

SHORT
COMMUNICATIONS

Cycling a Sulfur Electrode in Electrolytes Based on Sulfolane and Linear Ethers (Glymes) in an LiCF_3SO_3 Solution

V. S. Kolosnitsyn, E. V. Karaseva, N. V. Shakirova, D. Y. Seung*, and M. D. Cho*

*Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences,
pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia*

**Samsung Advanced Institute of Technology, Suwon, Korea*

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Abstract—The cycling of a sulfur electrode is studied in sulfolane mixtures with linear ethers (1,2-dimethoxyethane, diglyme, tetraglyme) in an LiCF_3SO_3 solution. The results confirm the assumption made previously that different forms of existence of lithium polysulfides in an electrolytic solution affect their electrochemical activity and the decrease in the sulfur electrode capacity during its cycling.

INTRODUCTION

The development of lithium–sulfur batteries has run into serious difficulty, namely, a substantial drop of the sulfur electrode capacity during prolonged cycling. Despite numerous studies, the reason for this phenomenon is not understood yet. Earlier we investigated the cycling of a sulfur electrode in mixtures of sulfolane (SL) with 1,2-dimethoxyethane (DME), dioxolane, and tetrahydrofuran and assumed that it is heavily dependent on the structure of ionic associates of polysulfides present in electrolytic solutions [1].

In solvents with close values of permittivity and donor numbers, the structure of ionic associates of polysulfides is largely defined by the size of the solvation sheath of lithium ions, which depends on the molar volume of solvents at the same solvation number.

To confirm these assumptions, it is of interest to examine the effect the molar volume of solvents has on the cycling of a sulfur electrode. This is precisely the aim of this work. For the objects to study we selected systems that comprise sulfolane and glymes with different numbers of ethylene oxide links, specifically, 1,2-dimethoxyethane (glyme), diglyme (DGM), and tetraglyme (TGM). Raising the number of ethylene oxide links in the glyme molecules permits the determination of the effect the molar volume of solvents exerts on the sulfur electrochemistry.

EXPERIMENTAL

The sulfur electrodes were cycled in 1 M LiCF_3SO_3 solutions in mixtures sulfolane–glyme, sulfolane–diglyme, and sulfolane–tetraglyme. The volume ratio sulfolane : glyme was equal to 1 : 1. The experimental procedure was identical to that described elsewhere [1].

The cycling was restricted to 101 cycles. The average capacity of the sulfur electrode in one cycle was

computed with the formula

$$Q_{\text{av}} = \frac{\sum_{i=1}^{101} Q_i}{101}.$$

All the potentials are referred to a lithium electrode.

RESULTS AND DISCUSSION

The experimental studies demonstrated that, indeed, the number of ethylene oxide links in the glyme molecules affects both the charge–discharge curves and the curves illustrating how the sulfur electrode capacity varies in the course of cycling (Figs. 1, 2). As we see, in the case of glyme and diglyme, the charge–discharge curves (Figs. 1a, 1b) are similar to those obtained in electrolytes based on sulfolane mixtures with tetrahydrofuran and dioxolane [1]. Here, too, each curve exhibits two plateaus. The initial specific discharge capacity depends on the number of ethylene oxide links in the glyme molecules and equals 1000 and 600 mA h per gram of sulfur for electrolytes containing glyme and diglyme, respectively. It should be noted that in the initial cycles the charge–discharge curves for the tetraglyme-containing electrolytes displayed each a single plateau (Fig. 1c). The second plateau would appear after 40–50 cycles.

The curves that illustrate how the sulfur electrode capacity alters in the course of cycling depend on the number of ethylene oxide links in the glyme molecules as well (Fig. 2). In electrolytes containing glyme and diglyme, the curves are similar. These are descending curves with small peaks in the initial portions. In tetraglyme-containing electrolytes, the sulfur electrode capacity depends on the number of charge–discharge cycles in an absolutely different manner: it passes through a distinctly pronounced maximum (Fig. 2c). It must also be stressed that increasing the number of eth-

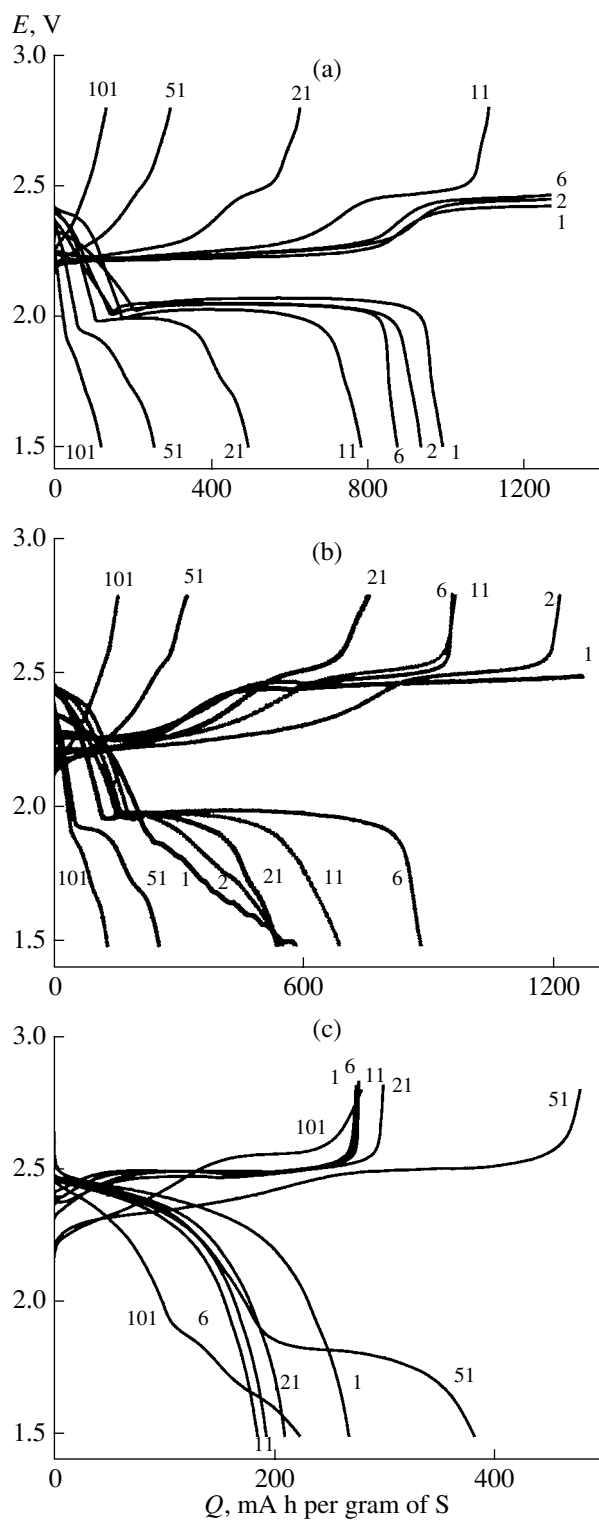


Fig. 1. Charge–discharge curves for sulfur electrode in 1 M LiCF_3SO_3 solution in the following 1 : 1 (vol %) mixtures: (a) SL : DME, (b) SL : DGM, and (c) SL : TGM; numerals near curves are cycle numbers.

ylene oxide links in the ether molecules reduces the initial sulfur electrode capacity and raises the final capacity, thus exhibiting a leveling effect.

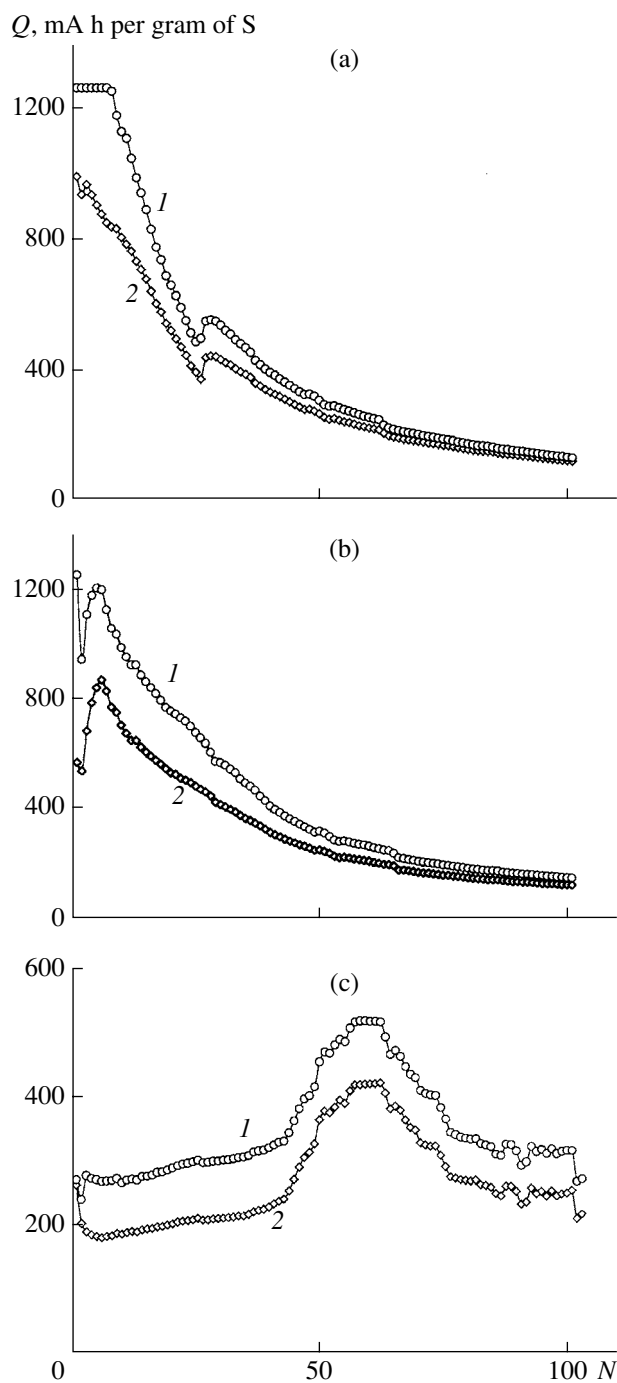


Fig. 2. Dependence of (1) charge and (2) discharge capacities of sulfur electrode on the number of cycles N in the following 1 : 1 (vol %) mixtures: (a) SL : DME, (b) SL : DGM, and (c) SL : TGM.

To determine the stage responsible for the emergence of maximums in the capacity dependence on the number of cycles, we plotted the dependence of the capacity released in the first and second plateaus of discharge curves for the diglyme-based electrolyte system (Fig. 3). As we see, the emergence of maximums is due

Table 1. Physicochemical characteristics of solvents studied

Solvent	Molecular weight	Density, g cm ⁻³	Molar volume, cm ³ mol ⁻¹	Viscosity, N s m ⁻²	Dipole moment	Permittivity	DN	AN
Glyme	90.1	0.861	104.6	0.41	1.71	7.1	24.0	10.0
Diglyme	134.2	0.940	142.8	1.01	–	7.2	24.0	10.2
Tetraglyme	206.3	1.007	204.9	3.67	–	–	–	–
Sulfolane	120.0	1.262	95.4	10.29	4.81	42.9	14.8	19.2

Table 2. Potential of the second plateau and the average capacity of sulfur electrode in a 1 M LiCF₃SO₃ solution in a sulfolane-glyme mixture

Type of glyme	$E_{av, 2}$, V	Q_{av} , mA h per gram of S		Cycling efficiency, %
		discharge	charge	
Glyme	2.07 (6th cycle)	355	446	80
Diglyme	2.00 (6th cycle)	338	460	74
Tetraglyme	1.82 (51st cycle)*	271	356	76

* In this particular electrolyte system no second plateau appears in the discharge curves.

to an increase in the capacity released in the second stage of discharge of the sulfur electrode.

The ethers we studied have similar values of permittivity, donor number, and acceptor number. However, they differ in viscosity and solvation ability (Table 1). The data we obtained suggest that increasing the number of ethylene oxide links in the glyme molecules affects the cycling of the sulfur electrode.

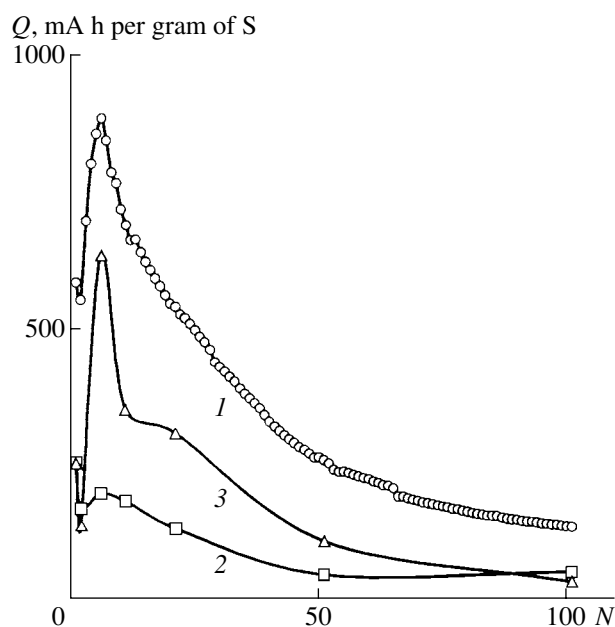


Fig. 3. Variations in (1) overall specific discharge capacity, (2) capacity released in the first plateau, and (3) capacity released in the second plateau of cycling a sulfur electrode in a 1 M LiCF₃SO₃ solution in a 1 : 1 (vol %) mixture of sulfolane and diglyme.

In a previous work we assumed that variations in the sulfur electrode capacity during cycling are defined by the form of the polysulfide anion in solution. The depth of the sulfur reduction is maximum when lithium polysulfides exist in the form of contact ionic pairs. Forms of ionic associates of salts in solutions are known to be determined by the polarity and solvation ability of solvent molecules. When the polarity and solvation ability increase, the degree of association of lithium salts diminishes.

As we showed previously [2], the lithium cation in the system consisting of sulfolane and 1,2-dimethoxyethane is solvated chiefly by molecules of dimethoxyethane, as the latter's donor properties are better than those of sulfolane and it is capable of forming chelates. Therefore, we assume that the lithium ion in the systems that comprise sulfolane and glymes is predominantly solvated by the glyme molecules. As the glyme molecules are polydentate, they interact most probably with the lithium ion by two oxygen atoms and form chelate cycles. Although the tetraglyme molecule contains five oxygen atoms, it is barely probable that all the oxygen atoms are coordinated by a single lithium ion. More likely than not, the lithium ion is also coordinated by two tetraglyme molecules.

We believe that in all the glyme-based electrolyte systems the coordinate number of the lithium cation is equal to four and the solvation number, to two. This being the case, the volume of the solvation sheath of the lithium ion will increase in the series DME < DGM < TGM. That is why it is likely that the degree of electrolytic dissociation of lithium polysulfides will increase and, consequently, the electrochemical activity of polysulfide ions will decrease in the same series. This assumption is substantiated by the decrease in the potentials of the second plateau of the reduction of lith-

ium polysulfides, E_{av2} , and by the decrease in the average discharge capacity of the sulfur electrode in the series glyme > diglyme > tetraglyme (Table 2).

The anomalous behavior of the sulfur electrode in an electrolyte system containing tetraglyme is probably due to lithium salts (lithium polysulfides among them) existing in the form of outer-sphere ionic pairs, due to a large volume of the solvation sheath of the lithium ion. That is the reason for the low electrochemical activity of lithium polysulfides in this system. This phenomenon reveals itself in the low specific discharge capacity and in the absence of the second plateau in the discharge curves.

Thus, the study we performed has confirmed the assumption we made earlier about a substantial influence the form of existence of lithium polysulfides in an electrolytic solution has on their electrochemical activity and on the decrease in the capacity of a sulfur electrode in the course of its cycling.

REFERENCES

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