

**Russian Academy of Science
Ufa Federal Research Centre
Ufa Institute of Chemistry**

On problems of optimizing amount of electrolyte in lithium-sulfur batteries

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Electrochemical system Li - S

Attractive do to its high theoretical specific energy (2654 Wh/kg), which makes it possible to develop energy-intensive electrochemical batteries on its basis.

$$\Delta G = 439 \text{ J/mol}$$

$$\text{EMF} = 2.275 \text{ V}$$

$$Q_{\text{Li}_2\text{S}} = 1.170 \text{ A}\cdot\text{h/g}$$

$$W = 2654 \text{ Wh/kg}$$

Lithium-sulfur batteries are being created during last 60 years - first patent was received in 1962 year (US Patent 3,043,896), - but there is still no commercially acceptable lithium-sulfur batteries.

Key barriers to develop lithium-sulfur batteries

1. Specific energy is still lower than expected

Theory: 2654 Wh/kg

Expected: 700-800 Wh/kg (24-28 % Theory)

Achieved : 350-400 Wh/kg (13-15 % Theory)

2. Rapid capacity decay during cycling and, as consequence, limited cycle life

Li-S batteries = 100-300 cycles

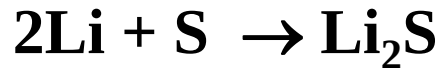
Li-ion batteries = 2000-3000 cycles

3. High rate of self-discharge and irreversible capacity loss during long-term storage

Li-S batteries $\approx$ 6-7% in month

Li-ion batteries $\approx$ 1-2% in month

Lithium-sulfur batteries – batteries with liquid cathode



S and Li₂S – are not electrochemically active in solid phase!

Properties	S	Li ₂ S
Molar mass, g/mol	32.066	45.95
Molar volume, cm ³ /mol	15.49	27.68
Density, g/cm ³	2.07	1.66
Conductivity, S/cm	$3.9 \cdot 10^{-16}$	$< 10^{-14}$
Solubility in aprotic solvents, mM	≈ 50-115	insoluble

Processes on positive electrode of the lithium-sulfur cells during discharge

Dissolution of sulfur, which is part of the positive electrode, in the electrolyte



Transfer to the surface of carbon particles that make up the positive electrode



Sorption on the surface of carbon particles

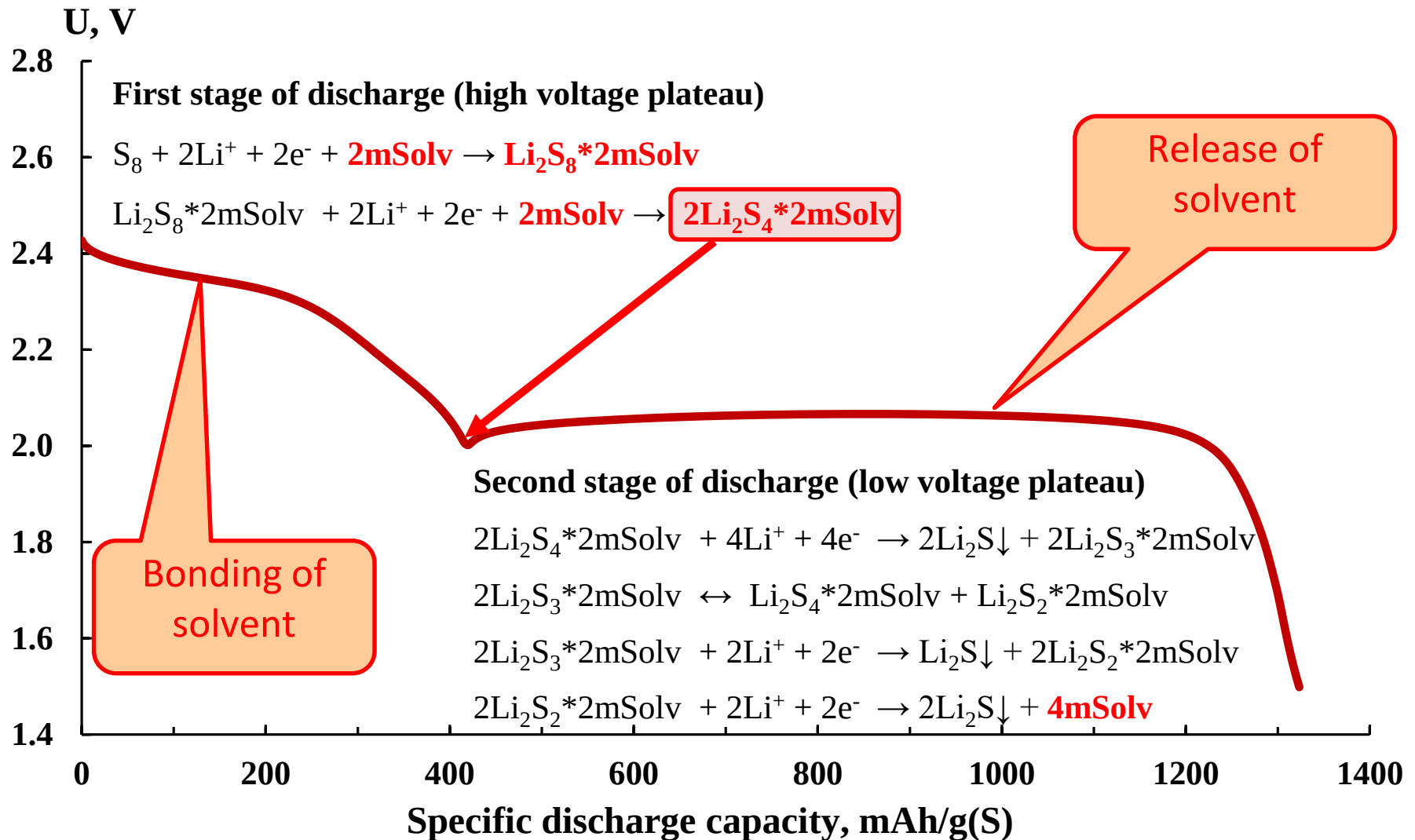


Electrochemical reduction of sulfur

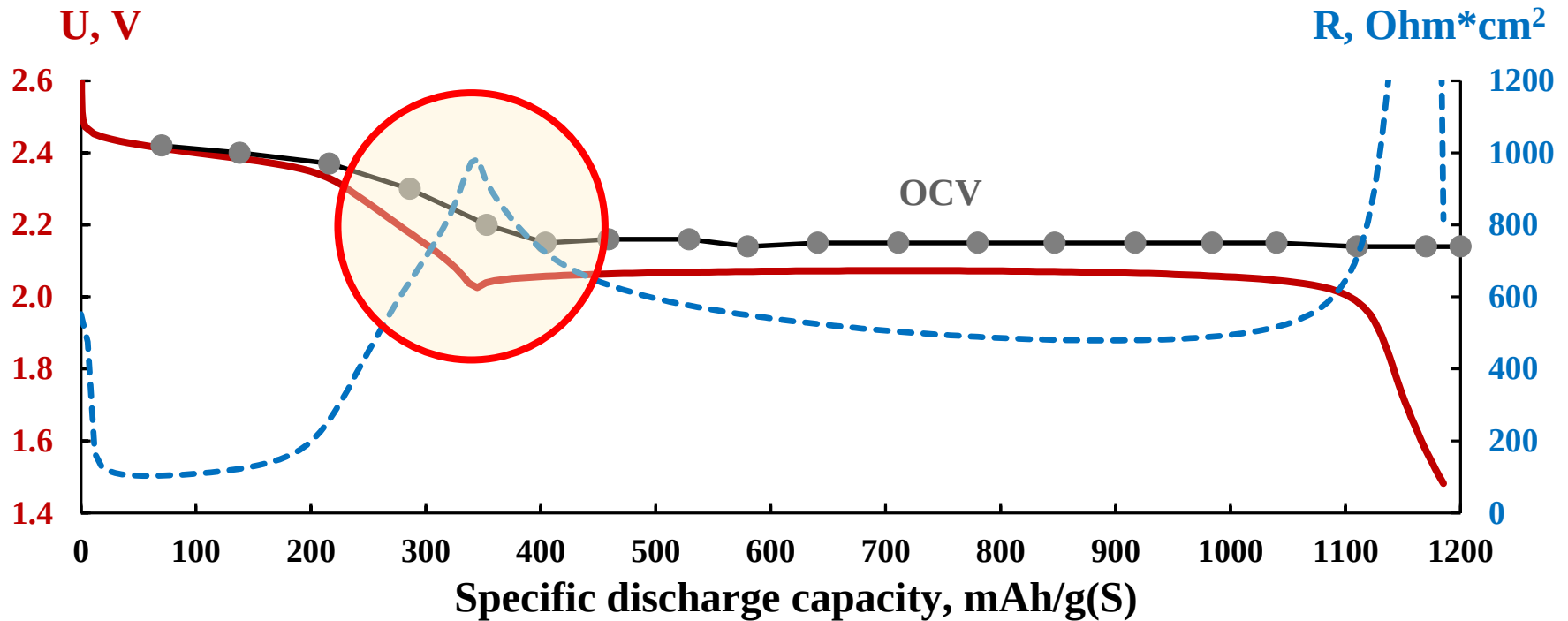


Desorption of products of sulfur reduction

Mechanisms of electrochemical processes when discharging lithium-sulfur cells

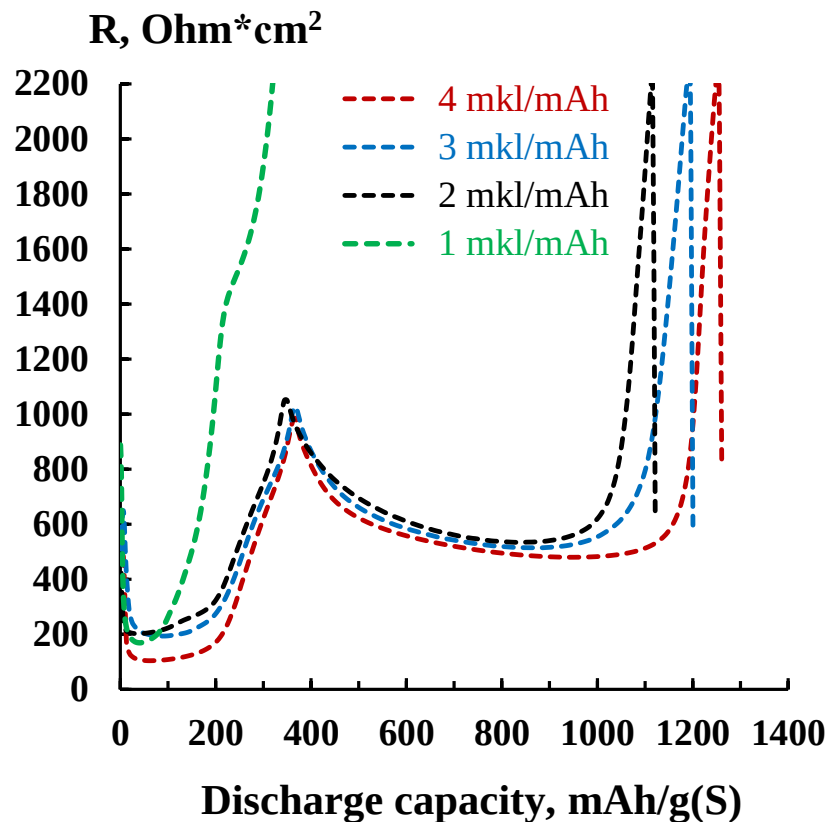
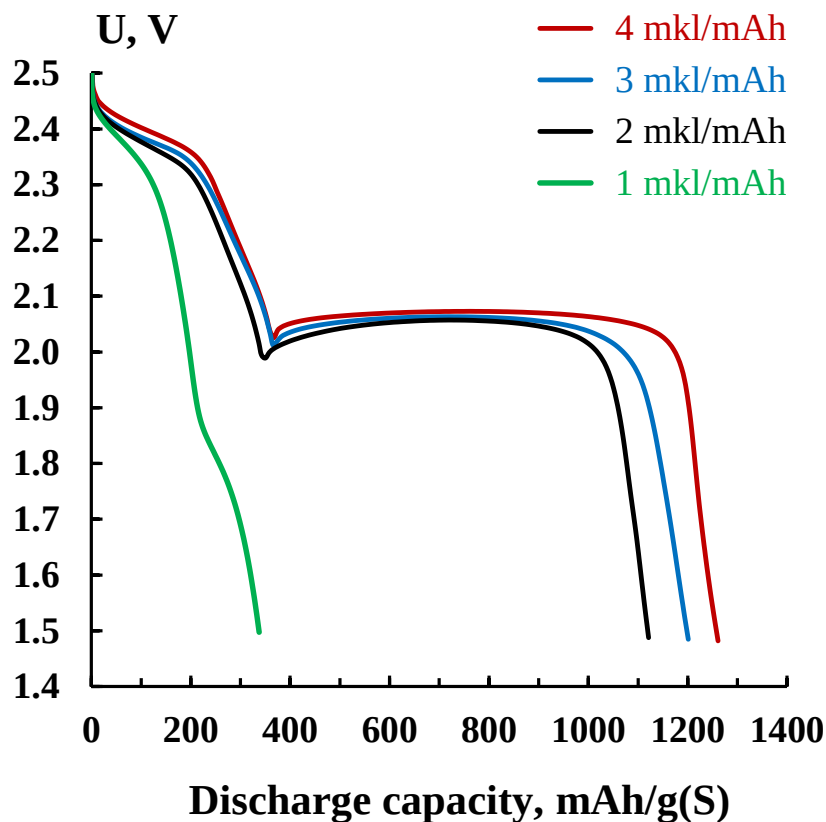


The composition of the electrolyte system at various stages of the discharge of lithium-sulfur batteries (2nd cycle)



$\text{LiA} \cdot \text{Solvent} + \text{Solvent}$	$\text{LiA} + \text{Li}_2\text{S}_n + \text{Solvent}$	$x\text{LiA} \cdot \text{Solvent} + y\text{Li}_2\text{S}_4 \cdot \text{Solvent}$	$y\text{Li}_2\text{S}_4 \cdot \text{Solvent} + z\text{Li}_2\text{S}_3 \cdot \text{Solvent} + m\text{Li}_2\text{S}$	$\text{Li}_2\text{S}_3 + \text{Li}_2\text{S}_2 + \text{Li}_2\text{S (Solid)} + \text{Solvent}$
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Effect amount of electrolyte on depth of electrochemical reduction of sulfur and internal resistance of lithium-sulfur cells (2nd cycle)



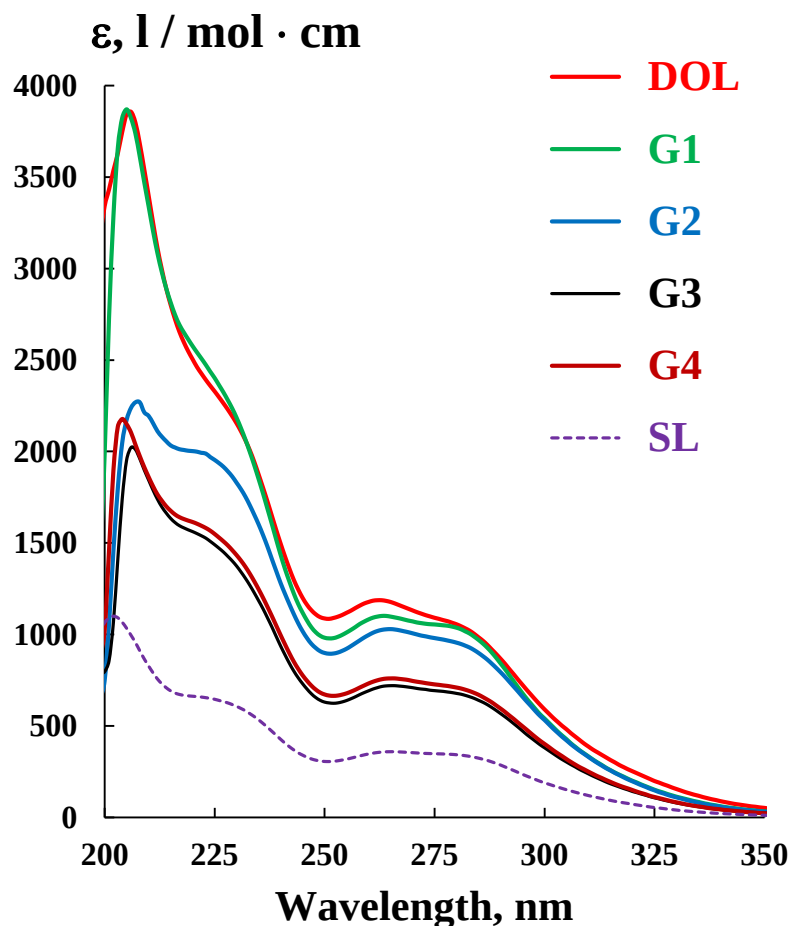
Electrolyte: 1M LiSO₃CF₃ in sulfolane

Sulfur electrodes: 70% S_10% Ketjenblack EC-600JD_20% Poly(ethylene)oxide (MW 4×10⁶)

Sulfur loading: 2 mAh/cm² (1.2 mg/cm²)

Solubility of sulfur in aprotic dipolar solvents (t=30 °C)

$$\varepsilon = \frac{D}{C l} \longrightarrow C = \frac{D k}{\varepsilon l}$$

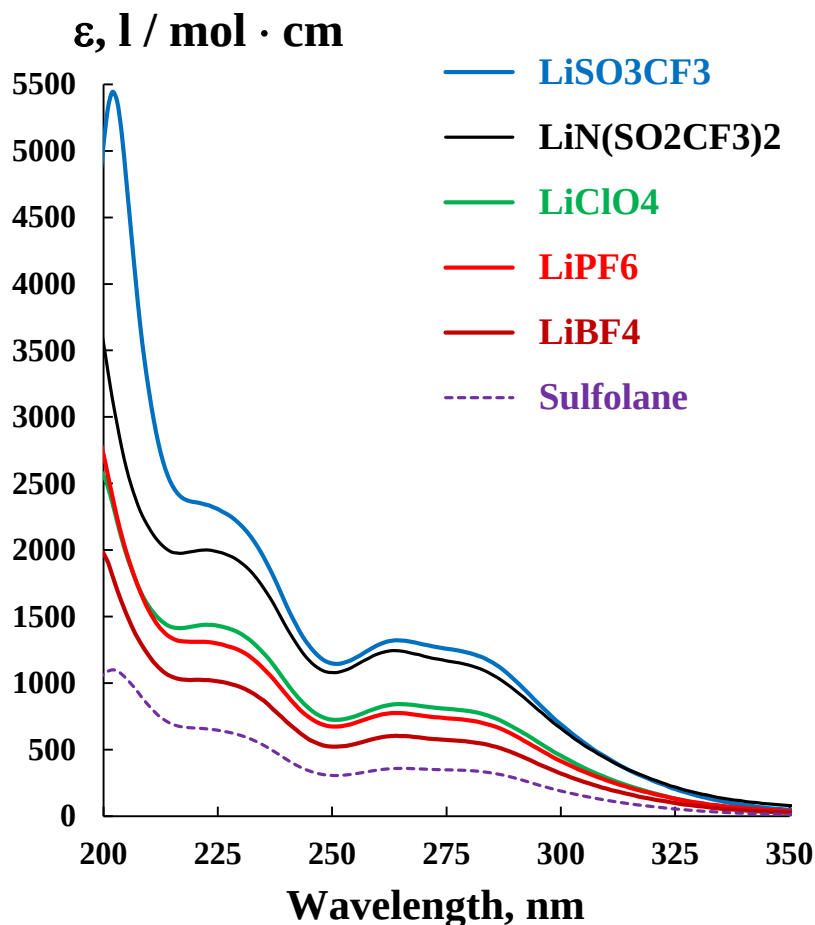


Solvent	Content of sulfur in saturated solution, mM			
	225 nm	265 nm	284 nm	Average
Diglyme (G2)	66.2	66.3	66.6	66.4
Sulfolane	80.7	84.0	81.1	82.0
1,3-Dioxolane	91.0	92.3	96.3	93.2
Tetraglyme	93.8	93.0	92.9	93.2
Glyme (G1)	113.8	119.6	109.6	114.2
Triglyme (G3)	118.4	115.2	112.2	115.2

Effect $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ on solubility of sulfur in aprotic dipolar solvents ($t=30\text{ }^\circ\text{C}$)

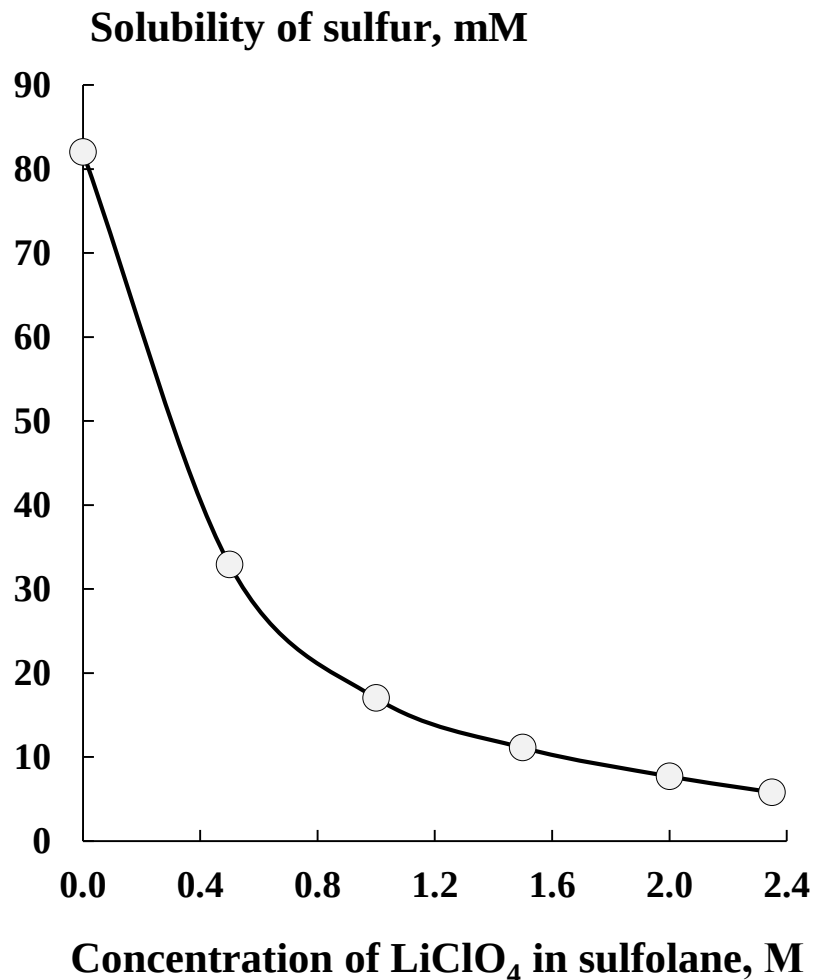
Solvent	Content of sulfur in saturated solution, mM	
	Without $\text{LiN}(\text{SO}_2\text{CF}_3)_2$	1M $\text{LiN}(\text{SO}_2\text{CF}_3)_2$
Sulfolane	82.0	9.0
Glyme (DME)	114.2	19.6
Diglyme	66.4	20.6
Triglyme	115.2	23.3
Tetraglyme	93.2	28.6
1,3-Dioxolane	93.2	30.3

Solubility of sulfur in sulfolane electrolytes for lithium-sulfur batteries ($t=30\text{ }^{\circ}\text{C}$)



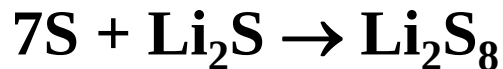
Lithium salt (1M)	Content of sulfur in saturated solution, mM			
	225 nm	265 nm	284 nm	Average
Sulfolane	80.7	84.0	81.1	82.0
LiBF_4	20.1	20.0	20.0	20.0
LiClO_4	17.1	16.9	17.0	17.0
LiPF_6	13.1	12.9	12.8	12.9
LiCF_3SO_3	9.7	10.2	10.2	10.0
$\text{LiN}(\text{CF}_3\text{SO}_2)_2$	9.3	8.7	8.9	9.0

Effect of lithium perchlorate concentration on the solubility of sulfur in sulfolane($t=30\text{ }^{\circ}\text{C}$)

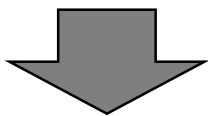


Concentration of LiClO_4 in sulfolane, M	Content of sulfur in saturated solution, mM			
	225 nm	265 nm	284 nm	Average
0	80.7	84.0	81.1	82.0
0.5	33.2	32.9	32.7	32.9
1.0	17.1	16.9	17.0	17.0
1.5	10.7	11.2	11.3	11.1
2.0	7.7	7.7	7.7	7.7
2.35	5.8	6.0	5.6	5.8

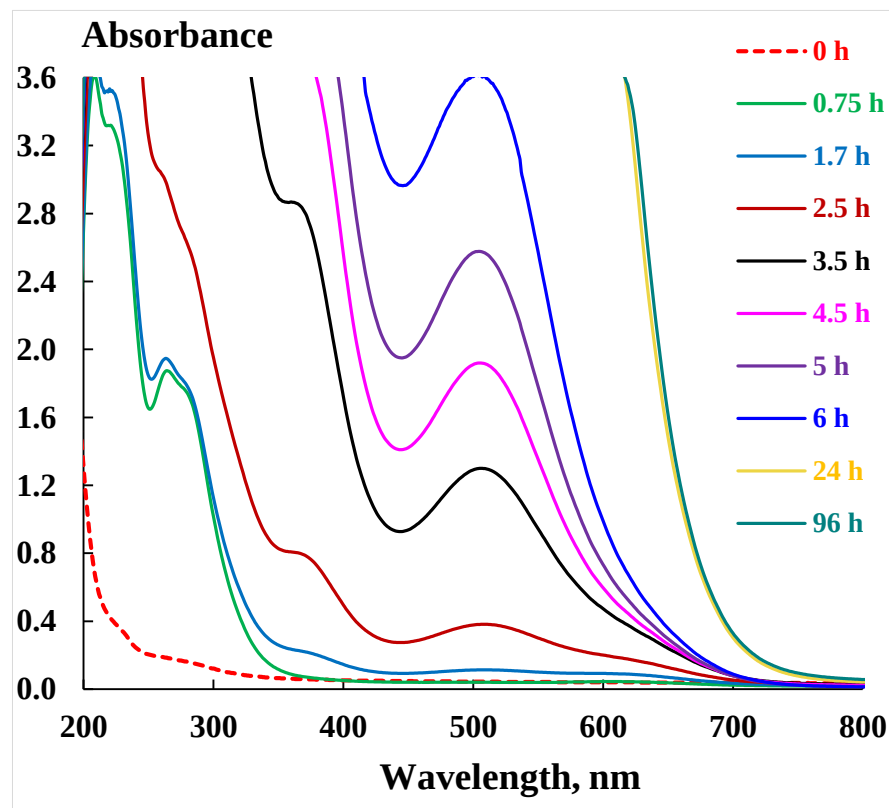
Solubility of long-chain lithium polysulfides in aprotic dipolar solvents (t=30 °C)



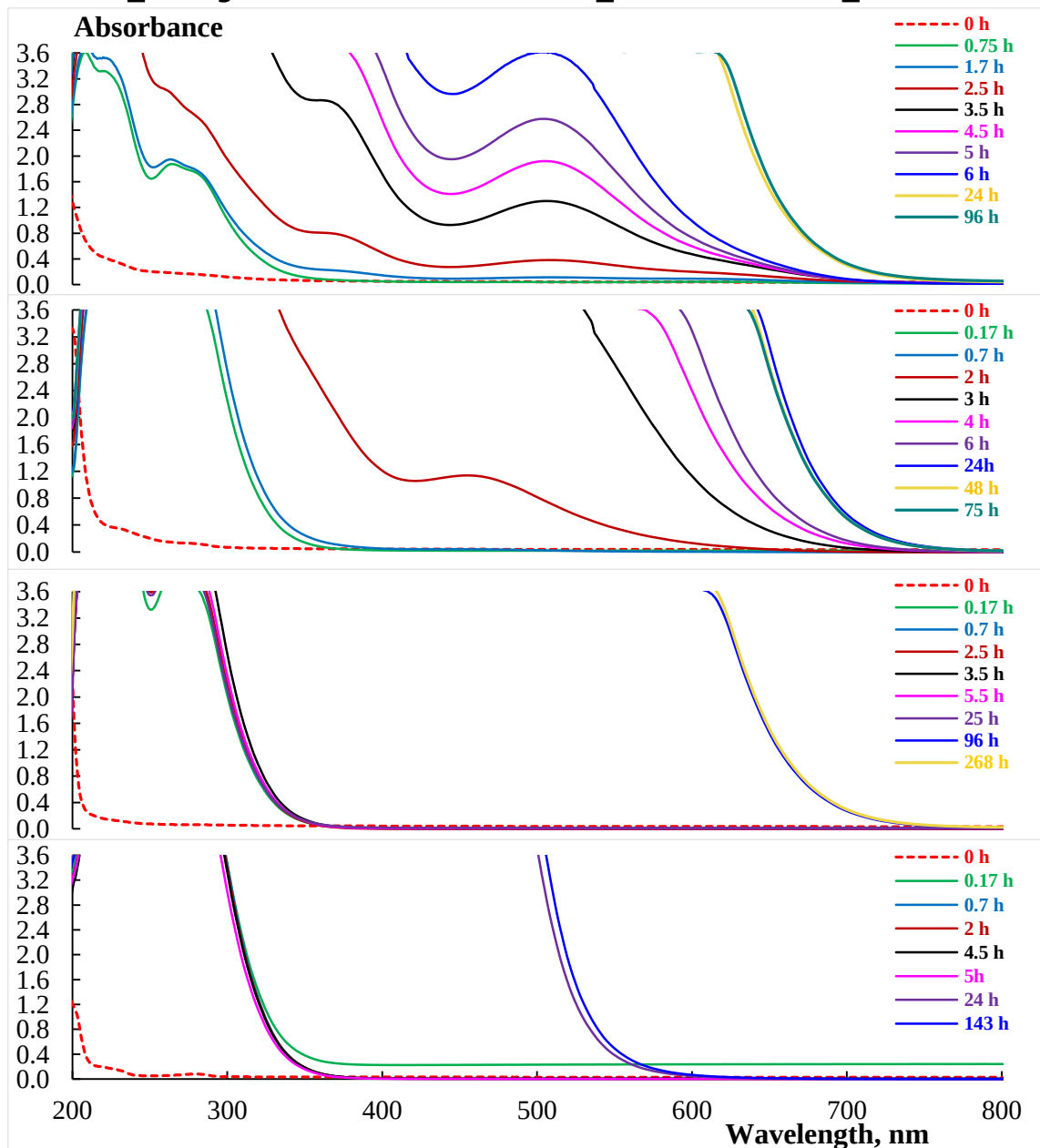
Weight ratio Solid : Liquid = 1 : 9



- Stirring at 30 °C
- Centrifugation at 30 °C
- Registration of spectra (UV, l=0.5 mm, 30 °C)
- Separation liquid and solid phases
- Storage liquid phase at 30 °C
- Iodometric titration of S²⁻



Absorption spectra and solubility of long-chain lithium polysulfides in aprotic dipolar solvents (t=30 °C)



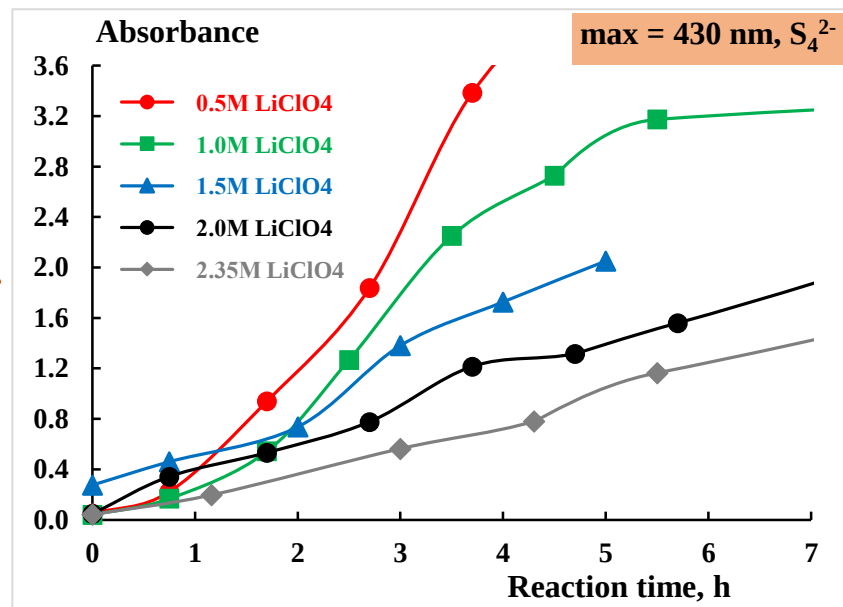
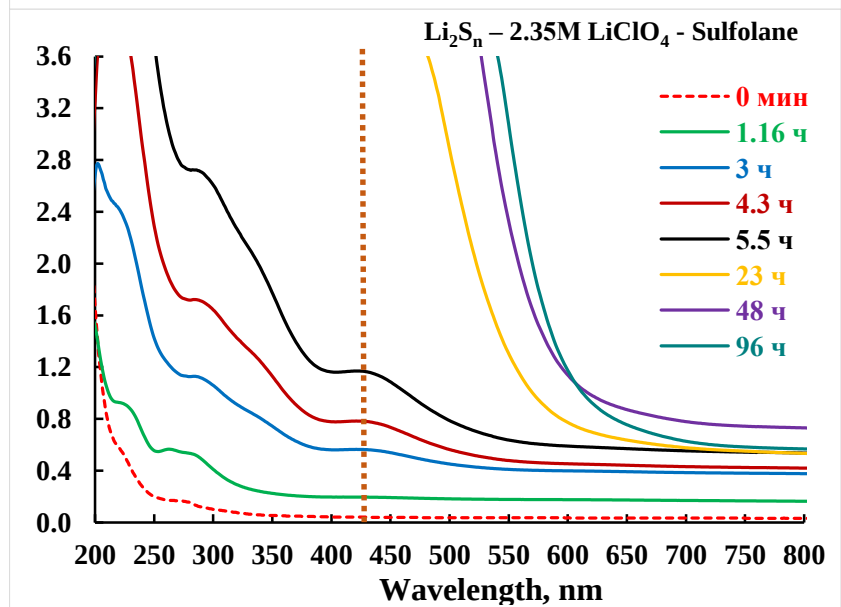
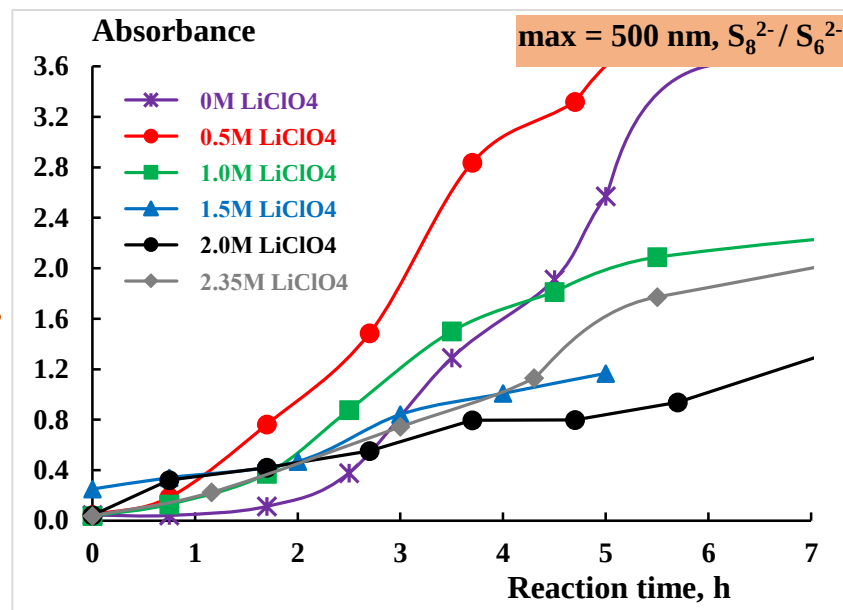
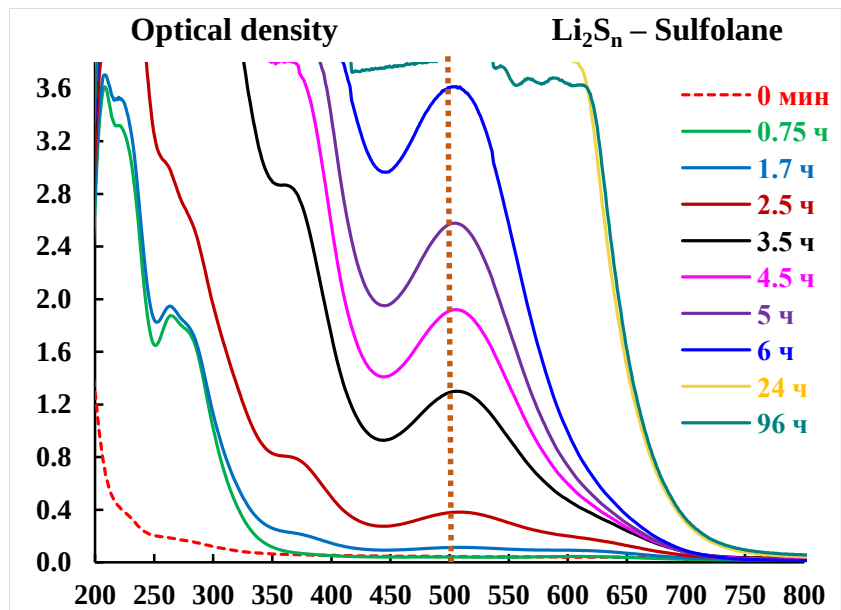
Solubility of $S^{2-} = 0.33$ m
Sulfolane (DN=14.8)

Solubility of $S^{2-} = 0.29$ m
Trygline (DN=14.0)

Solubility of $S^{2-} = 0.35$ m
Glyme (DN=18.6)

Solubility of $S^{2-} = 0.32$ m
1,3-Dioxolane (DN=18.0)

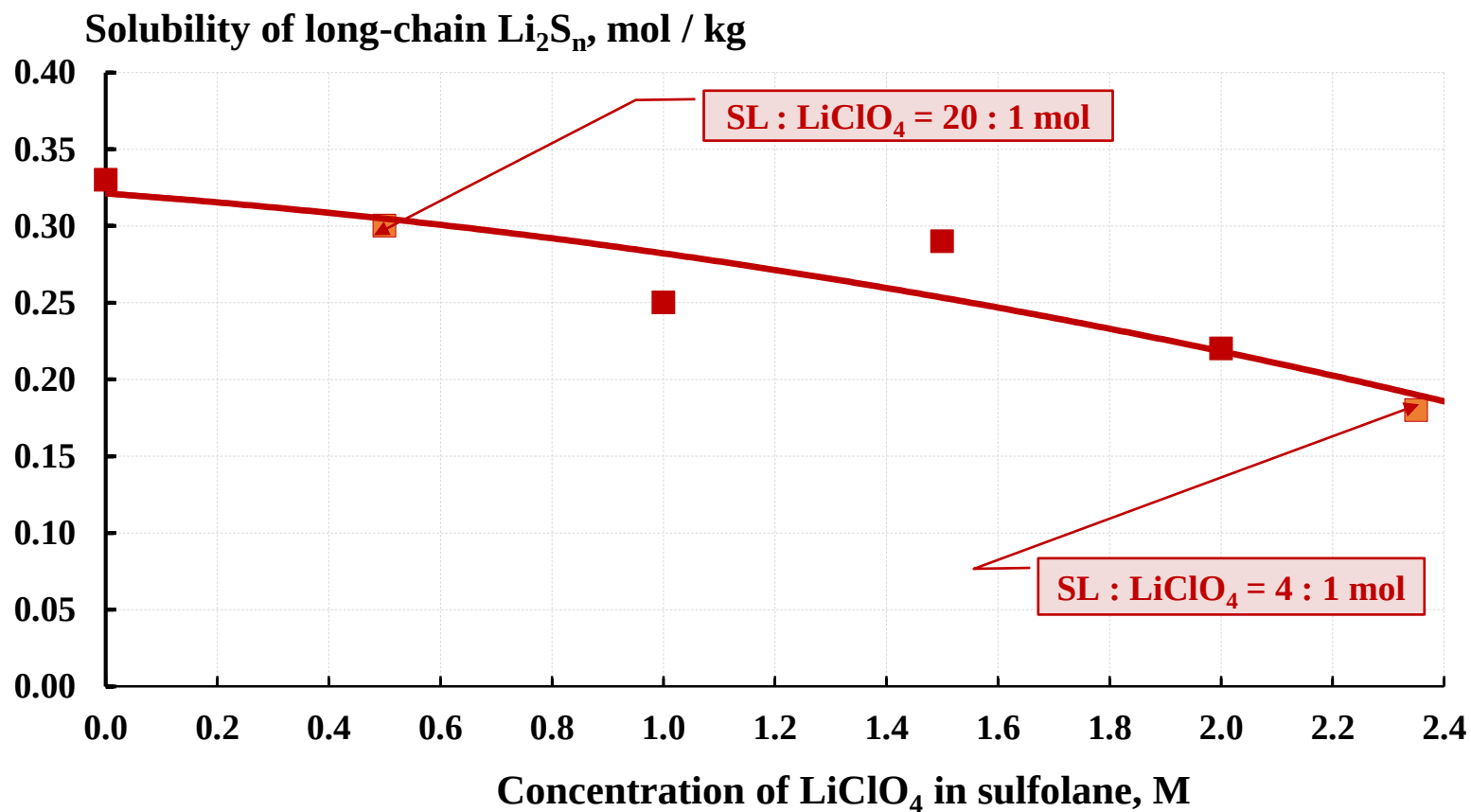
Effect of LiClO_4 concentration on formation rate of long-chain lithium polysulfides in sulfolane ($t=30^\circ\text{C}$)



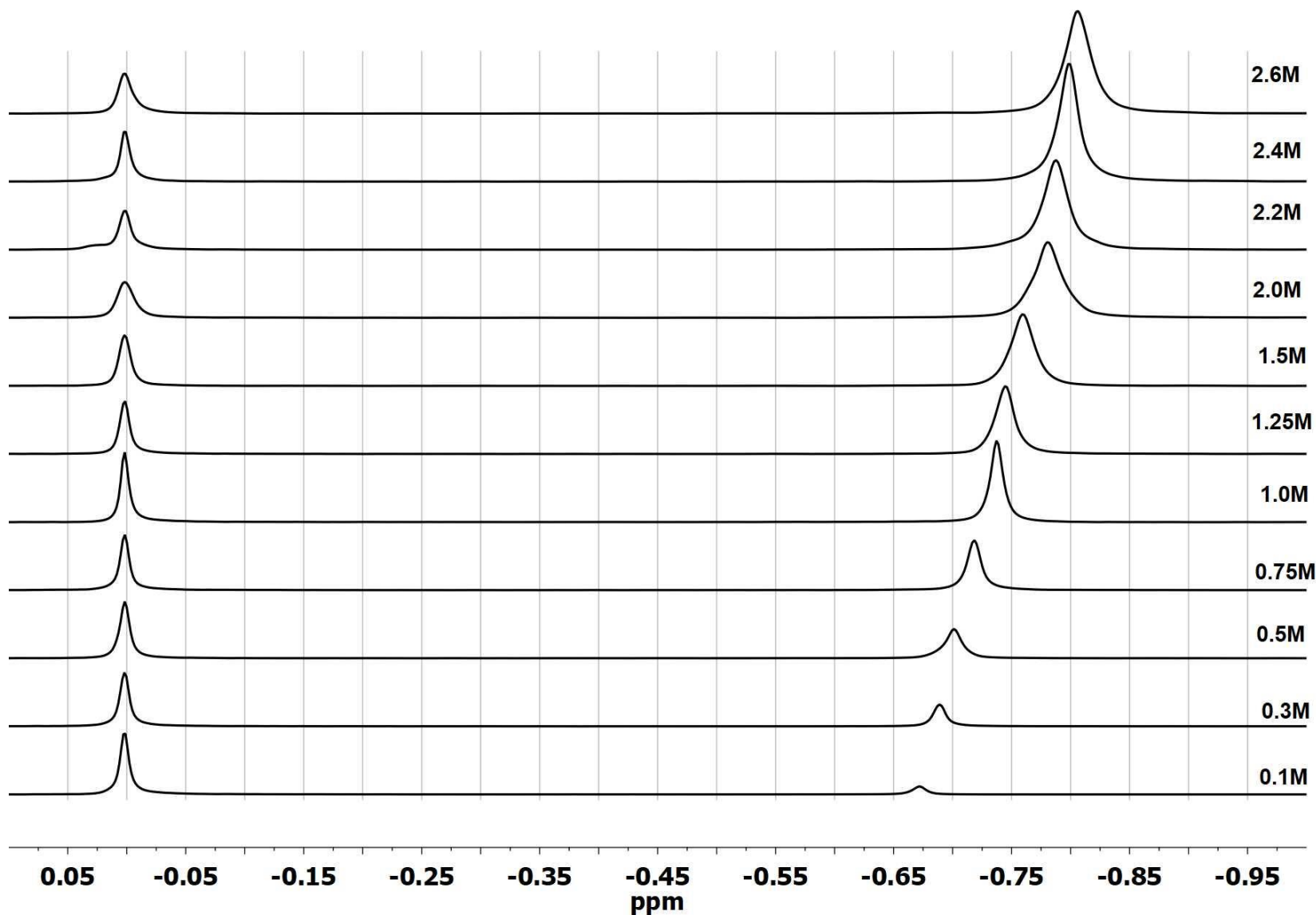
Effect of LiClO_4 concentration on the solubility of long-chain lithium polysulfides in sulfolane



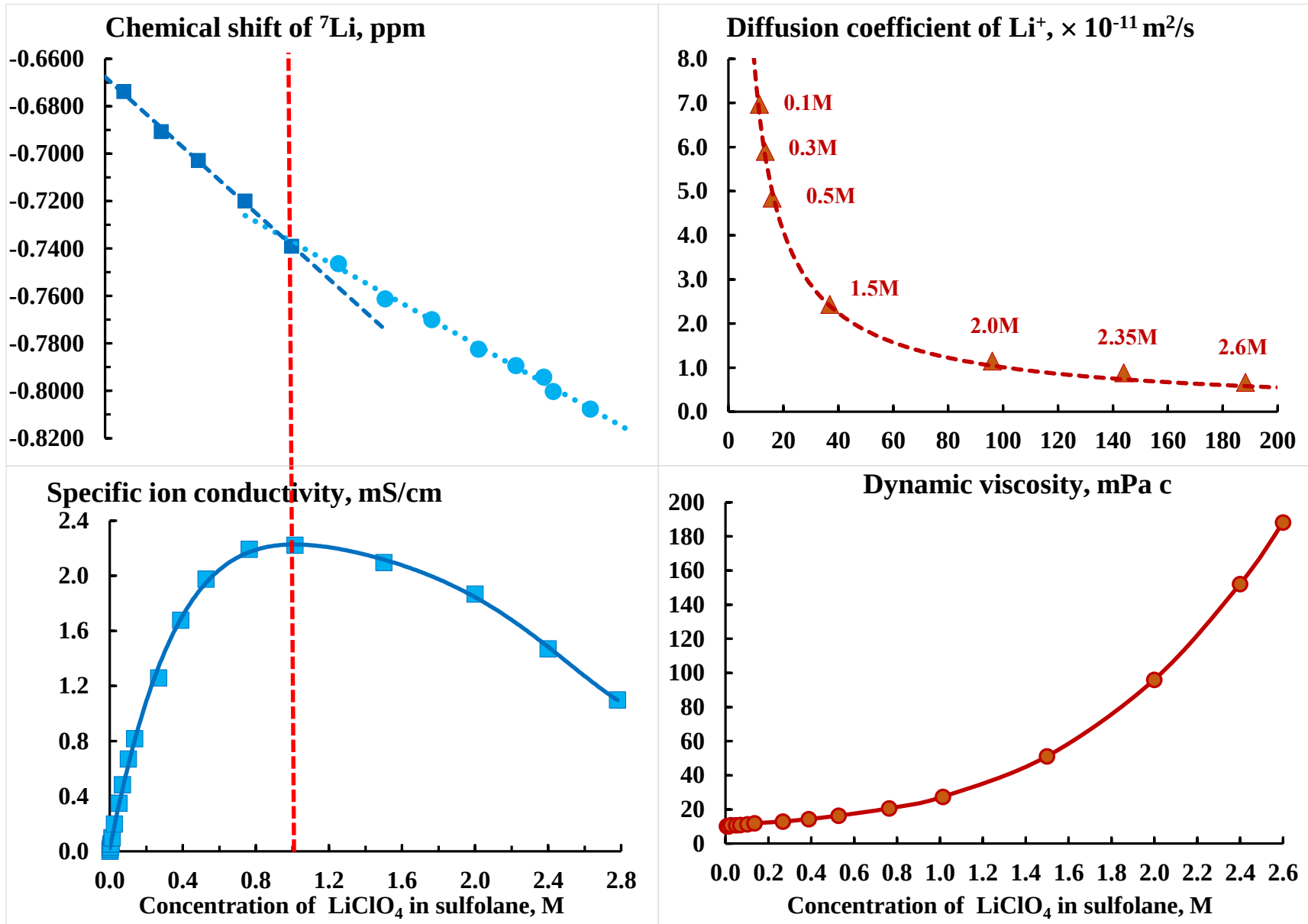
Weight ratio Solid : Liquid = 1 : 9



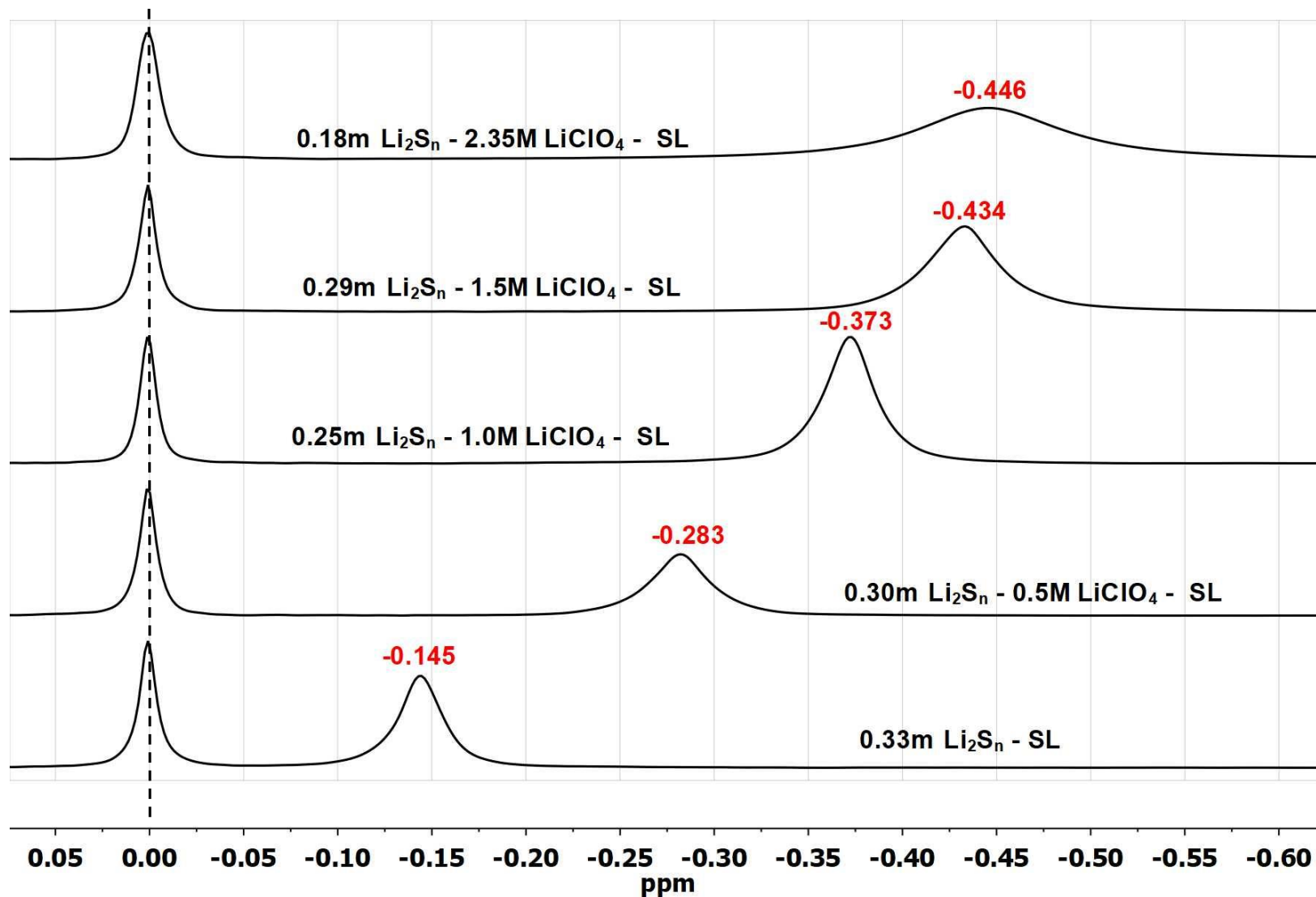
Effect of LiClO_4 concentration in sulfolane on the ^7Li NMR spectra



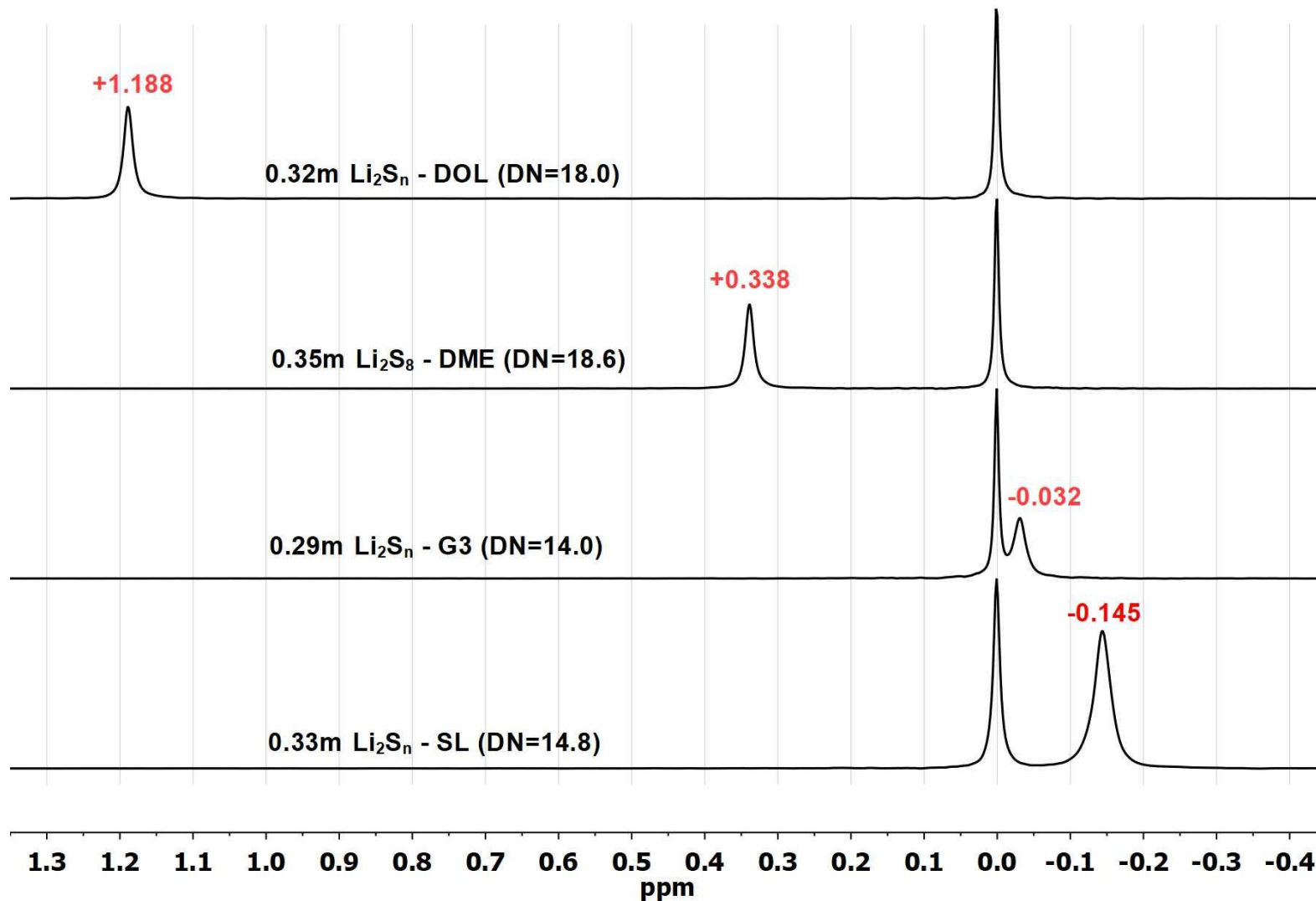
Effect of concentration of LiClO_4 in sulfolane on properties of its solutions ($t=30^\circ\text{C}$)



Effect concentration of LiClO_4 and long-chain lithium polysulfides in sulfolane on ^7Li chemical shift



^7Li NMR spectra of long-chain lithium polysulfides in aprotic dipolar solvents



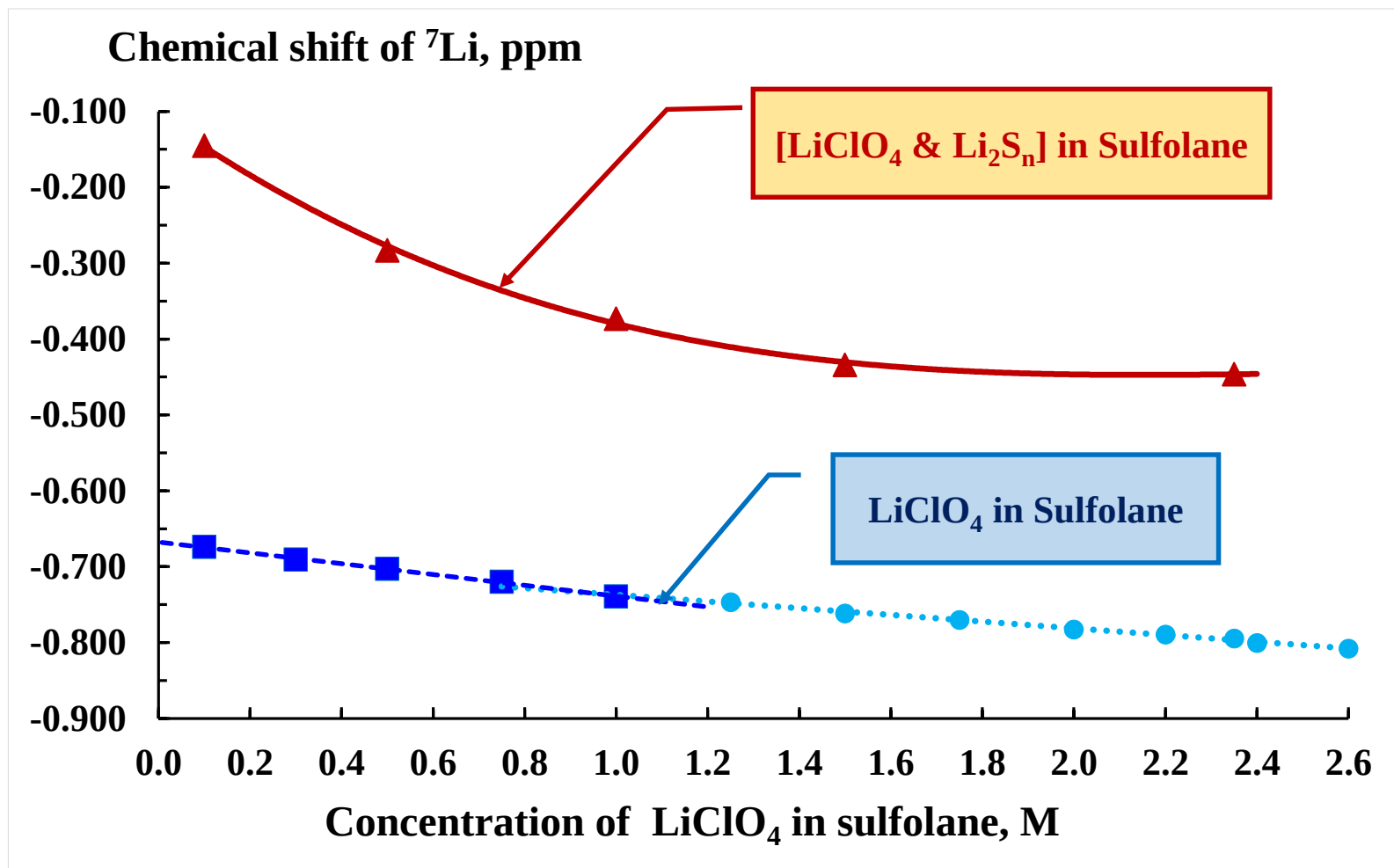
Solubility and ^7Li chemical shift of long-chain lithium polysulfides in aprotic dipolar solvents (t=30 $^{\circ}\text{C}$)

Solvent	DN	Dynamic viscosity, mPa s	Solubility of Li_2S_n , mol / kg	Chemical shift of ^7Li , ppm	Diffusion coefficient of Li^+ , m^2/s
1,3-Dioxolane	18.0	0.714	0.32 ± 0.01	+1.188	2.89×10^{-10}
Glyme (DME)	18.6	0.455	0.35 ± 0.01	+0.338	3.03×10^{-10}
Triglyme	14.0	1.886	0.29 ± 0.01	-0.032	6.81×10^{-11}
Sulfolane	14.8	10.019	0.33 ± 0.01	-0.145	7.80×10^{-13}

Solubility and ^7Li chemical shift of long-chain lithium polysulfides in sulfolane solutions of LiClO_4

Dynamic viscosity, mPa s	Concentration of LiClO_4 , M	Solubility of Li_2S_n , mol / kg	Chemical shift of ^7Li , ppm	Diffusion coefficient of Li^+ , m^2/s
10.02	0 (sulfolane)	0.33 ± 0.01	-0.145	7.80×10^{-13}
15.91	0.5	0.30 ± 0.01	-0.283	1.14×10^{-11}
26.98	1.0	0.25 ± 0.01	-0.373	6.37×10^{-12}
51.12	1.5	0.29 ± 0.01	-0.434	3.97×10^{-12}
143.98	2.35	0.18 ± 0.01	-0.446	1.44×10^{-12}

Chemical shift of ^7Li of sulfolane solutions of LiClO_4 saturated by long-chain lithium polysulfides

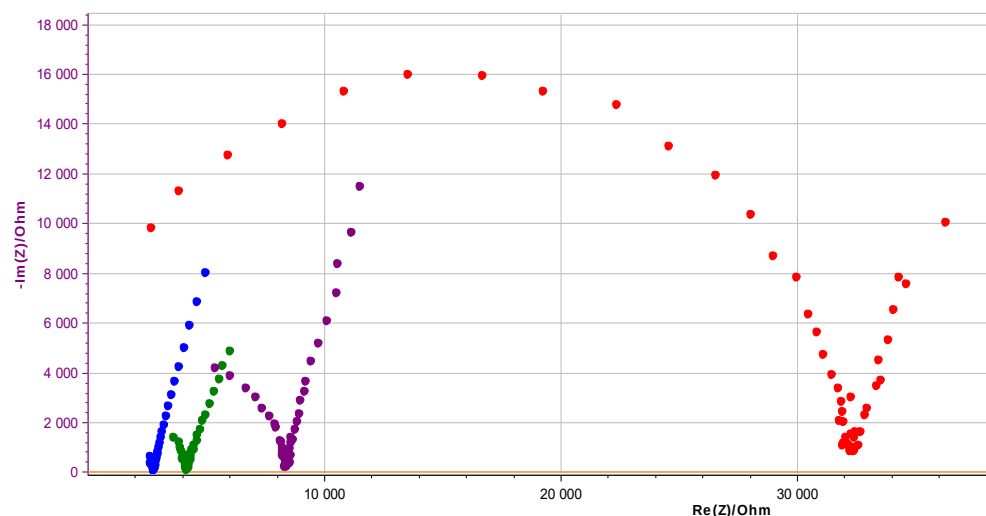


Specific ion conductivity of long-chain lithium polysulfide solutions in aprotic dipolar solvents (t=30 °C)

Solvent	Specific ion conductivity, $\text{mOhm}^{-1} \text{cm}^{-1}$	Solubility of Li_2S_n , mol/kg	DN	Dynamic viscosity, mPa s
Glyme (DME)	2.09	0.35 ± 0.01	18.6	0.455
Sulfolane	0.96	0.33 ± 0.01	14.8	10.019
Triglyme	0.84	0.29 ± 0.01	14.0	1.886
1,3-Dioxolane	0.20	0.32 ± 0.01	18.0	0.714



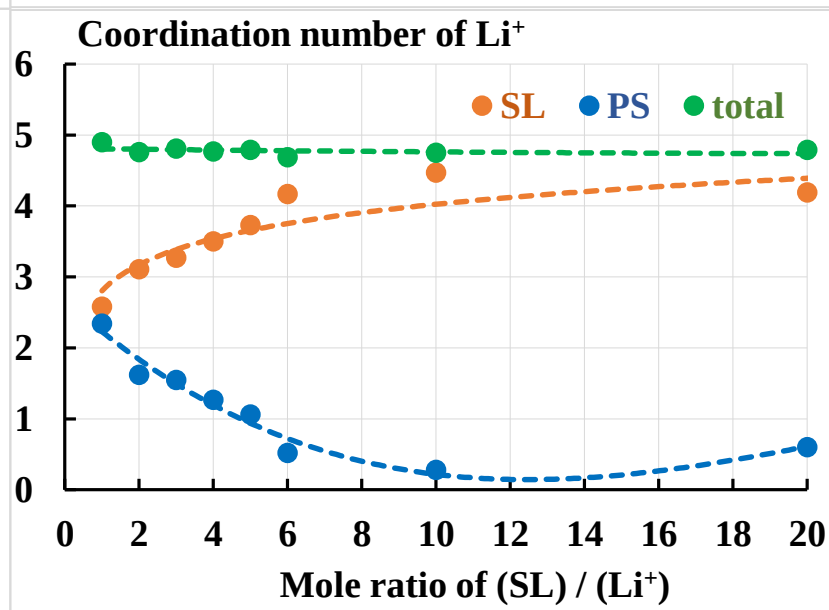
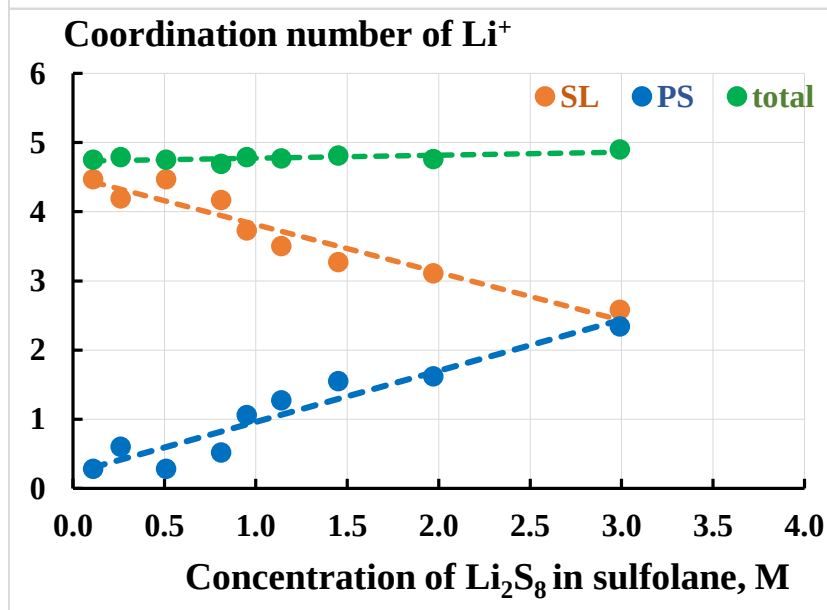
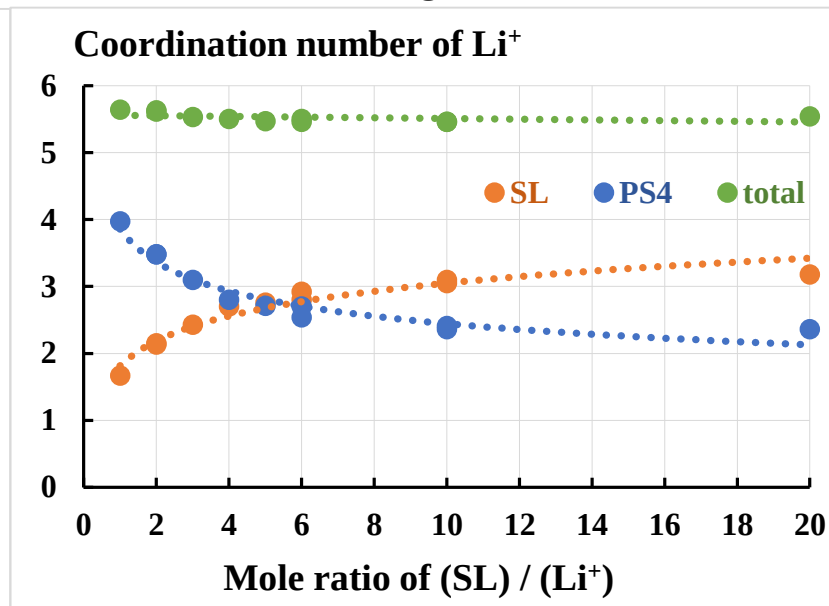
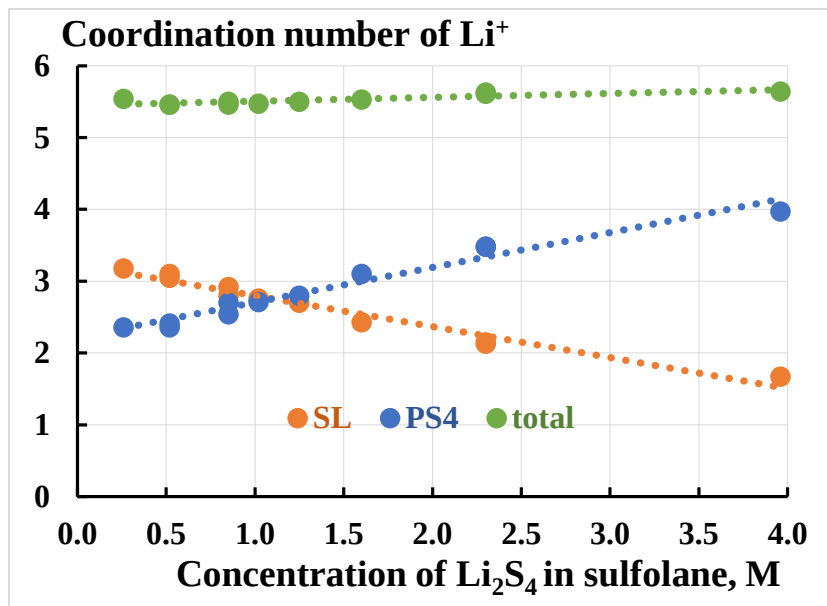
Micro cells with stainless steel blocking electrodes



Effect of LiClO_4 concentration on specific ionic conductivity of solutions sulfolane of long-chain lithium polysulfides ($t=30\text{ }^{\circ}\text{C}$)

Concentration of LiClO_4 , M	Specific ion conductivity, $\times 10^{-3} \text{ Ohm}^{-1} \text{ cm}^{-1}$		Solubility Li_2S_n , mol / kg
	without Li_2S_n	saturated with Li_2S_n (S: Li_2S =7:1)	
0 (sulfolane)	-	0.96	0.33 ± 0.01
0.5	1.908	1.08	0.30 ± 0.01
1.0	2.222	0.94	0.25 ± 0.01
1.5	2.096	0.74	0.29 ± 0.01
2.0	1.781	0.70	0.22 ± 0.01
2.35	1.464	0.72	0.18 ± 0.01

Change in the solvation numbers of the Li^+ with an increase in the concentration of Li_2S_4 and Li_2S_8 in sulfolane



Conclusions

1. During electrochemical transformations of sulfur and lithium polysulfides solvate complexes of lithium polysulfides are generated in lithium-sulfur batteries.
2. The energy and operating characteristics of lithium-sulfur batteries are largely determined by the specific ion conductivity of the associates of solvate complexes of lithium polysulfides with solvate complexes of lithium salts.
3. The kinetics of electrochemical processes in lithium-sulfur batteries can be determined by the rate of formation of lithium polysulfides, which, in turn, depends on the solubility of elemental sulfur in electrolytes.
4. The solubility of sulfur in electrolytes is significantly lower than in the solvents that make up the electrolytes; with an increase in the concentration of the support lithium salt, the solubility of sulfur in electrolytes decreases.

5. An increase in the coordination numbers of the lithium ion in sulfolane solutions of Li_2S_4 and Li_2S_8 with an increase in their concentration may indicate a decrease in the intensity of lithium ion solvation by sulfolane oxygen atoms and an increase by sulfur atoms of polysulfide chains.
6. Electrolyte systems for lithium-sulfur batteries, providing efficient solvation of lithium ions of support lithium salts and lithium polysulfides, as well as deep electrochemical reduction of sulfur and lithium polysulfides, while maintaining the required ionic conductivity of the electrolyte, can be created by combining solvents and lithium salts.
7. The use of electrolyte systems with optimal solvating properties with respect to lithium polysulfides will allow to reduce the amount of electrolyte in lithium-sulfur batteries and, thereby, increase their specific energy.

Acknowledgments

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THANK YOU FOR YOUR ATTENTION

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