

# 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  $^{13}\text{C}$ -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  $^{13}\text{C}$ -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  $600\text{mAh/g}$  at  $0.4\text{mA}/\text{cm}^2$  and a very stable reversible capacity of  $400\text{mAh/g}$  after 60 cycles in the electrolyte of  $\text{LiPF}_6$ . 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  $\text{N}_2$  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  $10^\circ\text{C}$  per minute until it reaches  $350^\circ\text{C}$ , and heat the mixture at this temperature for 3hrs before cooling. The heating and cooling process is carried out under the protection of  $\text{N}_2$ .

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  $298 \pm 1$  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<sub>6</sub> 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<sup>2</sup> and the cut-off voltage is from 3.0 to 1.0 V vs. Li/Li+.

### 3. Results and Discussion

The <sup>13</sup>C-NMR spectra of carbyne polysulfide is shown as in Figure 1.

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

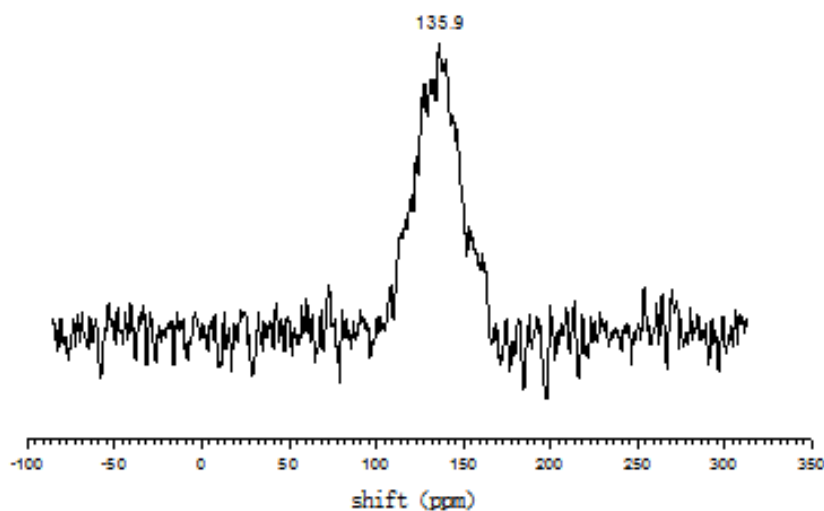


Figure 1: <sup>13</sup>C-NMR spectra of carbyne polysulfide

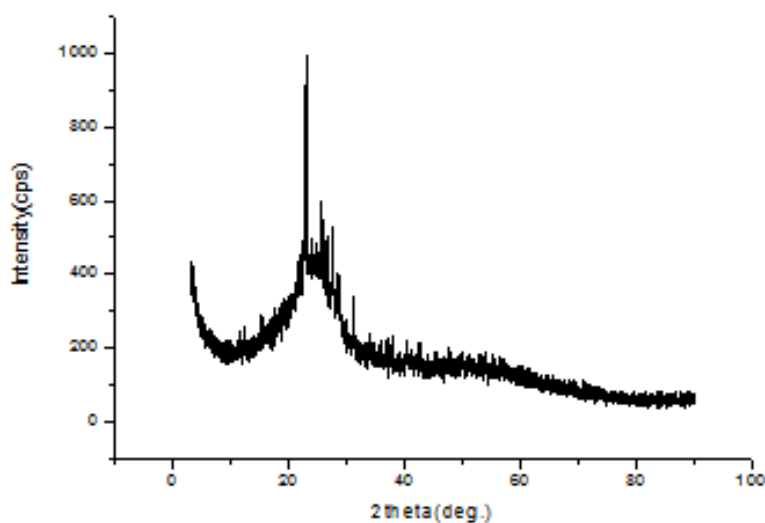
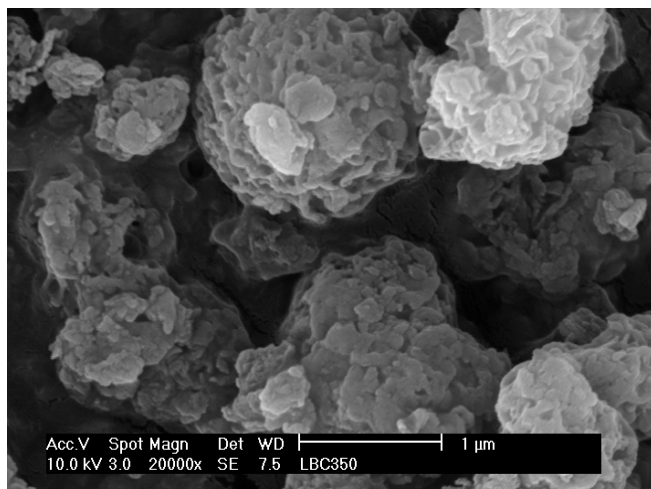
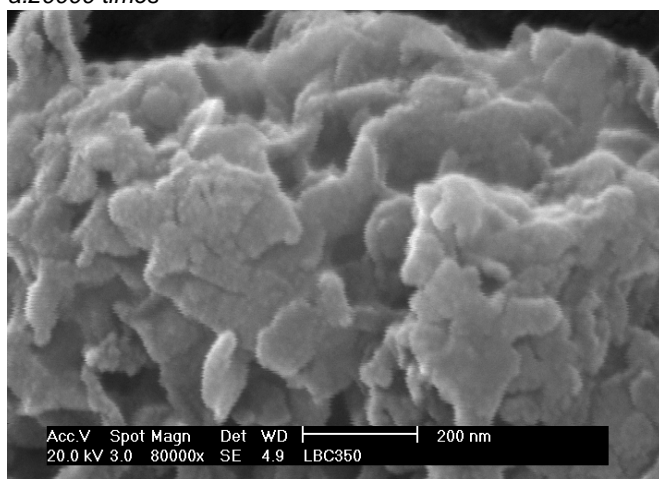


Figure 2: XRD spectra of carbyne polysulfide

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<sup>+</sup>. 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.

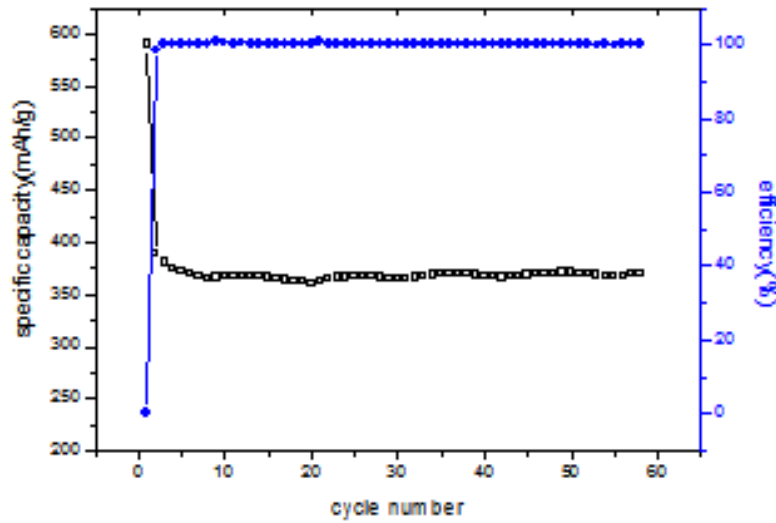


Figure 4: Efficiency of carbyne polysulfide

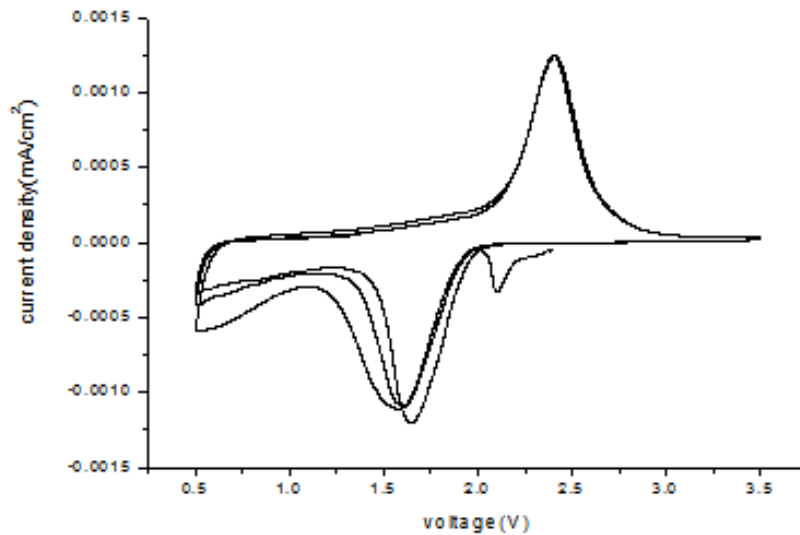


Figure 5: Cyclic voltammograms of carbyne polysulfide

#### 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.

#### References

- Ahn W., Kim K., Jung K., 2012, Synthesis and electrochemical properties of a sulfur-multi walled carbon nanotubes composite as a cathode material for lithium sulfur batteries, *Journal of Power Sources*, 202, 394-399.
- Alnaizy, R., 2008, Economic analysis for wet oxidation processes for the treatment of mixed refinery spent caustic. *Environmental Progress*, 27, 3, 295–301.

- Ateya, B.G., AlKharafi, F.M., Al-Azab, A. S., 2003, Electrodeposition of Sulfur from Sulfide Contaminated Brines. *Electrochemical and Solid-State Letters*, 6, 9, 137.
- Bassani A., Frau C., Maggio E., Pettinau A., Cali G., Ranzi E., Manenti F., 2017, Devolatilization of organo-sulfur compounds in coal gasification, *Chemical Engineering Transactions*, 57, 505-510, DOI: 10.3303/CET1757085
- Behm, M., Simonsson, D., 1997, Electrochemical production of polysulfides and sodium hydroxide from white liquor Part I: Experiments with rotating disc and ring-disc electrodes. *Journal of Applied Electrochemistry*, 27, 507–518.
- Ben Hariz, I. et al., 2013, Treatment of petroleum refinery sulfidic spent caustic wastes by electrocoagulation. *Separation and Purification Technology*, 107, 150–157.
- Byoung H.J., Jin H.Y., Kwang M. K., 2002, Preparation and electrochemical properties of lithium-sulfur polymer batteries, *Journal of Power Sources*, 109, 1, 89-97.
- Buckley, A.N., Hamilton, L.C., 1987, An Investigation of the Sulphur(-II)/Sulphur(O) System on Gold Electrodes. *J. Electroanal. Chem.*, 216, 213–227.
- Cardenas-Guerra J.C., Lopez-Arenas T., Hernandez S., Hernandez-Escoto H., Figueroa-Gerstenmaier S., ReyesAguilera J.A., 2017, Non-linear dynamics simulation study of a reactive distillation process for the ultra-low sulfur diesel production, *Chemical Engineering Transactions*, 57, 1681-1686, DOI: 10.3303/CET1757281
- Commision of the european Communities, 2005, Commission staff working paper. In Annex to : The Communication on Thematic Strategy on Air Pollution and The Directive on “Ambient Air Quality and Cleaner Air for Europe.”, 170.
- Crocker, L., Martin, D. A., Nissen, W. I., 1979, Citrate-Process Pilot-Plant Operation at the Bunker Hill Company, Bureau of Mines Report of Investigations 8374, p. 1-6.
- De Graaff, M. et al., 2012, Application of a 2-step process for the biological treatment of sulfidic spent caustics. *Water research*, 46, 3, 723–30.
- Dong, B. et al., 2014, The Impacts of European and Asian Anthropogenic Sulfur Dioxide Emissions on Sahel Rainfall. *Journal of Climate*, 27, 7000–7017.
- Du Y.H., 2017, Research on the prediction of nickel-metal hydride battery capacity based on artificial intelligence algorithm, *Chemical Engineering Transactions*, 59, 559-564, DOI: 10.3303/CET1759094
- Duan L., Lu J., Liu W., 2012, Fabrication of conductive polymer-coated sulfur composite cathode materials based on layer-by-layer assembly for rechargeable lithium–sulfur batteries, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 414, 98-103.
- Dutta, P.K. et al., 2010, Electrochemical sulfide removal and recovery from paper mill anaerobic treatment effluent. *Water research*, 44, 8, 2563–71.
- Fleming E. P., Fitt T. C., 1950, High Purity Sulfur from Smelter Gases – Reduction with Natural Gas, *Ind. Eng. Chem.*, 42, 2249-2253.
- Graham, M.C. et al., 2006, Calcium polysulfide remediation of hexavalent chromium contamination from chromite ore processing residue. *Science of the Total Environment*, 364, 1-3, 32–44.
- Heggie, T.W., 2009, Geotourism and volcanoes: health hazards facing tourists at volcanic and geothermal destinations. *Travel medicine and infectious disease*, 7(5), 257–61.
- Huang, H., Yu, Y., Chung, K.H., 2009, Recovery of Hydrogen and Sulfur by Indirect Electrolysis of Hydrogen Sulfide. *Energy & Fuels*, 23, 9, 4420–4425.
- Insinga M.G., Moncada A., Oliveri R.L., Ganci F., Piazza S., Sunseri C., Inguanta R., 2017, Nanostructured pb electrode for innovative lead-acid battery, *Chemical Engineering Transactions*, 60, 49-54, DOI: 10.3303/CET1760009
- Jeon B.H.Y., Gorenshstein A., Penciner J., 1988, Lithium sulfur battery oxidation/ reduction mechanisms of polysulfides in THF solutions, *Journal of the electrochemical society*, 135, 5, 1045-1048.
- Keller-Lehmann, B. et al., 2006, Preservation and Simultaneous Analysis of Relevant Soluble Sulfur Species in Sewage Samples. In 2nd international IWA Conference on Sewer Operation and Maintenance. Sewer Operation and Maintenance SOM 06, Vienna, Austria, 339–346.
- Knight, L.D., Presnell, S.E., 2005 Death by sewer gas: case report of a double fatality and review of the literature. *The American journal of forensic medicine and pathology* : official publication of the National Association of Medical Examiners, 26, 2, 181–185.
- Kohl, A. L., Nielsen, R. B., 1997, *Gas Purification*, Fifth Edition, p. 564, Gulf Publishing Co.
- Kwong, K. V., Meissner, R. E., Ahmand, S., Wendt, C. J., 1991, *Environmental Progress*, Vol. 10, No. 3, p. 211, August.
- Liang X., Liu Y., Wen Z., 2013, A nano-structured and highly ordered polypyrrole-sulfur cathode for lithium–sulfur batteries, *Journal of Power Sources*, 196, 16, 6951-9655.

- Lin F., Wang J., Jia H., 2013, Nonflammable electrolyte for rechargeable lithium battery with sulfur based composite cathode materials, *Journal of Power Sources*, 223, 18-22.
- Marmoustein D, Yu T.H., Striebel K.A., 2000, Electrochemical performance of lithium/sulfur cells with three different polymer electrolyte, *Journal of Power Sources*, 89, 2, 219-226.
- Nam I.K., Chae B.L., Jae M.S., 2004, Correlation between positive-electrode morphology and sulfur utilization in lithium-sulfur battery, *Journal of Power Sources*, 132, 209-212.
- O'Reilly, J.W. et al., 2001, Chromatographic and electrophoretic separation of inorganic sulfur and sulfur-oxygen species. *Analytica Chimica Acta*, 432, 2, 165–192.
- Paulino, J.F., Alfonso, J., 2012, New Strategies For Treatment and Reuse of Spent Sulfidic Caustic Streams from Petroleum Industry. *Química Nova*, 35, 7, 1447–1452.
- Pikaar, I. et al., 2011, Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities. *Water research*, 45, 6, 2281–2289.
- Rabaey, K. et al., 2010, Bioelectrochemical systems : from extracellular electron transfer to biotechnological application K. ; Rabaey et al., eds., IWA Publishing, London, UK.
- Slavov, S.V. et al., 1998, A proton-conducting solid state H<sub>2</sub>S—O<sub>2</sub> fuel cell. 1. anode catalysts, and operation at atmospheric pressure and 20–90°C. *International Journal of Hydrogen Energy*, 23, 12, 1203–1212.
- Smith, D. E., Timmerman, R. W., 2003, Carbon Disulfide, *Kirk-Othmer Encyclopedia of Chemical Technology*, October 17.
- Su Y.S., Manthiram A., 2012, A facile in situ sulfur deposition route to obtain carbon-wrapped sulfur composite cathodes for lithium-sulfur batteries, *Electrochimica Acta*, 77, 272-278.
- Yang G.M., Ma D.L., Liu L., Rong J., Yu X.H., 2017, Electrochemical behavior analyses of anodic oxide film obtained on ta2 pure titanium in sulfuric acid electrolyte, *Chemical Engineering Transactions*, 59, 157-162, DOI: 10.3303/CET1759027
- Yang Y.S., Wang W.K., Yuan K.G., 2002, Prospect of polysulfide as cathode for lithium Battery, *Battery*, 32, 1-5.
- Yushkevich et al, 1934, Article ZH. KHIM. PROM., No. 2, 33-37.
- Zhao Y., Zhang Y.G., Bake N., Zhu M., 2013, Electrochemical performance of lithium gel polymer battery with nanostructured sulfur/carbon composite cathode, *Solid State Ionics*, 234, 40-45.