Ionic transport in passivating layers on the lithium electrode

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Abstract

The processes of ionic transport in passivating layers on the surface of the lithium electrode in solutions based on thionyl chloride, propylene carbonate and γ-butyrolactone have been studied by means of pulse electrochemical methods. The data obtained are quantitatively described by a model which takes into account transport of both the intrinsic mobile lithium ions of the passivating layer and lithium ions injected into the passivating layer from the electrode or from the electrolyte solution under anodic or cathodic current directions, respectively. The values of mobility and concentration of mobile lithium ions in passivating layers formed on lithium in various solutions under open-circuit conditions have been determined.

Introduction

On the surface of lithium in electrolytes used in Li batteries, passivating layers (PL) are formed which, in a first approximation, may be considered as thin nonporous films of Li-conducting solid electrolytes [1]. Kinetics of electrode processes at the Li/nonaqueous-solution interface which was denominated by Peled [1, 2] as 'solid-electrolyte interphase' (SEI) is determined by peculiarities of the ionic transport in PL [1–4]. However, until recently the question concerning a model which would quantitatively describe the transport of ionic carriers in PL on Li for a wide range of variations of current densities and electrode polarizations remained open.

In the present work, studies of the ionic transport through SEI were performed using the method of single galvanostatic pulses.

Experimental

Polarization *j–E* curves on Li and its low-melting alloys were measured after ageing (storing) the electrode being studied in a solution under open-circuit conditions. The Li alloys had been obtained by the method of cathodic intrusion. A thin Li wire placed in the vicinity of the working electrode surface served as a reference electrode. The following solutions were used: 1 M LiAlCl$_4$ in thionyl chloride (TC), 1 M LiClO$_4$ in propylene carbonate (PC) and in PC mixtures with dimethoxyethane (DME),

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1 M $LiClO_4$ in γ-butyrolactone (BL). Water concentrations in the organic solutions did not exceed 0.005%. The procedure of electrochemical measurements was similar to that described elsewhere [3–5]. The j–E curves were obtained using stabilized time-independent polarization values after switching on current pulses with allowance for ohmic drops in solution. From the slopes of the initial parts of potential–time curves, the differential capacity values of the electrodes were obtained which were used for calculating the effective thicknesses of the PL by the formula of a plane capacitor, the values of relative dielectric constant being assumed equal to 10.6 and 7.0 for the PLs formed in TC and organic solutions, respectively. The use of short pulses of current enabled us to prevent destructive effects of measurements on PL and made it possible to obtain highly reproducible anodic and cathodic j–E curves in a wide range of current densities. All the measurements, until otherwise noted, were performed at 298 K.

Results and discussion

In Figures 1 and 2 polarization curves are presented for Li electrode in TC, PC and BL solutions after different storage periods. In all the systems at sufficiently high polarization values square j–E dependences are observed. The character of j–E curves obtained in the anodic and cathodic polarization regions was the same. Plotting the data from ref. 3 for Li in PC solutions also yields straight lines in the $j^{1/2}$–E coordinates (Fig. 2). As can be seen from Fig. 3, at low polarizations, experimental j–E dependences
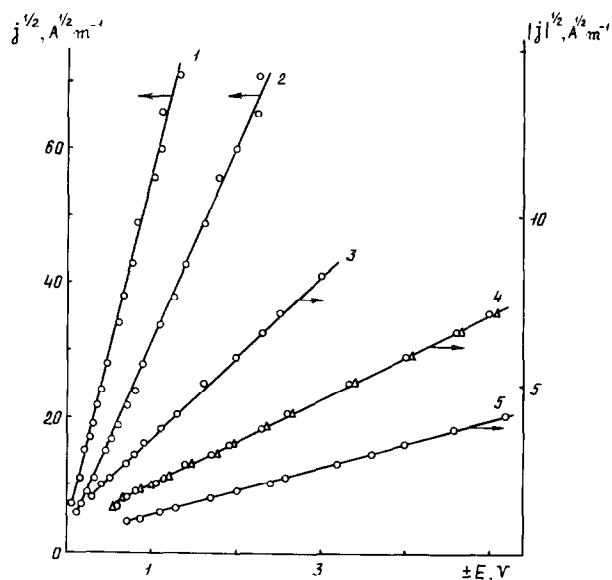

Fig. 1. (○) Anodic and (△) cathodic polarization curves of the Li electrode in 1 M $LiClO_4$/ BL, curves (1) and (2), and 1 M $LiAlCl_4$/TC (curves (3)–(5)) solutions. Storage duration: curve (1) 6 h, curve (2) 880 h, curve (3) 360 h, curve (4) 1130 h, and curve (5) 2550 h. Due to the difference between the signs of the anodic and cathodic currents, their absolute values have been used.
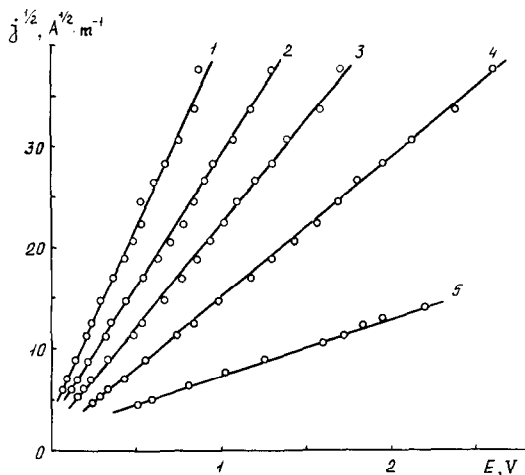
Fig. 2. Anodic polarization curves of the Li electrode in 1 M LiClO$_4$/PC solution. Storage duration; curve (1) 0.5 h, curve (2) 48 h, curve (3) 216 h, curve (4) 1320 h, and curve (5) plotting the polarization curve from ref. 3 for PL thickness equal to 138 Å.
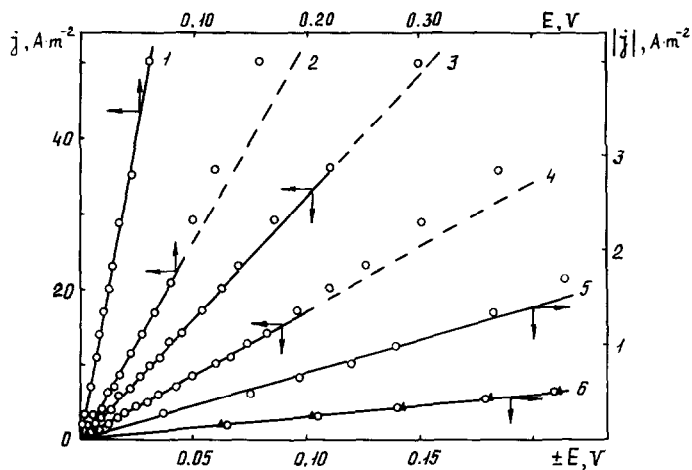

Fig. 3. Initial parts of (O) anodic and (△) cathodic polarization curves of the Li electrode in (curves (1) and (2)) 1 M LiClO$_4$/BL, (curves (3) and (4)) 1 M LiClO$_4$/PC, and (curves (5) and (6)) 1 M LiAlCl$_4$/TC solutions. Storage duration; curve (1) 6 h, curve (2) 880 h, curve (3) 48 h, curve (4) 216 h, curve (5) 360 h, and curve (6) 1130 h.

both in the anodic and cathodic regions form straight lines coming out from the origin of coordinates. The values of ionic resistivity of PL determined from the slopes of these lines grow with increasing storage duration. The square dependences of ionic current on potential found here allow one to assume the existence of ionic space-charge-limited currents (SCLC) flowing through SEI. The limitation of a flowing electronic current by the spatial charge of injected electronic carriers is well known

for solid systems [6]. Ionic SCLCs have been studied in a much lesser extent, although some communications have been published in which they were observed [6, 7]. During monopolar injection into a trapless dielectric, the flowing current must be proportional to the squared potential difference applied and inversely proportional to the third power of the thickness of the layer into which the carriers are being injected [6]. As can be seen from Fig. 4, the squared slope of the straight lines in the $j^{1/2}$–E plot is proportional to the third power of the value of differential capacity (C) or inversely proportional to the third power of the PL thickness thus pointing to the SCLC mechanism involved.

In the model proposed for describing ionic transport through SEI [5, 8, 9], the Li electrode or Li salt solution are considered as ion reservoirs (ionic emitters). Lithium ions can be injected into a PL from Li metal or from the electrolyte (during anodic or cathodic polarizations, respectively) and create in the PL a spatial charge limiting the flow of ionic carriers*. An increase in electrode polarization, according to the model proposed, leads not to an increase in the mobility of Li ions in the PL, as it was assumed in refs. 3 and 4, but to a concentration growth for ions within the PL bulk caused by their injection from the contact reservoirs.
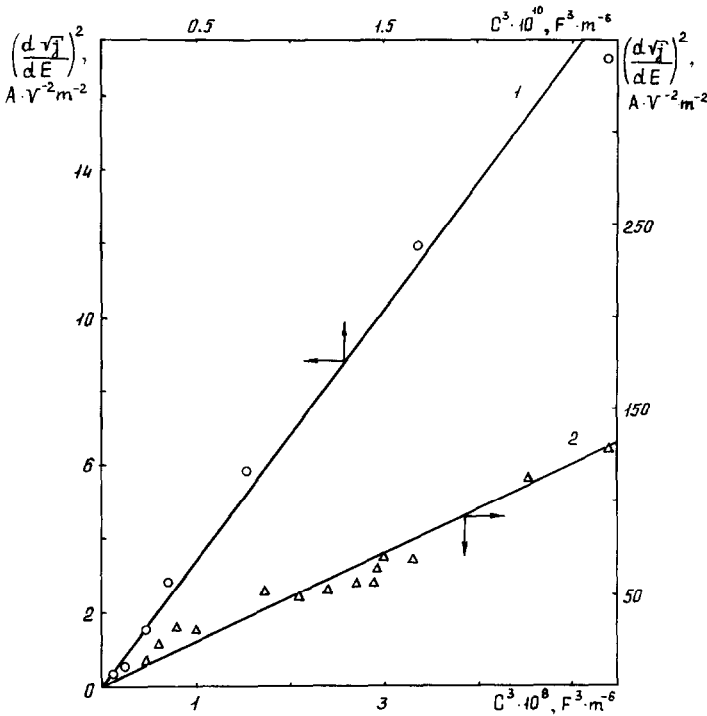

Fig. 4. $(dj^{1/2}/dE)^2$–C^3 plot for the systems: curve (1) Li/TC, 1 M LiAlCl₄, and curve (2) Li/PC, 1 M LiClO₄.

*In the simple model considered here it is assumed that the injecting contact can maintain any indefinitely high concentration of ions at the interface. As is shown in ref. 10, in the region of highest injection currents, deviations from the square j–E dependences may be observed connected with limitedness of ion concentration at the ionic emitter/PL interface.

PLs formed on the Li surface are characterized by their intrinsic ionic conductivity not connected with the injection of ions from the contacts. The latter is demonstrated, in particular, by the linear character of the $j–E$ dependences in Fig. 3. Assuming that injected as well as intrinsic carriers in PL are particles of the same type, a current–potential characteristic should be written for monopolar injection into a material containing mobile carriers. However, there is no explicit analytical form for current–potential dependence in this case [6]. In view of that, in order to describe ion transport through SEI in a wide range of polarizations, we used the following equation:

$$j = \frac{q n_o \mu E}{L} + \lambda \frac{\epsilon \epsilon_o \mu E^2}{L^3} \tag{1}$$

where n_o is the intrinsic concentration of mobile Li ions in a PL of the thickness L, μ their mobility, q the elementary charge, ϵ_o the permittivity of vacuum, ϵ the dielectric constant of the PL material; λ is the coefficient with the values ranging from 0.5 up to 1.125 at polarizations changing from zero to an infinitely high value which is approximated by the following expression:

$$\lambda = 0.5 + 0.625 \frac{\left(\dfrac{\epsilon \epsilon_o E}{q n_o L^2} + 0.586 \right)^{1.6} - 0.586^{1.6}}{\left(\dfrac{\epsilon \epsilon_o E}{q n_o L^2} + 0.586 \right)^{1.6} + 0.586^{1.6}} \tag{2}$$

The approximation made enabled us to use eqn. (1) with the error being less than 1% instead of the exact theoretical dependency [6]. In Table 1, as an example for PC- and TC-based systems, the values of current density and corresponding electrode polarization values are presented, the latter calculated according to eqn. (1) for n_o and μ values corresponding to the condition of minimal dispersion.

As can be seen from Table 1, a good agreement is observed between experimental and calculated $j–E$ curves in the whole region of polarizations investigated here. In Fig. 5, polarization curves for some systems have been plotted in full logarithmic coordinates. The latter form of data presentation clearly demonstrates the existence of two characteristic regions on the experimental $j–E$ dependences. The linear dependence with the slope equal to unity in the region of low polarizations corresponds to the transport of intrinsic mobile Li ions in PL and is described by the first term in eqn. (1). In the region of high polarizations, in conformity with eqn. (1), $j–E$ dependences transform into straight lines with a slope equal to 2, which corresponds to the square law under the conditions of an essential excess of the current of injected carriers over that related with the intrinsic conductivity of PL. The data presented show the possibility of quantitative description for ionic currents flowing through SEI within the framework of the model of ionic SCLC taking into account the intrinsic conductivity of PL.

Using eqn. (1), the values of mobility and concentration for intrinsic mobile Li ions in PLs formed in different solutions, which are absent in literature, were calculated from experimental $j–E$ curves. In Fig. 6, the values of concentration and specific ionic conductivity (σ) for PLs formed in PC solution are presented for different storage periods (σ was calculated from the values of concentration and mobility obtained). For this system, the mobility of Li ions in PL exhibits a negligible dependence on storage duration which results in a similar character of concentration and specific conductivity variations with time. Variation curves of the transport parameters for PL during storage in TC solution are presented in Fig. 7. The latter shows that during

TABLE 1

Comparison of experimental and calculated polarization curves for various periods of Li storage in different solutions under open-circuit conditions

j (A/m^2)	Storage duration (h)[a]					
	1		2		3	
	log E_{exp} (V)	log E_{calc} (V)	log E_{exp} (V)	log E_{calc} (V)	log E_{exp} (V)	log E_{calc} (V)
Li/TC, 1 M LiAlCl$_4$						
0.34	−1.79	−1.764	−1.50	−1.492	−1.33	−1.320
0.67	−1.46	−1.467	−1.20	−1.199	−1.02	−1.028
1.01	−1.30	−1.294	−1.03	−1.030	−0.86	−0.861
1.68	−1.08	−1.078	−0.82	−0.823	−0.67	−0.658
3.37	−0.79	−0.792	−0.55	−0.557	−0.40	−0.400
5.05	−0.63	−0.630	−0.40	−0.414	−0.27	−0.261
13.5	−0.27	−0.271	−0.11	−0.104	0.03	0.039
25.2	−0.07	−0.068	0.06	0.072	0.22	0.210
50.5	0.13	0.132	0.25	0.252	0.40	0.386
67.3	0.21	0.210	0.33	0.324	0.47	0.462
101.1	0.31	0.316				
Li/PC, 1 M LiClO$_4$						
1.43			−2.33	−2.341	−1.83	−1.804
4.29	−1.99	−1.961	−1.89	−1.867	−1.35	−1.341
10.0	−1.60	−1.598	−1.50	−1.505	−1.00	−1.001
20.0	−1.26	−1.305	−1.20	−1.215	−0.73	−0.746
35.7	−1.06	−1.066	−0.97	−0.980	−0.54	−0.553
78.5	−0.73	−0.757	−0.70	−0.682	−0.30	−0.319
157	−0.51	−0.511	−0.45	−0.447	−0.11	−0.133
286	−0.30	−0.320	−0.26	−0.265	0.03	0.019
500	−0.17	−0.157	−0.11	−0.109	0.15	0.155
800	−0.03	−0.030	0.02	0.015	0.25	0.267
1430	0.11	0.120	0.16	0.161	0.37	0.403

[a]Li/TC, 1 M LiAlCl$_4$: 1–47 h, 2–120 h, 3–360 h; Li/PC, 1 M LiClO$_4$: 1–5 h, 2–53 h, 3–990 h.

first 9 to 10 h of storage, a mobility growth* and concentration drop of mobile Li ions are observed leading to a weak dependence of specific conductivity on time. Increasing storage duration is accompanied by stabilization of the mobility values and by an essential decrease in the concentration of mobile Li ions and specific ionic conductivity. The concentration decrease with time which is characteristic for all the systems studied, is evidently related to the existence of nonequilibrium ionic current carriers in freshly formed PLs, as well as to the PL perfection process occurring during storage. It should be noted that the n_0 values found characterize the concentration

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*Within this time interval, the mobility appears to be a function of PL thickness which leads to deviations from the above-discussed characteristic dependence of current on thickness.
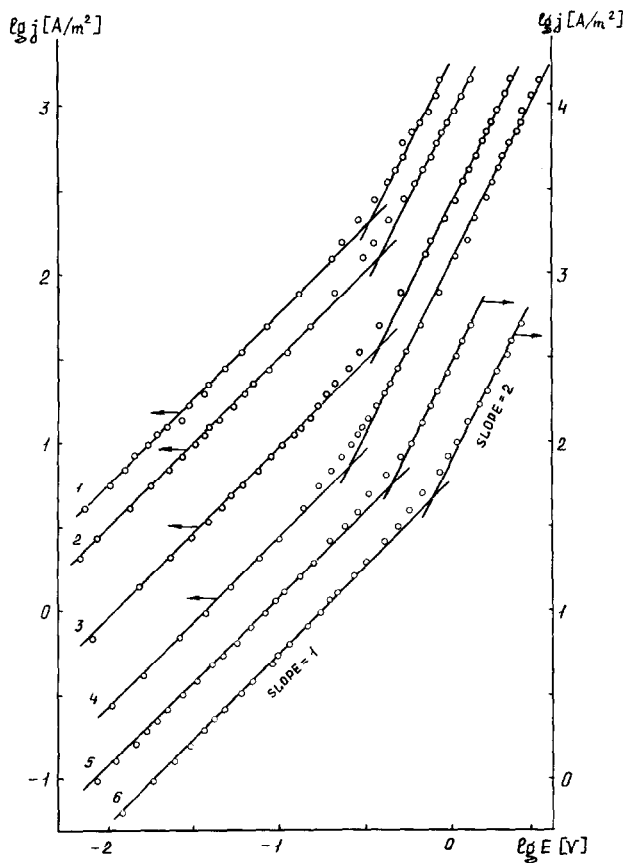
Fig. 5. Anodic polarization curves of the Li electrode (curves (1)–(4)) in 1 M LiClO$_4$/PC and (curves (5) and (6)) Li$_{12}$Sn$_{3.8}$Cd alloy electrode in 1 M LiClO$_4$/PC+DME solution. Storage duration; curve (1) 0.5 h, curve (2) 48 h, curve (3) 990 h, curve (4) 2160 h, curve (5) 3 h, and curve (6) 310 h. Dots represent experimental data; solid lines drawn with the slopes equal to 1 and 2.

of mobile Li ions averaged by the PL thickness* since, on account of the PL thickness growth, 'fresh' layers having an increased concentration of ionic carriers are being formed.

Temperature dependences of transport characteristics for PLs formed on Li in PC and BL solutions are presented in Fig. 8. As can be seen from the latter, the temperature dependences of specific ionic conductivity and concentration of mobile ions are linearized in the log σT, $1/T$ and log n_o, $1/T$ plots, respectively. The value of activation energy of conduction obtained for PLs formed in PC solutions is 0.60 ± 0.06 eV which agrees well with the data reported in the literature [3]. Activation energy values close to those presented above have been obtained for the BL-based system (see Fig. 8).

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*Specific features of time dependences of local concentrations of mobile Li ions in PL which characterize the relaxation kinetics of nonequilibrium ionic conductivity are discussed in ref. 12.
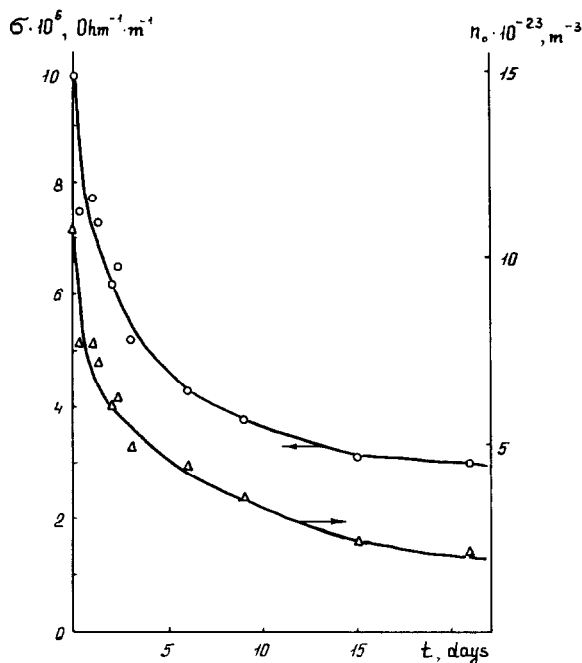
Fig. 6. Time dependences of ($\triangle$) mobile Li ion concentration and ($\bigcirc$) specific ionic conductivity of PL on the Li electrode in 1 M LiClO$_4$/PC solution.

General discussion and conclusions

In spite of quantitative differences, some common regularities can be observed in the behaviour of the studied systems of different nature. This makes it possible to assume that the ionic SCLC provides a general mechanism of ion transport through PLs formed on Li and its alloys in nonaqueous solutions under open-circuit conditions.

Using experimental j–E curves obtained in a wide range of current densities and polarizations, within the framework of the model proposed one can determine the basic transport characteristics of PL, i.e., the values of specific conductivity and mobility of ionic current carriers, depending on the composition of the solution and storage conditions of the system. This enables one to distinguish the effects exerted both by admixtures added to the electrolyte in order to modify the PL and impurities present in the electrolyte on the values of concentrations of ionic carriers and their kinetic characteristics in the PL. Note that measurements may be performed directly in Li batteries [13].

The experimental data obtained make it possible to draw some conclusions on the nature of ionic current carriers and the character of their transport within the PL bulk. First, it appears interesting to discuss the possibility of injection of cation vacancies from the solution into the PL as a basic mechanism limiting the rate of the anodic process in the region of high polarizations. Considering the similarity of the j–E profiles in the anodic and cathodic polarization regions, it follows from the afore-mentioned assumption that cathodic currents are also limited by injection of cation vacancies into PL. However, in this case Li metal should be regarded as an emitter
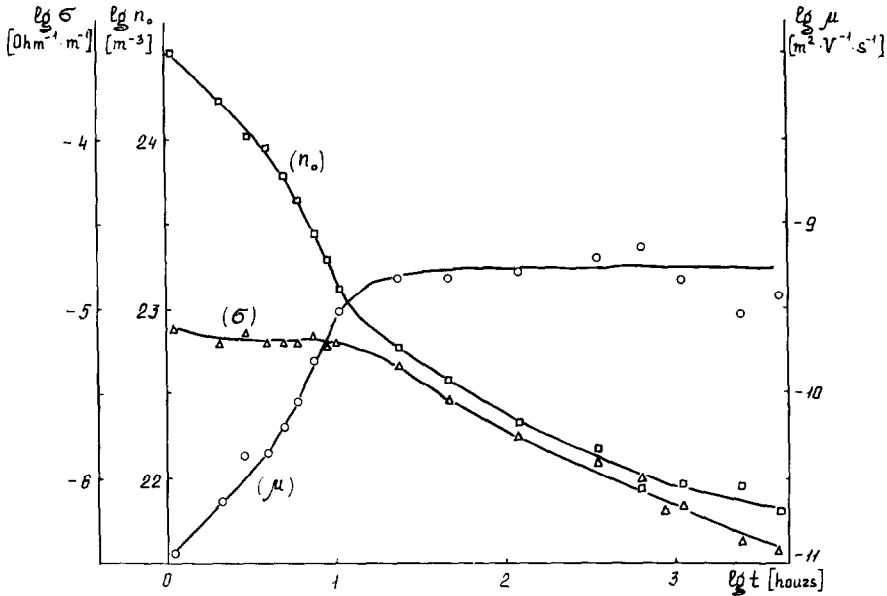
Fig. 7. Time dependences of concentration of mobile ions, their mobility and specific ionic conductivity of PL on the Li electrode in 1 M LiAlCl$_4$/TC solution.

of Li vacancies, which has absolutely no physical foundation. Hence, it may be concluded that experimentally observed ionic SCLCs are related to the processes of monopolar injection of Li ions from Li metal and from electrolyte during the anodic and cathodic processes, respectively, as we assumed earlier.

As for the nature of intrinsic ionic current carriers, the appearance of which in the PL bulk is not connected with injection from the contacts, analysis of experimental data also shows that they are not Li vacancies. As a matter of fact, the observed compliance of the experimental data with the model of monopolar injection into a solid containing particles of the same kind as the injected ones shows that in the region of low polarizations as well, which is characterized by linear j–E dependences, the basic current carriers are mobile Li ions. Therefore, from the viewpoint of ionic transport, PLs on Li differ significantly from monocrystals of alkali-metal haloid compounds the conductivity of which is connected with the presence of cation vacancies [14, 15]. Besides that, the values of transport parameters found differ significantly from those typical for monocrystals. In particular, for PLs based on LiCl formed on Li in TC solutions, the specific ionic conductivity values exceed that of LiCl monocrystals (taken from ref. 15), extrapolated to ambient temperature from the region of intrinsic disordering, by 9 to 10 orders of magnitude. (Extrapolation of the values of conductivity induced by impurities, which were presented in ref. 15, to ambient temperature appears inadequate due to exerting effects of association of defects and segregation of impurities during temperature decrease [14]). Hence, it can be assumed that, from the viewpoint of the defect structure and ionic transport mechanism, monocrystals of Li compounds seem to be very far analogues of PL formed on the Li surface. Taking into account the results of the present work and the data on the PL structure reported in the literature [16], it appears most likely that in such polycrystalline highly-disordered objects as PL, ionic transport proceeds mainly by Li ion transfer within the PL bulk
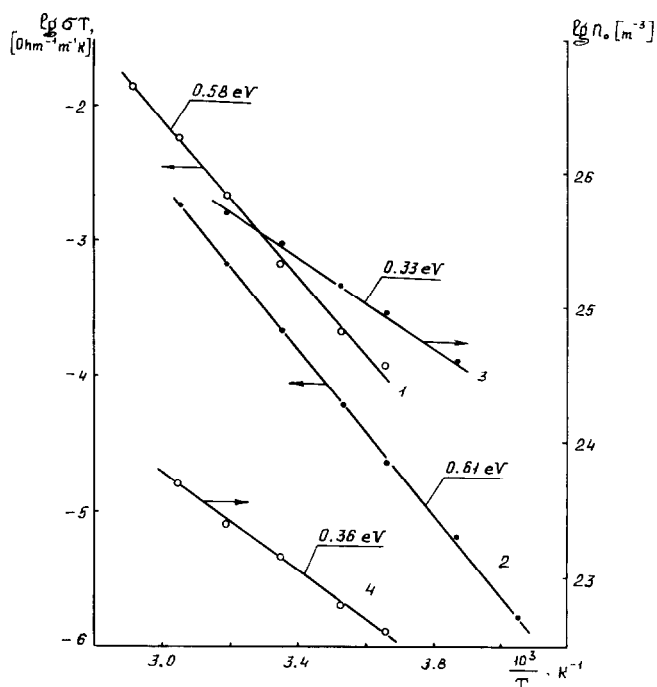
Fig. 8. Temperature dependences of specific ionic conductivity and concentration of mobile ions in PLs formed on Li in (curves (1) and (4)) 1 M LiClO₄/PC and (curves (2) and (3)) 1 M LiClO₄/BL solutions.

along the intergranular boundaries and phase boundaries having specific transport properties [17].

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