

# PREPARATION OF ELECTRODES OF LI-S BATTERIES USING INVERSELY VULCANIZED SULFUR

**David Trochta**

Bachelor Degree Programme (3), FEEC BUT

E-mail: [xtroch00@stud.feec.vutbr.cz](mailto:xtroch00@stud.feec.vutbr.cz)

Supervised by: Ondřej Čech

E-mail: [cechondrej@feec.vutbr.cz](mailto:cechondrej@feec.vutbr.cz)

**Abstract:** This paper focuses on manufacturing of Li-S batteries, which in theory have higher energy density than the currently most popular Li-ion battery. Before putting the Li-S battery on the market, several problems which prevent its practical use have to be solved. These issues include short longevity, which could be solved by manufacturing the electrode using inversely vulcanized sulfur. This method could eliminate the immediate issue and enable the rise of the Li-S battery on the market.

**Keywords:** Li-S battery, inverse vulcanization, inversely vulcanized sulfur, electrochemistry

## 1 INTRODUCTION

We can notice a rising trend of mobile electronic assets in today's quickly developing world. Be it in phones or new models of electric cars, the demand for new types of batteries is becoming apparent, batteries which are able to satisfy and keep up with the growing demands of the current age.

The answer could be a battery composed of the combination of lithium and sulfur (Li-S). Due to its on-paper energy density, which goes up to 2600 Wh/kg, it is considerably higher than the currently most popular lithium-ion (Li-ion) batteries which only boast on-paper energy density of up to 600 Wh/kg. However, there are standing issues which cause low longevity of the Li-S battery still waiting to be solved [1].

Solution to this problem could come in the form of amorphous sulfur, which can be obtained using inverse vulcanization. The final product - inversely vulcanized sulfur (IVS) is more stable and and resilient to backwards recrystallization, which makes it a particularly fitting material for manufacturing of the Li-S battery [2].

## 2 Li-S BATTERY

The Li-S battery is a promising candidate for the next generation of electric energy storage systems. It has taken a lead position namely thanks to its high on-paper energy density combined with its low cost. In practice, values of up to 600 Wh/kg have been achieved so far. Its theoretically high energy density is rooted in the conjunction of lithium and sulfur. The cathode which is made of sulfur has on-paper capacity of 1675 Ah/kg. In the case of metal lithium, its on-paper capacity is exactly 3860 Ah/kg [1].

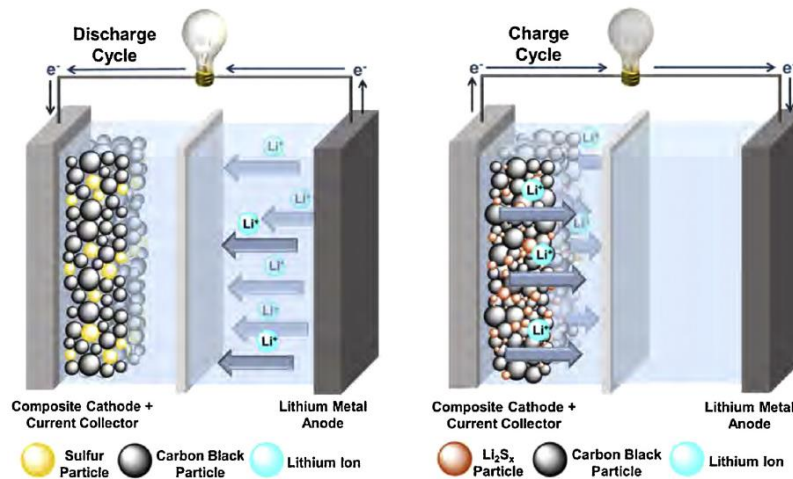
Despite the many advantageous properties of elemental sulfur, no-one has been able to create an optimal cell when it comes to its technical parameters (especially longevity) and thus compete with the currently dominant Li-ion batteries. Issues of the Li-S battery can generally be divided into three groups. First issue is the low electrical conductivity of elemental sulfur itself and its products. (i.e.  $\text{Li}_2\text{S}$ ). Second is migration of higher polysulfides through the separator and its reactions with the lithium anode (the so-called sulfur shuttle effect). These polysulfides consequently reduce the effective area of the lithium anode and contribute to the decrease of conductivity. The last of the

serious issues is cracking and disintegration of the electrode due to thermal expansion. During the cyclical conversion of  $S_8$  and  $Li_2S$  the volume of the electrode changes by 79%. Noteworthy is also the fact that carbon added into the cathodic slurry decreases the theoretical maximum energy density of the cell. For this reason, optimized sulfur/carbon ratio is needed to be achieved, as to keep the amount of sulfur as high as possible while preserving sufficient electrical conductivity.

## 2.1 PRINCIPLE OF THE LI-S BATTERY

A traditional Li-S cell has the same internal structure as common batteries. The casing, which protects the internal components against mechanical damage and oxidation, contains the cathode (composite of sulfur and carbon), anode (metal lithium) and the separator, which separates both electrodes and prevents short-circuiting in between. The separator is filled with electrolyte - usually lithium salt dissolvable in organic solvents [2].

The internal process of charging and discharging itself is depicted in Image 1. It is apparent from the image that as soon as the electrons begin to flow through the outer circuit, lithium ions simultaneously start to break loose. These lithium ions then diffuse through the separator using the electrolyte and get stuck to the cathode. On the cathode, the reactions between sulfur, lithium ions and electrons are realized, consequently leading to conversions. During charging, the whole process is inverted - polysulfides convert back to sulfur and the lithium ions as well as the electrons return to the anode [2].



**Image 1:** Charging and discharging principle of the Li-S cell [2].

## 3 INVERSE VULCANIZATION

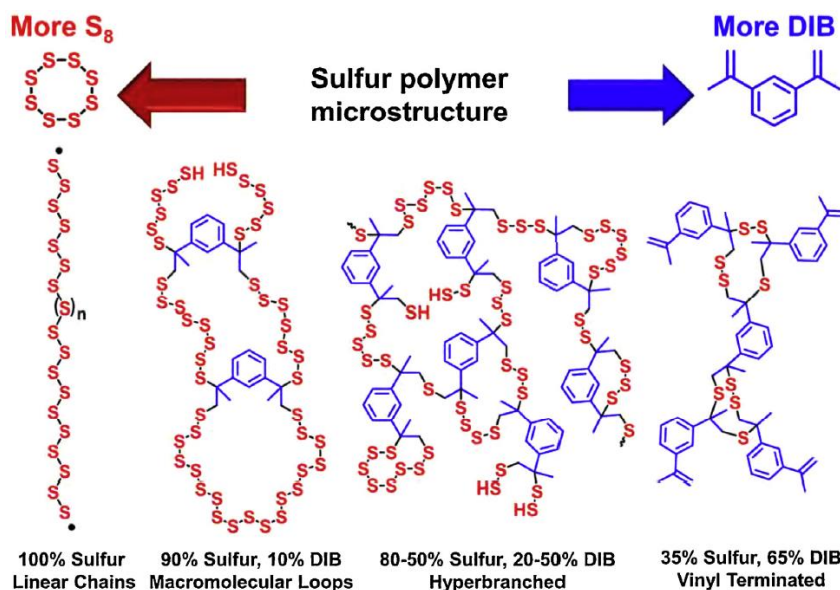
During traditional vulcanization, which is used to process natural rubber, sulfur creates bridges between sections of polymer chains. The situation during inverse vulcanization is similar, however the roles are different. Sulfur is the main material and a stable co-polymerous product is created using a crosslinker in this case, which is resistant to backwards depolymerization [2; 3].

Inversely vulcanized sulfur is also able to change its physical properties, including Young's modulus, tensile strength and refractive index (up to 1.8). Therefore the resulting material can additionally see value in application as a thermal insulator, infrared optic materials, or a cleaning material for water sources and natural environments.

### 3.1 PROPERTIES OF INVERSELY VULCANIZED SULFUR (IVS)

The final properties of IVS are affected particularly by the type and the amount of crosslinker used (sulfur and crosslinker weight percentage ratio). In general, the final form depends on the structure, as seen in Image 2. The first case contains only pure sulfur, which forms a linear polymer chain.

While in the case of the structure containing 90 wt. % of S and 10 wt. % of 1,3-diisopropenylbenzene (DIB) formation of macromolecular loops can be observed. Should more DIB be added, a so-called hyperbranched structure will be created. In the last scenario, a vinyl grouping is attached to the ends of the sulfur chains.



**Image 2:** Schematic of the IVS microstructure based on various S and DIB ratios [2].

### 3.2 MANUFACTURING OF INVERSELY VULCANIZED SULFUR

Manufacturing of IVS involves elemental sulfur and DIB crosslinker. The process begins by heating the elemental sulfur, which is placed in a vial along with a magnetic stirrer. The vial is then placed in an oil bath, which is heated until it reaches the temperature of 185°C. Before reaching the desired temperature however, several changes can be observed. The first change happens at the temperature of around 124°C when the elemental sulfur melts to become a yellow liquid. While rising the temperature, its color gradually changes from yellow, then light red until it becomes crimson red. As the temperature reached 185°C we added DIB into the vial and left the mixture to stir. The mixture immediately changed color back to yellow, but over the time it became crimson red again. The mixture was kept at 185°C for the following 24 hours.

Using this method we were able to prepare samples of IVS containing various ratios of input precursors. Specifically speaking S:DIB 70:30, 60:40 and 50:50 wt. %. We also attempted to create a S:DIB 80:20 wt. % sample, but this sample was crosslinked incorrectly - became plastic and sticky. IVS samples containing various ratios of input precursors do not vary in color. Subsequently we verified the internal structure using x-ray diffraction (XRD).



**Image 3:** IVS sample containing a ratio of S:DIB 70:30 wt. %.

## 4 ELECTRODE PREPARATION

To prepare the electrode slurry, it is necessary to grind down IVS into a powder. A vibration mill was used for this purpose with IVS being placed inside for 30 minutes to grind. Before the grinding itself the mill container along with IVS was put into a freezer to achieve higher brittleness of IVS and therefore higher grinding quality.

Afterwards, a mixture of IVS powder was prepared, Super P carbon and CMC (carboxymethylcellulose) binder in a ratio of 60:30:10 wt. %, with demineralized water being used as a dissolvent for CMC. The mixture was thoroughly mixed using a planetary mill by means of three 10 mm-diameter grinding balls, with a stirring speed of 350 revolutions per minute. The stirring was not continuous however, instead it included breaks during which the container cooled. Should these breaks be omitted from the mixing process, there's a risk of the mixture melting together as a result of high temperatures. The mixing duration without accounting for breaks was 8 hours. After the planetary mill procedure, a full week of additional mixing using a magnetic stirrer followed.

Upon processing the electrode slurry this way, it was coated onto an aluminum foil (current collector) using a coater and left to dry. First, the drying was done at room temperature and later proceeded in a dryer at the temperature of 50 °C. This step was necessary to prevent the cracking and peeling of the coated electrode slurry layer. The thickness of this layer was 100 µm. The drying was followed by cutting 18 mm diameter electrodes out of this coated foil and their consequent pressing using a force of 1600 kg/cm<sup>2</sup>.

## 5 CELL ASSEMBLY

The last step of the manufacturing process of the cell is its assembly within a glovebox containing an argon atmosphere. This argon atmosphere is necessary particularly due to the reactive nature of lithium. The assembly itself proceeds by forming a so-called electrochemical cell, which gets hermetically closed off in the box and thereafter it is able to be safely manipulated with and measured. The cell contains a lithium anode and the examined cathode. The electrodes are divided via a separator, which is filled with electrolyte. Then, the galvanostatic cycling with potential limitation (GCPL) and the electrical impedance spectroscopy (EIS) methods are used in order to test the cell.

## 6 CONCLUSION

In this project we presented a manufacturing process of inversely vulcanized sulfur which uses the 1.3-diisopropenylbenzene (DIB) crosslinker, carried out using various ratios of input precursors. Utilizing our method, we successfully synthesized IVS containing ratios of S:DIB 70:30, 60:40 a 50:50 wt. %. Subsequently, we described a process of electrode manufacturing optimized particularly for inversely vulcanized sulfur. Through this approach, we have proved that electrodes which use IVS as its active material can work and thus possess potential for further research.

## REFERENCES

- [1] LIU, Tiefeng, Hualiang HU, Xufen DING et al. 12 years roadmap of the sulfur cathode for lithium sulfur batteries (2009–2020). *Energy Storage Materials* [online]. 2020, **30**, 346-366 [cit. 2021-03-12]. ISSN 24058297. Accessible from: doi:10.1016/j.ensm.2020.05.023
- [2] GRIEBEL, Jared, Richard GLASS, Kookheon CHAR a Jeffrey PYUN. Polymerizations with elemental sulfur: A novel route to high sulfur content polymers for sustainability, energy and defense. *Progress in Polymer Science* [online]. 2016, **58**, 90-125 [cit. 2021-03-12]. ISSN 00796700. Accessible from: doi:10.1016/j.progpolymsci.2016.04.003
- [3] CHUNG, Woo Jin, Jared J. GRIEBEL, Eui Tae KIM, et al. The use of elemental sulfur as an alternative feedstock for polymeric materials. *Nature Chemistry* [online]. 2013, **5**(6), 518-524 [cit. 2021-03-12]. ISSN 1755-4330. Accessible from: doi:10.1038/nchem.1624