

Short communication

Cost-effective and ecologically safe electrolyte for lithium batteries

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Abstract

The electrochemical characteristic of solutions of lithium benzolsulfonate in dimethylsulfoxide is considered. DTA/TGA is employed to analyze the thermal stability of salt. The conductivity of solutions was determined. So, for example, conductivity lithium benzolsulfonate in dimethylsulfoxide is 3.8 mSm/cm. The area electrochemical stability of solutions is in an interval 4.5–4.6 V. Electrochemical properties of lithium manganese oxide spinel in tested solutions were investigated. The charge–discharge capacity of lithium manganese oxide spinel is 65 mAh g⁻¹ (in interval of potentials from 3.2 to 4.4 V Li/Li⁺) and 190 mAh g⁻¹ (in interval of potentials from 1.8 to 4.0 V Li/Li⁺) for vanadium oxide (V).

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Mass manufacture of lithium batteries requires cost-effective electrolytes that would have the acceptable electrochemical characteristics: electroconductivity, wide range potentials of oxidation and reduction components of electrolytes, inactivity to chemical interaction between components of electrolytes and electrode materials, especially, lithium metal. As the solvents for lithium batteries, organic carbonates (propylene carbonate, ethylenecarbonate and dimethylcarbonate), ethers (glyme and diglyme), cyclic ethers (γ -butyrolactone) and their mix are widely used. As salt component of electrolytes LiPF₆, LiClO₄, LiBF₄ and some other are used. All components of electrolytes have the positive and negative sides; therefore quest for the new solvents and salts is urgent.

The valuable property of dimethylsulfoxide (well known aprotic solvent) is its ability to dissolve many inorganic salts. The properties of dimethylsulfoxide (DMSO) were already investigated. The electroconductivity [1,2] and viscosity [2] of solutions lithium salts in mix solvents (DMSO-containing) were obtained. Lithium exchange currents in solutions LiClO₄ in mixes DMSO + propylenecarbonate was determined [3]. On the

other hand, there are a lot of investigations in which DMSO as the solvent is used in other directions of electrochemical researches. The solutions on a basis of DMSO are used in electrochemistry organic substances [4], for the study of electrode kinetics of reduction–oxidation ions of rare metals [5], for electrochemical deposition alloys [6], etc. For the last 20 years in some monographs and articles [7–9] dedicated to lithium batteries DMSO-containing solutions were mentioned as electrolyte, but electrochemical characteristics were not described. The need for rather inexpensive and safe electrolytes with acceptable electrochemical characteristics justifies main objective of this research to confirm the applicability of lithium benzolsulfonate solutions in DMSO as electrolyte for lithium batteries.

1. Experimental

1.1. Salts, solvents and materials

The lithium benzolsulfonate (BSLi), perchlorate and tetrafluoroborate lithium were synthesized by reaction between acids and lithium alkali. Water solutions of salts were evaporated and crystalline hydrates were dried by Fisher pistol. The trifluoromethene sulfonate lithium (Merck) was dried a little too.

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DMSO has been boiling with calcium hydride for 6 h, then distilled at the lowered pressure (temperature 50–60 °C). All operations with electrolytes, filling conductivity and electrochemical cells were performed in dry argon box.

Compatibility electrolyte with cathode materials estimated on LiMn_2O_4 and V_2O_5 . The lithium manganese oxide (LiMn_2O_4) was synthesized by modified sol–gel method. The crystalline vanadium oxide (V) was ground in a planetary mill with tiny quantity of carbon black in argon atmosphere.

1.2. Cells

The conductivity of electrolytes was measured in cell with platinum electrodes. The constant of cell was 1.5 cm^{-1} .

Three electrode cell was used for electrochemical investigations. The Pt-foil of square form ($5 \text{ mm} \times 5 \text{ mm}$) was as worked electrode and Li as reference and counter electrodes. Impedance analyzer “E7–14” was used.

1.3. Apparatus

Impedance analyzer “E7–14” was used. The electrochemical measurements were made with potentiostat “PI-50-1”.

2. Results and discussion

It is known that for the use of organic solvent and lithium salt as components of electrolyte, they should meet the following requirements:

- (1) The lithium salt should be dissolved in the solvent and produce sufficient concentration (about 1 mol l^{-1}).
- (2) The conductivity of solutions should not be less than $10^{-3} \text{ S cm}^{-1}$.
- (3) The solvent and lithium salt should be inert to anode and cathode materials and also to other lithium batteries components.
- (4) The electrolyte should have a wide temperature interval in liquid condition.
- (5) The solvent and salt should be neither inflammable, nor toxic and also cost-effective.

Also, it is known, that DMSO can dissolve many organic and inorganic substances. In particular, the solutions of perchlorate and tetrafluoroborate lithium in DMSO have concentration of salt greater than 1 mol l^{-1} . We found out that lithium salt of benzenemonosulfonic acid also gives with DMSO high concentrate solutions. In general, the solutions of BSLi in DMSO meet most of the above-mentioned requirements. As the benzenemonosulfonic acid is low-cost and widely used in some chemical manufactures, then lithium salt also will be accessible and low-cost in comparison with other salts [7–10].

As to ecological safety of DMSO and BSLi, it should be noted that both are low toxic components and solutions as a whole, as well as products of interaction electrolyte with an atmosphere and environment in the case of lithium batteries depressurizing.

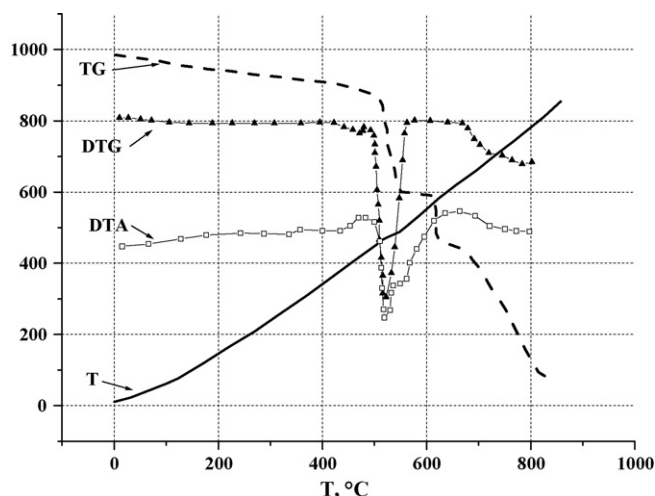


Fig. 1. DTA-, DTG- and TG-curves of lithium benzolsulfonate.

2.1. Thermal stability of lithium benzolsulfonate

The chemical and thermal stability is important for the stability of electrolyte as a whole. On DTA-, DTG- and TG-curves of BSLi in an interval of temperatures from 30 °C up to 800 °C are shown in Fig. 1.

The change of weight and thermal effect of decomposition of salt begins after 400 °C. Thus thermal stability of BSLi considerably exceeds this value when compared to LiBF_4 , LiPF_6 and others used as electrolyte component.

2.2. Electroconductivity of BSLi solutions

The dielectric constant ϵ [10] of solvent substantially influences the conductivity of solutions. The solvents can be classified according to the value of dielectric constant as highly polarized with $\epsilon > 35$ (organic carbonates, amides, sulfoxides and sulfones) and low polarized with $\epsilon < 15$ (ethers and esters). DMSO has $\epsilon = 46.5$ [11], therefore it is possible to expect values of conductivity not less than $10^{-3} \text{ S cm}^{-1}$.

The experimental results of measured conductivity of 1 M solutions of various lithium salts in DMSO are given in Table 1 and the literature data [11–15] on conductivity of 1 M solutions lithium salts in aprotic solvents in Table 2 are presented.

From submitted data on conductivities of lithium salts solutions in DMSO it is possible to draw a conclusion that among salts conductivity is increasing like this $\text{LiSO}_3\text{CF}_3 < \text{LiBF}_4 < \text{LiClO}_4$. Similar dependence is typical for others aprotic solvents. Absolute values of conductivity of accordingly DMSO solutions are close to the values of con-

Table 1
Electroconductivity 1 M solutions of lithium salts in DMSO

Electrolyte	Concentration of salt (mol l^{-1})	Conductivity (mS cm^{-1})
$\text{LiClO}_4 + \text{DMSO}$	1	10.9
$\text{LiBF}_4 + \text{DMSO}$	1	10.1
$\text{LiSO}_3\text{CF}_3 + \text{DMSO}$	1	8.4

Table 2
Electroconductivity 1 M solutions of lithium salts in aprotic solvents

Electrolyte	Concentration of salt (mol l ⁻¹)	Conductivity (mS cm ⁻¹)	References
LiClO ₄ + DMSO	1	10	[11]
LiCl + DMSO	1	5.9	[12]
LiClO ₄ + γ -BL	1	11	[13]
LiBF ₄ + γ -BL	1	7.5	[13]
LiBF ₄ + glyme	1.25	5.2	[14]
LiClO ₄ + glyme	1	3.6	[15]

ductivity of those salts in others highly polarized solvents (γ -Butyrolactone, propylencarbonate) and exceed the values of conductivity in low polarized solvents (glyme and diglyme). So, for example, conductivity of 1 M LiClO₄ in DMSO is 10.9 mS cm⁻¹, and for 1 M LiClO₄ in γ -BL and glyme are 11 and 3.6 mS cm⁻¹, respectively.

The experimental results on conductivity of 1 M BSLi in DMSO and in DMSO mix with others aprotic solvents are shown in Table 3.

The conductivity of DMSO-based solutions of BSLi is lower than the conductivity of other lithium salts solutions. However, the value of conductivity is enough for its use as electrolyte.

2.3. Electrochemical measurement

The important feature of electrolytes is the interval of potentials, in which the components of electrolytes are electrochemically inactive (the so-called “electrochemical window”). It is known that “electrochemical window” of electrolytes on the basis of organic carbonates, ethers and esters is in the range of 4.2–5.0 V. Recently, the wide range of electrochemical inactivity (more than 5.0 V) for sulfon electrolytes has been shown [16]. The valency of sulfur in sulfons is six whereas in sulfoxides—four. Thus oxidation of DMSO to dimethylsulfon and reduction to dimethylsulfide is possible. The oxidative and reducing processes in solutions could be determined by using cyclic voltammetry (CV). The CV curves 1 M solutions of lithium salts in DMSO (Fig. 2) for definition of stability to electrochemical oxidation–reduction both DMSO and BSLi were obtained. The CV curves 1 M solutions of BSLi in DMSO (Fig. 3) were obtained too. The stationary potential of Pt-electrode in DMSO-based solutions as with BSLi so other salts

Table 3
Electroconductivity 1 M solutions of lithium salts in aprotic solvents

Electrolyte	Conductivity (mS cm ⁻¹)	Electrochemical stability interval (V)
1 M LiSO ₃ C ₆ H ₅ + DMSO	3.8	4.6
1 M LiSO ₃ C ₆ H ₅ + DMSO, PC (1:1 vol.)	3.4	4.5
1 M LiSO ₃ C ₆ H ₅ + DMSO, γ -BL (1:1 vol.)	3.5	4.5
1 M LiSO ₃ C ₆ H ₅ + DMSO, glyme (1:1 vol.)	3.6	4.4
1 M LiSO ₃ C ₆ H ₅ + DMSO, diglyme (1:1 vol.)	3.2	4.4

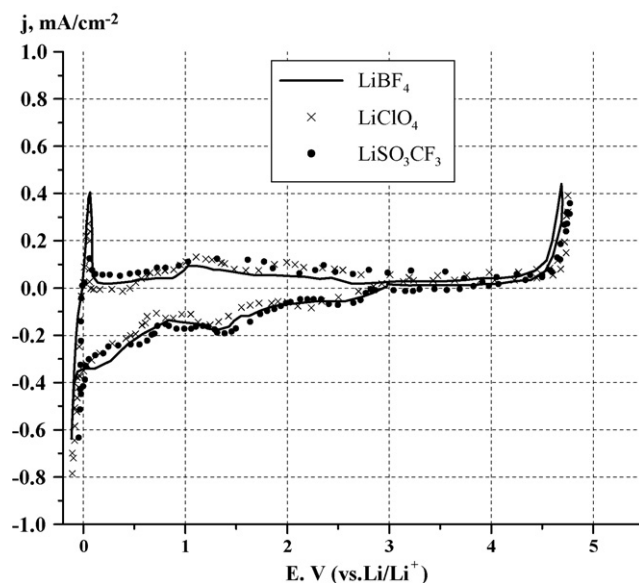


Fig. 2. CV-curves Pt-electrode in 1 M solutions of LiClO₄, LiBF₄ and LiSO₃CF₃ in DMSO at scan rate 50 mV s⁻¹ and temperature 25 °C.

is in range from 2.7 to 2.85 V (vs. Li/Li⁺). The reduction current in an interval of potentials from stationary to potential of lithium plating is less than 0.2 mA cm⁻², which corresponds to the background currents of electrolytes for lithium batteries on a widely used basis aprotic solvents. The oxidation potentials of investigated solutions are about 4.5 V (vs. Li/Li⁺).

The slices of Li were immersed in electrolyte for a long time to estimate of DMSO-containing solutions compatibility and BSLi with lithium. The visual changes of shine metal lithium were not observed after 48 h. Later on, lithium surface slightly darkened. Thus visual control of lithium surface testifies to stability of solutions BSLi in the DMSO-containing mixed solvents at contact with metal lithium. The fact of stability of DMSO solutions with other lithium salts at contact with metal lithium is shown [1], where the charge efficiency of lithium plating/stripping

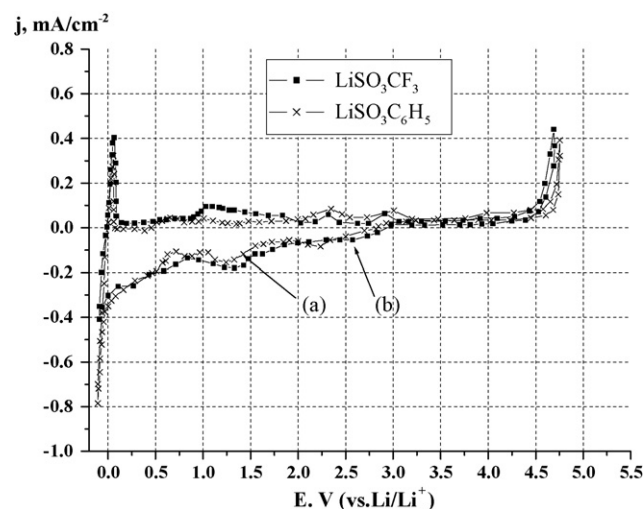


Fig. 3. CV-curves Pt-electrode in 1 M solutions of (a) C₆H₅SO₃Li and (b) CF₃SO₃Li in DMSO at scan rate 50 mV s⁻¹ and temperature 25 °C.

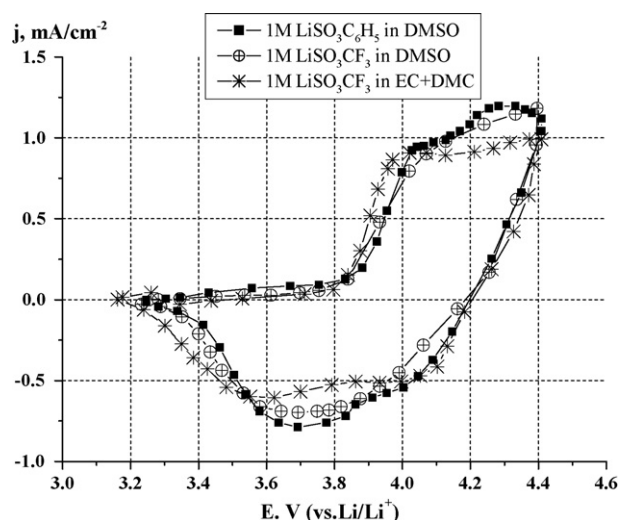


Fig. 4. The CV-curves (2nd cycle) $\text{Li}_{0.5}\text{MnO}_2$ in 1 M solutions of $\text{LiSO}_3\text{C}_6\text{H}_5$ and LiSO_3CF_3 in aprotic solvents at scan rate 2 mV s^{-1} and temperature 25°C .

on nickel substrate was investigated. Depending on lithium salt and solvents the efficiency on 20th cycle was in an interval from 60% up to 85%. Such efficiency of lithium cycling is characteristic of electrolytes not containing DMSO.

Stability to chemical oxidation and compatibility of DMSO + BSLi electrolytes with cathode materials was investigated using the charge/discharge efficiency manganese spinel— $\text{Li}_{0.5}\text{MnO}_2$ (Fig. 4) and vanadium oxide (V)— V_2O_5 (Fig. 5). The CV curves for estimation of influence of solvent nature and BSLi on cathode materials were received in three solutions: (a) 1 M BSLi in DMSO; (b) 1 M LiSO_3CF_3 in DMSO; (c) 1 M LiSO_3CF_3 in EC + DMC. Lithium trifluoromethanesulfonate (TfLi) was chosen for comparison with BSLi because conductivity of solutions of this salt is similar to conductivity of

benzenesulfonic solutions, and also TfLi unlike fluorocomplex lithium salts is not hydrolyzed in solutions. The CV-curves for $\text{Li}_{0.5}\text{MnO}_2$ were received in an interval of potentials from 3.2 up to 4.4 V (vs. Li/Li^+). In 2nd cycle in all electrolytes the value of capacity is about $63\text{--}65\text{ mAh g}^{-1}$.

In next cycling process the form of CV-curve for solution 1 M LiSO_3CF_3 in EC + DMC got stabilized and remained practically unchanged to the 30th cycle. It testifies to the absence of processes influencing the structure of cathode material. The form of CV-curve for DMSO containing solution changed from cycle to cycle to decrease charge–discharge capacity. After the 30th cycle specific capacity was 45 and 40 mAh g^{-1} in solutions $\text{LiSO}_3\text{C}_6\text{H}_5$ and LiSO_3CF_3 in DMSO, respectively. The similar decreasing of the capacitive characteristics spinel in $\text{LiSO}_3\text{C}_6\text{H}_5 + \text{DMSO}$ and $\text{LiSO}_3\text{CF}_3 + \text{DMSO}$, apparently, is related to interaction cathode material with the solvent.

For more convincing conclusions on stability of BSLi and DMSO that influence cathode materials, vanadium oxide (V) was used in 1 M solutions of lithium salts in DMSO and mix DMC and EC. The CV-curves for V_2O_5 were obtained in an interval of potentials from 1.8 to 4.0 V (vs. Li/Li^+). The forms of CV-curves stabilized after the 8th cycle and did not change until the 30th. The forms of V_2O_5 curves are similar in all electrolytes, that proves close specific capacity charge/discharge of V_2O_5 in these solutions. Starting from CV-curves charge/discharge capacity of V_2O_5 is about 190 mAh g^{-1} . On whole, the electrochemical behavior of $\text{Li}_{0.5}\text{MnO}_2$ and V_2O_5 in BSLi and TfLi solutions in aprotic solvents confirms probable oxidation DMSO, which is the solvent for BSLi, with salt component— $\text{LiSO}_3\text{C}_6\text{H}_5$ being inert.

3. Conclusions

- (1) The solutions of $\text{LiSO}_3\text{C}_6\text{H}_5$ in DMSO have high enough conductivity, that is a necessary condition for their use as electrolytes for lithium batteries.
- (2) The electrochemical and chemical stability of solutions of $\text{LiSO}_3\text{C}_6\text{H}_5$ in DMSO in contact to electrode materials is confirmed, using as the example metallic lithium inertness, and on the basis of the charge/discharge manganese spinel and vanadium oxide (V).

In general, it is necessary to note, that the solutions of BSLi in the DMSO have negative characteristics. DMSO has a high melting point (18.5°C), low efficiency of Li^+ -cation intercalation into graphite. Thus, developments of DMSO-included electrolytes with BSLi demand to find satisfactory solution next tasks. First of all, it is necessary to select co-solvent for increase interval of liquid condition. In the second, there is a need to choose cathode and anode materials for the best efficiency of battery. It is possible to expect good specific characteristics from balanced system.

The above conclusions allow us to make the following generalization: it is possible to use $\text{LiSO}_3\text{C}_6\text{H}_5$ in mixes DMSO and other solvents in electrolytes for lithium chemical power sources.

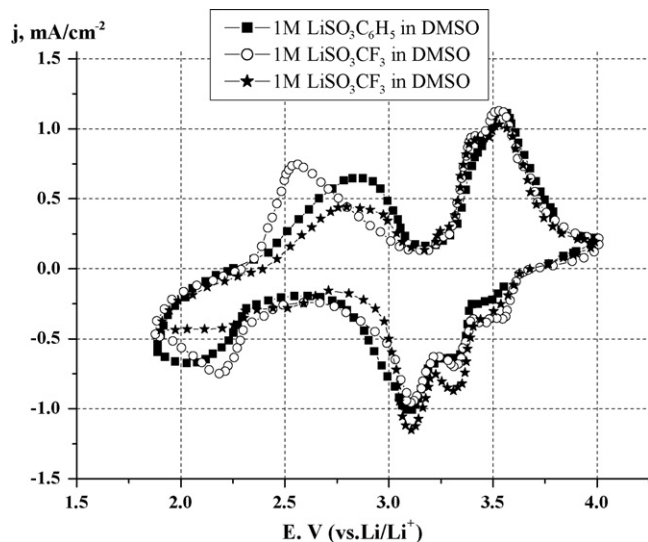


Fig. 5. The CV-curves (8th cycle) $\text{Li}_{0.5}\text{MnO}_2$ in 1 M solutions of $\text{LiSO}_3\text{C}_6\text{H}_5$ and LiSO_3CF_3 in aprotic solvents at scan rate 2 mV s^{-1} and temperature 25°C .

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