

LITHIUM SULPHUR BATTERIES

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Abstract: S+C cathode material was prepared by simple solid-state reaction in ball mill. Content of sulphur was approximately 80 wt. % in final sample. Cyclic voltammetry and galvanostatic charge/discharge techniques were used for characterization of the samples. Initial discharge capacity observed for S+C sample was 600 mAh/g_{sulfur}. Capacity loss for S+C sample after 30th cycles was 66 %. Cycling loss is due to insoluble polysulfide formation.

In this paper I present fundamental characteristics of Li-S batteries. This paper presents a principle of Li-S batteries, fundamental measurement and their evaluation. I present the techniques of measurement and preparation of cathode materials.

Keywords: Lithium, Sulfur, Li-S, batteries, cell, polysulfides, charge, discharge.

1. INTRODUCTION

Li-S batteries have attracted much attention lately because they have very high theoretical specific energy 2500 Wh kg⁻¹, five time higher than that of the commercial LiCoO₂ graphite batteries. Poor cycling life and low capacity retention are main factors limiting their commercialization. Large number of electrode and electrolyte materials address these challenges have been investigated [1]. For various cathode materials are theoretical capacities shown in Figure 1.

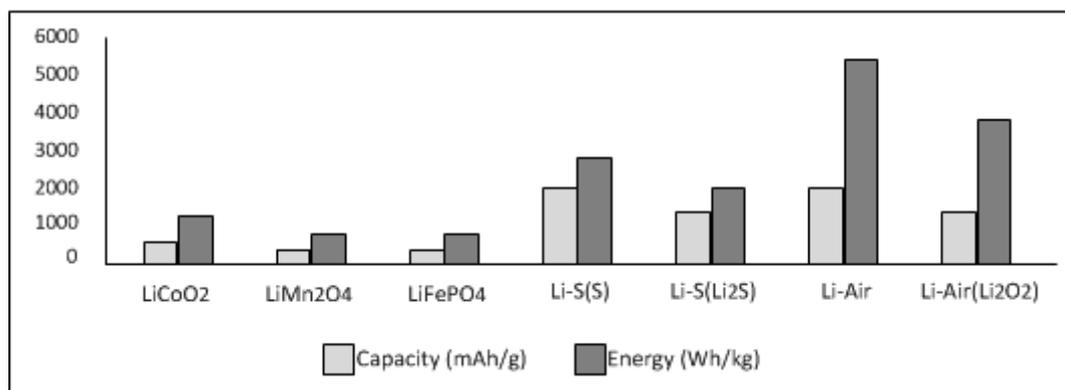


Figure 1: Theoretical capacity and energy density of various cathode materials of rechargeable lithium batteries [4].

In this review I present basic principle of operation Li-S batteries. I present basic principle of measurement and evaluation. Typical rechargeable Li-S cell consist of a sulphur cathode, a metallic lithium anode, non-aqueous electrolyte and a separator. Cell operation scheme can be illustrated in Figure 2 [4]. For basic measurement cathodes are consist only from sulphur and carbon. The aim of this research is achieving the minimum decline of charge/discharge diagram on Figure 4.

2. LITHIUM - SULFUR BATTERY OPERATION

The practical application of the Li-S batteries has to face some serious problems of low active material utilization and poor rechargeability, due to the insulating nature of sulphur and solid reduction products and the loss of active material in the form of soluble polysulfide reaction products [2]. At the cathode, elemental sulphur S_8 is readily reduced to a series of intermediate lithium polysulfides Li_2S_n upon discharge. Most of these species are soluble in the organic electrolytes except Li_2S_2 and Li_2S . Simultaneously, lithium is oxidized at the anode and lithium ions diffuse through the separator to the cathode to balance the negative charges. The overall reaction is written as [4]:



There are mainly two stages of the discharge reaction of sulphur cathode [5]:



The first discharge region attributes to the dissolution of solid sulphur and formation of high order polysulfides (Li_2S_x ; $x > 3$). As the discharge process continues, the low order, insoluble polysulfides (Li_2S_x ; $x < 2$) accumulate at cathode surface at the second discharge region and lead to an irreversible capacity [5].

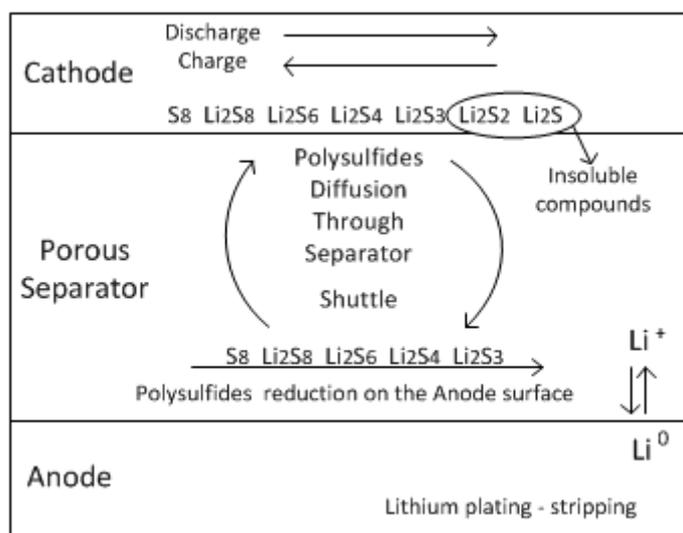


Figure 2: Cell operation scheme [4]

2.1. LITHIUM SULFUR BATTERY PREPARATION AND MEASUREMENTS

The main components of the cathode are sulphur and carbon. Cathode preparation consists from several parts. There is a need to mix sulphur α cyclo- S_8 (cyclo-octasulphur) with carbon in accurate ratio 5:1 in the first part. Used carbon is the type Super P®. The main characteristics of Super P® is high purity, high structure and his moderate surface area. The high purity is evidenced by the low ash, moisture, sulphur and volatile contents, while his high structure is expressed by oil absorption and electrical conductivity [7]. In the next step it is possible to grind up S+C mixture in ball mill and use this mixture for production of cathode or it is possible to heat up S+C mixture to the temperature 50-60 °C for a period of 15-20 minutes. By heating the S+C mixture the sulphur binds to carbon better. In the case of grinding in a ball mill, sulphur and carbon are grind up to parts of size about 200 μm and S+C mixture is more homogeneous. Both procedures for the preparation of S+C mixture were tried.

It is necessary to do a solution from each prepared S+C mixture. Solution will be applied to the thin cathode sheet and after the solution is dry it will, the electrodes with a 18 mm diameter will be cut out from the sheet. For the production of 7-12 pieces of electrodes it is necessary to use 0,32 g of prepared S+C mixture, which is mixed with 0,04 g carbon (for better conductivity) and 0,04 g of Poly(vinylidene fluoride) (PVDF). PVDF is used as a binder. After application of this procedure the 0,4 g of new mixture is created, which is mixed with N-Methyl-2-pyrrolidone (NMP). NMP works as a solvent. It is necessary to stir this mixture for at least 24 hours. After the solution is perfectly stirred it is possible to apply it on the prepared cathode sheet. The cathode sheet consists of aluminium sheet covered with carbon layer. The thickness of the applied layer was chosen 80 μm . After application of the layer it is necessary to dry the sheet for the next 24 hours. After drying the circle electrodes will be cut out. These electrodes are ready for use now. Before use, it is recommended to place the prepared electrodes to the vacuum pump for elimination of air from the pores in a deposited layer.

It is necessary to assemble the measured cell in the Glove Box in an inert argon atmosphere because of very high reactivity of lithium. Type of porous separator is non-aqueous. The volume of electrolyte for wetting of separator is 160-200 μl . The used electrolyte is a mixture of solution 0,25M LiNO_3 and 0,7M LiTFSI in ratio 2:1. After the assembly the cell is ready for measurement in the BioLogic.

The results of measurements are on the Figures 3,4 and 5. Overall the 6 cells were measured and results were similar. In this review I present the best measured sample. The Cyclic Voltammetry, Potentiostatic Impedance and Galvanostatic Cycling with Potential Limitation were measured on the all cells. Descriptions of the techniques used are on the following sections.

Cyclic Voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions. CV provides information on redox processes, heterogenous electron-transfer reactions and adsorption processes. It offers a rapid location of redox potential of the electro active species. CV consists of linearly scanning the potential of a stationary working electrode using a triangular potential waveform. During the potential sweep, the potentiostat measures the current resulting from electrochemical reactions. The cyclic voltammogram is a current response as a function of the applied potential [6].

The Potentiostatic Impedance (PEIS) experiment performs impedance measurements into potentiostatic mode by applying a sinus around a potential E that can be set to a fixed value or relatively to the cell equilibrium potential [6].

The Galvanostatic Cycling with Potential Limitation (GCPL). This technique corresponds to battery cycling under galvanostatic mode (essentially), i.e. with an imposed current, but with possible potential limitations under current for both charged and discharge and tests on potential values during open circuit period [6].

Electrochemical reduction of sulphur is very complicated process and cyclic voltammetry (CV) is important method how to describe this reaction. CV analysis is summarized in Fig. 3. When sweeping in the cathodic direction three reduction peaks are observed. These peaks are attributed to formation of Li_2S_6 (peak at 2 V) Li_2S_5 (peak at 1,5 V) and Li_2S , Li_2S_2 (peak at 1 V). When the potential is swept in the anodic direction, only one oxidation peak is observed. This peak is associated with simultaneous oxidation of all polysulfides to elemental sulphur. The current decreases with the number of cycles because of formation of insoluble and insulating polysulfides (Li_2S , Li_2S_2). The overall energetic yield from the cell is lowered by formation of insoluble polysulfides.

Figure 4 shows the cell potential versus time during the C/10 charge/discharge cycling.

Galvanostatic charge-discharge profiles are shown on Fig. 5. The flat plateau between 2,1 – 2,4 V was observed for charge and discharge process. Initial discharge capacity of S+C sample was 600 $\text{mAh/g}_{\text{sulfur}}$. It was also found that increasing the number of cycles resulted in an increase in the

potential difference between the charge and discharge plateau. Plateau difference in Fig. 5 is caused by formation of polysulfides. Discharge capacity after 30. cycles was approximately 200 mAh/g_{sulfur}. Capacity loss after 30. cycles is about 66%.

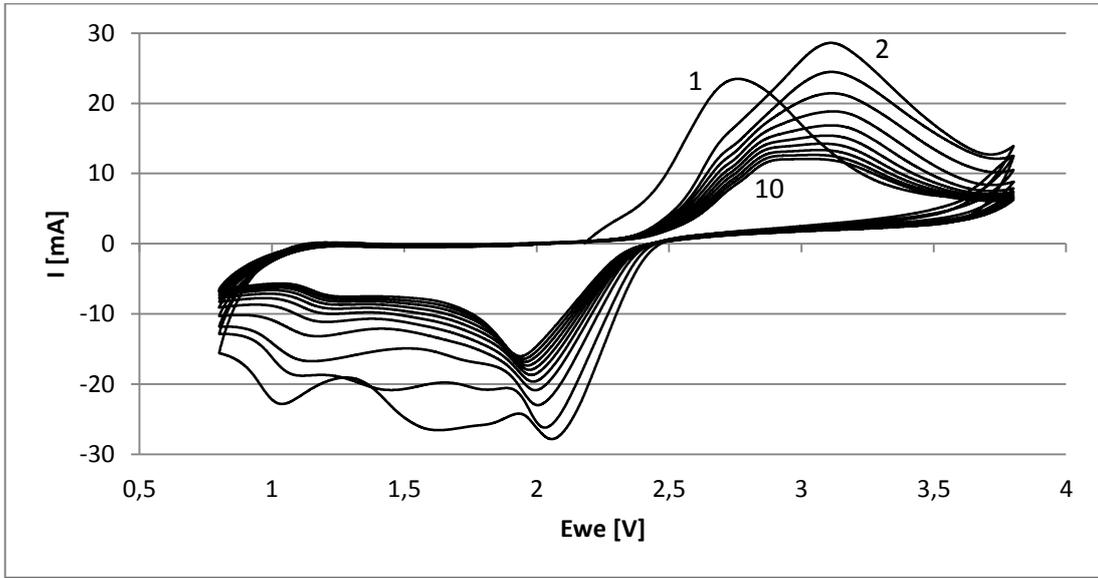


Figure 3: Cyclic Voltammetry characteristics. Charge (oxidation) is direction from left to right on upper part and discharge (reduction) is direction from right to left on lower part. Cyclic voltammograms (10 cycles) of S+C electrodes measured at potential scan rate 20 mVs⁻¹ and room temperature vs. Li/Li⁺ reference electrode in the potential range of 0,8 – 3,8 V.

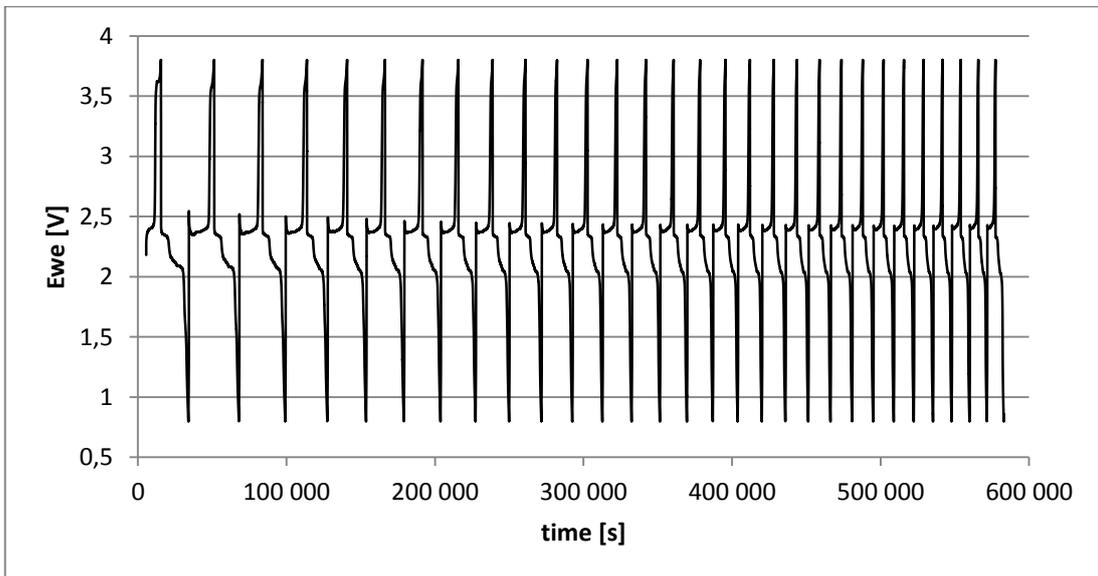


Figure 4: Cell potential vs. time during the C/10 charge/discharge cycling at room temperature (Li/Li⁺ reference electrode).

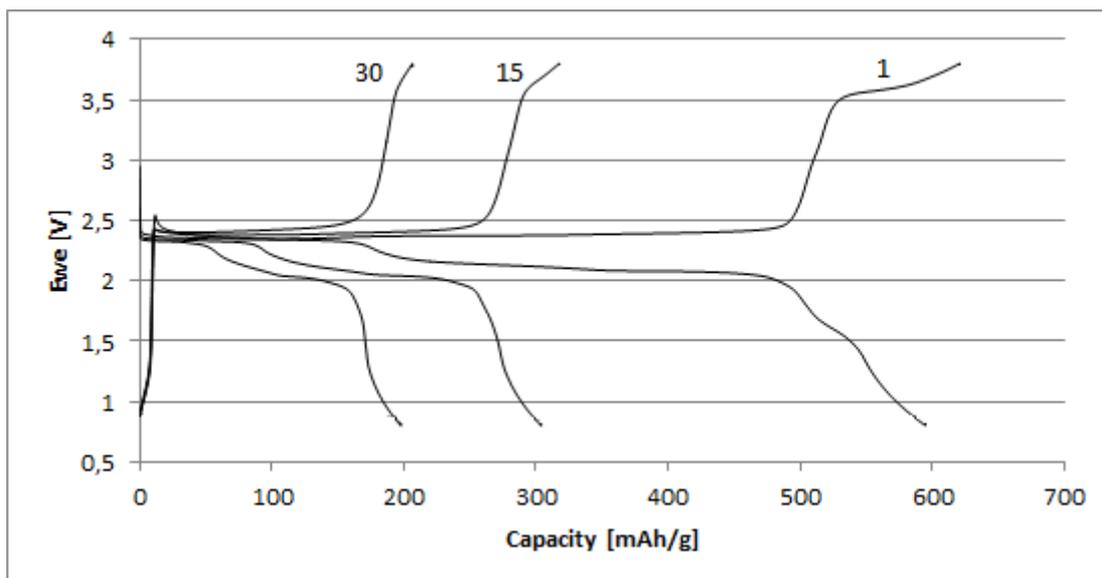


Figure 5: Galvanostatic charge/discharge profiles of S-C sample at the constant rate of C/10.

3. CONCLUSION

I have demonstrated that the discharge of Li-S battery unavoidably causes the formation of insoluble polysulfides Li_2S_2 and Li_2S . Sulphur-based electrodes were prepared by planetary ball mill a mixture of sulphur and carbon.

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