

Sulfolane as Solvent for Lithium Battery Electrolytes

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Abstract: *The properties and applications in lithium batteries of solutions containing lithium perchlorate dissolved in sulfolane have been studied. Due to the high cryoscopic constant of sulfolane (85 K/mole), the freezing point can be considerably decreased. Also the viscosity can be decreased in a way similar to the idea of mixed carbonate solvents. Viscosity and conductivity obey the modified Walden rule. The addition of sulfolane to carbonate solvents increases their flash point fairly considerably. The capacity of experimental cells containing a LiCoO₂ cathode and a carbon anode was ca. 33.33 mAh/g (related to anode material). The internal resistance of the cell increased, and an irreversible charge was observed on discharge curves and described. To some extent, the battery had the capability of a rechargeable one.*

The use of sulfolane (SL) as a highly polar solvent for electrochemical purposes has been the subject of previous studies [1] – [6]. Its advantages are high permittivity, excellent thermal stability and resistance to strong oxidation potentials. However, there are some disadvantages such as rather high viscosity and correspondingly also low conductivity of salt solutions in this solvent, and a rather high freezing point (+ 28.4 °C).

A similar problem arises in ethylene carbonate which exhibits excellent electrochemical properties if solvents with a sufficiently low freezing point and viscosity are added. It is commonly known that the loss of conductivity is not so detrimental, and the freezing point depression can make such mixed solvents useful. Therefore the blends of ethylene carbonate (abbreviated as EC) with other solvents (mostly dimethyl carbonate DMC) are used as solvents for preparation of electrolytes for lithium batteries.

The main objective of the present paper is to attempt to suppress the weaknesses of sulfolane by adding a solvent with a sufficiently low freezing point and viscosity in order to facilitate the use of sulfolane for various electrochemical applications in electrochemical science and technology.

Keywords:

1. THEORY

The model of electrolyte solutions based on the viscosity and the balance between the electric force and hydrodynamic drag of an ion assumes that the drag is being controlled by the Stokes law. It is supposed that the ion is of spherical shape without any considerable attraction to other ions in the solution. Under such presumptions, the product of viscosity η and specific conductivity σ should be constant. This relation has been known as the Walden rule for more than one century :

$$\eta \cdot \sigma = \text{const} \quad (1)$$

However, the fundamental presumption is valid to some extent only. The essential presumption is that the ionic radius and charge of the ion are invariant. Any deviation from this presumption causes a deviation from Eq. (1). An empirical formula

$$\eta \cdot \sigma^\alpha = \text{const} \quad (2)$$

is used for empirical description of the processes in solutions. The parameter α ($0 < \alpha < 1$) is the lower the stronger the changes that the ions undergo. These changes may consist in changed solvation envelope and its radius or some dissociation which

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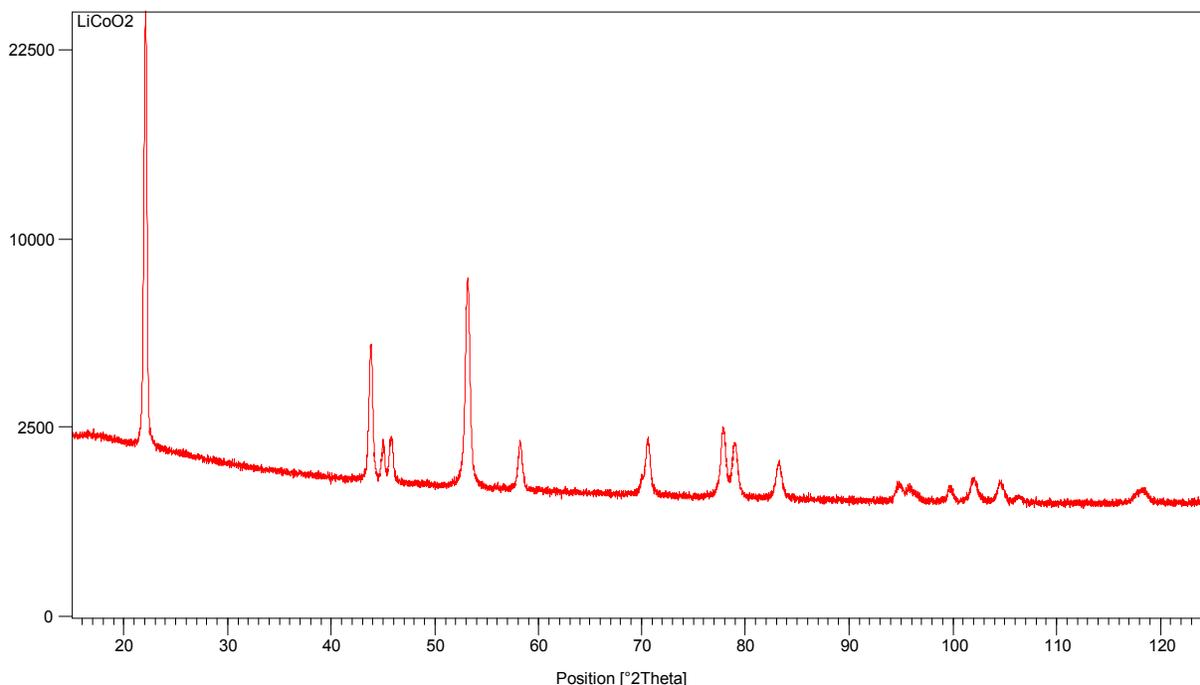


Figure 1. XRD pattern of LiCoO_2 used (direct output from the diffractograph)

would affect the effective charge of the solvated ion. Also ion pairing may be responsible for the lower value of the exponent.

Equation (2) has often been used for description of ionic liquids [7] – [11].

Both viscosity and conductivity are usually plotted in logarithmic scales and the exponent can be obtained by comparison of the slopes of their almost linear plots.

Another group of properties would be illustrated by the phase diagram of the binary mixture of SL and other solvents and the viscosity of a binary mixture of liquids at a temperature below the freezing point of one component. Finally, the dielectric properties expressed by the apparent permittivity ϵ at various frequencies could help to understand the behavior of two mixed strongly polar liquids.

2. EXPERIMENTAL

2.1. Preparation of solutions

Sulfolane (SL), dimethyl carbonate (DMC) and propylene carbonate (PC) were distilled and used as solvents. Lithium perchlorate LiClO_4 was dried for 24 hours at 130°C in air.

The following solutions were prepared:

- sulfolane + 1M LiClO_4
- sulfolane (70 %) + propylene carbonate (30 %)
- sulfolane (70 %) + propylene carbonate (30 %) + 1M LiClO_4

The solvents are fairly hygroscopic. Due to extreme values of sulfolane cryoscopic constant (*vide infra*), all preparations were performed in dry atmosphere of a glove box.

2.2. Instrumentation

The conventional device for cryoscopy was applied. The cooling

was done by liquid air. Measurements were performed at temperatures from $+30^\circ\text{C}$ to -40°C .

Electrical conductivity was measured in a temperature range from 22°C to 90°C in a commercial conductivity cell and a RCL meter.

The cell Agilent 16452A connected to the RCL meter Agilent 4284 was used for estimation of sulfolane permittivity.

The flash point was estimated by open crucible method.

Dynamic viscosity was observed using the falling ball Höppler viscosimeter.

Viscosity and conductivity were measured in the temperature range from 22°C to 90°C .

2.3. Electrode materials and experimental cell

Cathode material was prepared in the laboratory from lithium carbonate and cobalt nitrate by sintering, grinding and repeated sintering. Ten percent of carbon Super C and 10 percent of PVDF were added to the substance. The XRD spectrum of this sample is shown in Fig. 1. Apparently, its major constituent was LiCoO_2 . Its capacity was the capacity of 130 Ah/g in a conventional metallic cell (El-Cell) in connection to lithium metal counter electrode and an electrolyte of LiPF_6 in the mixture of ethylene carbonate and dimethyl carbonate (unpublished results).

Anode material was natural graphite powder ČR 595 (Graphite Týn Czech Republic) with 10% of PDFE.

Electrode materials were deposited in a slurry on metallic discs (2.5 cm in diameter) and pressed in heat of $200 - 400^\circ\text{C}$.

The metallic cell (El-Cell, GmbH, Germany) was assembled from both positive and negative electrodes and a sheet of non - woven glass separator in a glove box with controlled argon atmosphere.

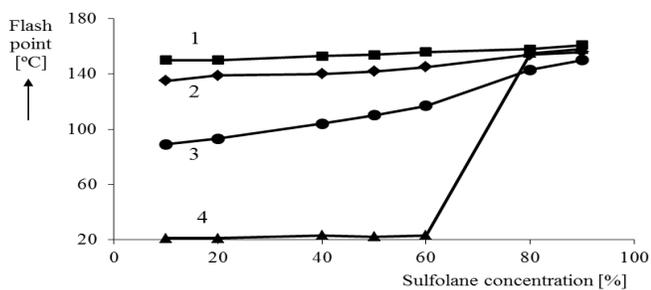


Figure 2. Increase of the flashpoint of organic solvents caused by addition of sulfolane. Curve 1: sulfolane + ethylene carbonate, 2: sulfolane + propylene carbonate, 3: sulfolane + dimethyl sulfoxide, 4: sulfolane + dimethyl carbonate.

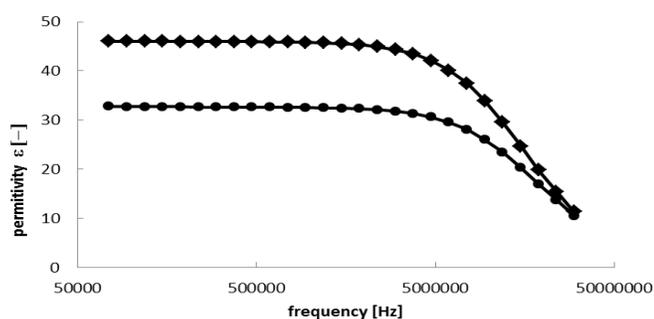


Figure 3. Relative permittivity ϵ' in frequency range 0.075 to 30 MHz for mixtures containing 20 % of PC (upper curve, diamonds) and of 100 % sulfolane (lower curve, circles).

3. RESULTS

3.1. Flash point

The flash point of SL mixtures with several other solvents is indicated in Fig. 2. Apparently, the flash point of solvents with an intrinsically high flash point is not considerably influenced by an addition of SL. However, in more flammable solvents such an increase of flash point can be enhanced to a high degree. The highest flash point increase was observed in the system SL – DMC as the latter is rather volatile. However, the self-ignition temperature of SL on air is between 500 °C and 600 °C, indicating a high temperature safety limit of SL systems.

3.2. Permittivity of sulfolane – propylene carbonate mixtures

The permittivity of two SL + PC mixtures in the frequency range between 75 kHz and 30 MHz is shown in Fig. 3, where we can see that it approaches the static permittivity of both substances, and its value decreases monotonously to values close to optical permittivity accessible from the value of refractive index.

At the frequency below 2 MHz, ϵ' approaches some steady value close to tabulated data and the imaginary permittivity ϵ'' begins to rise simultaneously. This indicates that the conductance of the liquid starts to prevail over the capacitance of the substances in that frequency range.

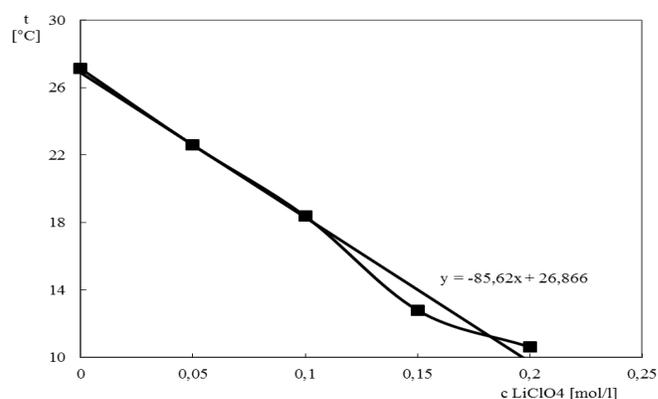


Figure 4. Freezing point of solutions of LiClO_4 in sulfolane.

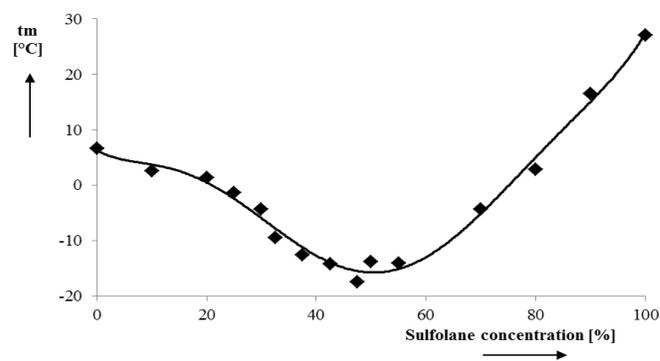


Figure 5. The phase diagram of the system SL – DMC.

3.3. Cryoscopy and phase diagram

The melting (or freezing) point of sulfolane appears to be extremely sensitive to any dissolved substances. For example, due to addition of lithium perchlorate, LiClO_4 , the freezing point decreases as shown in Fig. 4.

Even if it is not accurate, a straight line could be drawn and the cryoscopic constant as high as 85.6 estimated from its slope. Therefore, the latent heat of solidification is more than 10 or 15 times lower than that of water. For more exact values further investigation would be necessary, as they are influenced by the effect of ion association in the system.

The data concerning the system SL - DMC are shown diagrammatically in Fig. 5.

First, the freezing point depression is very markedly visible for high SL concentrations 10 % of DMC is not far from 10 mol. % and the freezing point depression 11.5 °C was observed.

Therefore, the heat of melting can be estimated at 65 J/g.

Apparently, we can find fairly easily the regions where the freezing point is suppressed well below zero, and therefore the sulfolane solutions can be used in practical applications. This is emphasized even more by the addition of inorganic lithium salt.

The rather high freezing point of sulfolane can clearly be depressed to values which would make the use of SL possible.

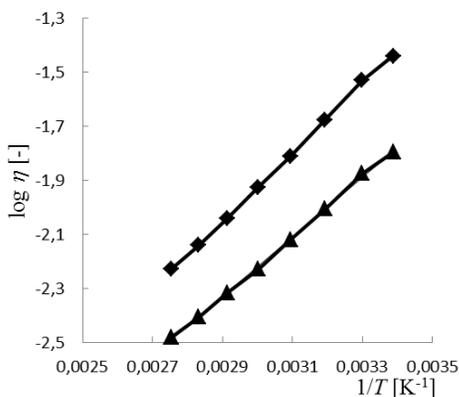


Figure 6. Viscosity η at different temperatures. Diamonds: sulfolane, triangles : SL + 30 % PC.

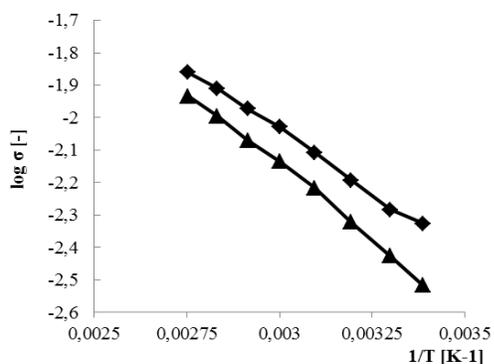


Figure 7. Conductivity σ at different temperatures. Meaning of symbols the same as in Fig. 5.

3.4. Viscosity and conductivity

Solutions of 1 M LiClO_4 in 100 % SL and in a mixture containing 70 % vol. of SL and 30 % vol. of PC were used for the measurement of conductivity and viscosity. Moreover, the viscosity of pure SL and the mixture of 70 % vol. of SL and 30 % vol. of PC were measured in parallel.

Viscosity and conductivity were measured in a 1 M solution of LiClO_4 in SL, in the binary solvent consisting of 70 % vol. SL and 30 % vol. PC. The results are shown in Figs. 6 and 7. The values of apparent activation energy of both viscosity and conductivity profile are listed in Table 1.

The rightmost value ΔW is the difference between activation energy values for viscosity and conductivity. Its average value, $\Delta W = 0.0672$ eV, is approximately twice or three times as high as the value of thermal energy (equal to $k.T = 0.021$ eV). Hence, the

Table 1. Apparent activation energies of viscosity, conductivity and their differences for 1M LiClO_4 in SL and SL+PC solvents.

system	W (η) [eV]	W (σ) [eV]	D W [eV]
SL	0.246	0.1825	0.0654
SL + 30% PC	0.2189	0.1512	0.0657

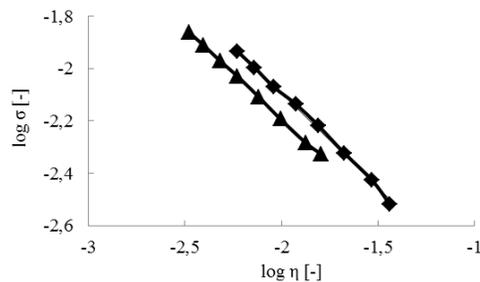


Figure 8. Logarithmus of conductivity and viscosity for a solution of SL + 1M LiClO_4 (diamonds) and a mixture of SL + PC + 1M LiClO_4 (triangles), plotted according to modified Walden rule.

increase of temperature from +20 to +90 °C can play an important role if some structural change of the ionic milieu should be considered. Such a change can be formation and dissociation of ion pairs. Their existence would cause a decrease in conductivity due to the mutual compensation of their charges while their dissociation would increase the total number of charged ions present in the solution.

A similar effect could be associated with ion pairing on viscosity. The viscosity of SL+ PC without LiClO_4 (equal to 0.006517 Pa.s at 22 °C) increased to 0.00160 Pa.s if 1M LiClO_4 was added.

3.5. Walden Rule

The modified Walden Rule was applied for the correlation of viscosity and conductivity of 1M LiClO_4 solutions in SL and SL + PC solvents. Results are shown in Fig. 8. The trend of both correlations is similar and an exponent $\alpha = 0.6$ to 0.7 was evaluated for both of them. *In the Walden theory the value is supposed to be equal to unity and the difference indicates ion association as mentioned above.*

Hence, the modified Walden Rule is applicable to sulfolane containing electrolytes.

The use of the Walden plot and its modified version was described even for aprotic systems containing ionic liquids [8] - [11].

3.6. Basic properties of sulfolane - Discussion

Let us suppose that the change of conductivity is influenced by the association of ions to some extent. For example, ionic pairs of one cation and one anion cannot be contributed to the conductivity due to the fact that they behave as an uncharged particle in external electric field. Simultaneously, they cause some hindrance of movements in the electrolyte, thus influencing the viscosity. Then we can postulate an assumption that the difference in apparent activation energy ΔW can show us the measure of such phenomenon as the degree of ion pairing of equivalent circuits.

The energy of ion pair formation can be estimated from the assumption of energy associated with the electrical field between two ions according to principles of electrostatic phenomenon. However, it would be close to 0.02 eV in a solution of relative permittivity equal to 30 and the distance between ions solvated by sulfolane as low as 0.2 nm. However, the polarizability in a rather strong electric field of ions should be nearly saturated, which

would result in apparent permittivity decrease, and energy will be close to 0.067 eV as follows from observations of viscosity and conductivity.

3.7. The experimental lithium - ion cell

3.7.1. Visual observations of sulfolane stability

A lump of lithium (cca 1 – 1.5 g) was immersed in 20 ml of 1M LiClO₄ dissolved in sulfolane. Visually, no changes of clean lithium surface were observed. Therefore, if any passivation layers or similar substances were formed, they were so thin that they were not visible with a naked eye.

3.7.2. Charging - discharging curves

Cell No. 1 was assembled using negative electrode of the mass of 3.5 mg and positive mass of 6.5 mg.

After assembling, the voltage of the cell was virtually zero, as both materials (graphite and cathode) were in fully discharged state.

The first three charging / discharging cycles are shown in Fig. 9. Apparently, the charging section is longer than the discharge one and the difference is smaller in the second cycle. Moreover, any plateau cannot be observed in the charging process. Further, the duration of the first part of the charging cycle is much longer than in the other two parts. This effect is generally known in aprotic electrolytes and is called “irreversible charge”. It should be noted that the voltage is well within the expected limits for such a system.

In the mode of charging and discharging by constant current, five subsequent cycles were performed and the cycle ability was similar to the previous cycles.

The superposition of charge - discharge curves No.1 to No.3 is shown in Fig. 10. The shortening due to formation of a surface layer and its completion in subsequent cycle is clear after that. The mass of negative electrode was 3.15 mg, as mentioned above, and the charge seems to be limited by it. The discharge times and charges are summarized in Table 2. The charge constitutes 30 to 50 % of the theoretical value for a negative electrode and it diminishes gradually.

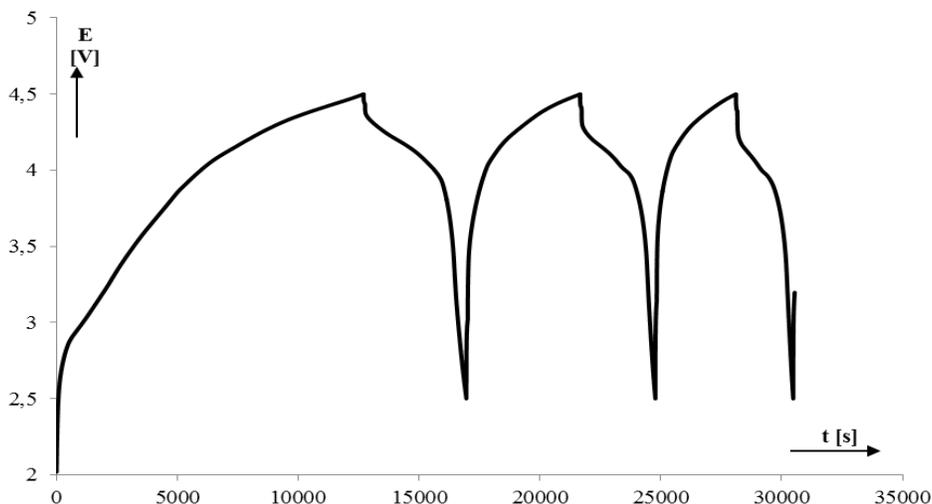


Figure 9. First three cycles of charging the cell containing 3.5 and 6.5 mg [anode and cathode] with current 0.6 mA.

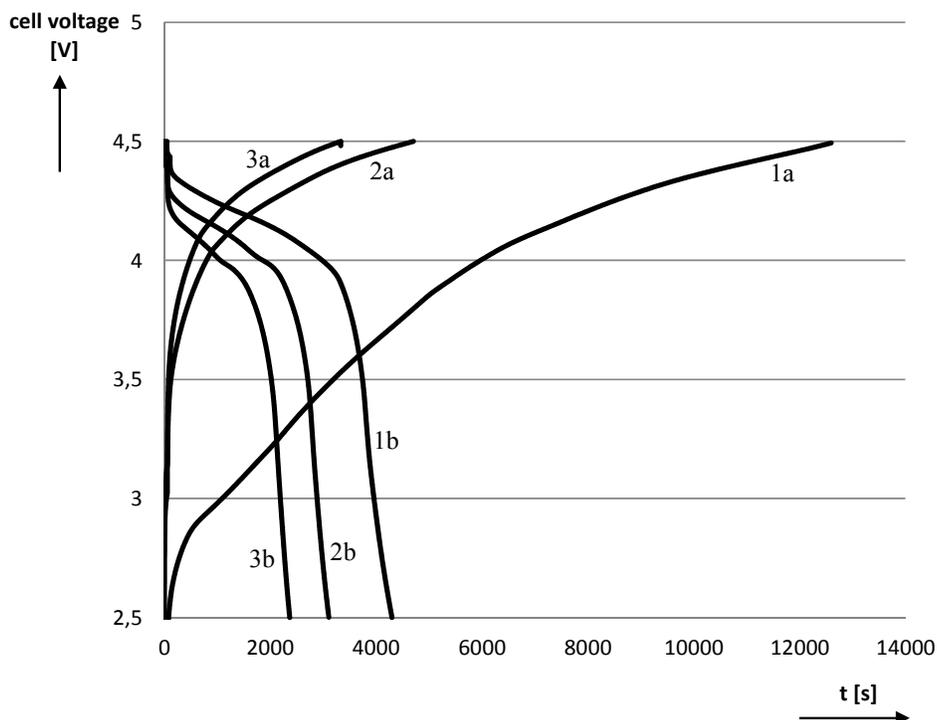


Figure 10. Galvanostatic cycling at current 0.6 mA. Charging of cell No. 2 to 4.0 V. Curve 1a is first charge, 1b is first discharge, 2a second charge, 2b second discharge, 3a third charge and 3b third discharge.

Table 2. Specific charge of three galvanostatic discharge cycles

cycle	duration	charge	As/g	mAh/g
1	3800	0.70	2.01E+02	55.794
2	2670	0.49	1.41E+02	39.202
3	1986	0.37	1.05E+02	29.160

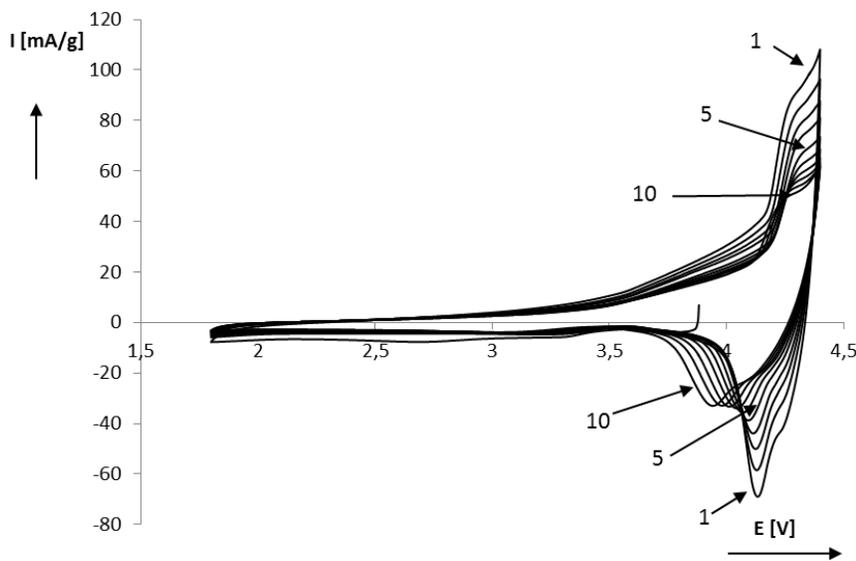


Figure 11. First 10 voltammetric scans of cell No. 2. Scan rate 0.481 mV/s.

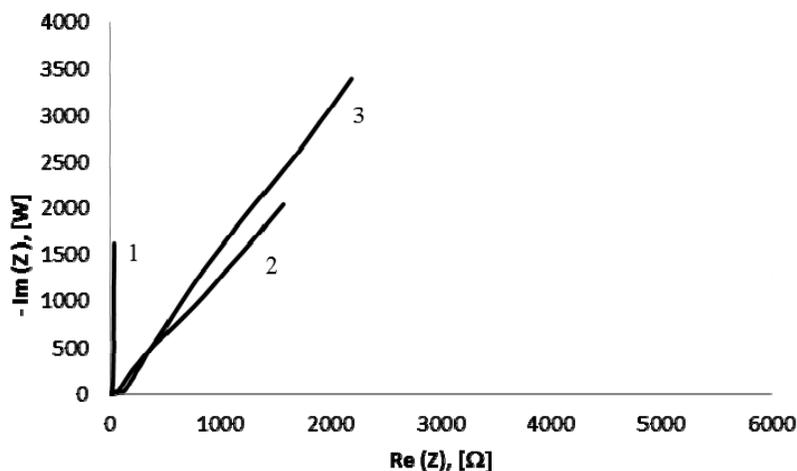


Figure 12. EIS spectra of a freshly assembled uncharged cell.

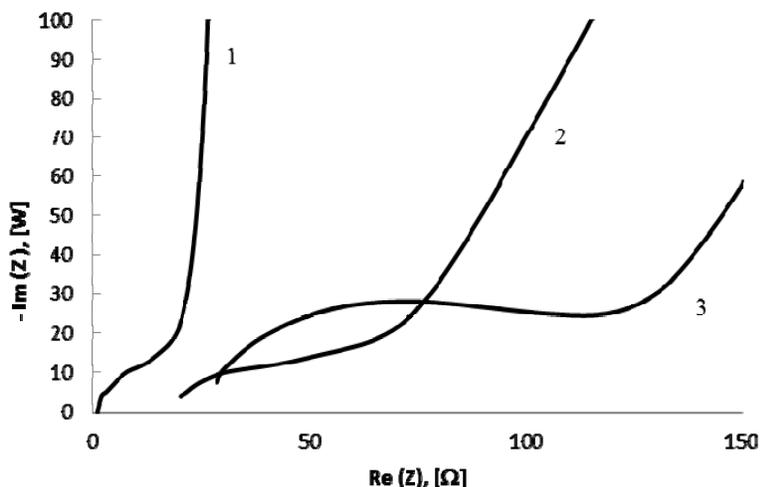


Figure 13. EIS spectra of the cell after 10 voltammetric cycles.

3.8. Voltammetry

Cell No. 2 was assembled using a 6.21 mg anode and a 4.24 mg cathode and a scan of 0.481 mV/s.

First, an EIS spectroscopy was performed at a voltage of 0.039V. Then the cell was charged with 4.0 V.

Then 10 voltammetric cycles were recorded. The result with overlapping voltammograms is in Fig. 11. We can see that the charging (cathodic) part is flattened during the cycling process. Its charge is not much decreased during consecutive cycles. It should be noted that the position of charging peaks is shifted so that the difference between charging and discharging potentials increases. For example, the cathodic peak area decreased from 8.61 mAh/g for the first peak to 7.44 mAh/g for peak No. 3 and to 4.91 mAh/g for peak No. 9 (also related to top 1 g of cathode material). Corresponding peak potentials were 4.136, 4.122 and 3.88 V (peaks No. 1, 3 and 9) Finally, the EIS spectroscopy was repeated. Impedances are described in the following subparagraph.

3.9. Impedance spectroscopy

The impedance at an open circuit potential of a freshly assembled cell is shown in Fig. 11 and – on an enlarged scale – in Fig. 12.

A constant-phase element CPE (in the notation of potentiostat software, Q) with exponent $n = 0.89$ and an almost negligible RC semicircle at highest frequencies were observed. The potential was close to zero.

The impedance EIS spectrum after 10 voltammetric cycles is also given in Figs 12 and 13. It was measured at an open circuit potential 1.8 V.

In Fig. 13 we can observe the presence of a rather well displayed semicircle and an increase of the series resistance of the cell. The high frequency component is increased more than twice and the resistance estimated from the semicircle is also rather high, so that the ohm components increased to nearly 50 Ω from the original value of 15 Ω . This can be ascribed to the formation of a passivation layer responsible for the changes in the course of cycling.

On the contrary, an almost ideal Warburg-like admittance is visible in the low frequency part of spectrum.

Finally, another spectrum was obtained after 30 hours of standing with opened circuit, the potential dropped from 3.8 to 1.8 V. The rather high series resistance sank to values closer to the values of a fresh cell.

Again, we ascribe this behavior to the passivation layer which partly dissolves in current - free state (open circuit).

Parameters obtained of suggested equivalent circuits by the software of the potential are listed in Tab. 3. Spectrums were interpreted by an equivalent scheme containing series resistance R1 in series with a parallel circuit containing capacity C2 a constant phase element close to Warburg admittance Q and a R2 and finally, another parallel R3 – C3 circuit. This was found to be the best representation for high frequency resistance, the semicircle arch at intermediate frequencies and low frequency loop or straight line with the nature of a diffusion process.

3.10. Discussion – Li ion batteries with sulfolane

Experimental data can be summarized in several points:

Firstly, the undesirably high freezing point of sulfolane can be decreased by addition of other polar solvents. Also viscosity and specific resistivity would be more favorable. The reason is extremely low latent heat of sulfolane fusion.

Secondly, this solvent seems to be favorable for systems that require stability towards oxidation. Lithium batteries with cathode voltages up to 5 V would offer a field to the use of sulfolane.

Thirdly, the formation of passive layer is highly probable if sulfolane is used in a negative potential range. Most likely, it would not be so detrimental for lithium batteries with higher anode potentials (e.g. lithium titanium oxides).

Fourthly, sulfolane as a solvent could help to increase the safety of secondary lithium batteries owing to its high boiling point and flash point temperature.

As a disadvantage, the high irreversible capacity of first charging cycles should be mentioned. If this hindrance can be suppressed, sulfolane - either alone or in combination with other solvents - could be used in practice.

4. CONCLUSIONS

The aim of this paper is to get a deeper insight in SL and its suitability to be used as a solvent for special electrochemical experiments and applications. It does not deal with electrochemical properties such as potential window or stability towards strongly negative potential of lithium or lithium intercalation compounds in lithium ion batteries.

Table 3. Parameters of equivalent circuit describing the EIS results

element	Initial. $i=0$	after cycling	after pause	units
E				V
R1	15.8	27.68	18.73	Ω
C1	1.634	0.299	0.415	$F \cdot 10^6$
R2	6.067	373	3.597	Ω
Q	3.966	2.934	0.38	$\Omega \cdot \text{Hz}^{1/2}$
a	0.563	0.394	0.401	-
R3	49.18	315	68.3	Ω
Q2	5.768	837.1	459	$\Omega \cdot \text{Hz}^{1/2} \cdot 10^{-6}$
C3	1.727E-6	185	199	$F \cdot 10^6$
R4	4.015	415	415	Ω

The main objection against the use of SL in lithium batteries is based on its poor resistance against reduction at negative potentials.

Two opinions are generally known. Firstly, sulfolane is a rather strong oxidant and cannot be in contact with a negative electrode. Secondly, the use of sulfolane in a lithium battery has already been described and its positive effect has been declared [12], [13]. Also, we have observed visually that a piece of lithium sulfolane can be immersed into sulfolane without any vivid reaction or visible changes.

Even if the stability of sulfolane at negative potentials were proved to be poor, we can benefit from SL stability towards oxidation. Hence, the batteries containing 5V cathodes and 1.5 V anodes (for example, lithium titanium oxides) can be assembled and used experimentally at least.

Electrochemical behavior of sulfolane and batteries with this solvent during prolonged cycling will be the subject of our future communications.

5. ACKNOWLEDGEMENTS

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