

Photoelectrochemistry of lithium

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Abstract

The results of investigation of the processes occurring at the lithium/nonaqueous solution interface under the influence of light irradiation are presented. The primary step of the cathodic photoeffect revealed is photoemission of electrons from lithium into passivating layers on its surface. The electron photoemission technique has been used for obtaining information about the composition and electric characteristics of the passivating layers during lithium storage in solution under open-circuit conditions.

Introduction

On the surface of lithium in nonaqueous solutions, passivating layers (PL) are formed, the properties of which exert a decisive influence on the electrochemical behaviour of the Li electrode [1]. Along with traditional electrochemical techniques for investigating the characteristics of a PL-covered Li electrode, it seems expedient to apply photoelectrochemical techniques which, in other electrochemical systems, enable one to obtain important and, in some cases, unique information about the properties of interfaces and characteristics of electronic current carriers [2, 3]. The first photoelectrochemical measurements on the Li electrode, which have, however, only a qualitative character, were conducted by Povarov *et al.* [4, 5]. The observed decrease in the anodic current and increase in the cathodic current under stationary illumination of the Li/nonaqueous solution interface by polychromatic light was explained in refs. 4 and 5 by internal photoeffect within the PL. In the present work, in order to separate the processes of different nature initiated by illumination of the Li/nonaqueous solution interface along with the experiments under stationary-illumination conditions, pulse photoelectrochemical measurements were conducted at various energies of light quanta. The photoelectrochemical technique was used also for investigating the properties of PL formed on Li in solutions of different composition under open-circuit conditions.

Experimental

Measurements were conducted in three-electrode electrochemical cells with a quartz optical window. Both the working electrode and counter electrode, as well as the reference electrode, were made of Li metal. The working end-face electrode was obtained by press-fitting Li into a glass tube. The following two procedures for

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pretreatment of the surface of the working electrode were used: (i) shear-cutting under a layer of the electrolyte solution and (ii) annealing in an atmosphere of dry oxygen at 373 K for 5 h. 1 M solution of LiAlCl_4 in thionyl chloride (TC), 1 M LiClO_4 in propylene carbonate (PC) and 1 M LiClO_4 in the mixture (1:1 by volume) of PC with dimethoxyethane (DME) were used as electrolytes. The water content of the organic solutions did not exceed 50 ppm. All measurements were conducted and electrochemical cells were stored at 298 K.

A DRSh-250 mercury-vapour quartz lamp served as a source of stationary illumination. Thermal radiation of the lamp was cut off by means of a water filter. For pulse illumination, an IFK-120 xenon flash lamp was used. Monochromatization of the illumination was performed using an optical monochromator. The working electrode was illuminated through a layer of the solution which has no absorption in the region of wavelengths studied.

Investigations of the influence of electrode potential on the time dependences of the current following illumination were conducted in the potentiostatic mode. In order to prevent destruction of PL formed on the surface of the electrode under study by 'dark' current, short potentiostatic pulses were applied.

By means of a device, which served for investigating the characteristics of cathodic photoeffect, depending on the parameters of both the electrochemical cell and measuring circuit elements, it was possible to register a signal proportional to either photocurrent or its integral over time (charge). It should be emphasized that the character of the spectral dependencies studied in the present work is independent from which of these two parameters is being registered. During studying the influence of electrode potential on the value of the 'red' limit of photoeffect, the potential was applied using a battery supplied with a voltage divider. The values of the photoeffect signal measured were recalculated to one and the same light intensity, which was measured using a calibrated photodiode FD-24K. Resistance of the passivating layer (R) at various moments of time after switching on the stationary illumination was measured using pulse galvanostatic method.

Calcium distribution through the thickness of the PL formed on Li in the TC electrolyte with $\text{Ca}(\text{AlCl}_4)_2$ added was determined by the method of secondary-ion mass spectrometry (SIMS). PL sputtering in the course of measurements was performed by bombardment with an argon-ion beam having the energy of 2 keV. Prior to analysis, the PL-covered electrodes were washed with pure TC up to the negative reaction for calcium.

Results and discussion

Figure 1 depicts the effect of stationary illumination on the current-voltage potentiodynamic curves of the Li electrode*. Upon illumination, a sufficient increase in the anodic current in the region of essentially positive potentials and appearance of a cathodic current at less positive potentials are observed along with a shift in the stationary potential value in the positive direction. It can be seen that the photocurrent (which is determined as a difference between the current under illumination and the dark current) changes its sign at some electrode potential value. Such behaviour is

*The curves obtained might have been somewhat distorted due to partial destruction of PL on Li during measurements; however, this does not influence the qualitative relationships which are of interest in this case.

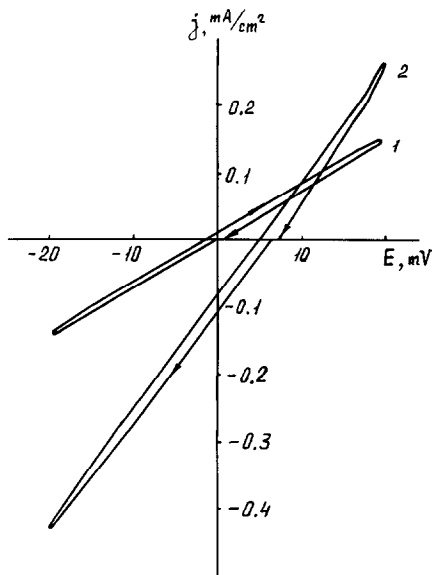


Fig. 1. The effect of illumination on the potentiodynamic curves of the Li electrode in PC + DME, 1 M LiClO₄ solution: (1) in darkness, and (2) under illumination by a DRS-250 lamp (potential sweep rate 0.2 mV/s); storage duration: 75 days. Anodic direction of current and polarization is regarded as positive.

not characteristic for internal photoeffect [3]. Hence, it seems unlikely that the cathodic photocurrents registered in refs. 4 and 5 in the region of low polarizations might be connected with internal photoeffect in PL. As follows from Fig. 2, switching on illumination under open-circuit conditions leads to a slow shift of the Li electrode potential in the positive direction. Under illumination an essential drop of ionic resistance of PL is also observed which is in agreement with the increase in the slope of the current-potential curves under illumination in Fig. 1. After switching off the illumination, both the electrode potential at open circuit and ionic resistance of PL returned to their initial (dark) values. We observed qualitatively similar relationships under stationary illumination on a nonilluminated Li electrode which was placed in the same electrochemical cell in the vicinity of the illuminated one. (Special experiments had shown that the potential of the reference electrode placed at a significant distance (1.0 to 1.2 cm) from the working electrode remained constant). The data obtained lead to an assumption that the light-initiated effects under stationary illumination are related mainly to warming-up the PL-covered Li electrode and the adjacent electrolyte layer. In this case light radiation serves only as a source of PL heating, alteration of electrical characteristics of the PL accounting for the effects observed.

Since the warming-up process is a slow-response one, in order to register the true photoeffect at the Li electrode it is necessary to apply short light pulses. Figure 3 shows typical time dependencies of current obtained under powerful flash illumination of the Li electrode surface. At potentials close to zero versus Li/Li⁺ electrode, a quick-response photocurrent in the cathodic direction is revealed. During increase of anodic polarization, the cathodic photocurrent amplitude decreases. Besides that, under these conditions after the cathodic overshoot an anodic photocurrent gradually develops

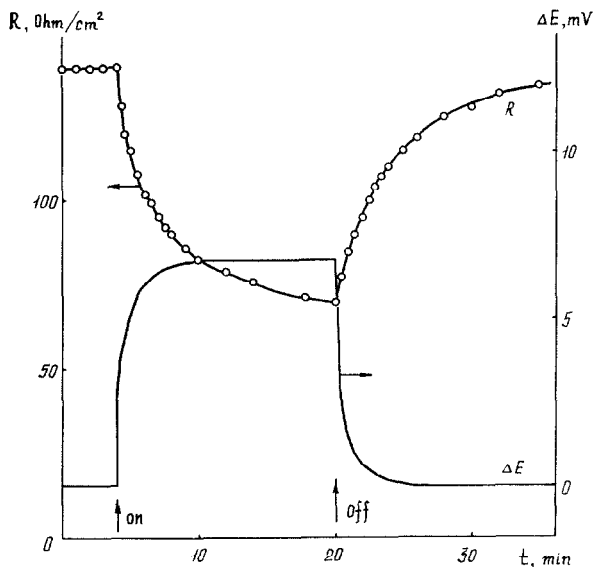


Fig. 2. The effect of illumination on PL resistance and potential of the Li electrode in PC + DME, 1 M LiClO₄ solution; illumination by a DRSh-250 lamp light, and storage duration: 75 days.

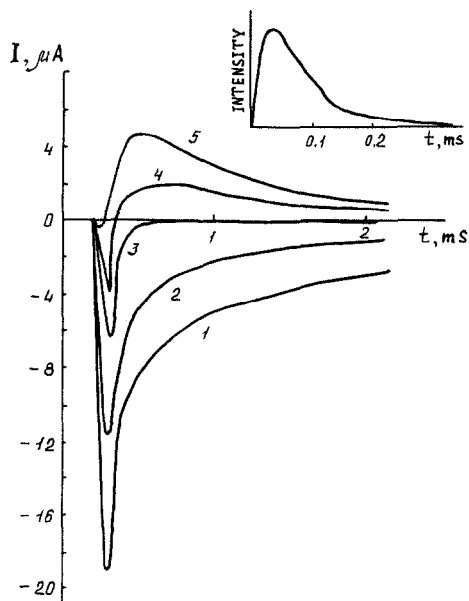


Fig. 3. Time-dependencies of current at the Li/PC+DME, 1 M LiClO₄ interface illuminated by a flash lamp. Electrode polarization: (1) -0.4 V, (2) -0.2 V, (3) 0 V, (4) +0.1 V and (5) +0.2 V. Anodic direction of current and polarization is regarded as positive. Inset: light pulse profile.

which, after reaching its maximal value, decreases slowly with time. At cathodic polarization along with the quick-response component of photocurrent, a slow response appears in the cathodic direction. At significant cathodic polarizations the appearance of the inertial component of the photocurrent is revealed by the sluggishness of the trailing edge of the signal. In view of the analogies in the behaviour of the slow-response component of photoeffect and photocurrents under stationary illumination, it may be assumed that the 'slow' photoeffect is related to warming-up the PL-covered Li by light. Further in this work we investigated the characteristics of the revealed 'quick' cathodic photoeffect.

In Figs. 4 and 5 for PC- and TC-based systems, the dependencies of the photocurrent I_{ph} on the photon energy $\hbar\omega$ are presented, plotted in terms of the $I_{ph}^{1/2}-\hbar\omega$ coordinates. As can be seen from these Figs, the experimental spectral curves fit the equation:

$$I_{ph} = A(\hbar\omega - \hbar\omega_0)^n \quad (1)$$

where, $n=2$; A and $\hbar\omega_0$ are constants. The $\hbar\omega_0$ value obtained from the intercept of the extrapolated straight lines in the $I_{ph}^{1/2}-\hbar\omega$ plot to the zero photocurrent value, is a function of electrode potential. Note that the effect of the potential on the threshold energy, $\hbar\omega_0$, decreases during an increase of the Li storage duration in solution under open-circuit conditions (Fig. 4). The observed square dependence of the photocurrent on photon energy is typical for electron photoemission from metals into low-conducting media and is known as the Fowler law [6]. In view of that, it may be assumed that the primary step of the cathodic photoeffect is photoemission of electrons from Li into PL [7, 8]. The $\hbar\omega_0$ parameter in eqn. (1) represents the photoelectric work function

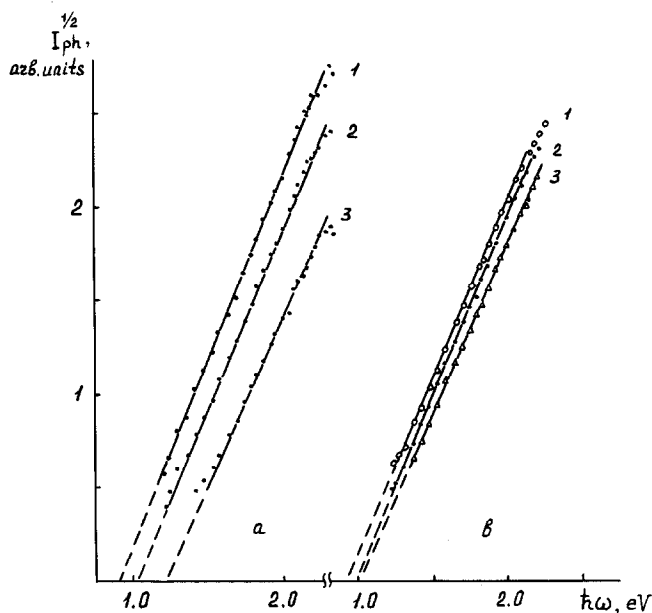


Fig. 4. Spectral dependencies of photoeffect at the Li/PC, 1 M LiClO₄ interface. Electrode polarization: (1) -0.2 V, (2) 0 V and (3) +0.2 V. Storage duration: (a) 2 days and (b) 38 days (arbitrary units).

for electron emission from Li into PL at given electrode potentials and characterizes the long-wave ('red') limit of the photoeffect. The decrease of the effect of potential during storage on position of the 'red' limit of photoeffect observed in Fig. 4 may be explained by a decrease in the fraction of externally applied potential corresponding to the Li-PL interface. This is connected with a growth of the PL resistance during storage of the system due to an increase in the PL thickness and a decrease in specific conductivity [9].

The fact that electron photoemission proceeds just into the PL on Li and not directly into the electrolyte solution is supported by the investigations of spectral and current-voltage dependencies of electron photoemission currents from a platinum electrode into 1 M LiClO₄ solution in PC performed in ref. 10. The work function value found for platinum at zero potential versus Li/Li⁺ electrode is higher than that for photoemission from Li. On the other hand, work function values for electron emission into the same media for different metals at one and the same electrode potential must coincide [2]. In view of this, the difference found between the above-mentioned values of work function shows that photoemission in those two cases proceeds into different media. Furthermore, photoemission by tunnelling of electrons through PL directly into electrolyte has a very low probability due to the significant PL thickness.

In discussions of photoelectron emission from Li into PL, the models may be used that have been developed for photoemission from metals into electrolyte solutions [2] and from metals into wide-bandgap semiconductors [11]. However, in the case of the present study, the specificity of solid layers with ionic conduction must be taken into account. After completion of the photoemission act, when the photoemitted electrons have been transferred to the PL, a number of processes may occur which influence both the magnitude and the characteristics of the photoeffect signal. After quick thermalization which proceeds on account of interaction with the condensed medium, photoelectrons can return to the surface of the electrode-emitter, be transferred to the PL/solution interface, as well as be captured by traps within the PL bulk. Redistribution of mobile Li ions in PL, the charge of which must compensate the excessive charge of photoemitted electrons, may also take place. General theoretical considerations of relaxation processes during photoemission of electrons into materials with mixed ionic and electronic conductivity, as well as a study of the photoeffect kinetics in the Li-PL-electrolyte system by means of pulse laser technique will be presented in ref. 12. As for the investigations of the spectral dependencies of the amplitudes of the photoeffect carried out in the present work, they make it possible to obtain information on the properties of PL.

The electronic work function values for electron emission from Li into PL (at zero potential versus Li/Li⁺ electrode) obtained from the data of Figs. 4 and 5 were found to be 1.0 and 1.3 eV for PC- and TC-based systems, respectively, and remained constant during storage. They allow one to estimate the value of thermoemission current I_T from Li into PL. For calculating I_T we used the equation of Richardson-Zommerfeld for thermoemission from metal into vacuum [6]:

$$I_T = A_0 T^2 \exp(-\hbar\omega_0/kT) \quad (2)$$

where the constant A_0 has the order of 10^2 A cm⁻² K⁻². The obtained value of thermoemission current from Li into PL formed in PC solutions is 10^{-10} A cm⁻², while for PL formed in TC solutions it is 10^{-15} A cm⁻². The orders of the values obtained allow one to assume that the thermoemission component in PC-based systems may make a significant contribution to the electronic current flowing through PLs

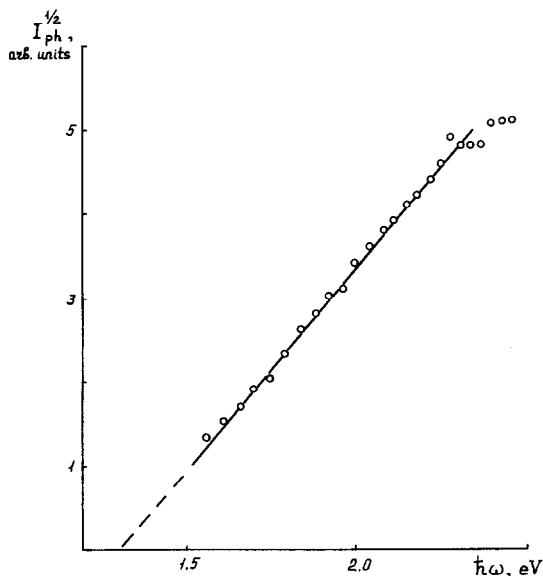


Fig. 5. Spectral dependence of photoeffect at the Li/TC, 1 M LiAlCl₄ interface. Storage duration: 73 h (arbitrary units).

which determines the Li corrosion rate [1], while the electronic current flowing through PL in TC systems may be of a different nature.

In Figs. 6 and 7, the spectral dependencies of the photoemission currents are presented which were measured in (PC+DME)-based solution on Li electrodes with different surface pretreatment. In both cases the spectral dependencies of the photocurrent for long storage periods are linear in the $I_{ph}^{1/2}-\hbar\omega$ plot. For short storage periods, the spectral dependencies obey a power law with an exponent (n) close to 5/2: $I_{ph} \sim (\hbar\omega - \hbar\omega_0)^{5/2}$. The '5/2 power law' was observed earlier during photoemission from metals into concentrated ionic systems — electrolyte solutions [2]. The physical cause of the difference between the exponents in the spectral law for emission into a dielectric and into a concentrated ionic system is attributed to the shielding of the long-range image forces which distinctly influence the character of movement of emitted electrons [2].

As can be seen from Figs. 6 and 7, the work function for electron emission from Li into PL coincides for both methods of surface pretreatment. This provides evidence that in both cases photoemission proceeds into materials of the same composition. On the other hand, the surface of Li annealed in oxygen is covered by lithium oxide. In view of that, the coincidence of the values of the work function allows one to conclude that in the organic solutions, the PLs are formed by the interaction of the Li with traces of water and consist mainly of lithium oxide. This conclusion is in concordance with the data on the important role of water which were presented in refs. 13 and 14.

Accuracy of determination of the exponent (n) in the spectral law of photoemission is essentially improved by using the method of data treatment proposed in ref. 15. In accordance with ref. 15, we presented experimental spectral dependencies in the form of logarithmic derivative:

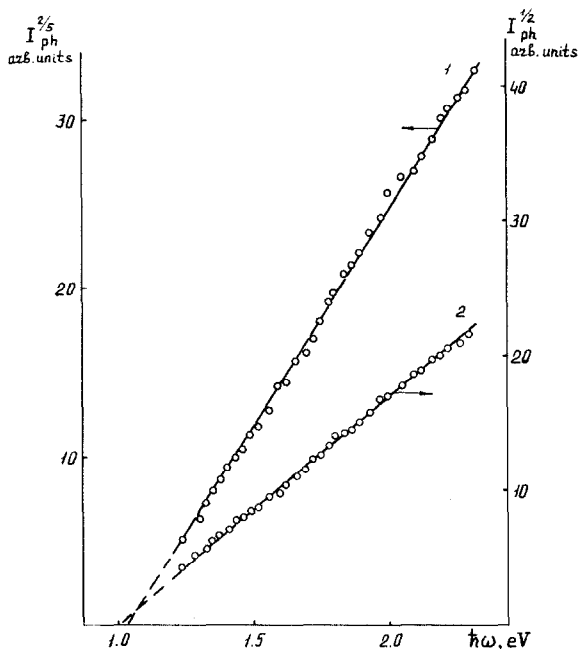


Fig. 6. Spectral dependencies of photoeffect in the system Li/PC+DME, 1 M LiClO₄ (the electrode surface was shear-cut under a layer of solution). Storage duration: (1) 1 h and (2) 41 h (arbitrary units).

$$\Phi = (d \ln I_{ph} / d \hbar\omega)^{-1} = (\hbar\omega - \hbar\omega_0) / n \quad (3)$$

From the slope of linear $\Phi - \hbar\omega$ dependence n was determined, while from the intercept at the abscissa axis $\hbar\omega_0$ was found. In Figs. 8 and 9, as an example, the results of treatment of the spectral dependencies from Fig. 7 are presented. The values of the parameters n and $\hbar\omega_0$ found, using this method, are in a good agreement with those presented above. The change of the exponent in the spectral law of photoemission found is in concordance with the data of ref. 9 on a significant concentration of ionic current carriers present in freshly-formed PLs and an essential decrease of this concentration during storage.

An alteration of the PL composition during storage may be monitored by measuring photoemission currents [8, 16]. As one way of improving the transport characteristics of PLs on Li in TC solutions, it was suggested [17] that the Li anode be covered with calcium. In view of this, it was of interest to investigate photoemission currents on Li electrodes in solutions of LiAlCl₄ in TC with additions of Ca(AlCl₄)₂*.

Figure 10 shows the calcium profiles in the PLs formed in 1 M LiAlCl₄ + 10⁻⁴ M Ca(AlCl₄)₂ solutions in TC obtained by the SIMS technique. Due to the fact that the main quantity of calcium transfers to a PL during the initial steps of its formation, as can be seen from Fig. 10, a decrease in the concentration of calcium compounds takes place near the Li-PL interface and in the PL bulk as a whole.

*Participation of Drs A. A. Senotov and A. G. Zhukov in this part of work is thankfully acknowledged.

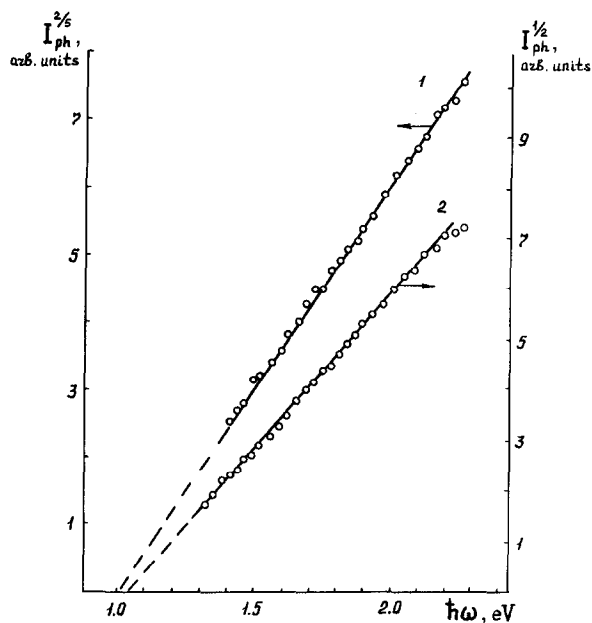


Fig. 7. Spectral dependencies of photoeffect in the system Li/PC+DME, 1 M LiClO₄ (the electrode surface was annealed in oxygen). Storage duration: (1) 1 h and (2) 300 h (arbitrary units).

In Fig. 11 the spectral dependencies of the photocurrents are presented for the Li electrode in electrolytes with Ca(AlCl₄)₂ added. For short storage periods in the region of high photon energies ($h\omega \geq 2.1$ eV), the spectral dependencies give a linear $I_{ph}^{1/2} - h\omega$ plot. An energy value of 1.8 eV is found by extrapolation of the straight line to the abscissa. At lower photon energies, significant deviations are observed from the straight line towards an increasing photocurrent. As a reason for similar deviations from Fowler straight lines for the case of photoemission from metals into dielectrics in sandwich-type structures, different heights of the barrier for emitted electrons at various regions of the metal-dielectric interface were considered in ref. 18. The presence of calcium compounds (presumably calcium chloride) along with lithium chloride in PLs formed on Li in the presence of Ca(AlCl₄)₂ in the electrolyte results in phase-nonhomogeneity of the Li-PL interface. Therefore, it may be concluded that at short-storage periods the electronic work function for a significant part of the Li-PL interface is equal to 1.8 eV, while for the other part of the interface $h\omega_0$ has smaller values.

As can be seen from Fig. 11, the spectral dependence of the photocurrent during storage approaches that typical for photoemission from Li into PLs formed in electrolytes without Ca(AlCl₄)₂, i.e., a straight line in the $I_{ph}^{1/2}$ plot with an intercept equal to 1.3 eV at the abscissa. The changes of the spectral characteristics with time are evidently caused by a decrease in the concentration of calcium compounds in the vicinity of the Li electrode surface. This is depicted by the data obtained by the SIMS method (see Fig. 10). As a result, during storage the part of the Li-PL interface for which the $h\omega_0$ value differs from 1.3 eV diminishes. The time dependencies of the work function for electron emission from Li into PLs formed in TC solution of LiAlCl₄ and in an electrolyte with added Ca(AlCl₄)₂ are presented in Fig. 12. The $h\omega_0$ values

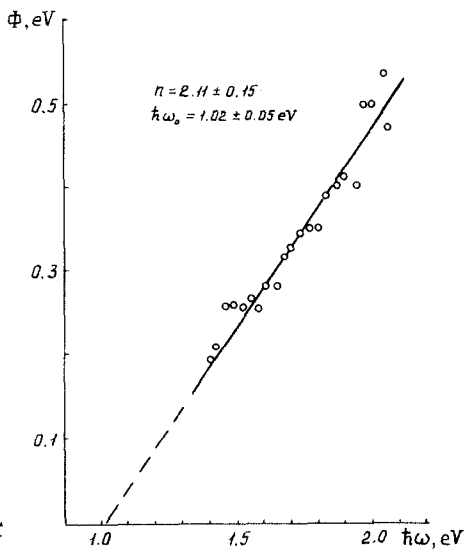
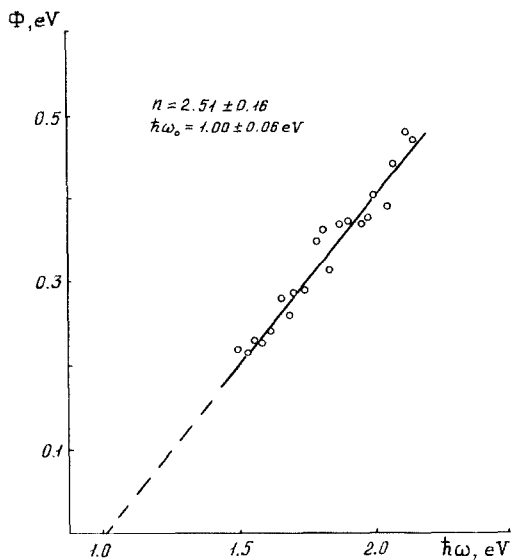


Fig. 8. Φ - $\hbar\omega$ plot for the system Li/PC+DME, 1 M LiClO₄ (the electrode surface was annealed in oxygen). Storage duration: 1 h.

Fig. 9. Φ - $\hbar\omega$ plot for the system Li/PC+DME, 1 M LiClO₄ (the electrode surface was annealed in oxygen). Storage duration: 300 h.

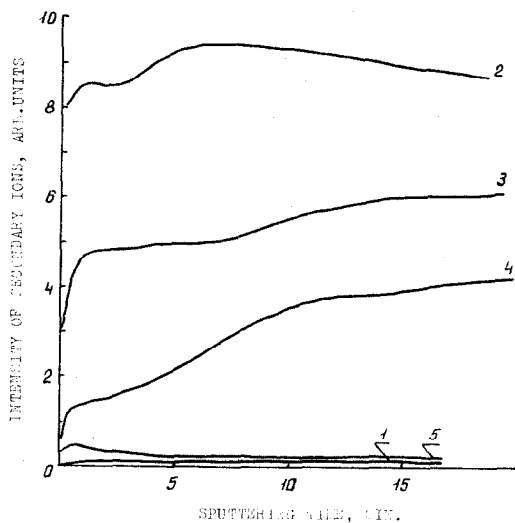


Fig. 10. Depth profiles of ⁴⁰Ca distribution in PL formed on Li in: (1) TC, 1 M LiAlCl₄ and (2-5) in TC, 1 M LiAlCl₄ + 1×10^{-4} M Ca(AlCl₄)₂ at different storage periods: (2) 9 days, (3) 22 days, (4) 42 days and (5) 102 days.

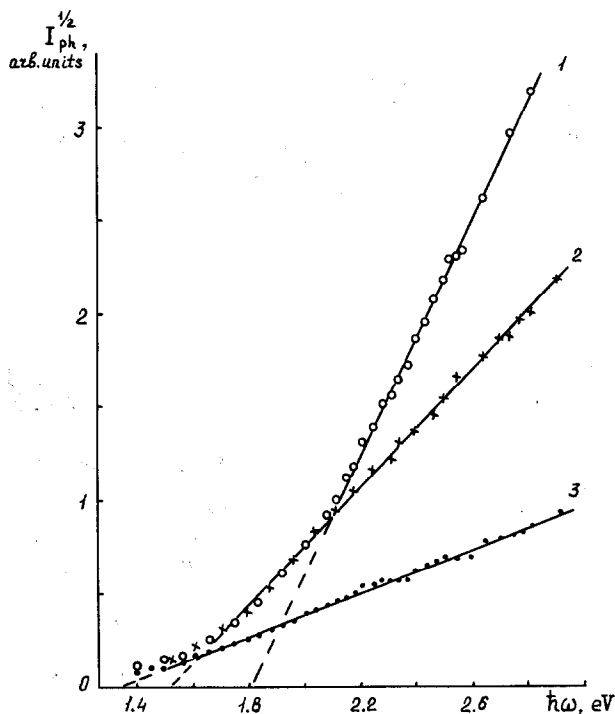


Fig. 11. Alteration of spectral dependencies of photoeffect at the Li/TC, 1 M LiAlCl₄ + 1 × 10⁻⁴ M Ca(AlCl₄)₂ interface during storage. Storage duration: (1) 1 day, (2) 46 days and (3) 70 days (arbitrary units).

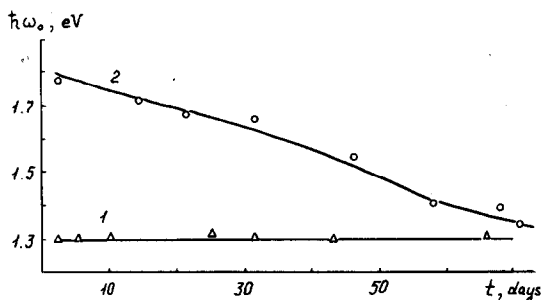


Fig. 12. Time dependencies of work function for electron emission from Li into PL formed in (1) TC, 1 M LiAlCl₄ and (2) in TC, 1 M LiAlCl₄ + 1 × 10⁻⁴ M Ca(AlCl₄)₂.

for the electrolyte with the calcium salt were found by extrapolating the straight lines in the $I_{ph}^{1/2} - \hbar\omega$ plot from the region of high quantum energies to zero photocurrent. The $\hbar\omega_0$ value for the electrolyte with the calcium salt decreased monotonously during storage from 1.8 to 1.3 eV, the latter value being typical for the system without any calcium salt. Intermediate $\hbar\omega_0$ values on curve 2 in Fig. 12 obviously do not characterize photoemission from Li into a PL having some definite composition, but represent only some work function averaged by the Li-PL interface.

Conclusions

A quick-response cathodic photocurrent at the lithium/nonaqueous solution interface has been observed which is related to photoemission of electrons from Li into PL.

The flow of electrons photoemitted from Li into PL has been shown to be sensitive to the composition and the electrical characteristics of PL, since both the position of the 'red' limit of the photoeffect and the exponent in the spectral law of photoemission current depend on the properties of the PL.

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