

Hierarchically Structured Sulfur/Carbon Nanocomposite for High Energy Lithium Batteries

Jane Y. Howe, Chengdu Liang, Nancy J. Dudney

Oak Ridge National Laboratory, Oak Ridge, TN 37831

1. Introduction

The current Li-ion battery technology does not meet the high energy and high power requirements such as electrical vehicles (EVs). One major obstacle lies in the fundamental cathode chemistry, which uses transition metal compounds to store electrical energy: the heavy transition metals put a theoretical limit to the current Li-ion batteries. Lithium-sulfur chemistry, though less studied, holds great promise for achieving the goal of EV battery applications based on the sulfur chemistry, which has a theoretical capacity of 1675 mAh/g, nearly ten times higher than that of LiFePO_4 at 176 mAh/g. Yet the Li/S system has two fatal hurdles: the poor electrical conductivity of elemental sulfur and the intrinsic polysulfide shuttle.

The electrical conductivity of elemental sulfur is as low as 5×10^{-30} S/cm at 25 °C, which causes poor electrochemical contact of the sulfur and leads to low utilization of active materials in the cathode. The sulfur in the cathode, except at the full charge state, is present as a solution of polysulfides in the electrolyte. The concentration gradients of the polysulfide species drive the intrinsic polysulfide shuttle between the electrodes, and lead to poor cyclability, high current leakage, and low charge/discharge efficiency. A portion of the polysulfide is transformed into lithium sulfide and deposited on the anode, which eventually leads to the complete loss of capacity of the sulfur cathode. The deposition of lithium sulfide also drives up the internal cell resistance because of the insulating nature of lithium sulfide. Recent reports suggest that porous carbons are the most promising materials for the sulfur cathodes: the cathode made of sulfur on mesoporous carbon shows an excellent rate performance while retaining good cyclability of the cathode at low sulfur loading, however, results in a low energy density; the cathode made of sulfur on microporous carbon shows an excellent cyclability but compromises the rate performance.

We report herein nanostructured sulfur-carbon composite cathodes that can significantly improve the cyclability of Li/S batteries and promote the utilization of sulfur in the battery cycles [1].

2. Experimental procedures

Preparation of the S/C composites. The mesoporous carbon (MPC) was synthesized through a soft-template approach reported by Liang et al with a minor modification[2]. After KOH activation, elemental sulfur was loaded to activated-MPC (a-MPC) through liquid phase infiltration by using a solution of 10 wt % sulfur in CS_2 . Sulfur loading was determined using thermal gravimetric analysis (TGA). A Micromeritic Gemini 275 system was used to measure the nitrogen adsorption isotherms. The specific surface areas

(SA) and pore size distributions (PSD) were calculated using the BET theory and the Barrett-Joyner-Halenda (BJH) method based on the adsorption branches of the isotherms.

Scanning electron microscopy (SEM) The specimens were dispersed onto a lacey carbon film supported on a 200-mesh Cu grid without using any dispersing agent, then analyzed using a Hitachi HF-3300 TEM/STEM with a Thermo Noran Si(Li) EDS detector at 300 kV and -120 °C.

Preparation of cathode and electrochemical evaluation. Slurries were prepared using the ball-milled S/C composite mixed with a solution of 1 wt % poly(vinylidene fluoride) (PVDF) in N-methyl-2-pyrrolidinone (NMP). Batteries were assembled as Swagelok cells by using the S/C composite coated aluminum foil as the cathode, and a lithium foil as the anode, a Celgard 3225 separator, and an organic electrolyte (bis-(trifluoromethane) sulfonimide lithium (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and dimethoxyethane (DME) with volume ratio of 55:40. The batteries were tested in a Maccor 4000 series battery tester, cycled between 1.0 to 3.6 V. Each cycle was started with the discharge half-cycle. The calculation of specific discharge capacities is based on the mass of elemental sulfur.

3. Results and Discussion

A bimodal meso/microporous carbon has been synthesized as a high-surface-area cathode material for Li/S batteries. The starting mesoporous carbon (MPC) is an electrically conductive material with a low electrical resistivity at 4 Ωcm . Illustrated in Fig.1, a uniform mesoporous carbon was activated using potassium hydroxide (KOH); the activated mesoporous carbon has a hierarchical structure with a bimodal pore size distribution of micropores (<2 nm) and mesopores (7.3 nm). The micropores are presented as intrawall porosity of the mesoporous frameworks. These two sets of pores were utilized to carry out two functions: (1) the micropores were used as microcontainers for elemental sulfur; the high surface area of the micropores provides sufficient contact to the insulating sulfur and conveys a high electrical conductivity to the composite material; and (2) the mesopores facilitate the transport of Li ions during the electrochemical cycling and accommodate the polysulfides and sulfide ions resulting from the electrochemical reactions. The large internal porosity and surface area of the meso/microporous carbon is essential for achieving the high utilization of sulfur.

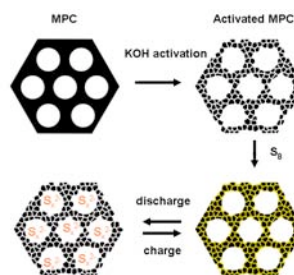


Fig.1 Illustration of the S/C composite cathode material by using a bimodal porous carbon as the support.

To demonstrate the advantageous properties of the S/C composites prepared from the a-MPC, we prepared two additional S/C composite cathodes: one using the original MPC containing only mesopores, and a second using WVA-

1500 (Mead Westvaco Corp.), an activated microporous carbon that contains mainly micropores. The surface area of WVA-1500 is 1760 m²/g, comparable to that of the a-MPC. The specific capacities of these cathodes are plotted versus cycle numbers in Fig.2. Sulfur content in samples S_C01 to S_C07 range from 12 to 52 wt%. The S/C composites prepared from mesoporous carbons including a-MPC and MPC had high initial discharge capacities. The initial discharge capacity decreased with the increase in sulfur loading: when the sulfur loading was 12 wt % (sample S_C01), the specific capacity of the initial discharge was as high as 1585 mAh/g, which was about 94.6% of sulfur utilization based on the theoretical maximum 1675 mAh/g; when the sulfur loading was 52 wt % (sample S_C07), the initial discharge capacity was 818 mAh/g. It is worth noting that the MPC supported S/C composite with 24 wt % S (S_C03) had an initial discharge capacity of 1136 mAh/g. Of striking contrast, the S/C composite prepared from WVA-1500 with 25 wt % S-loading displayed a very low initial discharge capacity of only 388 mAh/g. Therefore, the presence of mesopores accounts for the high initial discharge capacity. Although the MPC supported S/C composite had a high initial discharge capacity, it had a very fast decay of capacity in the following cycles. The capacity of the MPC supported S/C composite dropped to 163 mAh/g at the sixth cycle. The a-MPC and WVA-1500 supported S/C composites showed high retention of capacities in the cell cycling. The sample S_C01 retained a capacity of 805 mAh/g after 30 cycles; and the WVA-1500 supported S/C composites had a capacity of 154 mAh/g after 30 cycles; however, its initial discharge capacity was only 388 mAh/g.

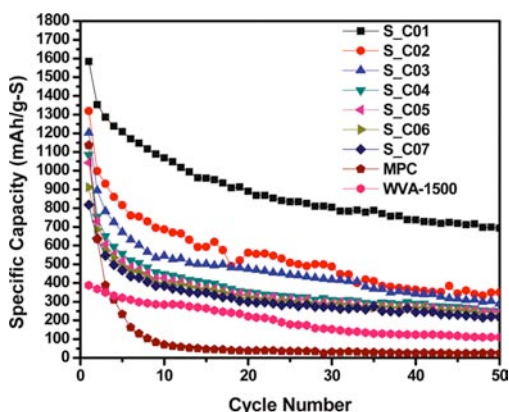


Fig.2 Specific discharge capacity of S/C composites that cycled in 1.0 M LiTFSI in DOL/DME (55:40) at 25 °C.

Shown in Fig.3 are the HRSEM images of the pristine bimodal porous carbon and the sample S_C02. The images confirm the porous nature of bimodal carbon before and after sulfur loading. These two images show undistinguishable difference in morphology because that the sulfur resides inside the micropores (pore size less than 2 nm), which are not able to be observed in these HRSEM images. Therefore, the comparison of the HRSEM images of the bimodal porous

carbon before and after sulfur loading is the direct evidence that the sulfur is loaded inside the micropores as we expected. This HRSEM observation coincides with the TGA and N₂ sorption measurements. Shown in panels C and D in Fig.3 are the elemental maps of carbon and sulfur for the S/C composite. These elemental maps confirm the sulfur is homogeneously distributed on the porous carbon.

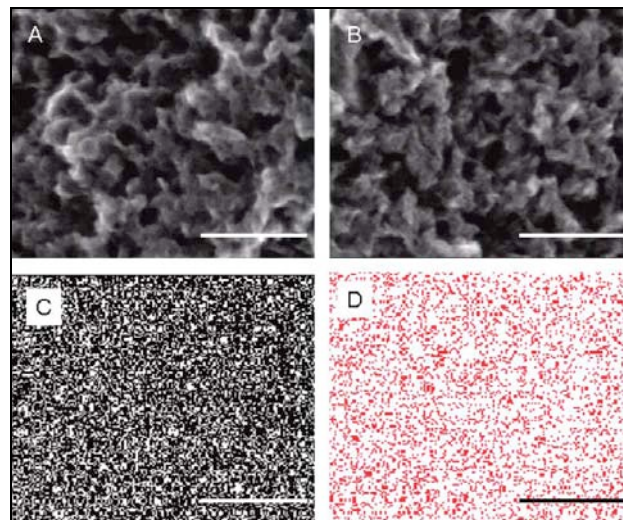


Fig. 3 HRSEM images of (A) the bimodal porous carbon and (B) the S/C composite with 18.7% sulfur loading. Elemental maps of (C) carbon and (D) sulfur of the S/C composite. Scale bars represent 50 nm.

4. Conclusions

This bimodal porous carbon material is a suitable substrate for the S/C composite cathode material that possesses advantageous properties of high-energy and high-power over the cathodes made of mesoporous carbon or microporous carbon. The promising performance of the bimodal porous carbon-supported S/C composite cathode is likely attributed to the synergetic effect of the hierarchically structured meso/micro-porosity: The microporosity gives high surface area and the micropore volume functions as a container that retains the sulfur species at the cathode region; the mesoporosity provides an avenue for the mass transport of Li-ions and thus confers a high ionic conductivity to the cathode. Therefore, the cells can be discharged and charged at a high current density without compromising the cell capacity.

Acknowledgments

Research sponsored by the LDRD program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC, for the U. S. Dept. of Energy (USDOE). CDL's work at the Center for Nanophase Materials Sciences at ORNL was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, USDOE.

References

- [1] Liang CD, Dudney NJ, Howe JY. Chem. Mater. 2009;21(19): 4724-4730 and references therein.
- [2] Liang CD, Hong KL, Guiochon GA, Mays JW, Dai S. Angew. Chem, Int. Ed. 2004; 43: 5785-5789.