

## Cycling a Sulfur Electrode in Mixed Electrolytes Based on Sulfolane: Effect of Ethers

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**Abstract**—The cycling of a sulfur electrode is studied in 1 M  $\text{LiCF}_3\text{SO}_3$  solutions in sulfolane mixtures with ethers 1,2-dimethoxyethane, dioxolane, and tetrahydrofuran. The results suggest that the electrochemical behavior of sulfur is defined by the forms of existence of lithium polysulfides in the electrolyte.

### INTRODUCTION

The major problem that hampers the development of lithium–sulfur batteries is a substantial drop of the sulfur electrode capacity during prolonged cycling. The depth and efficiency of cycling a sulfur electrode are extremely sensitive to properties of electrolytes [1, 2]. Despite numerous studies devoted to the sulfur electrochemistry in aprotic bipolar solvents, the reason for this phenomenon is still not fully understood. To fully solve this problem systematic research into the effect the physicochemical properties of electrolytes have on the cycling of a sulfur electrode is called for. Of special interest are electrolytes based on mixtures of solvents of different nature, as by selecting a proper solvent and a mixture composition one can vary their properties in a broad range.

Earlier, the cycling of a sulfur electrode was studied in sulfolane [3]. This work continues the studies begun previously. The aim of this work is to investigate regularities that govern the cycling of a sulfur electrode in mixtures of sulfolane and such ethers as 1,2-dimethoxyethane, dioxolane, and tetrahydrofuran and reveal factors that mostly affect the sulfur electrode capacity in the course of cycling.

### EXPERIMENTAL

The cycling of sulfur electrodes was realized in two-electrode cells. For the negative electrode we used lithium foil 200  $\mu\text{m}$  thick. The positive electrodes comprised 70 wt % of sulfur (Aldrich 21523-6 power-100 mesh., sublimed), 10 wt % of carbon (Ketjen Black International Co., Japan), and 20 wt % of polyethylene oxide (Aldrich 18946-4 Mw.ca 4 000 000). The thickness of the active electrode layer was 25–30  $\mu\text{m}$ . The specific capacity of positive electrodes was equal to 0.9–1.1  $\text{mA h cm}^{-2}$ . For the support (current collector) we used aluminum foil. The separator was a layer of a separation material Celgard 20  $\mu\text{m}$  thick. All operations

involving the preparation of sulfur electrodes and electrolytes and the assembling of the cells were done in a dry room, where the dew point was equal to  $-80$  to  $-90^\circ\text{C}$ . Prior to assembling the cells the separators and sulfur electrodes were impregnated with electrolyte in a vacuum.

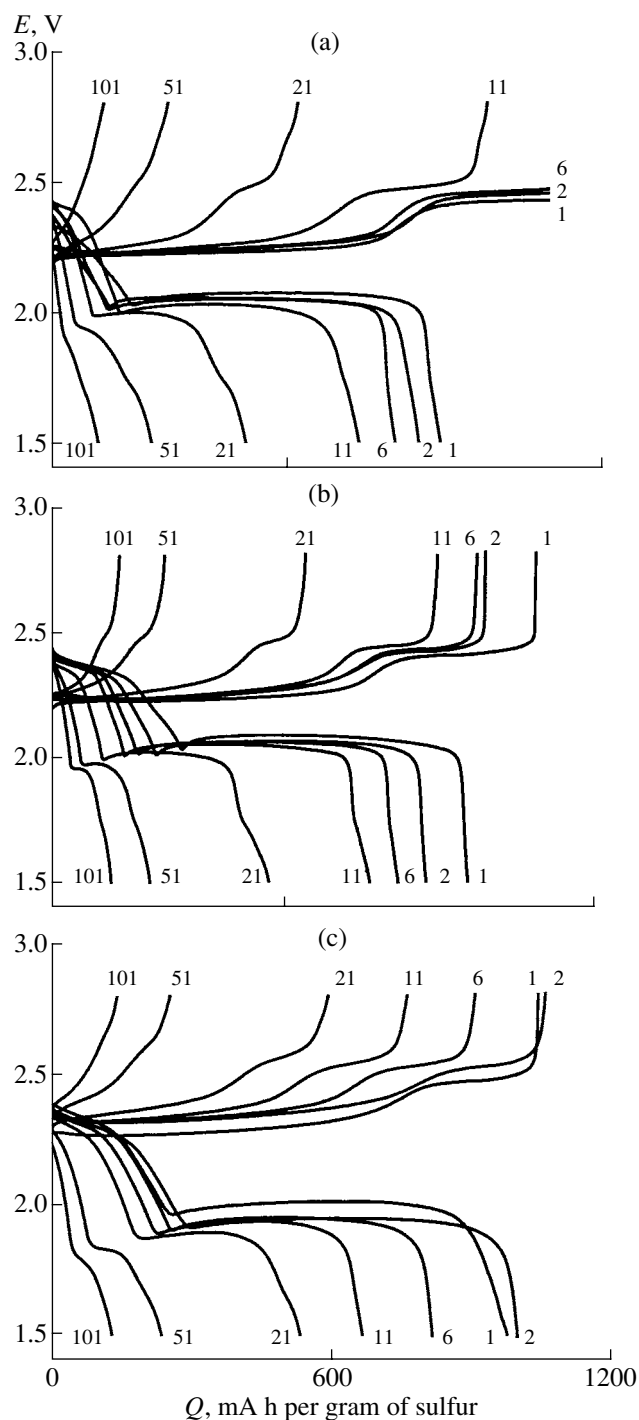
The cells were cycled in a galvanostatic mode with a Toscat 3000 cycler. The range of cycling potentials was 1.5 to 2.8 V. The first cycle (forming) was performed in the mode 0.25C, all the rest, at 0.5C. Before commencing the cycling, the assembled cells were kept for 24 h in order to establish equilibrium. In order to estimate reproducibility of results, five parallel experimental runs were performed. The scatter of results was  $\pm 10\%$ .

The cycling of sulfur electrodes was studied in 1 M  $\text{LiCF}_3\text{SO}_3$  solutions in mixtures comprising sulfolane (SL) and 1,2-dimethoxyethane (DME), sulfolane and dioxolane (DOL), as well as sulfolane and tetrahydrofuran (THF). The sulfolane : ether volume ratio was 1 : 1. The ethers and  $\text{LiCF}_3\text{SO}_3$  were manufactured by Samsung Sheil Industries Co. and sulfolane, by Merck. The purity of solvents and the supporting salt was 99.8 to 99.0%. The water content in the electrolytes did not exceed 0.003–0.005% as determined by coulometric titration in a K. Fischer titrant.

Specific charge and discharge capacities of the sulfur electrode were determined from the intersection of tangents to linear portions of charge and discharge curves (from an inflection).

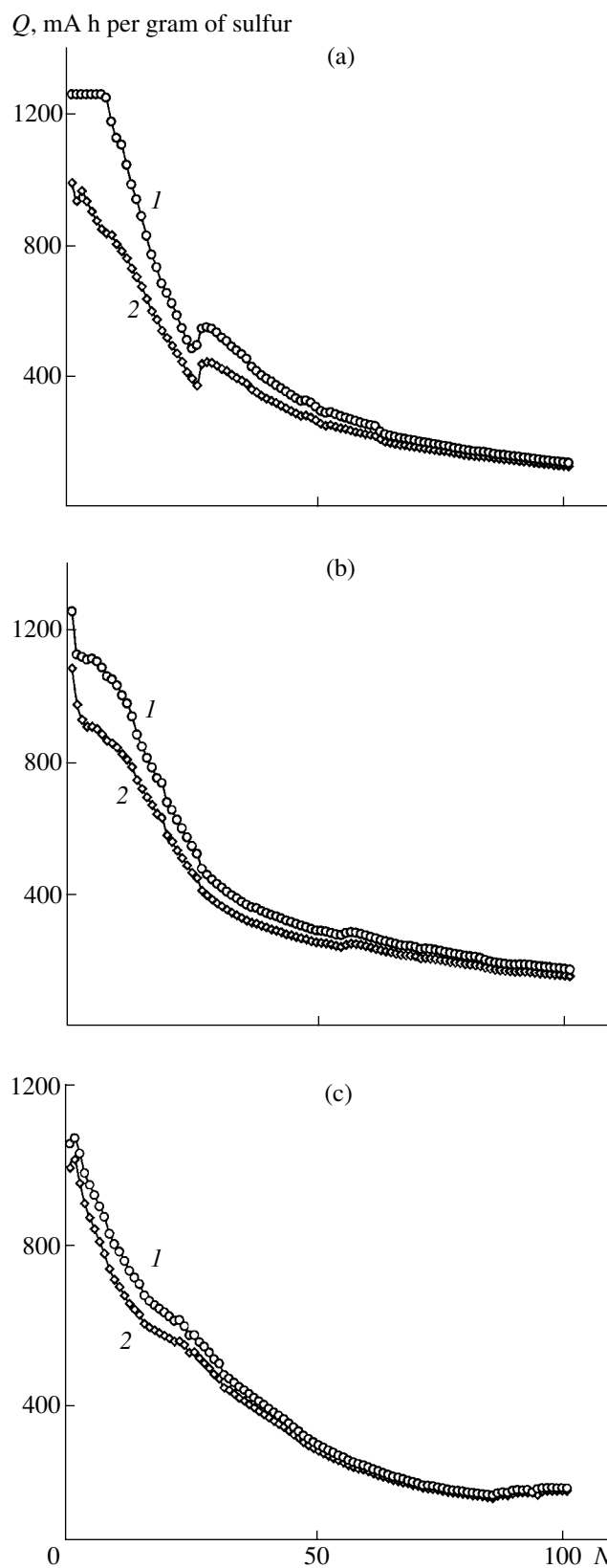
### RESULTS AND DISCUSSION

Figures 1 and 2 present charge–discharge curves and curves of variation in the sulfur electrode capacities during cycling in 1 M  $\text{LiCF}_3\text{SO}_3$  solutions in sulfolane mixtures with DME, DOL, and THF. As we see, both the charge and the discharge curves are shaped similarly (Fig. 1). Each curve exhibits two plateaus. A potential dip may be seen in between the plateaus. In



**Fig. 1.** Charge–discharge curves for sulfur electrode in 1 M  $\text{LiCF}_3\text{SO}_3$  in the 1 : 1 (vol %) mixtures as follows: (a) SL–DME, (b) SL–DOL, and (c) SL–THF; numerals next to curves are cycle numbers.

the course of cycling there appears in these curves one more, weakly pronounced plateau (inflection) at 1.7–1.6 V. The initial specific discharge capacity was nearly 900 mA h per gram of sulfur for electrolytes containing DME and THF and 1100 mA h per gram of sulfur, for electrolytes containing DOL.



**Fig. 2.** Dependences of (1) charge and (2) discharge capacities of sulfur electrode on the number of cycles  $N$  in 1 M  $\text{LiCF}_3\text{SO}_3$  solution in the 1 : 1 (vol %) mixtures as follows: (a) SL–DME, (b) SL–DOL, and (c) SL–THF.

The lengths and potentials of the plateaus in the charge and discharge curves gradually alter in the course of cycling. The nature of an ether solvent affects the potential of the second plateau and the degree of the overvoltage increase in the course of cycling. For example, the potential of the “two-volt” plateau in the discharge curves obtained in electrolytes containing DME and DOL diminishes in the course of cycling from 2.07 to 1.95 V, whereas in the case of THF, it reduces from 2.00 to 1.80 V.

The shapes of curves illustrating variations in the charge and discharge capacities depend, albeit weakly, on the composition of the electrolyte system (Fig. 2). Attention is drawn to the fact that small maximums or inflections appear in the initial portions of these curves. The most pronounced maximum is observed in the electrolyte containing DME.

The cycling efficiency substantially depends on the nature of the co-solvent. The maximum efficiency is observed for the electrolytic solution containing tetrahydrofuran and the minimum, for that containing dimethoxyethane.

#### *Mechanisms of the Effect of Electrolyte Systems on the Sulfur Electrode Cycling*

Processes that occur in the lithium–sulfur batteries in the course of their cycling are tremendously complicated and interrelated. As the electroreduction of sulfur and the oxidation of sulfide ions of different stoichiometry involves liquid-phase stages, properties of electrolyte systems exert a substantial influence on the regularities of their occurrence. Therefore, before discussing the results we obtained, let us briefly consider feasible mechanisms that govern the effect the properties of solvents have on the forms and electrochemical activity of sulfur and products of its reduction in the electrolytes.

The solubility of sulfur and lithium polysulfides and their electrochemical activity is known to be substantially dependent on the properties of the electrolyte system [4–6]. For example, long-chain lithium polysulfides  $\text{Li}_2\text{S}_n$  ( $n > 3$ ) are fairly well soluble in solvents with a low permittivity and high basicity, while short-chain ones ( $n < 3$ ), in highly-polar solvents.

The electrochemical activity of polysulfides is defined by the length of the polysulfide chain (the degree of polysulfidity) and by the form in which polysulfides are present in electrolytes. With increasing degree of polysulfidity  $n$ , the electrochemical activity of lithium polysulfides rises. This is explained by the fact that the electron density on the sulfur atoms decreases with increasing length of polysulfides due to its delocalization over the polysulfide chain. This follows from the change in their basicity as a function of the composition [7].

We believe that the electron density distribution over the polysulfide chain depends also on the structure of ionic associates of polysulfides present in solutions.

The salts may exist in solutions in several forms, specifically, as free solvated ions, outer-sphere ionic pairs, solvation-separated ionic pairs, and contact ionic pairs. The stronger the interaction between the lithium cation and a sulfide anion, the greater the differences in the electron density on the “end” and “inner” sulfur atoms of a polysulfide chain. This leads to an increase in the electrochemical activity of inner sulfur atoms. That is why we presume that the ease, with which a polysulfide anion undergoes reduction, will increase in the series free solvated ion < outer-sphere ionic pair < solvation-separated ionic pair < contact ionic pair. The form assumed by salts in solutions (supporting salts, lithium polysulfides) is defined by both the properties of ions constituting them and the solvent properties (permittivity, solvation ability).

The degree of association of lithium polysulfides increases with decreasing size of solvated ions and the strength of solvation shells. That is why the degree of association of lithium sulfides in solution increases with decreasing molar volume and donor properties of solvent molecules. The increase in the degree of association of lithium sulfides is facilitated also by an decrease in the environment permittivity. It should also be noted that aprotic bipolar solvents are capable of solvating not only ions of supporting salts but polysulfide anions as well, at the expense of a  $\pi$ -dative interaction between  $d$  orbitals of sulfur and  $p$  orbitals of oxygen atoms in the solvent molecules [8].

When analyzing mechanisms of functioning of lithium–sulfur cells, it is necessary to take into account the fact that, due to the formation of well soluble compounds and to incomplete reversibility of electrochemical processes in the course of electroreduction of sulfur, properties of an electrolyte system continuously vary both during an individual cycle and in the course of the entire cycling process. In an individual cycle, during the sulfur reduction process, the electrolyte becomes saturated with polysulfides; as a result, the electrolyte polarity decreases. Then the latter starts growing again owing to the decrease in the concentration of polysulfides in electrolyte because of the precipitation of final products of their reduction (short-chain lithium polysulfides) in the form of a solid phase.

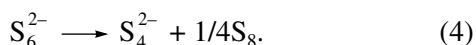
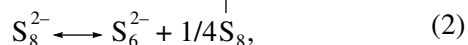
We assume that the incomplete reversibility of electrochemical processes in the course of prolonged cycling will lead to a gradual accumulation of short-chain lithium polysulfides with a poor solubility and the least electrochemical activity. Due to the poor solubility, short-chain polysulfides will precipitate as a solid phase, thus excluding themselves from the electrochemical process. As a result, the discharge capacity of a sulfur electrode will diminish.

### The Mechanism of Discharge Processes

In view of the foregoing, we offer the following mechanism for the processes that occur in lithium-sulfur cells in the course of their cycling.

The sulfur electroreduction involves two electrochemical stages. This follows from the presence of two plateaus in the discharge curves of a sulfur electrode. In the first stage (high-voltage plateau), there occurs a two-electron reduction of an octet of elemental sulfur [4, 7, 9] with the formation of  $S_8^{2-}$ . The anion thus formed is unstable and experiences a number of chemical conversions leading to the formation of sulfur and sulfide anions with a smaller number of sulfur atoms.

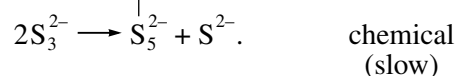
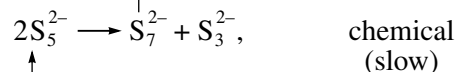
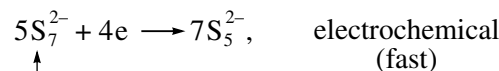
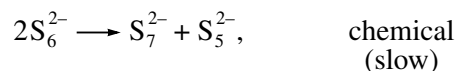
According to the literature data and the results of our studies, the aggregate of processes that occur in the first stage of reduction may be described by the following equations of reactions:



The  $S_8^{2-}$  anion dissociation with the expulsion of elemental sulfur leads to an increase in the capacity released in the first stage. In the case of formation of anions  $S_6^{2-}$  and  $S_4^{2-}$ , the overall capacity will amount to 280 and 420 mA h per gram of sulfur, respectively. As the discharge capacity in dioxolane-containing electrolytes is equal to approximately 350 mA h per gram of sulfur, we assume that reaction (4) also occurs in the first stage. However, additional studies are warranted in order to confirm this assumption.

The second stage probably involves the reduction of long-chain polysulfides dissolved in the electrolyte system. These polysulfides form in the first stage as a result of disproportionation reactions leading to the formation of both long- and short-chain polysulfides. It is mainly long-chain polysulfides that undergo electrochemical reduction, while the short-chain ones enter subsequent reactions of disproportionation, leading in the long run to the formation of lower polysulfides with a poor solubility in the electrolyte system, which become deposited in the electrode pores. The occurrence of a chemical reaction in between the first and second stages follows from the presence of a potential dip between the first and second plateaus in the discharge curves. The emergence of such a dip is probably connected with the low rate of the disproportionation reaction, which leads to the formation of electrochemically active polysulfides. One of the feasible schemes of reactions that

could occur in the second stage is the following:



An analysis of the obtained results readily reveals that the reduction depth of a sulfur electrode nicely correlates with the molar volume of co-solvents. The molar volume of the ethers decreases in the series DME ( $104.6 \text{ cm}^3 \text{ mol}^{-1}$ ) > THF ( $81.7 \text{ cm}^3 \text{ mol}^{-1}$ ) > DOL ( $68.6 \text{ cm}^3 \text{ mol}^{-1}$ ). The capacity released in the first stage increases in the same series. As we have shown in the foregoing, the electrochemical activity of polysulfide anions is a function of the form in which they exist in solution. The maximum electrochemical activity is inherent in the polysulfide anions of contact ionic pairs.

Suppose that the solvation number of lithium in the electrode systems studied is the same (4). Then the strength of ionic associates of lithium polysulfides in dioxolane-containing electrolytes is greater than in any other electrolyte system studied, and the polysulfide anion enters a contact ionic pair. This is what leads to the increase in the depth of electrochemical reduction of sulfur in the dioxolane-containing electrolytes.

Elemental sulfur that forms in the disproportionation of the  $S_8^{2-}$  anion also undergoes electrochemical reduction in the first stage. This fact allows us to assume that the disproportionation reactions involving expulsion of elemental sulfur occur most easily and most deeply in the electrolyte systems where polysulfides exist in the form of contact or solvation-separated ionic pairs.

### The Mechanism of Charge Processes

The charge curves for a sulfur electrode also exhibit each two plateaus. We attribute the low-voltage plateau to the oxidation of soluble polysulfides, which leads to an increase in the degree of polysulfidity (formation of long-chain polysulfides), and the high-voltage plateau, to the oxidation of long-chain polysulfides to elemental sulfur. Reactions of electrochemical oxidation of polysulfides are, probably, accompanied by reactions of disproportionation as well.

The emergence of maximums and inflections in the initial portions of dependences of the sulfur electrode capacity on the number of charge-discharge cycles may be attributed to accumulation of soluble polysulfides in electrolytes as a result of incomplete oxidation

of lithium polysulfides during the charging process. As a fraction of sulfur leaves the electrochemical system in the form of lower polysulfides during further cycling, the content of soluble polysulfides in the electrolytic solution decreases, which is manifested as the decrease in the length of the second plateau in the discharge curves.

The decrease in the sulfur electrode capacity in the course of cycling is, more likely than not, also caused by a fraction of sulfur leaving the electrochemical system in the form of lower lithium polysulfides. These have a low reactivity and are barely capable of undergoing electrochemical reduction. Depositing themselves on the surface and in the pores, lower lithium polysulfides block the electrode surface, thus hampering the electrochemical reactions, which follows from an increase in the overvoltage of anodic and cathodic process with increasing number of cycles. This assumption is also confirmed by the results reported in [10], whose authors demonstrated that a cathode containing lithium sulfide cannot be charged.

We believe that the relatively low efficiency of the sulfur electrode cycling in the initial stage is due to the interaction of lithium polysulfides dissolved in the electrolyte with the freshly-deposited metallic lithium:  $2\text{Li}^0 + \text{Li}_2\text{S}_n \rightarrow 2\text{Li}_2\text{S}_{n/2}$ . The rate of the interaction between lithium polysulfides and metallic lithium is defined by their concentration in the electrolytic solution and chemical activity. The maximum chemical activity is probably intrinsic to lithium polysulfides that exist in electrolytes containing DME.

Thus, the studies we performed has confirmed the assumptions about a substantial influence the nature of the electrolyte system has on the regularities of electrochemical behavior of a sulfur electrode. The maximum effect is exerted by the molar volume of solvents, their solvation properties, and their polarity, as it is precisely these factors that define the form in which lithium polysulfides exist in solutions.

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