

Cycling a Sulfur Electrode: Effect of Physicochemical Properties of Electrolyte Systems

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Abstract—A sulfur electrode is cycled in mixtures of 3-methoxysulfolane and sulfolane with linear ethers (glyme, diglyme, tetraglyme) and lithium trifluoromethane sulfonate (lithium triphlate) as the supporting electrolyte. The decrease in the electrode capacity, observed with an increase in the number ethylene oxide links in glyme molecules and in the number of donor centers in sulfone molecules, is attributed to changes in the form taken by lithium polysulfides in solutions and the increase in the electrolyte viscosity.

Keywords: sulfur electrode capacity, sulfolanes, lithium triphlate

INTRODUCTION

In our earlier studies dealing with cycling a sulfur electrode in mixtures of sulfolane with cyclic and linear ethers and lithium triphlate as the supporting electrolyte, we assumed that the form taken by lithium polysulfides in electrolyte solutions substantially affects the electrochemical behavior of sulfur electrodes [1, 2].

It is known that the solubility and the form taken by lithium sulfides in solution are determined by physicochemical properties of solvents, viz., permittivity, basicity, and molar volume. According to [3, 4], solvents with high permittivities and donor numbers well solvate and stabilize both long- and short-chain lithium polysulfides, whereas solvents with low permittivities and high basicities well solvate only long-chain lithium polysulfides. Solvents with weak donor abilities poorly solvate lithium polysulfides.

Despite the data available, it still remains unclear how the physicochemical properties of electrolyte systems affect the mechanism of electrochemical reduction of sulfur. To solve this problem, we studied the cycling of sulfur electrodes in mixtures of 3-methoxysulfolane and linear ethers (glymes).

EXPERIMENTAL

We used 3-methoxysulfolane (3-MeSL) as the main solvent and linear ethers with different numbers of ethylene oxide links in molecules [glyme (GL), diglyme (DGL), and tetraglyme (TGL)] as the co-solvents. The volume ratio sulfone : ether was 1 : 1. Lithium triphlate served as the supporting electrolyte. Lithium triphlate

and ethers were supplied by Samsung Sheil Industries. Synthesis of 3-methoxysulfolane was carried out according to the procedure proposed in [5]. The purity degree of all solvents was 99.8–99.0%, according to gas–liquid chromatography data. The water content in electrolytes found by coulometric titration in the Fischer's salt medium did not exceed 0.005–0.008%.

The composition of sulfur electrodes, the technology of their preparation, and the procedure of electrochemical experiments were similar to those described in [1]. The cycling time of lithium–sulfur cells was limited by 101 cycles in all experiments.

RESULTS

Figure 1 shows chronopotentiograms of the cathodic reduction of sulfur (discharge curves) and anodic oxidation of its reduction products (charging curves) measured in 1 M LiCF₃SO₃ solutions in mixtures of 3-MeSL and sulfolane (SL) with glyme, diglyme, and tetraglyme.¹ The experimental results have shown that the nature of sulfone affects sufficiently strongly the shape of chronopotentiograms, the value of specific discharge capacity of sulfur electrode, and its variation in the course of cycling.

The shape of sulfur-electrode chronopotentiograms in electrolyte systems 3-MeSL–GL–LiCF₃SO₃ and SL–GL–LiCF₃SO₃ are similar. However, they show certain differences. Thus, the potential dip between the first and second plateaus in sulfur-electrode discharge curves and the increase in the overpotential during cycling in 3-MeSL-based electrolyte systems are more

¹ The data of sulfur electrode cycling in mixtures of sulfolane with glymes are taken from [2].

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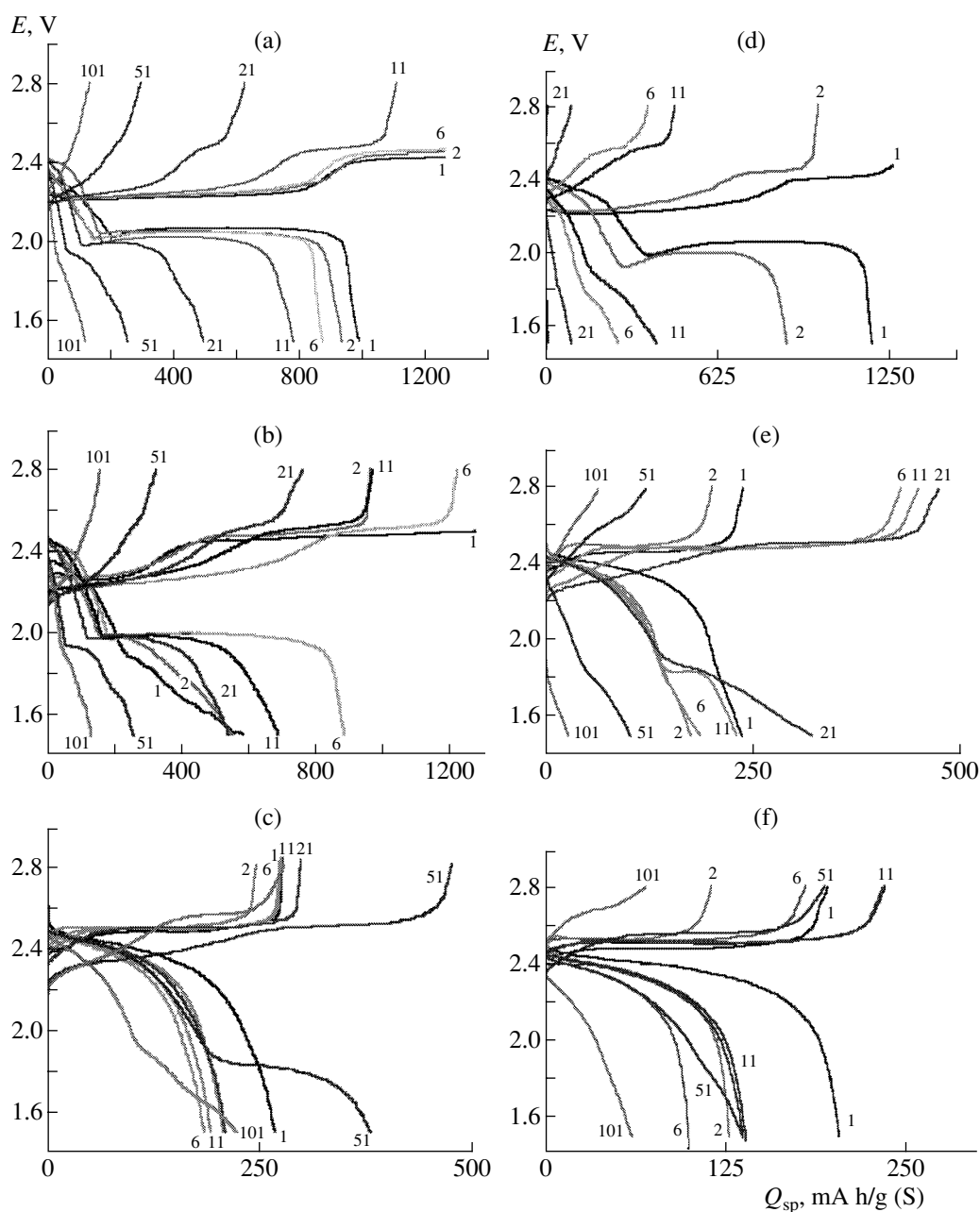


Fig. 1. Chronopotentiograms of cathodic reduction of sulfur and anodic oxidation of its reduction products in 1 M LiCF_3SO_3 solutions in mixtures of sulfones with glymes (volume ratio 1 : 1): (a) SL-GL, (b) SL-DGL, (c) SL-TGL, (d) 3-MeSL-GL, (e) 3-MeSL-DGL, and (f) 3-MeSL-TGL; cycling mode 0.5 C, $t = 25^\circ\text{C}$; numerals at the curves mark cycle numbers.

pronounced than for those based on SL. Another strong difference lies in the length of the first plateau in discharge curves in the initial period of cycling: this length is 350 mA h/g (sulfur) for electrolyte systems based on 3-MeSL and 200 mA h/g (sulfur) for those based on SL.

When diglyme was used as the co-solvent, the differences in the chronopotentiogram shapes became more pronounced. In the electrolyte system based of the 3-MeSL-DGL mixture, in the initial cycles, only a single plateau is observed in charging and discharge

curves of a sulfur electrode, whereas the second plateau appears only after 10 cycles.

In electrolyte systems based on mixtures of SL and 3-MeSL with TGL, the second plateau is absent in initial cycles. It appears only for the SL-TGL system after 30–40 cycles.

The dependences of the specific discharge capacity of a sulfur electrode on the number of cycles (Fig. 2) measured in 3-MeSL mixtures with SL and GL are similar and represent descending curves with small peaks

in initial cycles. Substitution 3-MSL for SL in electrolyte mixture shifts the peaks, increases the curve slope, and decreases the specific discharge capacity of the sulfur electrode.

When DGL was used as the co-solvent, the Q_{sp} vs. N dependences that demonstrate the cycling behavior of specific discharge capacity of sulfur electrode are also similar to one another. As in the previous case, they represent descending curves with sufficiently well pronounced peaks in initial cycles. In contrast to the case above, the maximum of sulfur electrode capacity in 3-MeSL appears in later cycles (25th–30th cycles) as compared with the SL-containing electrolyte (the 6th cycle). Substitution of 3-MeSL for SL also decreases the specific discharge capacity of sulfur electrode.

In contrast to the aforementioned cases, the Q_{sp} vs. N dependences obtained in 3-MeSL–TGL and SL–TGL electrolyte systems substantially differ from one another. For example, in SL–TGL mixtures, this dependence passes through a well pronounced maximum (45th–75th cycles), whereas, in 3-MeSL–TGL, the dependence has a wide “plateau” (10th–60th cycles). As in both previous cases, the specific discharge capacity of a sulfur electrode is lower in systems based on 3-Me–SL, as compared with those based on SL. Thus, in the 101st cycle, the specific discharge capacitance of a sulfur electrode is about 220 mA h/g (sulfur) for SL-containing electrolyte and 60 mA h/g (sulfur) for 3-MeSL electrolytes.

DISCUSSION

The table lists physicochemical properties of solvents under study. Here ρ is the density, V_{mol} is the molar volume of solvents, η is the dynamic viscosity, D is the dipole moment, ϵ is the permittivity, DN is the donor number, AN is the acceptor number.

From the results obtained, it follows that the solvent nature has a sufficiently strong effect on the electrochemical behavior of sulfur electrodes, although the donor properties and polarity of studied sulfones and ethers are much similar (table).

Prior to discussing the effect of solvent properties on the electrochemical behavior of a sulfur electrode, we note certain common features in the evolution of the chronopotentiogram shape with the properties of com-

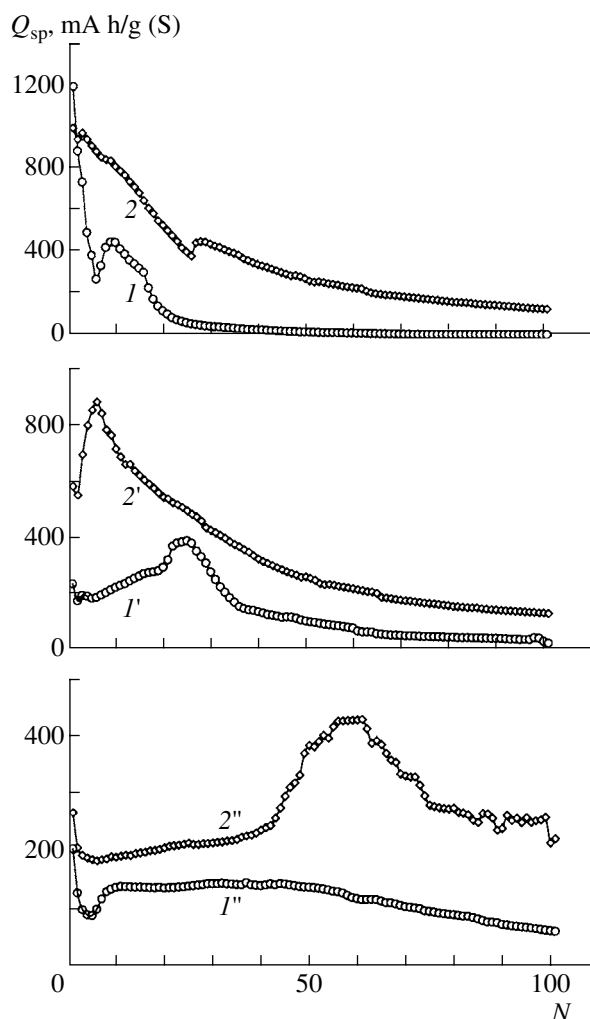


Fig. 2. Dependences of specific discharge capacity of a sulfur electrode on the number of cycles N in 1 M LiCF_3SO_3 solutions in mixtures of sulfones with glymes (volume ratio 1 : 1): (1) 3-MeSL–GL, (2) SL–GL, (1') 3-MeSL–DGL, (2') SL–DGL, (1'') 3-MeSL–TGL, and (2'') SL–TGL; cycling mode 0.5 C; $t = 25^\circ\text{C}$.

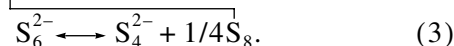
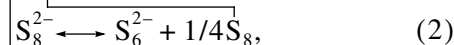
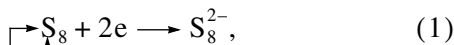
ponents of electrolyte systems. Thus, in all the cases, the enhancement in the dentate structure of solvents (both sulfones and ethers) narrows and even eliminates the second plateau in sulfur electrode chronopotentiograms. The dentate structure of sulfones also affects the

Physicochemical properties of solvents

| Solvent | ρ , g/cm ³ | V_{mol} , cm ³ /mol | η , N s/m ² | D | ϵ | DN | AN |
|-----------------------------|----------------------------|----------------------------------|-----------------------------|------|------------|------|------|
| 3-Methoxysulfolane (3-MeSL) | 1.277 | 117.5 | 15.15 | – | 50.4 | – | – |
| Sulfolane (SL) | 1.262 | 95.4 | 10.29 | 4.81 | 42.9 | 14.8 | 19.2 |
| Glyme (GL) | 0.861 | 104.6 | 0.41 | 1.71 | 7.1 | 24.0 | 10.0 |
| Diglyme (DGL) | 0.940 | 142.8 | 1.01 | – | 7.2 | 24.0 | 10.2 |
| Tetraglyme (TGL) | 1.007 | 204.9 | 3.67 | – | – | – | – |

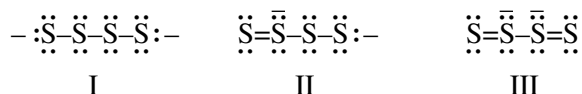
length of the first plateau; however, this effect is observed only in electrolytes containing glyme as the co-solvent. The viscosity of solvents also has an effect on the lengths of first and second plateaus.

The electrochemical reduction of sulfur involves two electrochemical steps² [1]. The first step involves the following reactions:



As follows from the specific discharge capacity values of the sulfur electrode obtained in the first step, the stability of the dianion S_8^{2-} formed in reaction (1) depends on the medium properties. With an enhancement of the dentate structure of the solvent, the stability of S_8^{2-} decreases, whereas, an increase in the viscosity stabilizes the dianion.

These facts can be explained as follows. In [3], it was assumed that polysulfide ions can exist in three forms

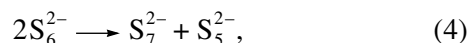


Double bonds in structures II and III are formed as the result of the d_π - d_π interaction due to electron transfer from nonbonding π -orbitals onto terminal sulfur atoms to d -orbitals of central sulfur atoms. Conjugation in I and III structures decreases the electronic density at terminal sulfur atoms, and they easily enter into electronic donor-acceptor interactions with solvents.

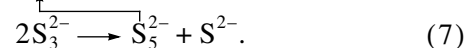
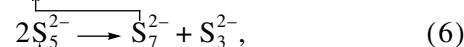
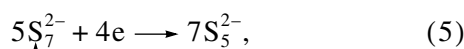
Most probably, it is these interactions that finally lead to dissociation of the polysulfide anion to give elemental sulfur. Hence, with an increase in the solvation ability (dentate structure) of solvents, the equilibrium of the reaction of the primary dianion S_8^{2-} [reactions (2) and (3)] dissociation shifts to the right, which results in an increase in the Q_{sp} of the sulfur electrode in the first step due to the involvement in reaction (1) of elemental sulfur formed in reactions (2) and (3).

The increase in S_8^{2-} stability with an increase in the solvent viscosity can be explained by the "cage-effect."

In the second step of sulfur reduction, the following reactions are most probable:



² Here, the term step means a combination of electrochemical and chemical reactions occurring in a narrow potential range.



In Eqs. (6) and (7), we underlined those sulfide anions which form soluble salts with lithium cations.

The solvent properties affect also the mechanisms of electrochemical and chemical reactions in the second step of sulfur reduction. With the formation of a more pronounced dentate structure and the increase in solvents viscosity, the second plateau in the sulfur electrode chronopotentiograms narrows.

It is known that, due to the chelate and polychelate effects, the more pronounced dentate structure of electron-donors increases the stability of their solvates and complexes with acceptors, thus decreasing the reactivity of the latter. In our case, in addition to lithium cations, polysulfide anions can also play the role of acceptors. The reactivity of lithium polysulfides decreases as the medium becomes more viscous. Probably, it is the decrease in the reactivity of lithium polysulfides with the enhancement of the dentate structure and viscosity of solvents that narrows the second plateau in the sulfur-electrode chronopotentiograms [reaction (5)].

The pronounced potential dip between first and second plateaus in the discharge curves of sulfur electrode indicates the inhibition of disproportionation of polysulfide anions (lithium polysulfides) [reactions (4), (6) and (7)]. One can assume the disproportionation of polysulfide anions to occur after their desolvation. Hence, with an increase in the stability of solvate sheaths, the reaction decelerates, which, ultimately, decreases the concentration of electrochemically active polysulfide forms and, hence, deepens the potential dip between first and second plateaus in discharge curves of the sulfur electrode. This is the case we observed when comparing the chronopotentiograms of sulfur electrodes in electrolyte systems 3-MeSL-GL and SL-GL.

The nature of sulfones also determines the length of the second plateau in the discharge curve of sulfur electrode. Thus, the plateaus are shorter in electrolyte systems based on 3-MeSL as compared with SL-based systems. In the previous studies dealing with the effect of solvents on the electrochemical behavior of sulfur electrodes, we assumed that the electrochemical activity of polysulfide ions is determined by the form of their existence in solutions. The lowest electrochemical activity was demonstrated by polysulfides present in solutions as outer-sphere ionic pairs.

One can hardly assume that substitution of 3-MeSL for SL changes substantially the form of polysulfide solvates. It is more probable that the length of the second plateau in sulfur-electrode chronopotentiograms depends on some other factors.

By comparing the properties of solvents under study, it becomes evident that they substantially differ

in viscosity, i. e., transport properties. The viscosities of electrolyte solutions differ still greater. Moreover, their viscosities substantially exceed those of individual solvents [6–8].

Being substantially slow and bimolecular, the reactions of polysulfide disproportionation can be assumed to be diffusion controlled. Hence, based on the viscosity values, we can expect that, due to the “cage-effect,” their rate will change by an order of magnitude with the transition from GL to TGL and by a factor of 1.5 with the transition from SL to 3-MeSL [9].

Based on the above reasoning and the results of [1, 2], one can attribute the narrowing of the second plateau in sulfur-electrode discharge curves observed with an increase in the number of ethylene oxide links in glyme molecules and the number of donor centers in sulfone molecules to both the changes in the form of existence of lithium polysulfides in solutions and the increase in the solution viscosity.

We assume that the shape of sulfur-electrode capacity dependence in the cause of cycling also reflects the character of changes in the reactivity of polysulfides. From Fig 2, it is clear that these dependences have maximums in all electrolyte systems. The position of a maximum is determined by physicochemical properties of the electrolyte system. Earlier, we have demonstrated that the appearance of maximums is defined by the changes in the length of the second plateau in sulfur-electrode chronopotentiograms in the cause of cycling [2].

The length and potential of the second plateau are determined by the reactivity and concentration of polysulfides in electrolyte solutions. A decrease in the polysulfide reactivity will increase their concentration in the electrolyte solution. Because the polysulfide disproportionation rate decreases with the increase of solvation ability and viscosity of solvents, the area under maximums in Q_{sp} vs. N dependences can be expected to increase with the increase in the number of ethylene oxide links in ether molecules and the number of donor centers in sulfone molecules. Most probably, the position of maximums is defined by the rate of formation of poorly soluble compounds, viz., lithium sulfide and dis-

ulfide. The slower their formation, the later the appearance of maximum in Q_{sp} vs. N dependences. Based on the above reasoning, we can conclude that the rate of this reaction also decreases with the increase in viscosity and solvation ability of solvents. The experimental results we obtained confirm this assumption.

Thus, the studies of the effect of physicochemical properties of electrolyte systems on the electrochemical behavior of sulfur electrodes have shown that the shapes of sulfur-electrode chronopotentiograms and the cycling-induced changes in the capacity curves strongly depend on the viscosity and solvation ability of solvents. It can be assumed that the increase in the viscosity and solvation ability of solvents inhibits the reactions of dissociation of primary dianion S_8^{2-} and disproportionation of lithium polysulfide in electrolyte solutions.

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