

Electrochemistry of a Lithium Electrode in Lithium Polysulfide Solutions¹

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Abstract—The effect of lithium polysulfides on the cycling of a lithium electrode and the corrosion rate of lithium cathodic deposits in sulfolane electrolytes is studied. Lithium polysulfides are found to affect the shape of polarization curves, the overpotential of electrode processes, and the cycling time. The presence of lithium polysulfides in electrolyte systems increases the cycling time of a lithium electrode and positively affects the quality of lithium cathodic deposits. A suggested reason for the positive effect of lithium polysulfides is the appearance of a surface film on metallic lithium: this film has quite high protective properties but does not inhibit electrochemical processes.

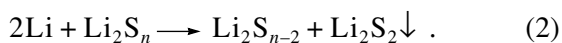
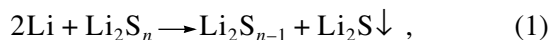
Key words: lithium electrode, cycling, lithium polysulfides, corrosion

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INTRODUCTION

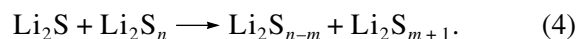
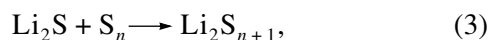
The electrochemistry of a lithium electrode in lithium polysulfide solutions in electrolyte systems based on dipolar aprotic solvents (DASs) is of great interest because of the development of lithium–sulfur batteries. Lithium polysulfides Li_2S_n appear as intermediates in electrochemical processes in lithium–sulfur batteries during charge and discharge [1–4]. Depending on the number of sulfur atoms n , short-chain ($n = 1–2$), medium-chain ($n = 3–5$), and long-chain ($n \geq 6–7$) lithium polysulfides are distinguished. Short-chain lithium sulfides are insoluble, while medium- and long-chain ones are well soluble in many DASs.

Lithium polysulfides are rather strong oxidizers and actively react with metallic lithium [5]. The reaction of long-chain lithium polysulfides with metallic lithium generates medium-chain polysulfides. A film consisting of sparingly soluble short-chain lithium polysulfides deposits on the lithium electrode:



This film inhibits corrosion, but does not inhibit electrochemical reactions on a lithium electrode [6–8].

Insoluble short-chain lithium sulfides can react with sulfur or long-chain lithium polysulfides to produce soluble polysulfides:



These reactions result in the dissolution of the sulfide film from the metallic lithium surface. The interplay between deposition and dissolution determines the thickness and properties of the surface film on a lithium electrode in electrolyte systems containing lithium polysulfides. The composition and properties of the surface film are also determined by the chemical and physicochemical properties of other components of electrolyte systems, in particular, solvents and lithium salts.

The electrochemical properties of a lithium electrode in lithium polysulfide electrolytes will be much dependent on the properties of the surface film deposited on lithium in sulfide systems. The surface sulfide film is expected to strongly affect the cycling and corrosion stability of metallic lithium, i.e., the properties of a lithium electrode that are most important for the creation of batteries with a metallic lithium electrode. Therefore, in this work we studied the effect of lithium polysulfides on the cycling of a lithium electrode and the corrosion rate of lithium cathodic deposits.

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EXPERIMENTAL

A lithium electrode was cycled in air-tight stainless steel cells equipped with planar-parallel disk electrodes. All electrodes were made of a lithium foil 38 μm thick (Chemetall Foote Corp., USA). The separator used was a combination of two Celgard 3501 separator layers (Tonen Chemical, Japan), which adjoined to the surface of lithium electrodes, and 10 nonwoven polypropylene layers in between. Cell cycling was performed at +30°C with the use of an MCV16-0.1-5 battery tester (Bitrode, USA) in the galvanostatic mode at the current density 0.2 mA/cm². The amount of electricity during the cathodic deposition and anodic dissolution of lithium was equal to 0.2 mA h/cm²; the cycling potential range was ± 1.0 V. All operations associated with lithium electrode manufacturing, electrolyte preparation, and cell assembling were carried out in a glovebox under a dry argon atmosphere.

In studying the corrosion properties of lithium cathodic deposits, lithium foil served as counter and reference electrodes; the working electrode was manufactured of stainless steel 12Kh18N10T. The separator used consisted of several nonwoven polypropylene layers with an overall thickness of ~ 600 μm . A VT4-1000 device for cycling lithium batteries, which was designed and manufactured in the Electrochemistry Laboratory of the Institute of Organic Chemistry, Ufa Scientific Center [9], was used in experiments. Lithium cathodic deposits were obtained at the current density 0.2 mA/cm² and various amounts of electricity. After the cathodic deposition, the circuit was broken and the potential of the working electrode was monitored.

Two to four replicate experiments were carried out for ascertaining the precision.

Lithium polysulfide solutions were prepared by the direct reaction of lithium sulfide (Li₂S, 98%, Aldrich) and sulfur (S, sublimed, 99.5%, Acros) in sulfolane. The apparent degree of polysulfidity n was calculated as the quotient of the total sulfur concentration to the sulfide sulfur concentration. Sulfur involved in sulfolane and lithium triflate molecules was included into the calculations. Total sulfur and sulfide sulfur were determined by routine procedures [10].

RESULTS AND DISCUSSION

Figures 1 and 2 displays the potential versus time curves of a lithium electrode measured during long-term cycling (cathodic deposition and anodic dissolution of lithium) in 1 M LiCF₃SO₃ solution in sulfolane and in 0.42 M Li₂S_{6.5} in 1 M LiCF₃SO₃ solution in sulfolane. Clearly, lithium polysulfides affect the shape of the polarization curves, the overpotential of electrode processes, and the cycling time.

Cathodic deposition of lithium in 1 M LiCF₃SO₃ solutions in sulfolane is initially unsteady (Fig. 1). The potential versus time curves of cathodic lithium deposition at the initial cycling stages (up to the 8th cycle) show noises and potential breakdowns. The cathodic overpotential increases during cycling. Then, as cycling progresses (10th to 66th cycle), cathodic deposition becomes steady. Noises decrease, and potential breakdowns disappear. The cathodic deposition overpotential starts to decrease. In the progress of cathodic deposition, however, instability appears again: noises increase, potential breakdowns appear, and the overpotential increases. Anodic lithium dissolution occurs steadily during the entire cycling. The anodic dissolution overpotential, as well as cathodic deposition overpotential, first increases, then decreases, and finally again increases during cycling. Calculations show that the figure of merit (FOM) for the system in question is 2.75 and the cycling efficiency is 64%.

In lithium polysulfide electrolytes (Fig. 2), cathodic deposition is stable; considerable noise or potential breakdowns are not observed. Cathodic and anodic overpotentials at the initial cycling stage slightly decrease, then increasing smoothly. Both the cathodic deposition and anodic dissolution of lithium are steady during the entire experiment; potential breakdowns are not observed. About 450 cycles are obtained before the overpotential increases abruptly. Calculations show that lithium polysulfides increase the FOM to 12.5 and the cycling efficiency to 92.5%. The different tendencies in lithium electrode cycling in similar electrolyte systems are likely due to the surface film appearing on the lithium electrode in the presence of lithium polysulfides, this film enhancing cathodic lithium deposition.

Cathodic lithium deposition on stainless steel substrates and its subsequent anodic dissolution were studied in 1 M LiCF₃SO₃ solution in sulfolane and 0.5 M Li₂S₈ in 1 M LiCF₃SO₃ solution in sulfolane. Figure 3 displays 1st cycle potential versus time curves. An plateau appears at about 2 V in the initial segment of the potential versus time curves during cathode polarization in the electrolyte containing lithium polysulfides; the potential versus time curve obtained in lithium triflate solution does not show this plateau. We think that this high-voltage plateau is due to the reduction of lithium polysulfides in the electrolyte to lithium sulfide and/or lithium disulfide:



These compounds being sparingly soluble in the electrolyte, they are deposited onto the electrode and form a lithium sulfide film, which inhibits the subse-

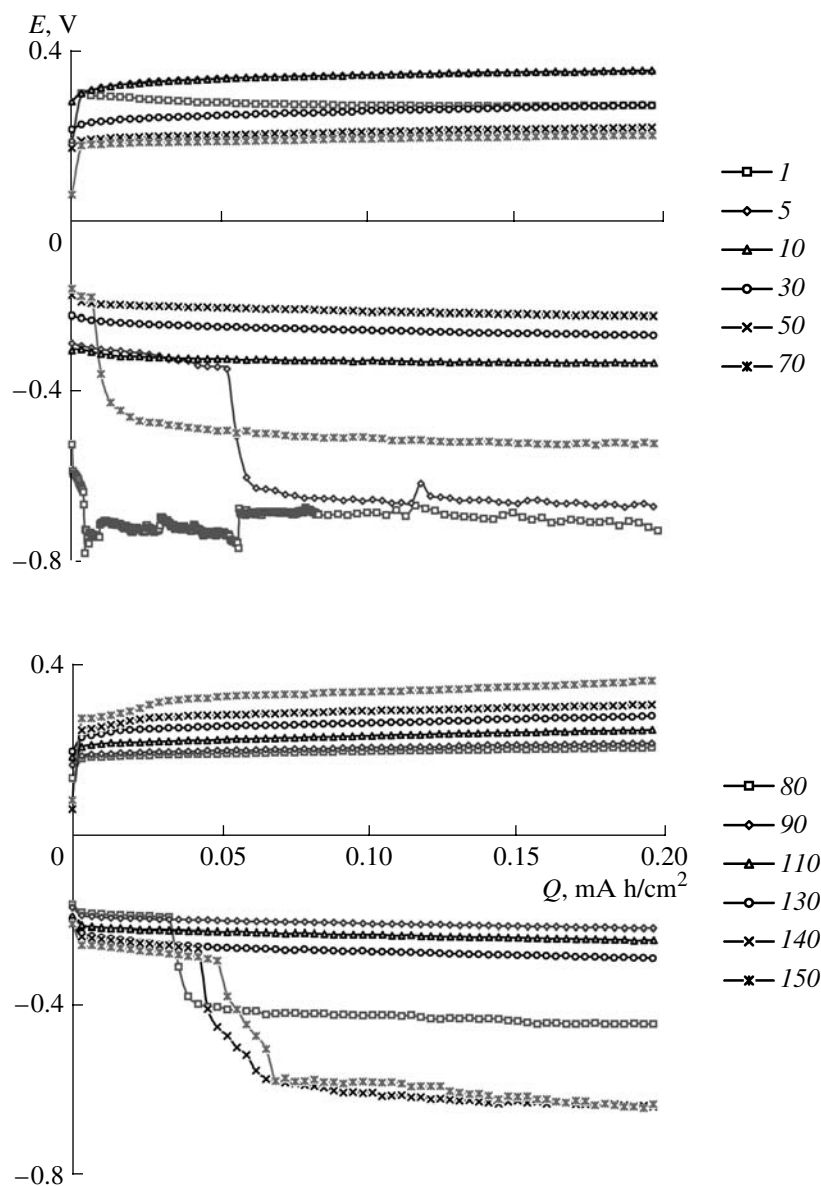
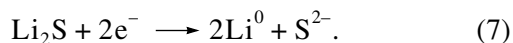


Fig. 1. Polarization characteristics of cells: Li/separator and electrolyte/Li. Electrolyte: 1 M LiCF_3SO_3 solution in sulfolane. Cycling potential range: ± 1.0 V. Current density: ± 0.2 mA/cm². Temperature: +30°C. Figures at data symbols are cycle numbers.

quent reduction of lithium polysulfides from the solution. As a result, lithium cations are reduced during further cathodic polarization:



After cathodic lithium deposition, the potential of the nonpolarizable working electrode is unstable and varies with time; first, it increases slowly; then, abruptly (Fig. 4). The rapid increase in the potential follows the complete dissolution of cathodic lithium. Additional visual investigations showed that the change in the potential of a steel electrode coated with cathodic lithium is due to corrosion. Comparing potential versus

time curves for the working electrode obtained after cathodic lithium deposition from various electrolytes, we find that the lithium corrosion rate in 1 M LiClO_4 solution is higher than in 0.42 M $\text{Li}_2\text{S}_{6.5}$ solution. The transition time, which was derived from the break point on the potential versus time curve, characterizes the corrosive activity of the electrolyte with respect to freshly deposited cathodic lithium. The corrosion rate of cathodic lithium was calculated from the transition times. In LiClO_4 solution, it was 30 ± 3 $\mu\text{A}/\text{cm}^2$; in $\text{Li}_2\text{S}_{6.5}$ solution, 23 ± 2 $\mu\text{A}/\text{cm}^2$.

The apparent controversy between the chemical reactivities and corrosive activities of sulfolane solu-

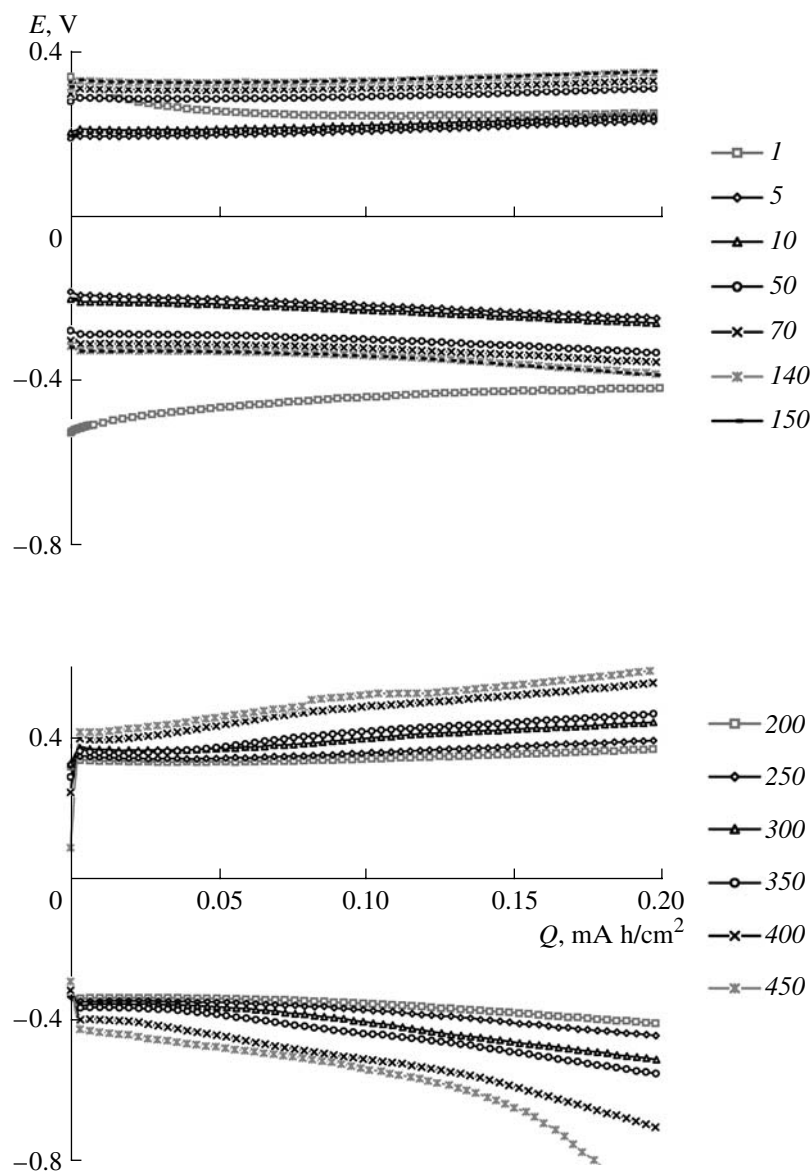


Fig. 2. Polarization characteristics of cells: Li/separator and electrolyte/Li. Electrolyte: 0.42 M $\text{Li}_2\text{S}_{6.5}$ in 1 M LiCF_3SO_3 solution in sulfolane. Cycling potential range: ± 1 V. Current density: ± 0.2 mA/cm². Temperature: +30°C. Figures at data notations are cycle numbers.

tions of lithium perchlorate and lithium polysulfides is likely explained by the different properties of surface films on fresh cathodic lithium deposits.

The lithium corrosion rate is also controlled by the thickness of the surface sulfide layer, which forms on the electrode surface during cycling. Figure 5 shows the transition time for electrodes with freshly deposited lithium as a function of amount of electricity Q_c after the 1st lithium cathode deposition cycle (panel a) and after multiple lithium deposition (panel b). In both cases, the transition time for electrodes in an electrolyte containing lithium polysulfides is longer than in an

electrolyte free of lithium polysulfides. The positive effect of lithium polysulfides on the deactivation time of cathodic lithium is manifested most brightly after multiple lithium deposition. For example, the corrosion rate of cathodic lithium in a sulfolane solution of lithium perchlorate is virtually independent of the amount of deposited lithium, whereas in an electrolyte containing lithium polysulfides, this rate decreases more than 1.5-fold.

In summary, our study shows that lithium polysulfides in electrolyte systems increase the cycling time of a lithium electrode and positively affect the quality of

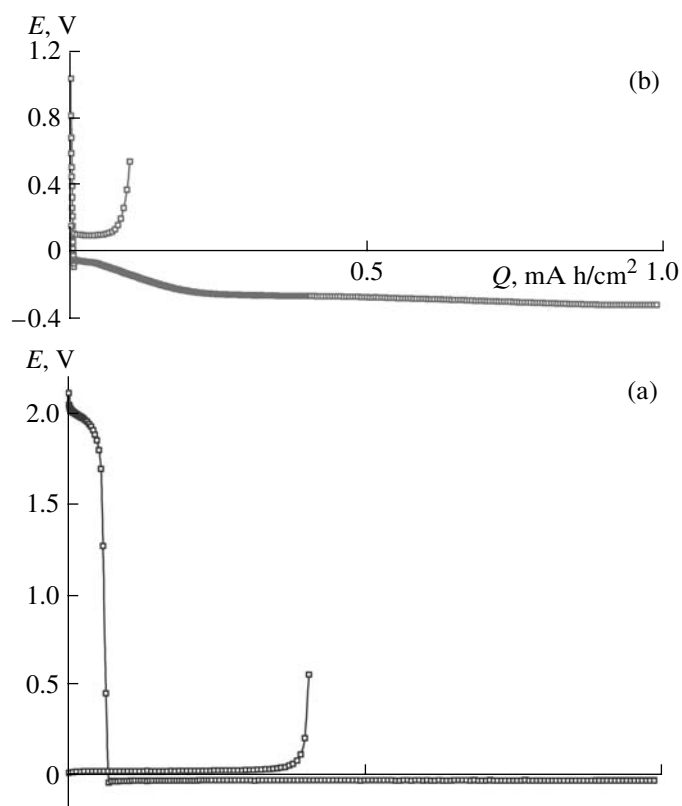


Fig. 3. Polarization characteristics of cells (1st cycle): Li/separators, electrolyte/stainless steel. Electrolyte: (a) 1 M LiCF_3SO_3 solution in sulfolane and (b) 0.5 M Li_2S_8 in 1 M LiCF_3SO_3 solution in sulfolane. Cycling potential range: $\pm 0.5.0$ V. Current density: ± 0.2 mA/cm². Temperature: $+30^\circ\text{C}$.

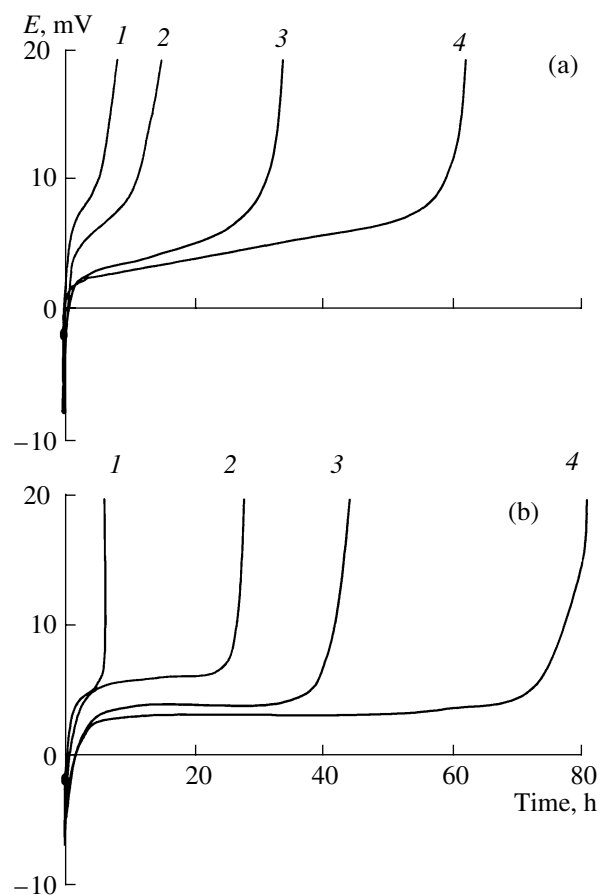


Fig. 4. Potential versus time curves of the working electrode after the 1st lithium cathodic deposition in 1 M LiClO_4 solution in (a) sulfolane and (b) 0.42 M $\text{Li}_2\text{S}_{6.5}$ solution in sulfolane. Amount of deposited lithium: (1) 0.2, (2) 0.5, (3) 1, and (4) 2 mA h/cm².

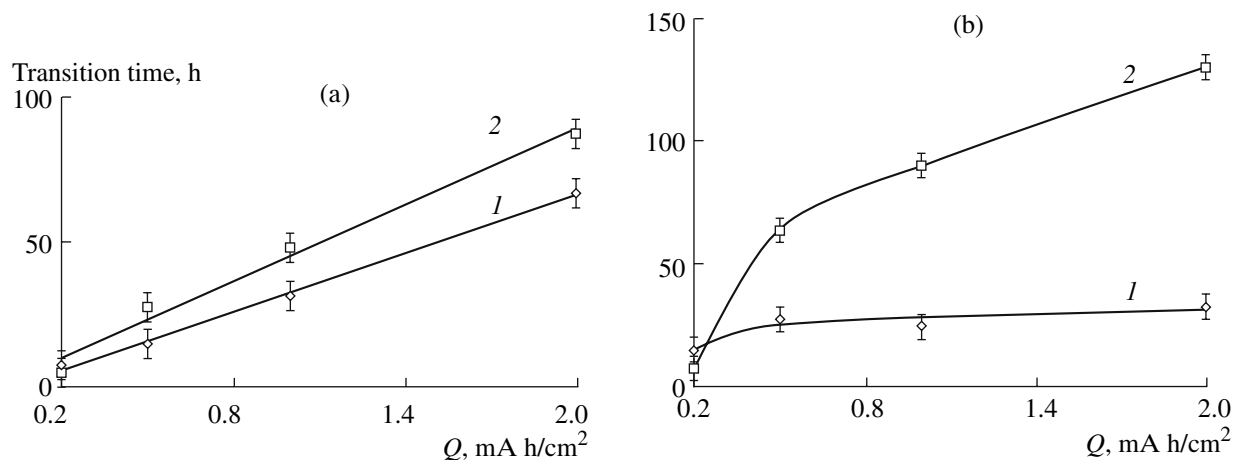


Fig. 5. Deactivation time of a cathodic lithium deposit vs. amount of electricity after (a) 1st and (b) 6th cathodic deposition cycle in (1) 1 M LiClO_4 solution in sulfolane and (2) 0.42 M $\text{Li}_2\text{S}_{6.5}$ solution in sulfolane.

cathodic lithium. The likely reason for the positive effect of lithium polysulfides is the appearance of a surface film on metallic lithium, which has quite high protective properties but does not inhibit electrochemical processes.

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