



## Sulfur redistribution between positive and negative electrodes of lithium-sulfur cells during cycling

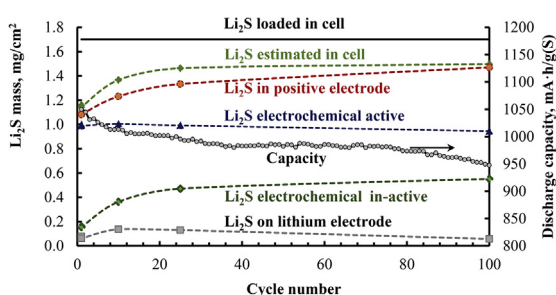
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### HIGHLIGHTS

- Lithium sulfide content in Li-S cells is studied.
- Lithium sulfide does not accumulate on lithium electrodes over 100 cycles.
- Lithium sulfide is blocked in the pores of carbon particles of positive electrode.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Lithium-sulfur battery  
Capacity fade  
Lithium sulfide  
Lithium polysulfide

### ABSTRACT

Change in the content of lithium sulfide is quantitatively studied through the methods of precipitation and back iodometric titration in lithium-sulfur cells during charge-discharge cycling for 100 cycles. It is shown that in the initial cycles (25 cycles) of charge-discharge cycling, electrochemically inactive lithium sulfide accumulates. The predominantly inactive lithium sulfide accumulates in the sulfur electrode. It is likely that lithium sulfide is deposited in the pores of the carbon material, blocks the pores and loses the ability to participate in the electrochemical reactions.

On the surface of the lithium electrode, a surface layer containing lithium sulfide is formed during the cycling of the lithium-sulfur cells and is in equilibrium with the electrolyte system. It is found that lithium sulfide does not accumulate on the lithium electrode for at least 100 charge-discharge cycles.

### 1. Introduction

The electrochemical system of lithium-sulfur has a high theoretical specific energy - 2650 Wh/kg, which predetermines the possibility of developing batteries with record power characteristics, i.e., specific energy of 350–500 Wh/kg and volumetric energy of 420–600 Wh/l [1]. Although the number of scientific and patent publications in the field of chemistry and technology of lithium-sulfur batteries is steadily increasing (Fig. 1), the main problems preventing the

commercialization of lithium-sulfur batteries (short cycle life, high self-discharge rate, low specific energy achieved in comparison with expected value [2,3]) have not been resolved to date.

A feature of lithium-sulfur batteries is the solubility in electrolyte solutions of lithium polysulfides - the intermediate products of electrochemical transformations of sulfur and the active component of the positive electrode [4,5].

In the dissolved form, lithium polysulfides are highly mobile and can be redistributed along the volume of the positive electrode,

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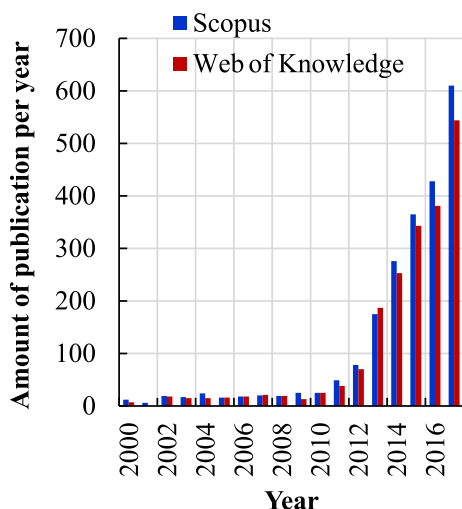


Fig. 1. Publication activity of lithium-sulfur batteries. Search terms are “lithium sulfur batteries” and not “lithium ion batteries”.

transferred to the surface of the negative electrode and reacted with it [6–11]. The final product of the interaction of lithium polysulfides and lithium metal is lithium sulfide ( $\text{Li}_2\text{S}$ ), which is insoluble in the electrolyte solutions. The insolubility of lithium sulfide in the electrolyte can lead to accumulation of lithium sulfide on the surface of the negative electrodes during cycling and storage of the lithium-sulfur batteries. Accumulation of sulfur in the form of lithium sulfide on the negative electrode will cause a decrease in the amount of electrochemically active sulfur in the lithium-sulfur batteries and a decrease in their capacity during charge-discharge cycling [12,13].

The deposition of lithium sulfide on the carbon components of the positive electrode is also considered as one of the main reasons for the decrease in the capacity of the lithium-sulfur cells [14–18].

The aim of this work was to study the redistribution of sulfur between the positive and negative electrodes of lithium-sulfur cells during charge-discharge cycling.

## 2. Experimental

### 2.1. Charge-discharge cycling

Lithium-sulfur cells were assembled in a prismatic dismountable case by own design and production (Fig. 2). The size of the positive electrode was  $6.0 \times 6.0 \text{ cm}^2$ , and the negative electrode was  $5.8 \times 5.8 \text{ cm}^2$ . The size of the separator was  $6.2 \times 6.2 \text{ cm}^2$ . The number of electrode pairs in the cells was 2.

The sulfur electrodes contain 70% wt. of sulfur (> 99.99%, Russia), 10% wt. of carbon (Ketjenblack EC-600JD, Akzo Nobel) and 20% wt. of polyethylene oxide (MM 4000000, Aldrich). The sulfur loading was 1.2–1.5 mg/cm<sup>2</sup> in the positive electrodes. The electrode layer was



Fig. 2. Photo of a prismatic dismountable cell case.

coated on aluminum foil with a double-sided carbon coating (XIAMEN TOB NEW ENERGY TECHNOLOGY Co., LTD). The electrodes were made as previously described [19]. Porosity of the electrode layer of the positive electrodes was 40%.

Lithium electrodes were made of lithium foil (> 99.9%, Russia) with a thickness of 120  $\mu\text{m}$ .

Microporous polypropylene (Celgard® 3501) was used as a separator. Two layers of the separator were placed between the positive and negative electrodes to separate the electrodes after cycling to perform the analysis.

The electrolyte was 1 M solution of lithium trifluoromethanesulfonate ( $\text{CF}_3\text{SO}_3\text{Li}$ ) in sulfolane. Sulfolane was used as the solvent as it is the promising solvent for lithium-sulfur batteries [20–25]. Sulfolane well solvates lithium salts, and the electrolyte solutions based on sulfolane have high chemical stability. It should be noted that sulfolane has a high FlashPoint (> 166 °C [25]). Gaseous products are not generated at the reaction of sulfolane with metallic lithium.

The electrolyte solution was prepared similar to that described in Ref. [19]. The amount of electrolyte in the lithium-sulfur cells was  $7.4 \pm 0.2 \mu\text{l}$  per  $1 \text{ cm}^2$  of the positive electrode. The electrolyte was injected into the cell with a 1 ml polypropylene syringe.

All operations of assembling the cells were conducted in an atmosphere of dry air (the water content did not exceed 10 ppm) in a glove box.

Galvanostatic charge and discharge cycling of lithium-sulfur cells were carried out using a BT-05PG battery tester in the potential range of 1.5–2.45 V at + 30 °C. The current density of the charge was 0.1 mA/cm<sup>2</sup> (0.05 C, 80 mA/g(S)), and the discharge current density was 0.2 mA/cm<sup>2</sup> (0.1 C, 167 mA/g(S)).

The results of the electrochemical studies were processed using the Data Analyzer program, which is part of the specialized ElChemLab V1 © software package. The Data Analyzer program is designed to build charge-discharge profiles and calculate the energy parameters of the battery (e.g., capacity, energy, Coulomb efficiency), the internal resistance of battery, corrosion current density, and the signals from external sensors (e.g., dilatometric, thermometer). The program allows to process files with experimental data presented in a table containing information on the change in time of the current, the voltage on the cell, the potential of the working electrode vs. the reference electrode and other information (for example, data from external sensors).

The internal resistance of the cells was calculated by Equation (1) at the specified depth of discharge.

$$R = |U_{ch} - U_{dch}| / (|i_{ch}| + |i_{dch}|) \quad (1)$$

where:

- R - internal resistance at the specified depth of discharge, Ohm·cm<sup>2</sup>;
- $U_{ch}$  - voltage on the cell at charge at the specified depth of the discharge, V;
- $U_{dch}$  - voltage on the cell at discharge at the specified depth of the discharge, V;
- $|i_{ch}|$  - module of current density of charging, A/cm<sup>2</sup>;
- $|i_{dch}|$  - module of current density of discharging, A/cm<sup>2</sup>.

### 2.2. Determination of pore volume of carbon materials

Nitrogen physisorption measurements at 77 K were performed on a NOVA 1200 (Quantachrome Instruments). Before performing the experiment,  $9.0 \pm 0.3 \text{ mg}$  of Ketjenblack EC-600JD sample was degassed and heat-treated at 300 °C for 16 h. The pore size distribution (PSD) was calculated by the Barrett, Joyner and Halenda (BJH) method and DFT method [26] from nitrogen adsorption isotherm using software NovaWin, provided with Quantachrome Instruments.

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