Preparation of nitrogen doped CNTs porous carbon materials based on MOF in situ growth and its application in lithium sulfur cathode

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Abstract. Porous carbon structure is widely used as sulfur carrier to improve the cycle stability and rate performance of lithium sulfur batteries. However, due to the amorphous carbon structure of porous carbon nanostructures, it is still a big challenge for porous carbon nanostructures to obtain high sulfur content and high sulfur surface density. In order to improve the electronic conductivity of porous carbon, maintain its long cycle life and good rate performance, we prepared N-doped graphitized CNTs by high temperature sintering. CNTs encapsulated bulk porous carbon was prepared using ZIF-67 and melamine as precursors(Co-NC@CNTs/S). The CNTs are "slubby" structure and the tube wall is graphite. Due to the unique structure of Co-NC@CNTs, the positive cathode of Co-NC@CNTs/S has better electrochemical performance than Co-NC/S positive cathode. Under the condition of high sulfur (82wt%), the cathode can not only obtain high discharge capacity (1293mAhg⁻¹ at 0.1C) and excellent rate performance (727.8 mAhg⁻¹), but also achieve long cycle stability of more than 100 cycles (capacity decay rate of each cycle is 0.17%).

1. Introduction
The next generation lithium battery is considered to have one of the highest specific energy density (2600 wh kg⁻¹) due to its high energy density. Although lithium sulfur battery has shown attractive performance, it has been widely studied and commercialized. In the field of energy storage and conversion, there are still many inherent problems hindering its practical application [1,2]. In particular, the electronic conductivity of sulfur is low, the blocking effect of long-chain polysulfides is severe, and the volume expansion rate during discharge is large [3-9]. In order to solve the above problems of sulfur cathode, researchers have proposed many strategies in the past few years, such as coating sulfur into various types of conductive carbon or polymer, adding conductive layer between sulfur cathode and membrane, or fixing sulfur with polar transition metal oxide or hydroxide [9-30]. Due to the high electronic conductivity, flexible pore structure design and good chemical sulfur affinity of carbon materials, new sulfur/carbon cathode structure design has made encouraging progress in recent years. Three dimensional conductive carbon structure has been widely studied due to its good conductivity, rich sulfur capacity pores and volume expansion pores, and good limitation of polysulfides, which are important factors affecting the energy density and cycle performance of lithium sulfur batteries [28-30]. In the past, the research on the structure of three-dimensional...
conductive sulfur cathode has made remarkable progress in improving electrochemical performance. For example, Yang et al. prepared a three-dimensional cross-linked porous carbon/nano sheet structure, which can still maintain a specific capacity of 882.8 mAh\textsuperscript{-1} after 150 cycles[30]. Zheng developed a three-dimensional foam structure based on CNTs. The conductive skeleton formed by CNTs is conducive to the rapid transmission of electrons, and the first discharge reaches the specific capacity of 1039 mAh\textsuperscript{-1}[31].

Song et al. prepared porous carbon materials with 0.5 nm and 22 nm pore structure using ZIF-8 as precursor, which inhibited the "shuttle effect" to a certain extent, and the capacity retention rate reached 82.6% after 100 cycles at 0.2C. Although the cycling performance of these composites has been greatly improved, their sulfur content is usually lower than 80wt% [32], sacrificing porosity to improve conductivity, which is unfavorable to improve the mass and bulk energy density of lithium sulfur battery. High sulfur and long life are still a great challenge for three-dimensional porous carbon cathode. In addition, the more pores in carbon materials, the stronger the physical adsorption of polysulfides, which is conducive to the cycle stability of lithium sulfur battery. The low sulfur loading of these three-dimensional conductive carbons may be due to their small pore volume (mostly less than 2.43 mAh\textsuperscript{-1}), small specific surface area and insufficient pore channels [16-29]. Another disadvantage may be that these porous carbon structures are usually amorphous, which can not make full use of the high electronic conductivity of \textit{sp}2 hybrid carbon. If we can improve the graphitization degree of these three-dimensional conductive carbon structures, even if the sulfur content increases, it can also provide fast electron transport for sulfur cathode. Therefore, the combination of carbon and sulfur is an effective way to obtain a stable three-dimensional structure. In this paper, three-dimensional porous carbon materials with N-doped graphitized CNTs coated porous carbon structure were obtained by grinding and mixing ZIF-67 powder and melamine powder, and annealing the mixed powder in Ar atmosphere. ZIF-67 is a kind of MOF material widely used in the preparation of porous carbon. Melamine is added as the carbon source of CNTs. The Co-NC@CNTs/S cathode can hold 82 wt% high sulfur and shows excellent rate performance (788.9 mAh\textsuperscript{-1} at 2C) and long cycle life (low capacity decay rate of 0.17%, 100 cycles), which shows better electrochemical performance than ZIF-67 single carbon-ized cathode. The results show that the nitrogen doped CNTs porous carbon material based on MOF is a promising cathode material for lithium sulfur battery with high sulfur load and long cycle life.

2. Experiment

2.1 Synthesis of Co-NC@CNTs/S
ZIF-67 precursor was prepared by classical method reported in literature. First of all, 18.624 g of Co(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O and 21.016g of 2-methylimidazole were dissolved in 800 ml of methanol solution, respectively, magnetic stirring was performed for 30 min until the solution was clarified. Then, the methanol solution containing 2-methylimidazole was quickly poured into the methanol solution of Co(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O to obtain the purple solution. After strongly stirring for 1h, it was put into the oven at 50 °C for 24h to obtain the lavender clear solution with purple precipitation. Part of the upper clear solution was poured out, the rest was washed with absolute ethanol, centrifuged and dried in 80 °C vacuum drying oven for 12 h to obtain ZIF-67 precursor. 2 g of ZIF-67 precursor and 3 g of melamine powder (mass ratio 1:1.5) were weighed and evenly mixed, heated to 750 °C in Ar atmosphere and kept for 2 hours, and then etched with 2M HCl solution for 2 hours to obtain black powder. The sulfur is then injected into the melt in the pores of the Co-NC@CNTs. The sulfur content in the composite can be calculated by the mass change before and after preparation, which is basically consistent with the TGA analysis results. The sulfur content is finally determined to be about 82%.

2.2 Materials Characterization
The structures of the prepared samples were characterized by XRD (SIEMENS D-500) using Cu Ka radiation. TEM was tested with a FEI Tecnai 2100 instrument. The thermogravimetric analysis (TGA)
was tested with a TGA-600 under N₂ atmosphere with a heating rate of 10°C min⁻¹ to confirm the content of sulfur in the composite.

2.3 Electrochemical characterizations
The 2016 button cell was used for electrochemical experiment. Using N-methyl pyrrolidone and water as solvent, sulfur cathode was prepared by mixing sulfur cathode, superconducting carbon and LA133 aqueous binder (mass ratio 80:12:8). The slurry was stirred and pasted on Al foil and dried at 65°C overnight. 0.5M lithium bis-trifluoromethanesulfonylimide (LiTFSI) in a solvent of 1,3-dioxolane and 1,2-dimethoxyethane (DOL/DME, 1:1 by volume) with 0.5M LiNO₃ (Fosai New Material Co. Ltd) was used as electrolyte, polypropylene membrane (Celgard Inc.) was used as the separators and lithium metal foil was used as the anode. About 130 μl electrolyte was used in the manufacture of button cell. Constant current charge and discharge tests were carried out at room temperature with a battery tester (land ct-2001a, Wuhan, China) at different current densities of 0.1C ~ 2C (1C=1672mAhg⁻¹).

3. Results and discussion

Figure 1. Schematic diagram of Co-NC@CNTs/S material preparation route

The Co-NC@CNTs/S positive cathode is synthesized by the method shown in Fig.1. Firstly, ZIF-67 precursor was prepared by classical method reported in literature. Secondly, the precursor of ZIF-67 was fully mixed with melamine, and then the mixed powder was annealed at 750 °C in Ar atmosphere, and then Co metal particles were etched to obtain the precursor. In the sintering process, the carbon containing gas from melamine pyrolysis was decomposed into carbon atoms by the catalysis of Co element, and deposited on the surface of Co metal particles to form a graphite layer. Under the effect of surface tension, the graphite layer fell off to form bamboo like carbon nanotubes. Finally, the sulfur element was melted into the water by melting method in the pores of Co-NC@CNTs/S.

Figure 2. a,b SEM and c,d,e TEM images of Co-NC@CNTs
The images of scanning electron microscope (SEM) and transmission electron microscope (TEM) are shown in Fig. 2. As shown in Fig. 2a, under the catalysis of Co element, a large number of CNTs are generated and interwoven to form a three-dimensional conductive network. The enlarged image of Fig. 2b clearly shows that the generated CNTs have higher length diameter ratio and more uniform diameter. Meanwhile, the inclusion of CNTs aggregation appears, and the CNTs extend outward with the inclusion as the center. Fig. 2c is the TEM image of the inclusion, which shows that the outer part of the inclusion is "bamboo" shaped CNTs, and the center is massive porous carbon, which is carbonized by ZIF-67. The enlarged image in Fig. 2d shows that the outer wall and "slub" of CNTs are composed of multilayer graphite. The diameter of CNTs is about 30nm, the thickness of carbon wall is 4.93nm, and the thickness of "slub" is 3.99nm. The thickness and the number of graphite layers at the "slub" are similar to those at the outer wall, which is mainly due to the decomposition of carbon containing gas by Co particles into carbon elements and deposition on the surface of Co particles, which precipitates under the effect of surface tension and forms carbon wall and "slub" spacing. Fig. 2e is a high-resolution TEM image of the CNTs (selected area in Fig. 2d) revealing Co-NC@CNTs. The crystal structure of the crystal. CNTs have a large number of microcrystalline structures, with a stripe spacing of 0.365 nm, corresponding to the (002) surface of graphite. This indicates that the graphitization degree of CNTs is higher under the catalysis of Co. In conclusion, the carbonized porous carbon structure of ZIF-67 is conducive to the infiltration and storage of sulfur, while the graphitized CNTs wrap the porous carbon and connect with each other to form a three-dimensional conductive network. This structure provides faster electron transfer for sulfur cathode, and both can improve the electrochemical performance of lithium sulfur battery.

![Figure 3. The full XPS spectrum of Co-NC@CNTs](image)

X-ray photoelectron spectroscopy (XPS) was used to analyze the structure of Co-NC@CNTs, the results are shown in Figure 3. In the XPS full spectrum shown in Fig. 3, there are characteristic signal peaks of C, N, O and Co. The element o comes from some oxygen-containing functional groups in the acid treatment process. The existence of oxygen-containing functional groups in the sulfur bearing matrix is conducive to the binding and fixation of sulfur in the matrix, and the oxygen-containing functional groups can inhibit the loss of sulfur to a certain extent. and Nitrogen doping in the samples can not only increase the conductivity of carbon materials, but also change the polarity of carbon materials, promote the chemical bonding between oxygen-containing functional groups and sulfur, increase the adsorption of sulfur cathode on polysulfide lithium during charging and discharging, and inhibit the "flying shuttle effect" to a certain extent. According to literature reports, the presence of Co has a certain catalytic effect on the electrochemical reaction of lithium sulfur battery.
Figure 4. The TGA curves of Co-NC@CNTs/S and Co-NC/S materials

For comparison, Co-NC composites were prepared with ZIF-67 as precursor and porous carbon obtained after high temperature carbonization under the same conditions. The elemental sulfur was injected into the reactor by melting method, and heat treatment, evaporation of excess sulfur. Co-NC/S and Co-NC@CNTs/S The TGA results of the composite are shown in Figure 4. The weight loss between 150 ° C and 300 ° C in the TGA curve corresponds to the evaporation of sulfur. Therefore, Co-NC@CNTs/S The sulfur content of the composite is 82%, while that of the Co-NC/S composite prepared under the same conditions is only 74%.

Figure 5. TEM images of Co-NC@CNTs/S materials

Figure 5 is an example of the 82% sulfur content in the porous carbon, which shows that the porous carbon is not filled with sulfur. Sulfur also appears in CNTs, indicating that CNTs are mainly used as electron transport framework and to provide sulfur containing space.

To prove the advantages of Co-NC@CNTs/S composite materials in improving the performance of lithium sulfur battery, the electrochemical performance of the cathode was studied. The results show that the positive cathode is between 1.7V and 2.8V, and its rate performance is poor. The capacity fluctuates greatly at 1C rate and remains at a low level (80 mAhg⁻¹) at 2C rate. Compared with the Co-NC/S positive cathode, Co-NC@CNTs/S cathode rate performance is more excellent. At the same time, The Co-NC@CNTs/S positive cathode provides 1264.8, 1031.4, 940.7 and 878.6 mAhg⁻¹ discharge capacities at 0.1C, 0.2C, 0.5C and 1C rates. When the current density is increased to 2C, the discharge capacity is still 788.9 mAhg⁻¹, and the discharge capacity of 10 charg-discharge cycles remains good. When the current density is restored to 0.1C, the discharge capacity is increased to 1062.5 mAhg⁻¹, the Co-NC@CNTs/S cathode can maintain good structural stability at high magnification. Figure 6b shows the results at different magnification, all the curves have two typical discharge platforms, even at the higher rate of 2C, the Co-NC@CNTs/S cathode still has a lower
polarizability at a higher rate. The Co-NC@CNTs/S positive cathode has better rate performance and lower polarizability. Compared with the porous carbon prepared by high temperature carbonization of ZIF-67 precursor, the porous carbon with three-dimensional conductive network formed by in-situ growth of CNTs not only has greater sulfur charging ability, but also can provide better electron transport due to the existence of graphitized $sp^2$ hybrid carbon.

Figure 6. (a) rate performance of the Co-NC@CNTs/S and Co-NC/S cathode, (b) charge-discharge profiles of the Co-NC@CNTs/S cathode at different C rate, cycling performance of the Co-NC/S and Co-NC@CNTs/S cathode at 0.1C rate

The cycling performance of the Co-NC/S and Co-NC@CNTs/S composite cathode at 0.1C rate is shown in Fig.7. Co-NC/S and Co-NC@CNTs/S initial discharge capacity of the composite cathode is 843.3 mAhg$^{-1}$ and 1293.6 mAhg$^{-1}$, respectively. In the following cycle, the discharge capacity of Co-NC/S cathode increases gradually and reaches 921.1mAhg$^{-1}$ in the fifth cycle, which indicates that the activation process of Co-NC/S cathode is slow and Co-NC@CNTs/S cathode initial discharge capacity of the composite is relatively high. The discharge capacity of the first six cycles decreases gradually, and then remains stable. The discharge capacity of the 100th cycle is 913.3 mAhg$^{-1}$. From the 10th cycle to the 100th cycle, the capacity decay rate is 0.17%, and the coulomb efficiency is close to 100%. The results show that the activation of the Co-NC@CNTs/S composites is faster, and the capacity of the decreases in the first six cycles, which may be due to the fact that a small amount of sulfur does not enter into the porous carbon and CNTs, and there is no binding of carbon structure. This small amount of sulfur gradually loses in the first few cycles, and finally only the active sulfur in the porous carbon and CNTs is left, and the discharge capacity tends to be stable in the next cycle. The different phenomena of the two cathodes in the initial cycle may be attributed to their different composite structures. The bulk porous carbons of Co-NC/S composites are relatively independent, and there is no conductive network between them. Especially when the sulfur content is high, the conductivity of the relatively independent porous carbons is worse. Therefore, the electrochemical activation requires multiple charge discharge cycles, while for Co-NC/S composites, the conductivity of the relatively independent porous carbons is worse, graphitized CNTs grown in situ are wrapped with porous carbon to form a three-dimensional conductive network, which is conducive to electrolyte permeation and electron transport, so activation process is not needed. Both cathodes showed stable cycling performance at 0.1C rate. Compared with Co-NC/S cathode, the Co-NC@CNTs/S cathode has
higher discharge capacity and more stable cycle performance, which may be due to the cathode has a three-dimensional interconnection structure of N-doped graphitized CNTs. The Co-NC@CNTs/S cathode provides easier electrolyte access and faster electron transport. For the cathode with high sulfur content, the large pore volume and high specific surface area of carbon nanostructures are needed to regulate sulfur and bulk expansion during the cycling process. The results show that the porous structure and three-dimensional conductive network of carbon are of great significance to maintain the structural integrity and high conductivity of sulfur cathode, especially the structural integrity and high conductivity of sulfur cathode with high sulfur content. The results show that the micropores formed by etching metal Co have strong adsorption and storage for polysulfides, and the N-doped graphitized sp2 hybrid CNTs have good chemical affinity with nonpolar sulfide nanoparticles and provide fast electron transport.

4. Conclusion

In conclusion, we prepared N-doped CNTs porous carbon (Co-NC@CNTs) by high temperature sintering using ZIF-67 and melamine as precursors materials. It has porous structure and N-doped graphitized three-dimensional conductive network structure. Because of the unique structure, the Co-NC@CNTs/S positive cathode has better electrochemical performance than Co-NC/S positive cathode. Under the condition of high sulfur (82wt%), the cathode can not only obtain high discharge capacity (1293.6 mAh g⁻¹ at 0.1C) and excellent rate performance (788.9 mAh g⁻¹ at 2C), but also achieve long cycle stability of more than 100 cycles (capacity decay rate of each cycle is 0.17%).

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