

MODIFICATION OF THE PRODUCTION OF POSITIVE ELECTRODES FOR LITHIUM-SULFUR BATTERIES

Kamil Jaššo

Doctoral Degree Programme (1), FEEC BUT

E-mail: xjasso00@stud.feec.vutbr.cz

Supervised by: Marie Sedlaříková

E-mail: sedlara@feec.vutbr.cz

Abstract: The rapid development of electrical wearable devices and electric cars is forcing battery industry into developing more efficient and economic energy storage systems. One of the attractive candidates among these systems are Li-S batteries. These next-generation high-energy rechargeable batteries are promising mainly thanks to their high theoretical energy density and low cost. However, the safety concerns of lithium anode, insulating properties of sulfur and rapid drop of capacity during cycling due to dissolution of polysulfides are key limitations of practical use. A cell composed of metal lithium anode and carbon doped sulfur cathode in environment of *LiTFSI:LiNO₃ DME:DOL electrolyte can be considered a basic lithium-sulfur cell. This type of lithium-sulfur cell is used in many scientific publications. This paper discusses the production of positive electrodes for lithium-sulfur cells and modifications of their production.

Keywords: Battery, Accumulator, Compaction pressure, Li-S, Lithium, Sulfur, Cathode, Modification, Production, Galvanostatic cycling, GCPL

1 INTRODUCTION

Currently, Li-ion batteries are used in a significant number of portable electronic devices. Their advantage over the older type of batteries (namely Ni-Cd, Ni-MH and Pb batteries) is notably higher energy density and longer life. There are several types of commercially used lithium-ion batteries differing in used materials. Despite their considerable use in modern electronic devices, their specific capacity ceases to be insufficient mainly due to the development of electric vehicles.

One of the most important areas of research of lithium-ion batteries is researching of new high-capacity materials. The most promising materials include especially sulfur and oxygen as a positive electrode active materials. The results of this research are new types of batteries (Li-S and Li-air) with a much higher energy density than that achieved by conventional lithium-ion batteries. Their high energy density makes them particularly prospective for electric cars industry.

However, lithium-sulfur battery technology does not come without problems. The main deficiency of this technology is rapid loss of capacity due to dissolution of polysulfides during life cycle of lithium-sulfur battery. Among others, the next problem is a large volume change of sulfur during charging and discharging of the accumulator. This volume change causes mechanical stress, which may result in poor electrical contact between carbon and sulfur and decomposition of positive electrode's material. Intensity of these negative phenomenons depends on positive electrode material composition and method of its production. One of the major parts of the lithium-sulfur positive electrode production is the compression of electrode. In this paper, will be discussed impact of the compression pressure used in production of the positive electrodes on electrochemical parameters of the lithium-sulfur cell.

*LiTFSI - Lithium bis(trifluoromethanesulfonyl)imide

LiNO₃ - Lithium nitrate

DME - 1,2-dimethoxyethane

DOL - 1,3-dioxolane

2 LITHIUM-SULFUR ACCUMULATOR

Unlike lithium-ion batteries, lithium-sulfur accumulators do not operate on the principle of intercalation process, but they work as a conversion type of batteries, which means that electrochemical reactions are involved in charging and discharging of the accumulator.

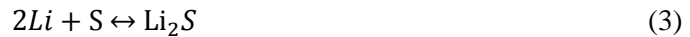
The negative electrode reaction:



The positive electrode reaction:



The overall reaction (\rightarrow discharging, \leftarrow charging):



The reactions described above (1-3) are simplified. In its most stable form, sulfur forms a molecular structure with a density of 2.07 g/cm^3 comprised of stacked eight atom rings (Li_2S density is 1.66 g/cm^3). During the discharge of the cell, the bonds are cleaved to open S_8 ring forming sulfur chain and lithium ions are accepted. After the formation of the polysulfide chain, further fragmentation occurs, leading to reduction of the chain length and creation of other polysulfides Li_2S_x . The actual overall redox reaction should be described as: [1][4]

The actual overall reaction (\rightarrow discharging, \leftarrow charging):



Sulfur as the active material of the positive electrode of lithium-sulfur batteries is particularly promising for its high theoretical capacity of 1672 mAh/g . From the economic perspective, sulfur is a low-cost and highly available material. These properties make it an attractive material for the positive electrodes.[1][2]

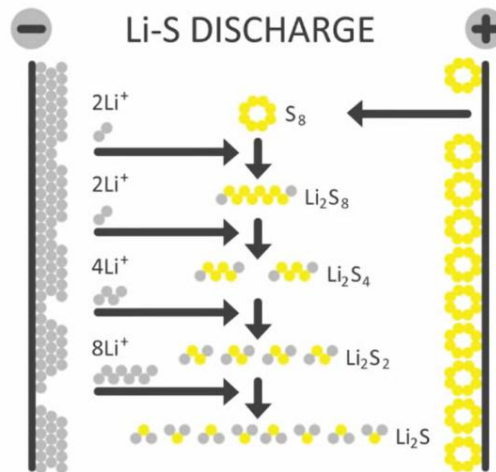


Figure 1: Electrochemical reactions occurring in a lithium-sulfur cell during its discharge. [5]

The electrochemical reactions occurring in lithium-sulfur batteries during life cycle are briefly shown in Figure 1. Li_2S forms during discharge by gradual transition from S_8 through polysulfides Li_2S_x ($2 \leq x \leq 8$) to Li_2S . Some of these intermediate products are soluble in the electrolyte and deposited on the surface of the lithium electrode, which results in a loss of active cathode material, the anode passivation and a rapid drop of capacity during cycling of the lithium-sulfur cell. Cycling of the lithium-sulfur cell causes also large volume differences due to different densities of S_8 and Li_2S .

Volume change of the material is circa 80% which causes high mechanical stress resulting in loss of electrical contact with conductive substrate or the current collector. [1][3][4]

3 EXPERIMENTAL TECHNIQUES

A range of techniques have been used to probe the operating mechanisms of Li-S cells, including electrochemical investigations and spectroscopic studies such as energy dispersive spectroscopy (EDS) in a SEM microscope. Methods such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), open-circuit voltage (OCV) and galvanostatic cycling (GCPL) were used for electrochemical analysis.

4 EXPERIMENTAL

For the purpose of this experiment, several positive electrodes were made. Material composition of these positive electrodes is shown in Table 1.

Percentage	Material
60%	Sulfur $\geq 99.5\%$
30%	Super P Carbon Black
10%	PVDF

Table 1: Material composition of positive electrodes used in experiment

Selected samples of positive electrodes were analyzed under the scanning electron microscope to observe the surface structure and to validate their identity. Analysis of the elemental distribution on the surface of sample electrodes confirmed the consistency of their layout. The surface structure and elements layout of one of the electrode samples is shown in Figure 2.

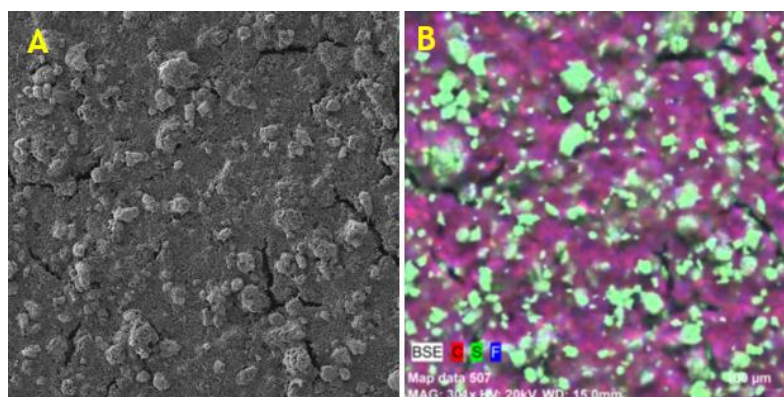


Figure 2: A) Surface structure (field of view 415 μm) and B) Elements layout (C, S, F) of the uncompressed electrode

Created positive electrodes were inserted in the standard electrochemical measuring cell (E1-Cell[®]). As a counter electrode, metallic lithium was used separated by a glass separator. Li-S cell was encapsulated in an environment of LiTFSI/LiNO₃ (DME:DOL = 1:1) electrolyte.

The assembled E1-Cell[®] was connected to the multi-channel potentiostat (Biologic VMP3) and measurements were carried out. First, OCV took place to determine the cell voltage. Next, electrochemical impedance spectroscopy was measured. Third, four cycles of cyclic voltammetry with 0.1 mV/s scanning rate and 1.8 – 3.0 V potential window were measured. Voltammograms of cyclic voltammetry were relatively stable, but with clearly visible capacity losses. All measured voltammograms were approximately the same as in the scientific literature. After cyclic voltammetry, two cycles of galvanostatic cycling were measured to determine the cell capacity. A potential window was set in the range of 1.8 – 2.8 V. Charge/discharge current was set to 0.1C provided that the active material

capacity is 1200 mAh/g. Capacity reached during the second cycle was used to determine charge/discharge current for the subsequent galvanostatic cycling. Finally, twenty cycles of galvanostatic cycling at 0.2C were measured followed by five cycles at 0.5C, 1C, 2C and again 1C, 0.5C and five cycles at 0.2C current. Figure 3 shows the measured results of galvanostatic cycling of samples of electrodes.

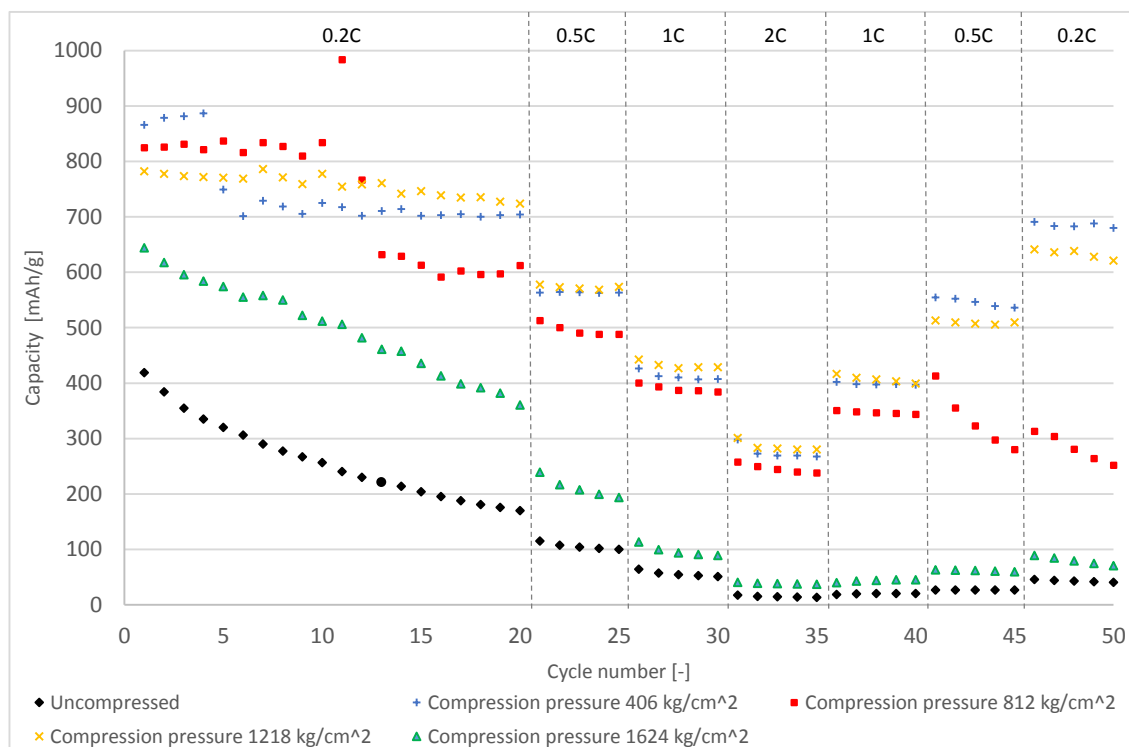


Figure 3: Comparison of galvanostatic cycling of the electrode samples.

5 RESULTS AND DISCUSSION

The comparison of galvanostatic cycling of the electrode samples (Figure 3) shows that:

- The uncompressed electrode reaches the lowest capacity
- The highest capacity in the first cycle of the galvanostatic cycling showed the electrode compressed by pressure equal to 406 kg/cm²
- The most stable in terms of cycling is the electrode compressed by 1218 kg/cm²
- The best return to the initial values of capacity has electrode compressed by 406 kg/cm²
- The electrode compressed by 1624 kg/cm² is approaching to the uncompressed electrode
- During the galvanostatic cycling of the electrodes compressed by 406 and 812 kg/cm², a sudden drop in capacity occurred due to the breakdown of cohesion of the material under mechanical stress
- In the 11th cycle of galvanostatic cycling of the electrode compressed by 812 kg/cm² a short circuit occurred, leading to mechanical stress in the structure and a significant decrease of capacity in the next cycle

It can be seen, from the measured results shown in the Figure 3, that it is important to choose the right compression pressure when manufacturing the electrodes. Too low pressure is not sufficient for a strong electrode structure and leads to a rapid disintegration of electrode material during cycling. On the contrary, too high pressure closes the pores of the structure against the intrusion of lithium

ions which leads to lower capacity. Higher pressures also caused delamination of the electrode material from the current collector.

From the measured results so far, it is clear that further research should be focused on finding a breaking pressure, at which further increase leads to a reduction in capacity.

6 CONCLUSION

From the research that has been up to now carried out, we can conclude that the amount of pressure used to compress the positive electrode has a significant impact on the electrochemical parameters of the lithium-sulfur cell. It was found that the effect of compression pressure follows a certain pattern. Using the higher pressure leads to strengthening the structure whereupon stability is improved. However, using too high compression pressure will close the pores of the structure and cause a decrease in capacity. Higher compression pressure in the production of electrodes also leads to delamination of the active material from the current collector, which can be considered as undesirable.

ACKNOWLEDGEMENT

This work was supported by the Internal Grant Agency of Brno University of Technology, grant No. FEKT-S-17-4595.

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