

Key parameters determining the performance of lithium sulfur batteries

P. Pórolniczak*, M. Przybylczak, K. Wasiński, M. Walkowiak

Institute of Non-Ferrous Metals, Division in Poznań, Central Laboratory of Batteries and Cells, Forteczna 12, 61-362 Poznań, Poland

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Lithium sulfur battery is a promising electrochemical system offers high energy density of 2500 Wh kg⁻¹, which is almost five folds higher than those of state-of-art Li-ion batteries. However, commercialization of Li/S batteries still cannot be realized due to many problematic issues, such as poor electronic conductivity of sulfur, solubility of lithium polysulfides in organic electrolytes and the use of highly reactive metal lithium as anode. In this paper we discuss key parameters, in particular carbon/sulfur ratio, carbon porosity, sulfur loading and electrolyte volume, which impact the battery performance. We found that increasing the carbon content in the sulfur cathode from 20 to 40% resulted in 30% capacity improving of the Li/S battery. The optimized sulfur loading was found to be 2.2 mg S per cm² and electrolyte volume should not be lower than 75 µl per mg of sulfur.

Keywords: Lithium sulfur battery, sulfur cathode, activated carbon, electrochemical performance

INTRODUCTION

Lithium-ion batteries since their first commercialization of more than 20 years ago have dominated the market of chemical power sources for portable electronic devices [1-3]. However, the limited energy density and the theoretical capacity of the Li-ion battery and the growing demand and requirements of the market forces searching for other solutions.

Metallic lithium with the lowest density and the highest theoretical capacity (3861 mAh g⁻¹) is considered the best anode material. The elemental sulfur with a theoretical capacity of 1673 mAh g⁻¹ appears to be preferred opposite electrode for lithium. Lithium-sulfur battery can potentially reach energy density of 2 500 Wh kg⁻¹, which is up to five times higher compared to lithium-ion batteries [4-6]. Low cost, non-toxicity and the natural abundance of sulfur in the environment is also conducive to the growing interest of the scientists. Nevertheless, there are still several major issues facing rechargeable Li-S batteries that impede their practical application, which include: low charging efficiency, poor cyclic stability and high self-discharge rate [7]. Disadvantages of Li-S batteries result from a number of reasons. Sulfur has a poor electrical conductivity, and therefore composing the cathode a large amount of conductive additive has to be added, which reduces the amount of sulfur itself and reduces the energy density of the cell. The second major problem is the solubility of lithium polysulfides formed during the electrode reaction in organic electrolytes

and their migration towards the anode, wherein further reaction of lithium leads to the formation of insoluble and non-conducting Li₂S and Li₂S₂. These polysulfides are accumulated at the anode causing the corrosion and polarization, and thus reduce the amount of the cathode active material [8-10].

In our study the influence of key parameters on the performance of Li-S batteries has been investigated. The impact of active material content, coating thickness and type of carbon additive on the specific capacity and cycle stability of the Li-S batteries have been studied. Different electrolyte composition has been proposed and tested towards polysulfides dissolution and Li-S batteries performance.

EXPERIMENTAL

The sulfur/carbon cathode composites were prepared by manually mixing elemental sulfur and carbon in different weight ratios in an agate mortar. The S/C mixture was dispersed in sodium carboxymethyl cellulose aqueous (Sigma Aldrich) solution to form a slurry which was subsequently casted onto Al foil as a current collector. The resulting cathodes were dried at 60°C under vacuum for 24 h. The cathodes were assembled in an argon-filled glove box (MBraunLABstar) in Swagelok-type cells with metallic lithium as the anode and Celgard 2400 as the separator. The electrolyte was a solution of lithium trifluoromethanesulfonate (0.5 M, Sigma Aldrich) and of LiNO₃ (0.5 M, Fluka) in a 1:1 mixture of 1,2-dimethoxyethane (DME, Sigma Aldrich) and 1,3-dioxolane (DOL, Sigma Aldrich).

* To whom all correspondence should be sent.
E-mail: paulina.porolniczak@claio.poznan.pl

The cells were galvanostatically charged/discharged at a current density of 0.005, 0.05, 0.1, 0.5 and 1 C between 1.7 and 2.7 V vs. Li/Li⁺. Cyclic voltammetry experiments were carried out at the scan rate of 0.05 mV s⁻¹ also between 1.7 and 2.7 V. All electrochemical measurements were carried out using multi-channel VMP3 potentiostat/galvanostat (Bio-Logic).

RESULTS AND DISCUSSIONS

Sulfur has poor electronic conductivity thus it needs to be blended with a conducting agent, e.g. carbon black. High sulfur content in the cathode favors high energy density, however, too low carbon amount in the cathode will lead to the formation of electrically isolated islands in the electrode [11]. It is crucial to have a balanced carbon to sulfur ratio in the cathode. The performance of Li-S batteries using S/C cathode with different S/C ratio is shown in Fig. 1. The Li-S battery with cathode composed of 70% of elemental sulfur and 20% of carbon black delivered 450 mAh g⁻¹ in the first cycle at 0.05 C and the capacity decreases in the next 10

charge/discharge cycles. As the carbon content was increased to 40%, the capacity in the first cycle at 0.05 C increases to 580 mAh g⁻¹. The cyclic stability was also improved. Higher carbon content (above 50%) leads to obtain electrodes mechanically unstable.

High capacity and good cycling life of Li-S batteries depends also on the structure, surface area and pore size diameter of the carbon added to the sulfur cathode. Following the first sulfur-carbon composite proposed by Wang et al.[12], and further work of Nazar's group [13], the approach was adopted by various groups, and new research avenues were opened, based on the concept of sulfur confinement inside a porous carbon structure. This strategy was the most studied one during last four years, since it was believed to solve both issues simultaneously, drastically improved high rate cyclability due to enhanced electronic conductivity and inhibited polysulfides migration due to confinement of sulfur and adsorption properties of carbon [14-16].

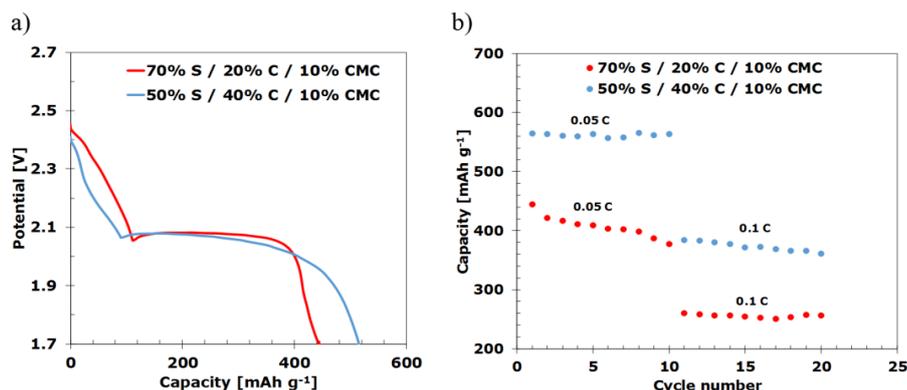


Fig. 1. a) Galvanostatic charge/discharge profiles of first cycle in the voltage window of 1.7-2.7 V at 0.05 C of S/C cathode with different S/C ratio, b) rate capability of S/C cathode with different S/C ratio

Three different carbons, depending on their porosity, were utilized as sulfur cathode component: carbon black, CMK-3 ordered mesoporous carbon and humic acid-derived mesoporous carbon (HAMC). CMK-3 and HAMC carbons have been synthesized according to procedures published elsewhere [17]. The carbon content in the cathode was 40% wt. The initial discharge profiles and cycling performance of S/C cathode with abovementioned carbons are shown in Fig. 2. The sulfur cathode with carbon black which is non-porous material with low surface area delivers capacity of about 550mAh g⁻¹ in the first discharge and the capacity significantly decreases with the next charge/discharge cycles. Surprisingly, sulfur

cathode with CMK-3 carbon, which is ordered mesoporous carbon with high specific area similar to HAMC carbon (see Table1), exhibits lower capacity of about 600 mAh g⁻¹ in comparison to 880 mAh g⁻¹ obtained for cathode with HAMC carbon. Such difference of electrochemical performance among S/CMK-3 and S/HAMC cathodes can be ascribed to the difference of pore size diameter and mesoporous structure perfection. Apparently, short range order with a significant amount of structural imperfections may favor faster mass transfer kinetics. Also relatively large pore diameter observed for HAMC (7.6 nm, in contrast with 3.8 nm for CMK-3) can facilitate sulfur species accommodation and release.

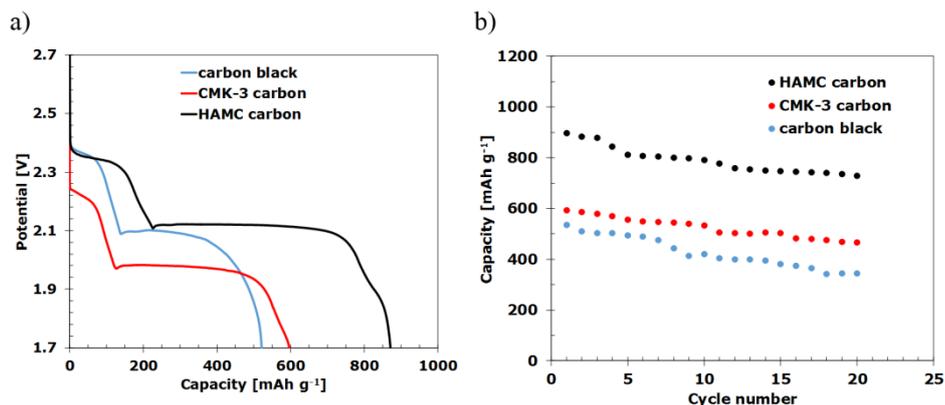


Fig. 2. a) Galvanostatic charge/discharge profiles of first cycle in the voltage window of 1.7-2.7 V at 0.05 C of S/C cathode with different carbon, b) cycling stability of S/C cathode with different carbon.

Table 1. Porosity data of different carbon materials used in sulfur cathode.

Carbon	Surface area [m ² /g]	Pore diameter [nm]
HAMC	670	7.6
Carbon black	45	Non-porous
CMK-3	740	3.8

The active material loading in electrode significantly impacts the energy density of an electrode. To improve energy density, the loading of sulfur and/or thickness of electrode can be increased. Sulfur/carbon black composites electrodes with different sulfur loadings were prepared using doctor-blade coating by changing blade thickness. Such obtained electrodes had increasing coating thicknesses (8, 16, 24, 28 μm), linearly proportional to the sulfur loadings (0.9, 1.7, 2.2, 2.7 mg S cm⁻²). The initial discharge profiles for S/C cathode with different sulfur loadings are displayed in Fig. 3 a). When the sulfur loading was increased from 0.9 to 2.2 mg cm⁻², the capacity per unit mass of sulfur was improved, from 541 mAh g⁻¹ to 752 mAh g⁻¹. But further increase of sulfur loading, to 2.7 mg cm⁻² resulted in a sharp capacity fade (394 mAh g⁻¹). The corresponding areal capacities at varied sulfur loading are calculated to be 0.49 mAh cm⁻² (0.9 mg cm⁻²), 1.02 mAh cm⁻² (1.7 mg cm⁻²), 1.65 mAh cm⁻² (2.2 mg cm⁻²) and 1.06 mAh cm⁻² (2.7 mg cm⁻²), respectively (Fig. 3 b). The cyclic stability of S/C cathodes with different sulfur loadings is presented on Fig. 3 c). The main problem with high loaded electrodes is the mechanical stability of the electrode. Thicker films from composite of sulfur and carbon are

brittle and tend to peel off from Al current collector. The second explanation of capacity fade in high loaded cathodes is the lithium polysulfides diffusion issue [18]. High loaded cathodes are thick and the polysulfides anions formed during discharge are unable to effectively diffuse out of the electrode. As a result, polysulfides anions stay on the carbon surface and isolate the remaining sulfur from the contact with carbon.

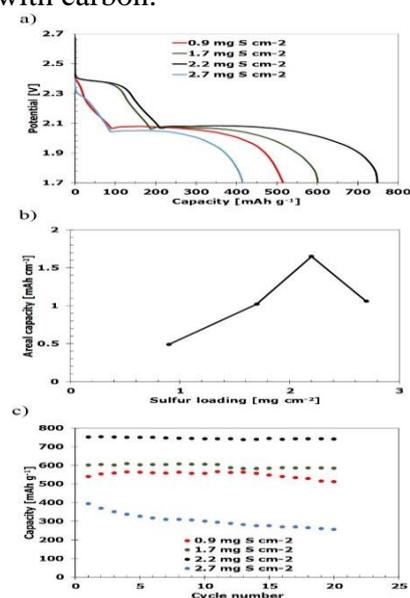


Fig. 3. a) Initial discharge voltage profile, b) areal capacity vs. sulfur loading curve, c) cycling performance of S/C cathode with different sulfur loading.

Electrolyte volume is another important parameter determining energy density and capacity of lithium-sulfur battery. Larger volume of the electrolyte better wet the electrode and dissolves more lithium polysulfides, but the brought-in drawback is the decrease of the energy density. The effect of the electrolyte volume on the capacity and cyclic stability is presented on Fig. 4. It can be seen that as the electrolyte volume was increased from 25

to 75 $\mu\text{l}/\text{mg S}$, the capacity increases from 115 to 500 mAh g^{-1} . As the electrolyte volume was further increased to 125 $\mu\text{l}/\text{mg S}$, the increase in capacity slowed down.

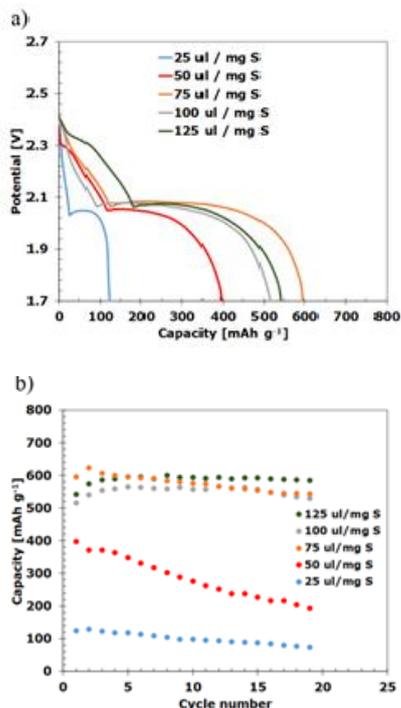


Fig. 4. a) Galvanostatic charge/discharge profiles of first cycle in the voltage window of 1.7-2.7 V at 0.05 C of S/C cathode with different electrolyte volume, b) cycling stability of S/C cathode with different electrolyte volume.

CONCLUSIONS

The performance of a Li-S battery is affected by multiple parameters such as electrolyte volume, carbon/sulfur ratio and sulfur loading, as well as the choice of carbon source. The development of a fully functional Li-S battery is a complex challenge to research and technology, and requires simultaneous optimization of a number of important parameters. At present, many problems remain unresolved,

despite intense efforts and the work carried out around the world.

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ОСНОВНИ ПАРАМЕТРИ, ОПРЕДЕЛЯЩИ ЕФЕКТИВНОСТТА НА ЛИТИЕВО-СЕРНИ БАТЕРИИ

П. Пулролничак, М. Пшибилчак, К. Васиньски, М. Валковиак

Институт за цветни метали, отдел в Познан, Централна лаборатория за батерии и клетки, 61-362 Познан, Полша

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(Резюме)

Литиево - сярната батерия е обещаваща електрохимична система, която предлага висока енергийна плътност от 2500 Wh kg^{-1} , което е почти пет пъти по-висока от тази на най-съвременните литиево-йонни батерии. Въпреки това, комерсиализацията на Li/S батерии все още не може да се осъществи поради съществуващи проблеми, като лошата електропроводимост на сярата, разтворимостта на литиевите полисулфиди в органичните електролити и използването на високо реактивен метален литий като анод. В тази статия са дискутирани основните параметри, по-специално съотношението въглерод/сяра, въглеродната порьозност, съдържанието на сяра и обема на електролита, които оказват влияние върху ефективността на батерията. Установено е, че увеличаването на количеството въглерод в серния катод от 20 до 40% води до подобряване на капацитета на Li/S батерия с 30%. Оптимизираното съдържание на сяра е $2,2 \text{ mg на S cm}^{-2}$, като обемът на електролита не трябва да бъде по-малък от $75 \text{ }\mu\text{l}$ на mg сяра.

Ключови думи: литиево - сярна батерия, серен катод, активен въглен, електрохимични характеристики.