

# INFLUENCE OF AMBIENT TEMPERATURE ON ELECTRO-CHEMICAL PARAMETERS OF LITHIUM-SULFUR BATTERIES

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**Abstract:** With the increasing popularity of electric vehicles, the demand for their range is increasing and thus demand for the batteries that power them. Range of current electric vehicles using Li-ion battery technology is around 250 miles (400 km). In the case of use of new prospective next-gen batteries such as Lithium-sulfur (Li-S) range of the electric vehicle may be doubled or even tripled. However, there are many challenges ahead of using these batteries in electric vehicles. Since the batteries in electric vehicles are largely affected by ambient temperature, this article deals with re-searching the effect of ambient temperature on lithium-sulfur batteries.

**Keywords:** Accumulator, Battery, Cathode, Li-ion, Li-S, Lithium, Lithium-ion, Lithium-sulfur, Sulfur, Temperature

## 1 INTRODUCTION

To increase the demand and acceptance of electric vehicles (EV's) among the public, there is a need to overcome two major shortcomings: insufficient range and expensive purchase price. Since the driving range of electric vehicles is highly dependent on their energy storage, there is a demand for a low cost and safe battery system with high specific energy.

Currently, the range of most popular electric vehicle (Tesla Model S) is around 250 miles (c. 400 km) when using an 80 kWh Li-ion battery pack. The 80 kWh battery pack of Tesla S contains around 7000 NCA<sup>1</sup> cells and weights approximately 500 kg which gives specific energy around 160 Wh/kg. In the case of replacement of Li-ion batteries with their Li-S dimensional equivalents, whose current specific energy is estimated around 500Wh/kg, theoretically the range of electric vehicles should triple. Moreover, since most of the Li-S battery materials are abundant, this technology has the potential of being cheaper than Li-ion batteries. Since the Li-S battery potentially fulfills all requirements for the EV batteries, it is a prospective replacement of the current Li-ion battery technology.

However, lithium-sulfur battery technology is still in research phase and before deployment to the commercial sector, certain shortcomings need to be overcome. Among the biggest shortcomings of this technology are the large volume change during cycling and the loss of capacity caused by the dissolution of some of the cycling intermediates in the electrolyte and their subsequent deposition on the negative electrode. As a result, there is a constant decrease in capacity during cycling. This decrease is highly dependent on the conditions of cycling of the battery and external conditions. Given that electric vehicles must endure different conditions during their operation, it imposes a high requirement on their batteries.

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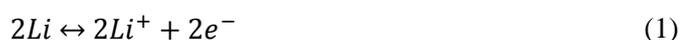
<sup>1</sup> Li-ion battery with LiNiCoAlO<sub>2</sub> electrode

## 2 ELECTROCHEMISTRY OF LITHIUM-SULFUR ACCUMULATOR

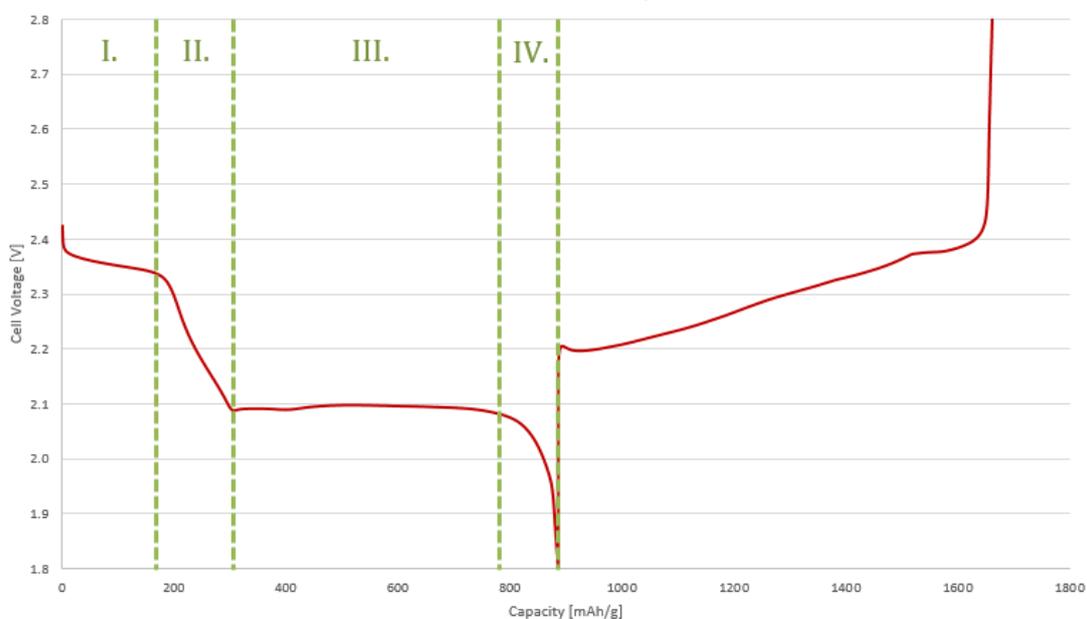
A typical lithium-sulfur battery is composed of metallic lithium on the side of negative electrode and sulfur-containing cathode material on the side of positive electrode. Due to the use of electrodes with high theoretical capacities (Lithium – 3860 mAh/g, Sulfur – 1672 mAh/g) and average working voltage of ca. 2.1 V, Li-S is a good candidate for high specific energy battery system. Sulfur has the great variety of molecular forms; therefore, the allotropy of sulfur is complex. The most wide-spread and most stable allotrope of sulfur in nature is the orthorhombic  $\alpha$ -form  $S_8$  molecule (cyclo-octasulfur) in the shape of a ring or “crown”. The  $\alpha$ -form  $S_8$  has a density of 2.069 g/cm<sup>3</sup> and is a great electrical insulator. Since sulfur is an insulator and therefore has weak conductivity ( $1 \times 10^{-15}$  S/m), the cathode material must contain a conducting element (most commonly carbon) and hence a binder (most commonly PVDF<sup>2</sup>). [1][2]

Unlike lithium-ion batteries, which are working on the principle of the intercalation process, the lithium-sulfur battery is the conversion type of the battery, thus its discharging and charging process involve electrochemical reactions. During discharging, the sulfur molecule ( $\alpha$ -form  $S_8$ ) reacts with lithium ions by a two electron reduction process to form a polysulfide intermediates ( $Li_2S_x$ ,  $2 \leq x \leq 8$ ) and to generate lithium sulfide ( $Li_2S$ ) as the final element of the discharge reaction.[2]

The negative electrode reaction:

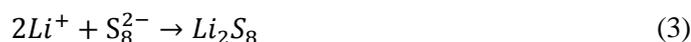


The positive electrode reaction:



**Figure 1:** A typical discharge-charge voltage spectrum of Li-S cell

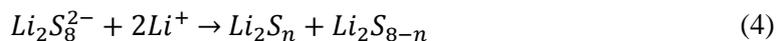
Figure 1 shows a typical discharge and charge characteristic of Li-S cell, which is divided into four reduction regions. In the first region, a solid-liquid reduction occurs from elemental  $\alpha$ -form  $S_8$  to  $Li_2S_8$ , forming the first upper plateau (at 2.2 – 2.3 V). However, liquid  $Li_2S_8$  dissolves into electrolyte to become a liquid electrode, which leaves numerous voids in the positive electrode material. [3]



In the second region, a liquid-liquid reduction from  $Li_2S_8$  to lower polysulfides occurs, during which voltage declines and electrolyte viscosity gradually increases while the polysulfides chain length

<sup>2</sup> PVDF – Polyvinylidene fluoride

shortens. Electrolyte reaches a maximum viscosity at the end of the region. This region together with first region shows the highest shuttle effect during which Li-S cell suffers from the highest self-discharge. [3]



Third region represent liquid-solid reduction from low-order polysulfide chains to insoluble  $Li_2S_2$  or  $Li_2S$  and second lower potential plateau is formed (at 1.9 – 2.1 V). These reactions mostly contribute to the resulting capacity of Li-S cell. [3]



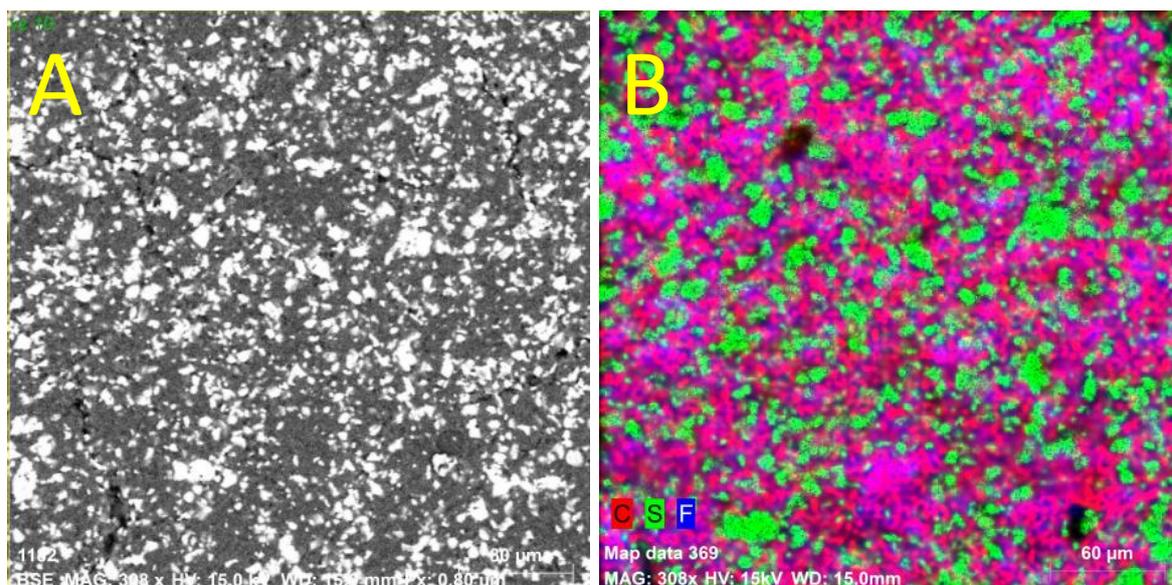
In last region, there is a solid-solid reduction during which last residues of  $Li_2S_2$  reduce to  $Li_2S$ . This reduction suffers from high polarization due to the insulant and insoluble nature of  $Li_2S_2$  and  $Li_2S$  and is kinetically slow. If reactions (6) are predominant in the third region, the cell reaches a higher capacities and last region becomes very short or even vanishes. [3]

Some of intermediates, which dissolves in the electrolyte are deposited on the surface of the metallic lithium counter-electrode, which results in so-called shuttle effect (or shuttle phenomenon). Shuttle effect results in passivation of metallic lithium electrode and loss of active material of positive electrode, which will reflect in self-discharging of the cell and lower coulombic efficiency. [2][3]

Another shortcoming of lithium-sulfur battery technology is a considerable volume change (circa 80%) during cycling of the cell, resulting from the fact that the final discharge product  $Li_2S$  has a different density ( $1.66 \text{ g/cm}^3$ ) than the initial  $\alpha$ -form  $S_8$ . This volume change causes an internal stress on the electrode material resulting in its disintegration and loss of conductive contact between electrode material and current collector and electrode material itself. [2][4]

### 3 EXPERIMENTAL

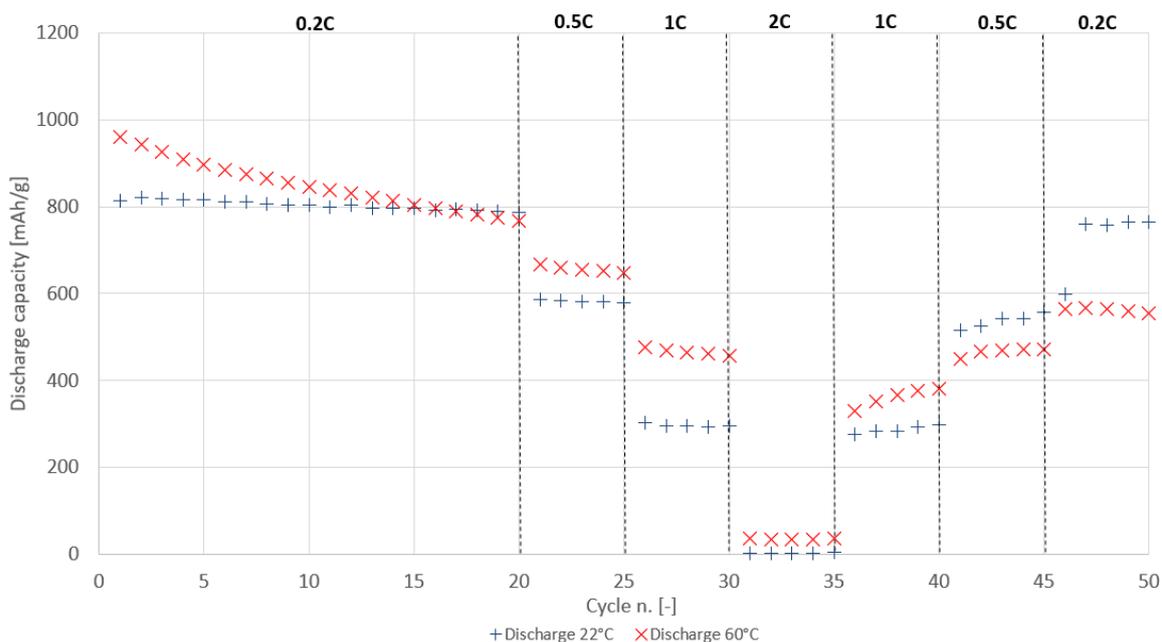
Samples of the electrodes composed of 60% Sulfur (Sigma Aldrich  $\geq 99.5\%$ ) 30% Super P Carbon Black and 10% PVDF were made. All measured electrodes were pressed with a pressure of  $350 \text{ kg/cm}^2$  and in the argon glove box assembled into the electrochemical measuring cells (El-Cell<sup>®</sup>). As a counter-electrode, the circular lithium metal was used and the  $130 \text{ }\mu\text{l}$  of electrolyte ( $LiTFSI/LiNO_3$  in DME:DOL) were dropped in the cell.



**Figure 2:** A) Surface structure of the electrode sample B) Elements distribution (C, S, F) on the surface of electrode sample

In an attempt to monitor operating mechanisms of Li-S sample cells, several techniques have been used, including spectroscopic and electrochemical analyzes. Energy dispersive spectroscopy (EDS) in scanning electron microscope (SEM) was used to analyze the surface structure of the electrode sample and the distribution of the elements on its surface. From the data obtained from the SEM (Figure 2) it is evident that the electrode surface is almost flat, and the element distribution is uniform with a high content of sulfur clusters.

Electrochemical measuring cells with electrode samples were subjected to electrochemical analyzes (particularly GCPL<sup>3</sup>) in different ambient temperatures (temperature range -20°C – 60°C). For the electrochemical analysis 2 cycles of GCPL at 0.1C were performed for all electrode samples assuming that the capacity of the active material is 1200 mAh/g. The capacity of the second discharge cycle was then used to recalculate the charging/discharging currents. After the recalculation of currents, another 50 cycles of GCPL were performed as follows: 20 cycles at 0.2C, 5 cycles at 0.5C, 5 cycles at 1C, 5 cycles at 2C and back to lower loads (see Figure 3).



**Figure 3:** Comparison of the GCPL results of the samples at different ambient temperatures

#### 4 RESULTS AND DISCUSSION

As can be seen from the comparison of GCPL of the electrode samples measured at different ambient temperatures (Figure 3), El-Cell<sup>®</sup> measured at room temperature reaches a capacity 813 mAh/g in the first cycle and is relatively stable during the first 20 cycles. On the other hand, El-Cell<sup>®</sup> measured at 60°C ambient temperature reaches higher capacity in the first cycle (959 mAh/g), however, capacity decline is significant in the first 20 cycles of GCPL. In the case of a sample measured at room temperature, the capacity drop in first 20 cycles is around 3%, while the capacity drop of sample measured at 60°C is slightly over 20%. As the load increases, this trend is maintained, while both samples failed at 2C. At the end of the measurement, capacity drop between 1<sup>st</sup> and 50<sup>th</sup> cycle of GCPL was slightly over 6% for the room temperature cell and over 48% for the cell measured at 60°C. With increased temperature, the internal resistance of the cell and the viscosity of the electrolyte decrease, supporting the transport of charged particles and accelerating electrochemical reactions. As a result, overall capacity increases at higher temperature at the expense of its faster decline during cycling due to the shuttle effect.

<sup>3</sup> GCPL – Galvanostatic Cycling with Potential Limitation

## 5 CONCLUSION

From the research that has been done so far, it is clear that the ambient temperature has a significant influence on the electrochemical properties of the Li-S battery. So far, only two samples at different temperatures were measured, whereas the planned temperature range for this research is from -20°C to 60°C. Currently, the cells at -20°C and 40°C are in the process of measuring.

## ACKNOWLEDGEMENT

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