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Effect of C/S ratio on the electrochemical properties of a Li-S cell

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Abstract

Lithium-Sulfur (Li-S) rechargeable batteries have gained a lot of attention since they have the potential to deliver high energy at low cost. However, before they can be deployed in commercial production, several problems associated with the use of a combination of sulfur and lithium metal still need to be resolved. The most significant problems include low conductivity of sulfur and its reaction products, lithium dendrite growth, sulfur electrode volume changes, and the shuttle effect. The combination of weak electronic and ionic conductivity of sulfur and its charge/discharge products with its poor electrochemical reversibility cause a relatively low-rate capability of Li-S cell. To improve the weak electrical conductivity, conductive additives, most often carbon, are added to the positive electrode material, thus reducing the sulphur content in the positive electrode volume at the expense of the conductive element. In this work, the impact of the C/S ratios on the performance of a Li-S cell is investigated.

Introduction

One of the fundamental drawbacks of using sulfur as an active material is its low potential vs. Li/Li+ and poor electrical conductivity (5×10^{-30} S cm^{-1} at 25°C) resulting from the fact that sulfur is an insulator **Chyba! Nenašiel sa žiaden zdroj odkazov.**. Due to its poor electrical conductivity and low electroactivity, sulfur has not been considered a suitable cathode material for low-temperature batteries in the past. Sulfur and its polysulfides (especially Li_2S_2 and Li_2S) exhibit poor ionic and electrical conductivity, which increases the internal resistance of the battery and deteriorates the reaction kinetics. This results in increased polarization, which reduces the resulting energy efficiency. In addition, during cycling, an insoluble passivation layer forms on the electrode surface that prevents further reduction, leading to impaired utilization of the active material [1].

Due to the insulating nature of sulfur and its products, the electrical conductivity is being increased by adding a conductive material to the electrode. To overcome the low conductivity, a large amount of carbon (up to 50 wt%) is often used, which results in low energy density cell. One of the crucial factors that significantly influences the electrochemical performance of the Li-S cell is the carbon-to-sulfur (C/S) ratio. Increasing the amount of carbon has been shown to improve the electrochemical properties of the Li-S cell, but together with the binder it forms an inactive part of the cathode, resulting in a decrease in the energy density [2]. However, as with Li-ion batteries, the aim is to reduce the amount of carbon down to 5% to ensure a high energy density Li-S batteries. Reducing the carbon content can affect several electrode properties and be beneficial in a number of ways [3][2]:

- **Porosity** – The density of carbon is very low and therefore its excessive use leads to highly porous electrodes. These electrodes often show good sulphur recovery, but a large amount of electrolyte is required to wet the entire electrode surface sufficiently, which increases the cell weight and reduces the energy density (increasing the electrolyte-to-sulfur [E/S] ratio).
- **Wettability** – Hydrophobicity of carbon impairs wettability by polar electrolyte. The high carbon content of the cathode material therefore limits the wetting of the active material by the electrolyte, resulting in poor ion transport and a reduction in cell capacity.
- **Bonding –** For efficient electron transfer it is important to create a good conductive path, which occurs when all electrode materials are sufficiently well bonded to each other. Non-polar carbon interacts poorly with polar polysulfides, leading to weak bonding and impaired electron transfer. This can lead to incomplete conversion of polysulfides to Li_2S and their release into the electrolyte, which causes the shuttle effect.

Most publications regarding the C/S ratio focus on the ratios of 0.5 and above. These high ratios often show an improvement in the electrochemical properties of the Li-S cell but are inapplicable to commercial Li-S pouch cells.

Experimental

Materials

The following materials were used to produce the positive electrode: Sulfur powder (Sigma-Aldrich, St. Louis, USA), Super P Carbon black (Timcal, Bodio, Switzerland) and CMC binder (CP Kelco, Atlanta, USA) in form of highly purified sodium carboxymethylcellulose. The electrolyte was prepared from 0,25M LiNO3 and 0,7M LiTFSI lithium salts dissolved in a mix of DME/ DOL (2:1) solvents (all Sigma-Aldrich, St. Louis, USA).

Preparation of the cells

First, cathodes with different S-C-Binder ratios were prepared by modifying the carbon and sulfur amounts in the slurry. The electrodes were prepared at a specified thickness; consequently, the sulfur loading in the cathode for each C/S ratio was different. Disc electrodes (Ø18mm) prepared from the slurries were placed in the electrochemical measurement cell (El-Cell®). Lithium metal (Ø16mm) was used as a counter electrode. The amount of electrolyte remained constant for all cells, which in effect means that the E/S ratio decreased with increasing sulphur loading. Selected properties of assembled Li-S cells can be seen in the table below.

Table 1. Li-S cell properties

S-C-Binder ratio [% wt.]	C/S ratio	Sulfur loading [mg cm^{-2}]	E/S ratio [µl mg^{-1}]
64-32-4	0,50	0,55	92
70-26-4	0,37	1,43	36
76-20-4	0,26	1,88	27
82-14-4	0,17	2,06	25
88-8-4	0,09	2,31	22

Electrochemical analysis

Assembled Li-S cells were subsequently subjected to electrochemical analyses. After initialization analyses, 50 cycles of galvanostatic cycling at variable loads (0.2C, 0.5C, 1C, 2C, 1C, 0.5C and again 0.2C) were performed (see Figure 1).

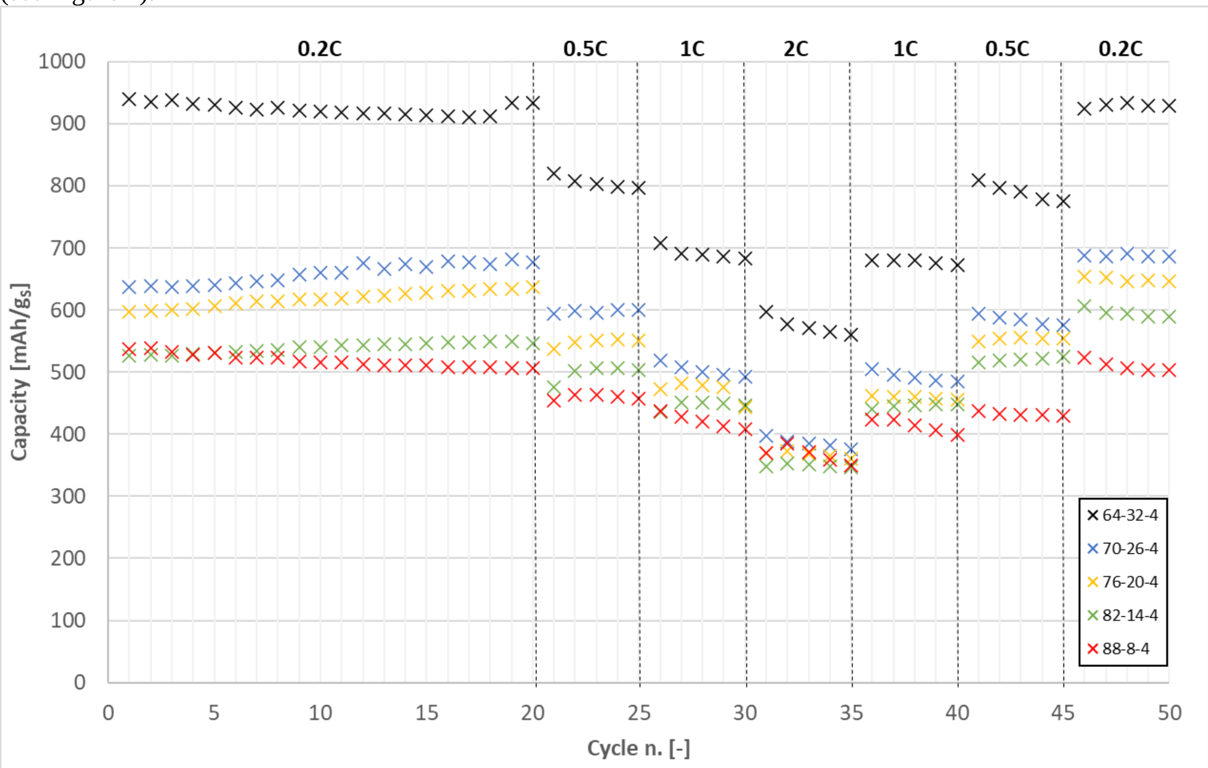

Figure 1. Specific discharge capacities of measured Li-S cells with different C/S ratio at different discharge rates

From the measured values of the specific discharge capacities, it can be seen that the electrode with the highest carbon content (32 wt.%) exhibits the highest capacity throughout the GCPL measurement, indicating the best sulphur utilization. As the carbon content decreases, the specific discharge capacities decrease, but the difference between the following cells is not so significant. The decrease in capacities in the first step of GCPL in response to decreasing carbon content is as follows: 940, 637, 598, 527 and 537 mAh g^{-1}. Thus, with decreasing carbon content, the sulfur utilization dropped from 56% to only 32%. It can be seen that in the first cycles of GCPL, the capacities of the electrode with the lowest carbon content (8% wt.) are slightly higher than the capacities of the electrode with the higher carbon content (14% wt.). However, towards the end of the GCPL cycling, this balances out and the electrode with the lowest carbon content shows the poorest sulfur utilization. The initial higher values can thus be attributed to the initial cell annealing. In the last step of GCPL, the decrease in capacities according to the decreasing amount of carbon is as follows: 929, 687, 646, 590 and 504 mAh g^{-1}. It is possible to notice a slight increase in sulfur utilization for electrodes with a moderately reduced carbon content (26% and 20% wt.). This phenomenon is not uncommon when using a given CMC binder. Based on the measured results, the dependence of sulfur utilization (at 0.2C) on the C/S ratio has been plotted (see Figure 2).

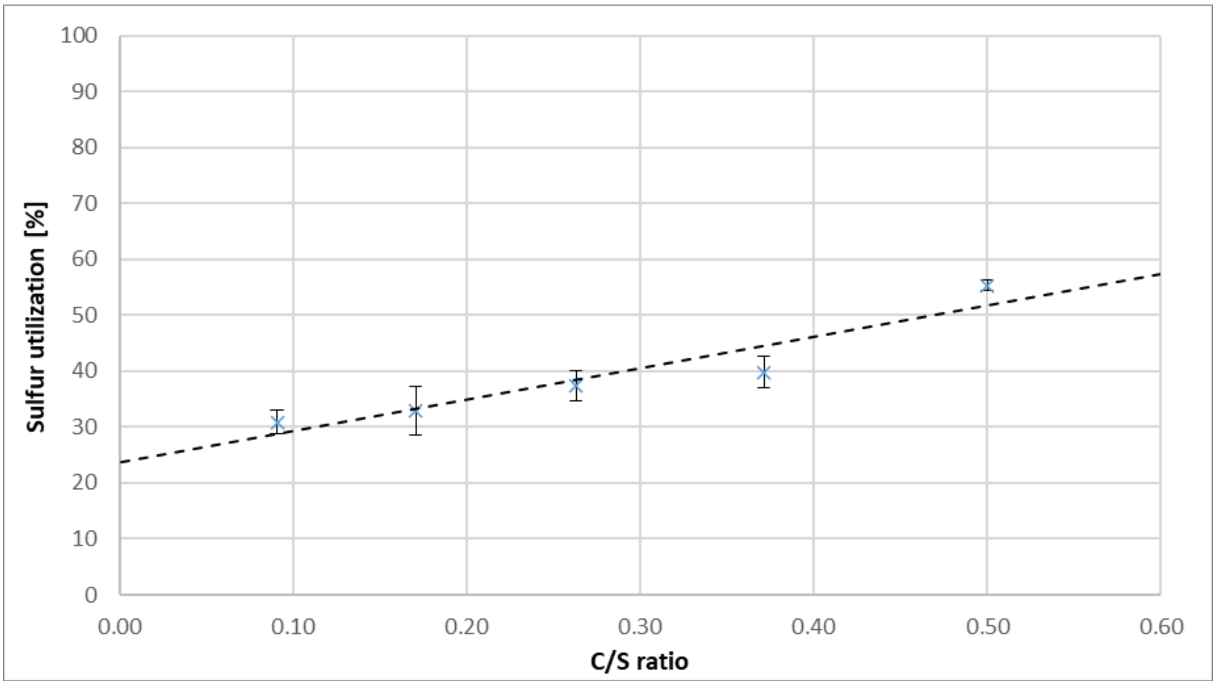

Figure 2. Dependence of sulfur utilization on C/S ratio (at 0.2C)

Figure 2 clearly shows the linear correlation of the sulfur utilization to the amount of carbon in the cathode material.

Conclusion

Five different C/S ratios were measured. The results show that the decreasing carbon content in the cathode has a significant negative effect on the sulfur utilization. However, this negative dependence can also be supported by the decreasing E/S ratio. To better understand this multi-parameter dependence, it is necessary to make multiple measurements where only one of these parameters will be altered.

Acknowledgements

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