Ni-NiS/NCF still showed excellent catalytic performance for Li_2S_6 (Figure S3).

To further reveal the catalytic effect of Ni-NiS heterojunction structure on LiPSs, Li_2S deposition experiments were carried out with different catalytic materials. The results

showed that Ni-NiS/NCF (154.43 mAh/g) (Figure 4d) had the highest deposition capacity for Li_2S compared with NiS/NCF (123.58 mAh/g) and Ni/NCF (25.0 mAh/g) (Figure 4e,f). Moreover, the LiPSs are the most converted by Ni-NiS/NCF. In addition, the nucleation reaction of Li_2S on Ni-NiS/NCF has an earlier peak time point and a higher response current, which indicates that the Ni-NiS heterojunction structure has a good electrocatalytic activity for LiPSs, and effectively accelerates the REDOX kinetic transformation between LiPSs and Li_2S in the electrochemical process.

To test the performance of lithium–sulfur batteries assembled with coated separator modified by Ni-NiS/NCF heterojunction composites, different coated separators were prepared by coating Ni-NiS/NCF, NiS/NCF, or Ni/NCF on Celgard-2400. Then the electrochemical properties of different Li–S cells with separators coated by Ni-NiS/NCF, NiS/NCF, or Ni/NCF were tested. As shown in Figure 5, the CV curves show that the Li–S cells assembled with different coated separators have two cathodic peaks (I_B and I_C) and one anode peak (I_A). Among them, I_B and I_C correspond to the conversion of S_8 to soluble long-chain LiPSs (Li_2S_8 , Li_2S_6 , and Li_2S_4) and then to insoluble short-chain lithium polysulfides (Li_2S and Li_2S_2), respectively. The oxidation peak at I_A corresponds to the progression from insoluble short-chain lithium polysulfides (Li_2S and Li_2S_2) to soluble long-chain LiPSs and finally to S_8 . For the cell with Ni-NiS/NCF-coated separator, the peak current was higher and the potential was lower than that of the cell with NiS/NCF or Ni/NCF coatings (Figure 5a–c), which prove that Ni-NiS/NCF could effectively enhance the kinetics of sulfur transformation. In order to quantitatively analyze the differences in electrochemical kinetics between different separator coatings, the Tafel diagrams of the initial potentials of reduction and oxidation processes are shown in Figure 5d–f, respectively. The Tafel slope of the cell with Ni-NiS/NCF coating separator during reduction and oxidation is the lowest, indicating that the order of lithium ion diffusion coefficient is Ni-NiS/NCF > Ni/NCF > NiS/NCF. Moreover, as shown in Figure S4, the electrochemical impedance test shows that the resistance of the cells assembled with different coated separator are Ni/NCF < Ni-NiS/NCF < NiS/NCF, indicating that the doping of metal Ni is beneficial to improve the charge transfer ability. Through the summary of the above experiments, in the Ni-NiS/NCF heterojunction, NiS can effectively capture and catalyze lithium polysulfide, while metal Ni can effectively accelerate the diffusion and charge transfer of lithium ions, thus the mutual coordination of uniformly distributed Ni-NiS heterojunction in Ni-NiS/NCF can inhibit the shuttle effect of LiPSs.

As shown in Figure 6a, when the current density is 0.5 C and the sulfur load is 1.8 mg/cm^2 , the Li–S cell with Ni-NiS/NCF coating has the best performance compared with that of NiS/NCF and Ni/NCF coating. The initial capacity of the cell with Ni-NiS/NCF coating is 1640.3 mAh/g, which is much higher than that of Ni/NCF with 954.4 mAh/g and NiS/NCF with 1311.2 mAh/g. Figure 6b shows the charge and discharge curves of Li–S cells assembled with different separator at 0.5 C at the initial cycle. The initial discharge capacity of the cell with Ni-NiS/NCF coating is up to 1128 mAh/g, which is much higher than that of Ni/NCF with 801.3 mAh/g and NiS/NCF with 876.5 mAh/g. In addition, the cell assembled with Ni-NiS/NCF-coated separator have a smaller polarization voltage, which is consistent with the adsorption and catalytic performance of Ni-NiS/NCF for LiPSs compared with NiS/NCF and Ni/NCF. Figure 6c shows the long cycle stability of the cells with different separators at larger currents. As shown in Figure 6c, after three cycles at 0.1 C, the cell with Ni-NiS/NCF coating could achieve long-term cycling stability at 1.0 C. When the current density changed from 0.1 C to 1 C, the reversible capacity is still 1109.6 mAh/g, and the reversible capacity can be well maintained with 618.0 mAh/g after 300 cycles.

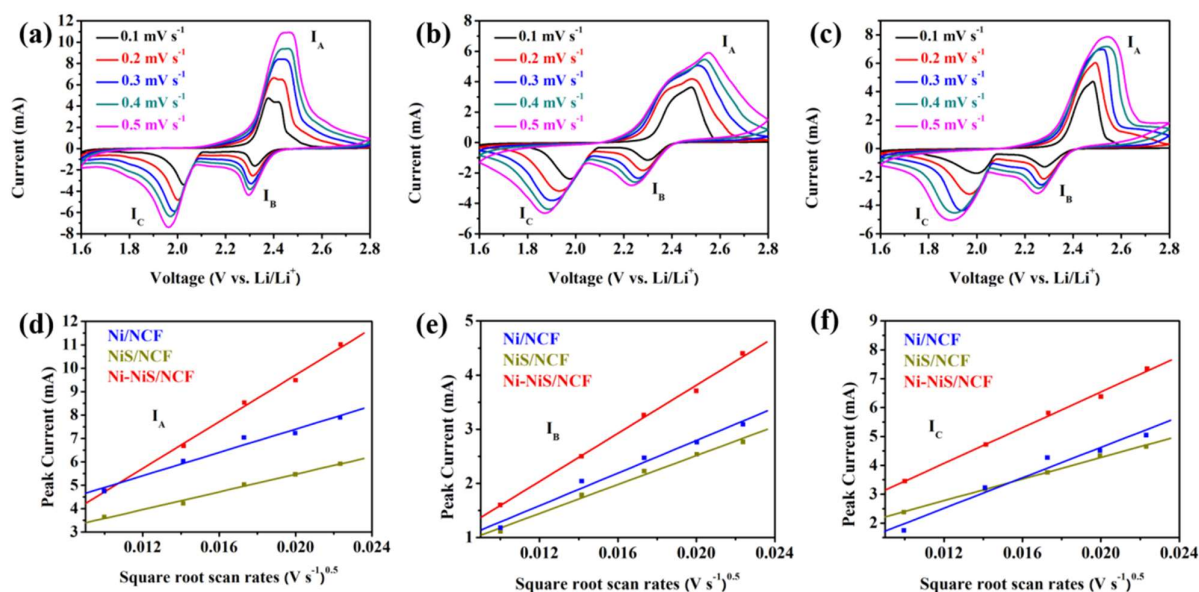


Figure 5. CV curves of the cells with separator coated by (a) Ni-NiS/CNT, (b) NiS/CNT, and (c) Ni/CNT at different sweep speeds. (d) I_A (anodic oxidation, Li₂S₂/Li₂S → S₈ + Li); (e) I_B (cathodic reduction, S₈ → Li₂S_x, 3 ≤ x ≤ 8); (f) I_C (cathodic reduction, Li₂S_x → Li₂S₂/Li₂S, 3 ≤ x ≤ 8).

Figure 6d shows the rate performance of different cells. The results show that the cell with Ni-NiS/NCF coating has the best rate performance. The specific capacity of the cell with Ni-NiS/NCF coating at different current densities is 1181.0 mAh/g, 939.1 mAh/g, 798.6 mAh/g, 639.1 mAh/g, 562.7 mAh/g, 549.8 mAh/g, and 511.6 mAh/g, respectively. Even at a current density of 5 C, the cell with Ni-NiS/NCF coating can still have a high specific capacity of 511.6 mAh/g. When the current density is restored to 0.1 C, the specific capacity of the cell with Ni-NiS/NCF coating can be well restored to 1078.0 mAh/g, showing good stability. In contrast, the specific capacity of cells assembled with NiS/NCF and Ni/NCF coatings decreases rapidly. The necessary role of the interaction between Ni and NiS in the catalytic process can also be observed from the charge and discharge curves at different current densities. As shown in Figure S5, the charge and discharge curves of the cell with Ni-NiS/NCF coated separator showed a clear charge and discharge plateau compared with the NiS/NCF and Ni/NCF, even at a high current density of 5 C. This is because that Ni-NiS/NCF can still effectively adsorb and catalyze the conversion of LiPSs at high current density, inhibit the shuttle of LiPSs, make the battery still have stable cycle at high current density, and achieve the high performance of the battery. In addition, we further explored the performance of the cell with Ni-NiS/NCF coated separator under high sulfur loading. As shown in Figure 6e, at 0.1 C and a higher sulfur load of 5 mg/cm², the cell can still cycle stably. These results indicate that the Ni-NiS/NCF coating with good conductivity and catalysis can still effectively inhibit the shuttle effect of LiPSs in the case of high sulfur load.

To further verify the effect of separator coating on shuttle effect, the cells with different coatings were disassembled after 100 cycles at the same current density to test the electrode morphology of the lithium anodes. As shown in Figure S6, compared with NiS/NCF and Ni/NCF, the surface of the lithium anode from the cell with Ni-NiS/NCF coated separator is still smooth. SEM image shows that there is no obvious lithium dendrite and yellow lithium polysulfides on the surface of lithium sheet after cycling (Figure S6b). However, the surface of the lithium sheet from the cell with the coating of NiS/NCF or Ni/NCF were rough and turned black, and SEM images showed obvious lithium dendrites (Figure S6d,f). This is because the Ni-NiS/NCF coating can effectively adsorb and catalyze LiPSs, thus, to inhibit the shuttle of polysulfide lithium, and reduce the corrosion of polysulfide lithium sheet.

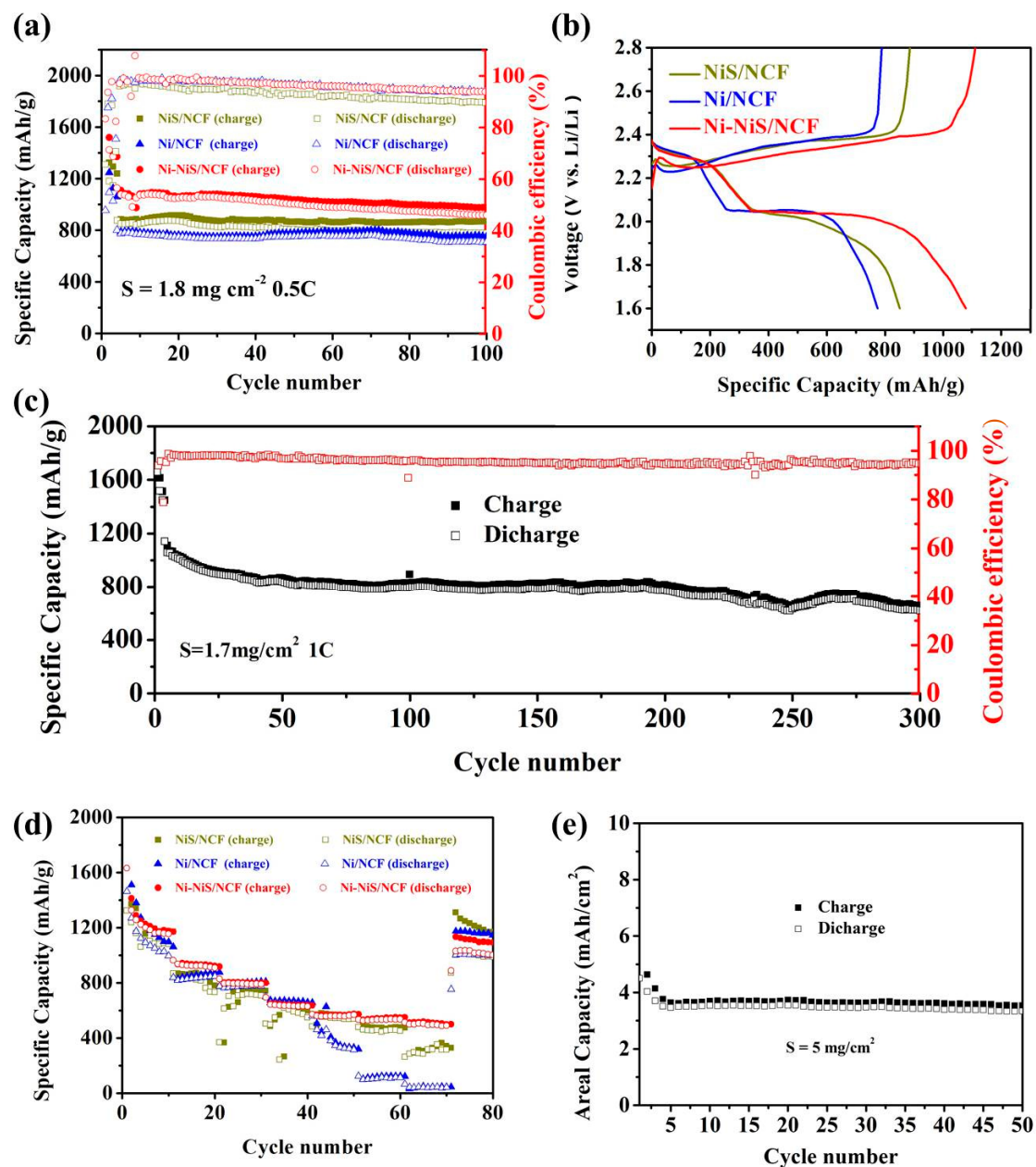


Figure 6. (a) Cycling performance of the cells with different separators at 0.5 C. (b) Charge and discharge curves of the cells with different separators at 0.5 C. (c) Long cycle performance of the cell with Ni-NiS/NCF-coated separator at 1 C. (d) Rate performance at different current densities for different cells. (e) Cycle performance of the cell with Ni-NiS/NCF-coated separator at 0.1 C with high sulfur load.

4. Conclusions

In conclusion, the Ni-NiS/NCF heterojunction composite prepared in this paper has a multistage pore structure and a large specific surface area, which can effectively capture LiPSs, provide more active sites for catalyzing LiPSs, and establish a high ion and electron conduction network, so as to achieve efficient mass and charge transfer capacity. NiS can effectively capture and catalyze lithium polysulfide, and Ni can effectively accelerate the diffusion and charge transfer of lithium ions. The mutual coordination of uniformly distributed Ni-NiS heterojunctions inhibits the shuttle effect of LiPSs. The nucleation of Li_2S in Ni-NiS/NCF cell is early, the deposition capacity of Li_2S is 154.43 mAh/g, and the conversion degree of polysulfide is deep. These results indicate that the heterostructure has

good electrocatalytic activity for LiPSs, and can effectively accelerate the REDOX kinetics of Li_2S in electrochemistry. When the sulfur load is 1.8 mg/cm^2 , the initial capacity of the cell with Ni-NiS/NCF coated separator at 1 C is 1109.6 mAh/g , and the final discharge capacity is maintained at 618.0 mAh/g after 300 cycles. At the same time, the reversible specific capacity was maintained at 674.0 mAh/g after 50 cycles even under high sulfur load.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12101557/s1>. Figure S1: (a) TEM images of Ni-NiS/NCF. (b) TEM images of carbon nanotubes in Ni-NiS/NCF. (c) HRTEM images of Ni and NiS. (d) Element mapping of Ni-NiS/NCF. Figure S2: High resolution Ni 2P XPS spectrum of Ni-NiS/NCF after adsorbing Li_2S_6 . Figure S3: CV curves of the symmetric cell assembled with Ni-NiS/NCF at different sweep speeds. Figure S4: The alternating-current impedance spectrum of the cells with different coated separators. Figure S5: The charge and discharge curves of the cells with different coated separators at different rates. (a) Ni-NiS/NCF (b) NiS/NCF (c) NiS/NCF. Figure S6: At 0.5 C, after 100 cycles, the picture of lithium anode: (a) Ni-NiS/NCF; (c) NiS/NCF; (e) Ni/NCF. SEM image of lithium anode surface: (b) Ni-NiS/NCF; (d) NiS/NCF; (f) Ni/NCF.

Author Contributions: Conceptualization, methodology, Z.-Y.W., X.-N.Z.; data curation, writing—original draft preparation, writing—review and editing, J.W. and Y.L.; project administration, funding acquisition, J.W. and S.H.; All authors have read and agreed to the published version of the manuscript.

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