

Preparation and Electrochemical Performance of Carbyne Polysulfide as a Cathode Material for Lithium Batteries

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The product obtained by co-heating carbon containing carbyne moieties and element sulfur was characterized by ^{13}C -NMR, XRD, and SEM, and it was proved to have carbon skeleton with polysulfide attached on it, which resembles the theoretical structure of carbyne polysulfide. This material exhibited a high capacity of $600\text{mA}\cdot\text{h/g}$ at $400\text{mA}/\text{cm}^2$ at first cycle and a very stable reversible capacity of $380\text{mA}\cdot\text{h/g}$ after 200cycles. This material is nearly 100% efficient during charge/discharge.

1. Introduction

As the cathode material with the highest specific capacity, elemental sulfur has many advantages like abundant reserves, inexpensiveness, and environmental-friendliness (Jeon et al., 1988; Byoung et al., 2002; Nam et al., 2004). Nevertheless, its application scope is mainly limited by poor electrical conductivity, solubility of lithium insertion product in organic solvent, and rapid capacity loss (Marmoustein et al., 2000). Currently, the major measures to improve the performance of elemental sulfur include adding a carbon type conductive agent or catalyst to the positive electrode, using solid or gel electrolytes, and forming a protective film on the negative electrode surface (Liang et al., 2013; Ahn et al., 2012; Lin et al., 2013; Duan et al., 2012; SU and Manthiram, 2012; Zhao et al., 2013; Yang et al., 2017; Bassani et al., 2017; Cardenas-Guerra et al., 2017). These methods can optimize the preparation process and battery performance to some extent, but is less effective than modifying platestructure (Du, 2017; Insinga et al., 2017). Accordingly, we design and prepare the cathode material with a conducting skeleton and energy-storing side chains (Yang et al., 2002). The conductive matrix is prepared by removing hydrogen halides from polyvinylidene chloride. The product obtained by co-heating carbon containing carbyne moieties and element sulfur has been characterized by ^{13}C -NMR, XRD and SEM, and it is proved to have carbon skeleton with polysulfide attached on it, which resembles the theoretical structure of carbyne polysulfide. It also showed that this material has good electric conductivity, with conducting polymer carbyne as the stable backbones of electric conducting channels, and high specific capacity, with polysulfide lines as side lines. The material exhibits a high capacity of 600mAh/g at $0.4\text{mA}/\text{cm}^2$ and a very stable reversible capacity of 400mAh/g after 60 cycles in the electrolyte of LiPF_6 . This material is nearly 100% efficient during charge/discharge.

2. Experimental

The experimental steps are: first, pour 20g PVDC into the mixture of 800ml KOH/ethanol saturated solution and 1200ml THF, and let them react with each other under the protection of N_2 for 1hr; then, neutralize the resultants with hydrochloric acid and filter out chloric ion, finally, wash the black precipitates by acetone, dry them in vacuum, and collect them.

Ball-mill the powder productions in a dry condition, and mix them with S (1mol :5mol), transfer the mixture into a tube furnace, raise the temperature by 10°C per minute until it reaches 350°C , and heat the mixture at this temperature for 3hrs before cooling. The heating and cooling process is carried out under the protection of N_2 .

The scanning electron microscope (SEM) is used to characterize the microstructure of carbyne polysulfide. The cyclic voltammograms measurements are performed in an electrochemical test station (Solartron 1, 280Z). The electrochemical performance is measured at the temperature of 298 ± 1 K.

CR2025-type Lithium coin cells are assembled in a glove box to evaluate the cyclic performance of carbyne polysulfide samples. The composite positive electrodes are fabricated in the following steps: mix carbyne polysulfide active material, acetylene black (AB) and LA132 binder thoroughly in n-propyl alcohol, at the weight ratio of 6:3:1, ball-mill the paste for 5hrs and spread it on a nickel film, cut it into a square at the diameter of 10mm. The cells, with a negative electrode of lithium, electrolyte containing 1M LiPF_6 plus ethylene carbonate (EC) + dimethyl carbonate (DMC) (1:1, v/v), are tested on a LAND electrochemical instrument at room temperature. The charge-discharge current density is 0.4mA/cm^2 and the cut-off voltage is from 3.0 to 1.0 V vs. Li/Li+.

3. Results and Discussion

The ^{13}C -NMR spectra of carbyne polysulfide is shown as in Figure 1.

There is only one peak ($\delta=135.9$) with sp^2 hybridization, which shows that the carbon base material is a complete π -electron conjugated structure.

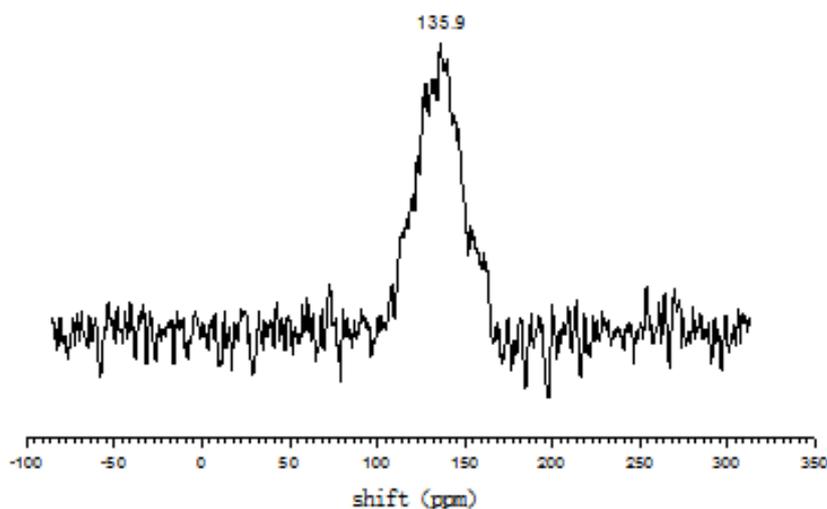


Figure 1: ^{13}C -NMR spectra of carbyne polysulfide

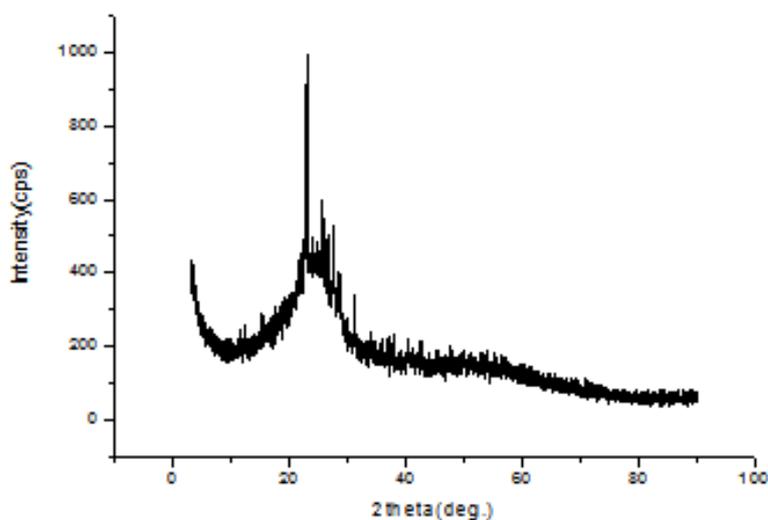
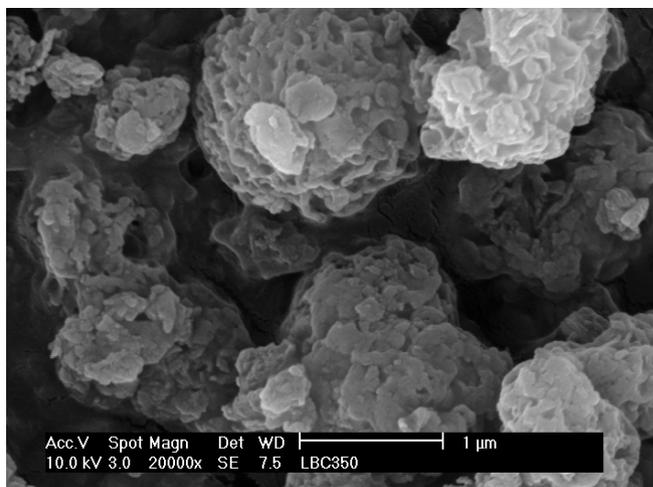
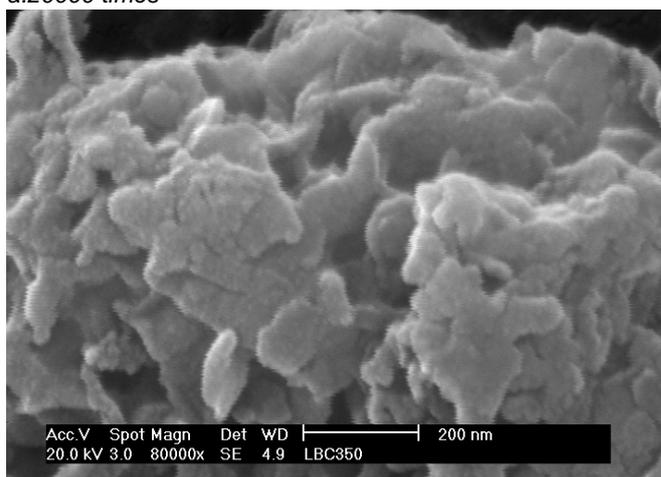


Figure 2: XRD spectra of carbyne polysulfide

In Figure 2, the XRD spectra of carbyne polysulfide demonstrate the diffraction characteristics of crystals and amorphous mixtures. The peaks of 24°C and 55°C show that the sample has an amorphous-carbon structure. The presence of crystal diffraction peaks shows that the product contains a small amount of elemental sulfur which is possibly embedded in the pores of the carbon matrix or combines with marginal carbon to form graphite crystallites that will not decompose at 350°C.



a. 20000 times



b. 80000 times

Figure 3: SEM spectra of carbyne polysulfide

Figure 3 is a SEM picture of carbyne polysulfide at different magnifications. The product is the aggregate of micron particles with a layered structure and internal micropores. Whether the electrolyte can contact the electrode material sufficiently will affect the performance of the battery. The structure of carbyne polysulfide is conducive to the penetration of electrolyte, and the utilization ratio of electrode material is improved.

The charge-discharge current density is $0.4\text{mA}/\text{cm}^2$ and the cut-off voltage is from 3.0 to 1.0 V vs. Li/Li⁺. This material exhibits a high capacity of $600\text{mA}\cdot\text{h}/\text{g}$ at $400\text{mA}/\text{cm}^2$ at first cycle and a very stable reversible capacity of $380\text{mA}\cdot\text{h}/\text{g}$ after 200cycles. This material is nearly 100% efficient during charge/discharge.

The potential sweep rate is $0.05\text{mV}\cdot\text{s}^{-1}$ and the voltage range is between 3.0 and 1.0V. In Figure 5, cyclic voltammetry is carried out to characterize the redox behavior and the kinetic reversibility of the cell at room temperature. In the first cycle, two reduction peaks appear at 1.7V and 2.1V which correspond to two deoxidization steps: the cleavage of polysulfide and the production of sulfur ion, one oxidation peak appear at 2.5V. The peak of 2.1V disappears in the subsequent cycle, showing that the first deoxidization is irreversible. There is a minor change in the area of the peaks, indicating better reversibility for the system. The electrochemical cleavage of sulfur-sulfur bond during discharge does not cause the depolymerization of skeletal chain and thus the lithium-insertion reduction product is almost non-soluble in solvent.

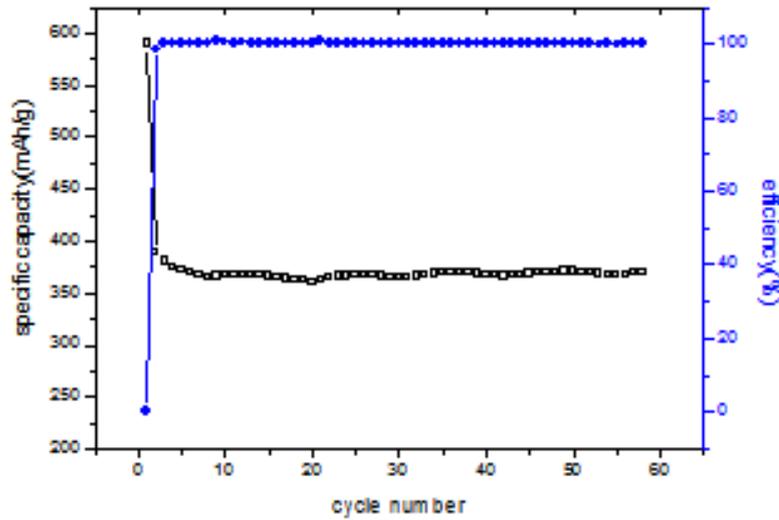


Figure 4: Efficiency of carbyne polysulfide

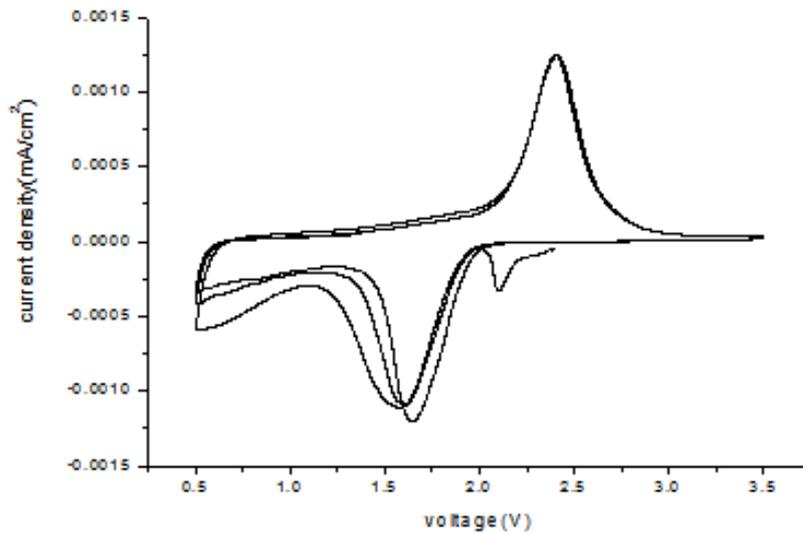


Figure 5: Cyclic voltammograms of carbyne polysulfide

4. Conclusions

The carbyne polysulfide materials found with such characteristic:

- (1) Irreversible capacity is high at first discharge.
- (2) This material is nearly 100% efficient during charge/discharge.
- (3) The cycle performance of this material is good and the capacity maintenance rate is over 90% from the second discharge.

The excellent cycle characteristics provide a good foundation for the practical application of this material in rechargeable lithium batteries.

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