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EFFECT OF CONCENTRATION AND NATURE OF LITHIUM SALT ON CHARACTERISTICS OF GEL ELECTROLYTES DMSO-PVDF-LiAn

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The results of the study of electrolytes based on gel solutions of DMSO-PVDF-lithium salt with concentrations up to 0.05 m.f. and above 0.1 m.f. are presented. It is shown that the conductivity of electrolytes is close to the conductivity of lithium salt solutions in pure DMSO and obeys the Arrhenius equation in the studied range of temperatures and concentrations. The calculated activation energies for electrolytes with a salt concentration of up to 0.05 m.f. are 14–15.4 KJ/Mol, and for electrolytes with a salt concentration above 0.1 m.f. - 16.9–20.6 KJ/Mol indicate a fast ion transfer, which in more concentrated solutions is inhibited by an increase in their crystallinity. The analysis of the equivalent circuit models of the Li-Li systems electrochemical impedance spectra showed the tendency of electrolytes to form capacitive elements at the lithium electrode-electrolyte interface. It was recognized the presence of semi-infinite diffusion in LiClO₄ and LiIm with salt concentration of 0.05 m.f., due to the imperfection of the film formed on the electrode surface. The efficiency of using DMSO-PVDF-lithium gel electrolytes on steel and platinum electrodes was analyzed by voltammograms.

Key words: polymer electrolyte, conductivity, lithium-electrolyte interface, conductivity activation energy, model circuit.

INTRODUCTION. Improving the performance of lithium-ion current sources is not possible without the development of electrolytes that are stable in a wide range of temperatures, charge- discharge voltages, and are indifferent to the main components of the current source. The development of gel-based polymer electrolytes has received considerable attention in the literature due

their sufficiently high viscosity, with retains the necessary level of electrical conductivity close to liquid solutions. The use of polymer electrolytes is also promising in lithium-oxygen current sources (LOCS) in addition to lithium-ion current sources with solid-phase cathodes and anodes. The main advantages of LOCS, in comparison with traditional battery systems, are in high theoretical

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capacity and energy, which is due to the use of molecular oxygen as a redox component [1, 2]. The range of potentials of electrochemical stability of non-aqueous electrolytes is significantly higher than that of water, which allows increasing the specific energy of LOCS in their application [3, 4]. However, issues related to the stability of the charge-discharge capacity during cycling remain unresolved, and this does not allow obtaining the capacitive characteristics necessary for practical use. One of the reasons for the decrease in capacitance during cycling is the formation of sparingly soluble products on the surface of the cathode and anode. In this case the resistance at the electrode-electrolyte interface increases, which leads to an increase of the current source total resistance. The choice of electrolyte systems that can reduce the resulting resistance is considered as a possible way to solve this problem. The required level of electrical conductivity, a wide range of potentials of electrochemical stability, ensuring high solubility of oxygen and its diffusion to the cathode surface, as well as the corrosion resistance of lithium during storage and cycling are the main requirements for electrolytes [5]. The use of electrolytes in the form of gels was suggested in [6–8], the advantages of which include increased chemical and thermal stability compared to liquid solutions [9, 10].

Polyvinylidene fluoride (PVDF) is one of the most commonly used polymers for producing gel and solid polymer electrolytes. The solubility of PVDF depends on the properties of organic solvents and reaches 500 g/kg of solvent, which makes possible to obtain gels with the necessary and

controlled viscosity. However, not all solvents capable of dissolving PVDF may be indifferent to the lithium electrode and cathode at the same time.

Dimethyl sulfoxide (DMSO) is one of the solvents that are relatively indifferent to the lithium electrode. Its use in electrolytes for lithium current sources with cathodes made of polycarbon fluoride, sulfur, and LOCS is described in the literature [11–14]. At the same time, DMSO was not widely used in current sources, which explains the relatively small number of publications, including those related to the electrical conductivity of solutions of lithium salts (LiAn) in a DMSO-PVDF mixture.

So, the purpose of this work is to determine the conductivity and electrochemical stability of DMSO-PVDF-LiAn solutions depending on the nature of the lithium salt anion and its concentration in a DMSO-PVDF solution over a wide temperature range. To establish the effect of the electrolyte composition on the transition resistance at the lithium electrode-electrolyte interface using the method of impedance spectroscopy. The obtained data will help to formulate some approaches to the formation of electrolytes for LOCS.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Lithium salts such as: lithium bis(trifluoromethane)sulfonimide $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ - LiIm ($\geq 99\%$), lithium fluoroborate LiBF_4 (98%), lithium trifluoromethanesulfonate LiCF_3SO_3 - LiTf (96%), as well as polyvinylidene fluoride hexafluoropropyl PVDF-HFP ($M = 400000$) (all Sigma-Aldrich) were dried in vacuum at $70 \pm 2^\circ \text{C}$ for 3 hours before the manufacture of electrolytes. Lithium bis(oxalato)borate

Table 1

Compositions of the studied electrolytes and their designations

Feature	Lithium salt									
	LiBOB		LiClO ₄		LiIm		LiBF ₄		LiTf	
Number of electrolyte	1	2	3	4	5	6	7	8	9	10
Salt concentration, m.f.	0.042	0.15	0.05	0.12	0.05	0.15	0.05	0.1	0.05	0.17
Solvate melting temperature, °C [16]	18	–29	10	–2,5	12	–23,6	12	–1	18	–22

— LiBOB was synthesized by the microwave method according to the procedure published in [15]. Before use, lithium perchlorate LiClO₄ (Sinbias, Ukraine) was recrystallized and dried in vacuum at a temperature of 160–170 °C for at least 14 hours. DMSO (99.7%, Sigma-Aldrich) was additionally dried over molecular sieves. To obtain solutions of electrolytes, a solution of PVDF in DMSO was initially prepared. The PVDF granules were dissolved in DMSO at a temperature of 70 °C until a clear solution was obtained. Then, the calculated amount of lithium salt was added to the resulting solution, and to speed up dissolution, the resulting mixture was heated for 10–15 minutes. The compositions of the solutions are given in table 1 (salt concentration is given in mole fractions (m.f.) and is calculated on a mixture of DMSO-PVDF). Electrolytes and cells for electrochemical studies were prepared and assembled in a dry glove box. The electrolyte conductivity was determined by the conductometric method using the impedance spectra obtained in the frequency range 10⁶–10³ Hz using the Z – 2000 impedance meter (Elins, Russia) and was calculated by the equation $k = l/RS$, l –

the distance between the electrodes, cm; R – the resistance determined using the impedance spectra, Ω ; S – the area of the electrodes, cm². To determine the conductivity, two-electrode Teflon cells with X18H10T stainless steel electrodes with a surface area – 2 cm² and fixed distance between them of 0.4 cm were used.

The change of the resistance at the lithium metal-electrolyte interface, depending on the electrolyte composition and storage time, was determined using impedance spectra obtained in the frequency range 10^{–1}–10⁵ Hz at an applied voltage of 20 mV and a temperature of 25±0.5 °C using a Z–2000 impedance meter (Elins, Russia). The range of electrolytes potentials of electrochemical stability was determined by voltammograms using a P-30 potentiostat (Elins, Russia) in a three-electrode cell with a platinum or steel working electrode, a lithium auxiliary electrode and a reference electrode. DMSO belongs to the class of highly polar organic solvents, which allows one to obtain its solutions with a high concentration of lithium salts [11, 14, 17]. According to the phase diagrams presented in [16], the melting points (T_m) of solvates with a salt concentration of up to

0.05 m. f. are in the range from 10 to 18 °C (Table 1). For more concentrated solutions corresponding to the eutectic point, T_m this temperature is much lower and, depending on the anion of the lithium salt, is in the range $-29 - 0$ °C. Based on this, for both salt concentrations selected for work, the crystallization temperature of the solution is below room temperature, which allows them to be in liquid conditions at room temperature.

The temperature dependences of the conductivity constructed in the Arrhenius coordinates are mainly linear, Fig. 1. Slight deviations in the tilt angles are observed depending on the concentration and nature of the anion of the lithium salt. The presence of PVDF in the electrolyte, although it leads to a significant change in the viscosity of solutions, which is observed visually, does not change the linear nature of the obtained polytherms. In the table 2 the values of the conductivity of DMSO - PVDF- LiAn solutions at a temperature of 25 °C are given for comparison. In accordance with the presented data, an increase in the conductivity of electrolytes with a lithium salt concentration ≤ 0.05 m.f. occurs in the following row: $\text{LiBOB} < \text{LiIm} < \text{LiTf} < \text{LiClO}_4 < \text{LiBF}_4$.

For solutions with salt concentration ≥ 0.1 m.f., the conductivity changes in a slightly different order: $\text{LiTf} < \text{LiBOB} < \text{LiIm} < \text{LiClO}_4 < \text{LiBF}_4$. This agrees well with a similar series characterizing the change in the degree of dissociation of lithium salts [18, 19]. An exception is DMSO-PVDF- LiBF_4 solutions, for which was obtained an abnormally high level of conductivity. For most salts, the conductivity in less concentrated solutions is higher than in concentrated ones. This is due to changes in the struc-

Fig.1 Polytherms of the DMSO-PVDF-LiAn solutions conductivity with lithium salt concentration ≤ 0.05 m.f. (a) and ≥ 0.1 m.f (b). The numbers on the curves correspond to the electrolyte number in the Table 1.

ture of the solvate because of increase in the degree of ordering of the solution due to the solvation of ions by solvent molecules.

The conductivity activation energy (E_{act}) was calculated graphically, based on the slope of the straight line constructed in Arrhenius coordinates ($\ln k - 1/T$), where $E_{act} = \text{tg } \alpha \cdot (-R)$. In accordance to Arrhenius equation, the activation energy values calculated on the basis of the linear sections of the $\ln k - 1/T$ curves. Results are presented in Table 3.

Table 2
The conductivity of gel electrolytes at 25 °C

Lithium salt	Concentration, m.f.	Conductivity, mS/cm	Concentration, m.f.	Conductivity, mS/cm
LiBOB	0.042	6.7	0.15	4.2
LiClO ₄	0.05	12.7	0.12	7.7
LiIm	0.05	9.5	0.15	6.1
LiBF ₄	0.05	13.7	0.1	11.1
LiTf	0.05	11.2	0.17	3.4

For comparison, the activation energies calculated by the authors of [16] for DMSO-LiAn solutions are presented. The obtained results show that the nature of the anion of lithium salt does not significantly affect the value of E_{act} and its order, which indicates a fairly fast ion transfer [20].

A slight increasing of the E_{act} value was observed in gel electrolytes and has been not significant after comparing with liquid DMSO-LiAn solutions. In accordance with the Stokes equation, such effect can be explained by an increase of the solutions viscosity with PVDF. However, according to experimental data, an increase of the solutions viscosity with increasing of PVDF content does not change the mechanism of the

conductivity process. This process depends on the salt concentration increasing. In this case E_{act} also increases. Such behavior may connect with the increase of the solutions crystallinity.

The interaction of the lithium metal with electrolyte components is very important for current sources with a lithium anode. As a result of the interaction of lithium with electrolyte components, a solid electrolyte film (SEF) is formed on its surface, the nature and composition of which is determined by the salt concentration, the nature of its anion, and the composition of the solvents. In order to determine the effect of the gel electrolyte composition on the resistance of the SEF formed on the surface of the lithium electrode and its change during storage, the electrochemical impedance spectra of Li|electrolyte|Li cells were recorded and analyzed.

The impedance spectra plotted in the Nyquist coordinates are shown in Fig. 2. They have a semicircle characteristic of such curves, the radius of which depends on the electrolyte composition. Such characteristic is mainly associated with the formation of a film on the surface of a lithium electrode.

Table 3
The conductivity activation energy of the studied electrolytes

Lithium salt	Concentration, m.f.	E_{act} , kJ/mol		Concentration, m.f.	E_{act} , kJ/mol	
		DMSO-PVDF	DMSO [16]		DMSO-PVDF	DMSO [16]
LiBOB	0.042	15.3	13.7	0.15	19.6	23.8
LiClO ₄	0.05	15.4	12.6	0.12	20.6	16.8
LiIm	0.05	14.0	13.4	0.15	20.0	17.5
LiBF ₄	0.05	14.2	13.0	0.1	16.9	13.5
LiTf	0.05	14.3	13.7	0.17	20.3	19.4

Fig.2 Impedance spectra of the Li | electrolyte | Li cell after 5 hours of storage at a temperature of $25 \pm 0.5^\circ \text{C}$ for electrolytes with a salt concentration of ≤ 0.05 m.f. (a) and ≥ 0.1 m.f. (b). The numbers on the curves correspond to the electrolyte number in the Table 1.

The structure of the film formed on the surface of the lithium electrode is quite complex and consists of both lithium inorganic compounds, which formed its dense part, and organic compounds, which formed a loose layer, consisting mainly of the products of the lithium interaction with solvent. The sum of the resistances of the dense and loose parts of the films corresponds to the total resistance.

In electrolytes with salt concentration ≤ 0.05 m.f., the resistance measured at the maximum frequency in the Li-Li electrode system after 5 hours of exposure changes in such order: $\text{LiBF}_4 < \text{LiTf} < \text{LiClO}_4 < \text{LiIm} < \text{LiBOB}$. With the exception of LiClO_4 , the presented series is in accordance with a series of the electrolytes conductivity changes. Thus, in the high-frequency region, the resistance in the Li-Li system is depended mainly by the conductivity of the gel electrolyte. This corresponds to generally accepted ideas about the formation of resistance in this frequency range. At the same time, the resistance of the SEF in the low-frequency region (1 Hz) changes in a slightly different order $\text{LiBOB} < \text{LiIm} < \text{LiBF}_4 < \text{LiTf} < \text{LiClO}_4$, and differs from changes in the conductivity of electrolytes. Such a mismatch may be due to the contribution of the SEF resistance the formation of which is affected by the electrolyte composition. In electrolytes with a salt concentration ≥ 0.1 m.f., under similar conditions, the SEF resistance in the high-frequency range changes in the order $\text{LiBF}_4 < \text{LiIm} < \text{LiClO}_4 < \text{LiBOB} < \text{LiTf}$. And also, with the exception of LiClO_4 , corresponds to the order of the conductivity of electrolytes changing. At low frequencies, this resistance has another order $\text{LiBOB} \approx \text{LiIm} \approx \text{LiBF}_4 < \text{LiTf} < \text{LiClO}_4$. The presented sequences of changes in the film resistance depending on the composition of the electrolyte are stored during storage, despite the fact that the film thickness and its composition, as well as the concentration of charge carriers, can vary.

The dynamics of the resistance changing Z' taken at a frequency of 1 Hz, depending on the storage time of the Li-Li electrode

Fig.3. Dynamics of the resistance Z' change at a frequency of 1 Hz in the Li | electrolyte | Li cell depending on the storage time τ for electrolytes with salt concentration ≤ 0.05 m.f. (a) and ≥ 0.1 m.f. (b). The numbers on the curves correspond to the electrolyte number in the Table 1.

couple for various electrolytes, is shown in.

In accordance to the experimental data, a constant change in the resistance value is observed, which is correlated with the films thickness and a change in its structure. In the initial period of time, after the assembly of the cells, the resistance on the axis Z' decreases, but after passing a certain minimum begins to increase. This behavior is explained by the dissolution of the primary sur-

face film formed upon contact of lithium with the environment, and the formation of a new film resulting from the interaction of lithium with an electrolyte. The chemical composition of the SEF is quite complex and depends on the composition of the electrolyte, which also affects its thickness, specific ionic and electronic conductivity. The data given in fig. 2 and 3 reflect the general picture of changes, which include changes in the current lead - lithium contact, the lithium-electrolyte interface, as well as in the electrolyte composition, and do not reflect changes in the dynamics of SEF formation. Model of the equivalent circuits 1 and 2, constructed from impedance spectra.

Scheme 1. Model equivalent circuit for electrolytes 1, 2, 6, 7, 8, 9

Scheme 2. Model equivalent circuit for electrolytes 3, 4 and 5

(Scheme 1, 2), demonstrate that in all electrolytes, contact with lithium leads to the formation of capacitive elements formed as a result of changes in ionic conductivity at the lithium electrode-electrolyte interface. This coincides with the general laws of charge transfer in SEFs formed on lithium in electrolytes of different compositions [24]. Only a perfectly polarized electrode can have an ideal impedance of the capacitance of a double electric layer (DEL), which is observed on geometrically and atomically homogeneous electrodes (liquid mercury or

monocrystals) [25]. In all other cases, on polycrystalline, including smooth solid electrodes, the impedance is not purely capacitive, because such surfaces contain several layers that are frequency-dependent in nature. To distinguish it from an ideal capacitance, such capacitance is called “frequency dispersion of capacitance”. For a simple description of the dispersion, the phase boundary is often approximated by a constant phase element (CPE), in other words, the capacitance C (frequency-dependent) is the frequency power function, ω , that is, $C(\omega) \propto (i\omega)^{-\alpha-1}$, where i - imaginary unit. In the theory of impedance, such capacitances are modeled by a shunted CPE element with a standard deviation not exceeding 7 [21].

For electrolytes containing LiClO_4 and an electrolyte with LiIm at a salt concentration of 0.05 m.f., an additional element appears in equivalent circuits - open Warburg (W_o), which characterizes the presence of semi-infinite diffusion. The reason for this may be the imperfection of the SEF formed on the surface of the lithium electrode [22], which can consist, for example, in the high porosity of the SEF, which facilitates the transfer of lithium ions, or in the presence of corrosion processes. Thus, electrolytes 3, 4 and 5 are modeled by circuit 2 with a standard deviation not exceeding 0.005.

For equivalent circuits containing an element of the CPE constant phase, an analysis was proposed in [23] using such parameter as the dispersion of the capacitance $C_{\min}$, which can be considered as an indicator of the imperfection of films formed on metal surfaces. The calculation of $C_{\min}$ was carried out using Bode diagrams according to equation 1:

$$C_{\min} = \frac{1}{3R_{\max}\omega_{\max}^{2-\gamma}} \quad (1)$$

The $R_{\max}$ and $\omega_{\max}$ are the resistance and frequency corresponding to the maximum of the semicircle, and the value of the exponent γ is determined by the slope of the impedance spectrum in the high-frequency region of the Nyquist diagram. The calculation of the maximum values of the differential capacitance $C_{\max}$ was carried out according to the Nyquist diagrams for different storage time ranges in accordance with equation 2:

$$C_{\max} = 3R_{\max}\omega_{\max} \quad (2)$$

After calculation this parameters the contour diagrams were built in 3-D coordinates (capacitance, capacity dispersion, frequency) (Fig.4). As result we received EIS images, which demonstrate a charges change of the lithium electrode surface in time. Using of the such was approaches based on the theory of transient processes and the Kirchhoff's laws for an electric circuit containing reactive elements. They were used to obtain some S-plane described by Duhamel integrals [26] and to apply a graphical method in the following time intervals: $0 < t < t_1$, $t_1 < t < t_2$ и $t > t_2$ [27]. In this case, the graph is presented in the form of a triple diagram of the dependence of the rate of change of capacitance C in a certain time interval Δt , which is proportional to the capacitance at the beginning of the time interval superimposed on the variation curve of the capacitance as a function of frequency. Taking into account that the dispersion of the capacitance reflects surface disorder arising due to the unevenness of atomic scales and energy inhomogeneities at the electrode – electrolyte interface [25- 29], this approach can be

Fig.4. EIS images of the changes of the lithium surface in the electrolytes depending on the storage time. The numbers in the diagrams correspond to the electrolyte number in the Table. 1

used as an integral characteristic of the degree of surface inhomogeneity in time. Thus, the switching of the rate of change of capacitance and the dispersion of the capacitance in the studied time interval can be considered as an integral picture of the changes in the SEF formed on the surface of the lithium electrode depending on the composition of the electrolytes, which is reflected in the EIS images (Fig.4). The X axis indicates the storage time, min, the Y axis shows the change in capacity over time calculated according to equation 2, and the Z axis represents the projection of the capacity dispersion $C_{\min}$ onto the $X - Y$ plane. The intensity of light tones corresponds to the maximum dispersion of the capacitance (charge) and can characterize the imperfection of the forming surface films.

The presented EIS images show a significant difference in the surface structure of the lithium electrode, depending on the storage time and electrolyte composition. In most electrolytes, with an increase in the duration of their contact with lithium depending on the storage time, a maximum of the dispersion of the capacitance is observed, depending on the composition of the electrolyte. After this, the formation of a more stable film is observed. The period of film formation is characterized by the presence of extrema, indicated in light diagrams by a light tone, which indicate the existence of a disordered SEF structure on the lithium surface. The presence of these extremes, as a rule, is observed in a relatively short period of time, which corresponds to the accepted ideas about the rapid formation of the disordered structure of the SEF [24]. An exception is electrolytes 3, 4, and 8, that is, elec-

trolites based on lithium perchlorate and fluoroborate, where the SEF disorder persists throughout the entire measurement time and may be due to corrosion processes, which is known for solutions with lithium perchlorate in DMSO [28]. With an increase in the contact time of lithium with an electrolyte, the degree of film ordering increases. This is characterized by a transition from light tones in the contour diagrams to darker ones. Thus, from the point of view of the structure of the electrode – electrolyte interface, electrolyte systems based on LiBF_4 and LiClO_4 salts can lead to an increase in internal resistance and, in the presence of corrosion processes, to decomposition of the electrolyte, which are undesirable effects that significantly affect the characteristics of current sources. An electrolyte based on LiBOB, at its high concentration, is also characterized by a rather long period of SEF formation, and from this point of view, its dilute solutions have advantages. In all other electrolytes, SEF is formed within $\sim 100\text{--}200$ min.

The efficiency of using electrolytes based on DMSO – PVDF gels in oxygen oxidation-reduction reactions was studied using voltammograms obtained on steel and platinum electrodes in the voltage range 1.8–4.6 V. The choice of electrode materials was based on differences in the catalytic properties of these metals in oxygen oxidation-reduction reactions. The obtained voltammograms are presented in Fig. 5. According to published data [13], the peak on the cathode branch of the curve obtained on the platinum electrode in the potential region close to 2.5 V (curve 1) can be attributed to the process associated with oxygen reduc-

tion. In the voltammogram obtained using a steel electrode, a similar peak is absent, since steel is not a catalyst in the processes of oxygen oxidation-reduction. The increase in current at voltages above 4.5 V on the steel electrode is explained by the decomposition of the electrolyte.

CONCLUSIONS. The study results of the conductivity of gel polymer electrolytes showed that the systems based on DMSO-PVDF solutions with lithium salts LiBOB, LiClO₄, LiIm, LiBF₄, LiTf are characterized by conductivity close to similar electrolytes, including lithium salt and DMSO. The conductivity activation energy calculated on the basis of the Arrhenius equation is 14–15.4 KJ/Mol for electrolytes with salt concentration ≤ 0.05 m.f., and 16.9–20.6 KJ/Mol for electrolytes with salt concentration ≥ 0.1 m.f. The obtained values of E_{act} indicate a fairly rapid transfer of ions, which in more concentrated solutions is inhibited by an increase in their crystallinity. A slight increase in E_{act} for gel electrolytes in comparison with DMSO-LiAn liquid solutions is not significant, and an increase in the viscosity of solutions due to PVDF does not change the mechanism of the conductivity process. The analysis of model equivalent circuits of the studied electrolytes did not establish significant differences in their structure, all electrolytes are prone to the formation of capacitive elements, which are formed as a result of changes in ionic conductivity at the lithium electrode-electrolyte interface. The changes on the surface of the lithium electrode have been recorded using EIS images based on capacitive elements and their frequency changing. The presence of diffusion in the LiClO₄ solution and LiIm

solution with a salt concentration of 0.05 m.f. was fixed by equivalent circuits of EIS spectra and by EIS images.

We are grateful to National Academy of Sciences of Ukraine for financial support of the project 011U000858.

ВПЛИВ КОНЦЕНТРАЦІЇ І ПРИРОДИ СОЛІ ЛІТІЮ НА ХАРАКТЕРИСТИКИ ГЕЛЕВИХ ЕЛЕКТРОЛІТІВ ДМСО-ПВДФ-LiAn

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В роботі приведені результати дослідження електролітів на основі розчинів гелів ДМСО-ПВДФ-сіль літію з концентраціями до 0,05 м. д. і вище 0,1 м. д. показано, що провідність електролітів є близькою до провідності розчинів солей літію в чистому ДМСО і підпорядковується рівнянню Арреніуса в досліджуваному інтервалі температур і концентрацій. Розраховані значення енергії активації для електролітів з концентрацією солі до 0,05 м. д. становлять 14-15,4 кДж/моль, а для електролітів з концентрацією солі вище 0,1 м. д. – 16,9-20,6 кДж/моль, що свідчить про достатньо швидкий перенос іонів, який у більш концентрованих розчинах гальмується збільшенням ступеню їх кристалічності. Аналіз модельних еквівалентних схем, отриманих в системі Li-Li, показав схильність електролітів до утворення ємнісних елементів, які формуються в результаті зміни іонної провідності на границі розділу літійовий електрод-електроліт. Для розчинів LiClO₄ та LiIm з

концентрацією солі 0,05 м. д. в еквівалентних схемах з'являється додатковий елемент W_0 (відкритий Варбург), який характеризує напівбескінечне дифузію, яка пов'язана з недосконалістю плівки, що утворюється на поверхні електроду. Присутність дифузії додатково підтверджена контурними діаграмами ємності та дисперсії ємності в широкому частотному діапазоні.

К л ю ч о в і с л о в а: полімерний електроліт, провідність, границя розділу літій-електроліт, енергія активації провідності, модельна схема.

ВЛИЯНИЕ КОНЦЕНТРАЦИИ И ПРИРОДЫ СОЛИ ЛИТИЯ НА ХАРАКТЕРИСТИКИ ГЕЛЕВЫХ ЭЛЕКТРОЛИТОВ ДМСО-ПВДФ-LiAn

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В работе приведенные результаты исследования электролитов на основе растворов гелей ДМСО-ПВДФ-соль лития с концентрациями до 0,05 м. д. и выше 0,1 м. д. Показано, что проводимость электролитов является близкой к проводимости растворов солей лития в чистом ДМСО и подчиняется уравнению Аррениуса в исследуемом интервале температур и концентраций. Рассчитанные значения энергии активации для электролитов с концентрацией соли до 0,05 м. д. представляют 14-15,4 кДж/моль, а для электроли-

тов с концентрацией соли выше 0,1 м. д. - 16,9-20,6 кДж/моль, что свидетельствует о достаточно быстром переносе ионов, который в более концентрированных растворах тормозится увеличением степени их кристалличности. Анализ модельных эквивалентных схем, полученных в системе Li - Li, показал склонность электролитов к образованию элементов емкости, которые формируются в результате изменения ионной проводимости на границе раздела литиевый электрод-электролит. Для растворов $LiClO_4$ и $LiIm$ с концентрацией соли 0,05 м. д. в эквивалентных схемах появляется дополнительный элемент W_0 (открытый Варбург), который описывает полу бесконечную диффузию, связанную с несовершенством пленки, образующейся на поверхности электрода. Присутствие диффузии дополнительно подтверждено контурными диаграммами емкости и дисперсии емкости в широком частотном диапазоне.

К л ю ч е в ы е с л о в а: полимерный электролит, проводимость, граница раздела литий-электролит, энергия активации проводимости, модельная схема.

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Надійшла 09.11.2019