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Fair performance comparison of different carbon blacks in lithium–sulfur batteries with practical mass loadings – Simple design competes with complex cathode architecture

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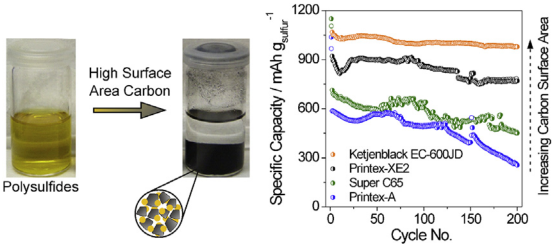
HIGHLIGHTS

- Electrolyte-to-sulfur ratio greatly influences the cycling performance.
- Nitrate is consumed continuously during cycling.
- Large amounts of nitrate are needed for long-term cycling performance.
- Carbon surface area correlates with polysulfide adsorption and specific capacity.
- High surface area carbons perform well (>800 mAh g_{sulfur}^{-1} at 1C over 600 cycles).

GRAPHICAL ABSTRACT



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ABSTRACT

The lithium–sulfur system is one of the most promising next generation battery systems, as elemental sulfur is cheap, abundant and has a high theoretical specific capacity. Although much research is conducted on complex sulfur/carbon composites and architectures, it is difficult to compare the performance of the cathodes to one another. Factors, such as different electrolyte composition and cell components strongly affect the cyclability of the battery. Here, we show the importance of optimizing "standard" conditions to allow for fair performance comparison of different carbon blacks. Our optimal electrolyte-to-sulfur ratio is 11 μL mg_{sulfur}^{-1} and high concentrations of $LiNO_3$ (>0.6 M) are needed because nitrate is consumed continuously during cycling. Utilizing these standard conditions, we tested the cycling behavior of four types of cathodes with individual carbon blacks having different specific surface areas, namely Printex-A, Super C65, Printex XE-2 and Ketjenblack EC-600JD. Both the specific capacity and polysulfide adsorption capability clearly correlate with the surface area of the carbon being used. High specific capacities (>1000 mAh g_{sulfur}^{-1} at C/5) are achieved with high surface area carbons. We also demonstrate that a simple cathode using Ketjenblack EC-600JD as the conductive matrix material can well compete with those having complex architectures or additives.

1. Introduction

The research and development of battery technologies for energy storage is of great importance, as our energy demands

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constantly increase. While Li-ion batteries have dominated the market since their introduction in the 1990s and have been improved significantly ever since, the physical energy density limit is almost reached [1]. Particularly, transportation is placing high demands on the energy density and a new generation of batteries is needed for extended range vehicles. At the present time, the lithium–sulfur battery system is one of the promising technologies as a power source because of sulfur's high abundance, making it inexpensive. Additionally, it has a high theoretical energy density of 2500 Wh kg^{-1} (or 2800 Wh L^{-1}) [2]. The working principle of lithium–sulfur cells and current challenges of this system are described comprehensively in several reviews [3–7]. Lithium is the only practical anode material to be used with the sulfur cathode thus far, as all other materials lead to a loss of energy capacity. Unfortunately, the use of lithium metal has severe drawbacks, like the steady consumption of electrolyte on freshly deposited lithium [8,9] and the polysulfide redox shuttle [10–13]. Briefly, the shuttle phenomenon can be noticed during charge: higher-order polysulfides diffuse away from the cathode where they should be fully oxidized and instead reach the anode where they are reduced to lower-order polysulfides. This results in overcharge of the battery and therefore low coulombic efficiency. The most efficient additive found up to date to reduce the polysulfide shuttle is lithium nitrate [8]. Commonly, some amount is added to the electrolyte. It seems to positively interfere as a solid electrolyte interface (SEI) stabilizing agent for lithium, although exact details on the mechanism are still under debate. A common hypothesis is that the nitrate, together with polysulfides, decomposes on the lithium surface forming an SEI layer [9]; eventually it is used up and thus the cell capacity fades at some point. Also, some of the nitrate can be lost on the cathode side during discharge below a potential of approx. 1.8 V [14]. We will discuss the aspect of nitrate consumption in more detail in this article.

Another critical component of the lithium–sulfur system is the leaching of polysulfides from the cathode. Recently, nanocomposite electrodes and complex carbon architectures have been reported in the literature, which improve the long-term cycling stability by encapsulation or coating of active material or enhanced adsorption of polysulfides within the composite cathode material [15–28]. Typically, these composite electrodes have low sulfur loadings (i.e., low areal capacities) or the loadings are not even mentioned and therefore become impractical for large scale applications. However, our group and others have shown the performance of highly loaded composite electrodes using e.g., nitrogen-enriched carbon as the host material [25,29–31].

Additionally, it has been shown that the electrolyte-to-sulfur ratio ($V_{\text{electrolyte}}/m_{\text{sulfur}}$, denoted as E/S in the following) is of great importance [32–34]. However, in all these works only small concentrations of nitrate were used and therefore low coulombic efficiencies were found or only a few cycles were shown. The performance of the lithium–sulfur cell is also dependent on the conductive carbon being used and most likely the Brunauer–Emmett–Teller (BET) surface area is a critical variable [35]. In the latter study, unfortunately, no lithium nitrate was used as an additive to demonstrate long-term performance.

Overall, the lack of standardized cell and cycling conditions and the use of different conductive carbons, binders and sulfur loadings make it virtually impossible to compare cathode performances to one another [34,36,37]. For this reason, we have established a standard cathode for lithium–sulfur batteries in our lab, which was previously reported [38]: a simple design, with a practical high sulfur loading of 2 mg cm^{-2}, containing a mixture of Super C65 and Printex-XE2 (1:1) as the conductive carbons and (poly)vinyl alcohol (PVA) as a binder. The electrolyte is composed of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (1:1), lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) as the conductive salt and lithium nitrate as a polysulfide shuttle suppressing additive. Herein, we report the systematic study of standard conditions for our cathode by varying the E/S ratio as well as the concentration of nitrate. With our optimized test conditions in the used coin cell design being an E/S ratio of 11:1 (μL:mg) and an electrolyte composition of 0.6 M $LiNO_3$ and 0.4 M LiTFSI we tested the effect of different carbon blacks, having different BET surface areas, on the cycling performance and specific capacity of the sulfur cathode. We chose Printex-A, Super C65, Printex-XE2 and Ketjenblack EC-600JD and compare the results to our standard. We finally show that a commercially available carbon can well compete with the performance of composite cathodes with complex architecture.

2. Experimental

2.1. Electrode processing and materials

For the preparation of the cathodes, sulfur (Aldrich, reagent grade) and either Printex-A (Evonik Industries), Super C65 (Timcal), Printex-XE2 (Orion) or Ketjenblack EC-600JD (AkzoNobel) in a ratio of 1.7:1 by weight were simply mixed by grinding (for the standard electrode Super C65 and Printex-XE2 were used in a ratio of 1:1). Poly(vinyl alcohol) Selvol 425 (Sekisui) dissolved in a mixed solvent of water, isopropanol and 1-methoxy-2-propanol was subsequently added to the blend. The amount of liquid was varied for each carbon black to optimize the consistency of the blend (more solvent is needed for higher surface area carbons). The resulting mixture was ball-milled for 20 h to form a homogeneous slurry. The slurry was then coated onto 8 μm-thick primed aluminum (as described elsewhere [38]) with a doctor blade and dried in vacuum at 40 °C for 16 h. The sulfur content in the final electrodes was 60 wt.% and sulfur loadings of 1.9–2.1 mg cm^{-2} (except 1.7 mg cm^{-2} for Ketjenblack EC-600JD) were obtained, as determined by weighing the electrodes before and after coating and knowing the nominal composition. Coin-type cells were assembled in an argon-filled glovebox using a polyethylene separator (Celgard EK2040) and lithium foil (China Lithium Ltd., 600 mm) as the negative electrode. The electrolyte was a solution of either 0.2, 0.4, 0.6, 0.8 or 1 M lithium bis(trifluoromethanesulfonyl)imide (Aldrich, 99.95%), and 0.8, 0.6, 0.4, 0.2 or 0 M lithium nitrate (Merck, 99.995%) keeping the total Li^+ ion concentration at a constant value of 1 M in a mixture of 1,2-dimethoxyethane (Alfa Aesar, 99+%) and 1,3-dioxolane (Acros, 99.8%) (1:1 by weight). The electrolyte-to-sulfur ratio was tested for 17:1, 11:1 and 7:1 (μL:mg) with the 0.6 M lithium nitrate composition. Prior to use, the solid electrolyte components were dried in vacuum and the solvents were purified by distillation from sodium potassium alloy under argon. The water content in the electrolyte was as low as 15 ppm, as determined by Karl Fischer titration.

2.2. Electrochemical testing

Electrochemical testing was done in a potential range between 1.7 V and 2.5 V with respect to Li/Li^+ using a MACCOR (Tulsa, Oklahoma) battery cycler. Prior to cycling, the batteries were kept at rest (open circuit) for 24 h to allow for equilibration. This resulted in a similar initial potential of each cell before cycling and therefore comparable conditions. After one cycle at C/50 (with 1C = 1672 mA g^{-1}_{sulfur}) was completed, the cells were cycled at charge and discharge rates of C/5, unless stated otherwise. All electrochemical experiments were carried out under stable environmental conditions in a BINDER cooled incubator.