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CHARGE TRANSFER IN THE LITHIUM CORROSION FILMS FORMED IN THE SOLUTIONS ON THE BASIS OF NITROMETHANE

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Abstract

Processes of polarization of films formed on the lithium electrode at corrosion in solutions of lithium bromide and iodide in the pyridine-nitromethane mix were investigated. It was shown, that the kind of polarizing curves was defined by speed of potential sweep and exposition time. The current restriction by a spatial charge was revealed at injection of additional carriers into the film, especially at high speeds of sweep.

At small sweep speeds and power failure indemnification in the solution the process is limited by charge transfer in high intensity fields. The assumption of double injection of additional carriers into the film was made.

Key words: *charge transfer, lithium corrosion film*

1. INTRODUCTION

The electrochemical behaviour of the lithium electrode is defined by a complex of the difficult phenomena occurring on its surface during the contact to environment. By present time it is known, that considering the lithium electrode kinetics it is necessary to take into account the film existence as a separately existing phase. In this connection there are complexities of the adequate description of behaviour of lithium-film-electrolyte system at use of laws of classical electrochemistry.

The layers of products of lithium-oxidizers interaction formed on the lithium surface are the non-stoichiometric ionic compounds having an essential disorder. Owing to it they possess both ionic, mainly, cationic, and electronic (p-type) conduction [1]. It allows considering it as a firm electrolyte.

Because of the surface film possesses firm electrolyte properties it leaves traces on kinetic of anode dissolution processes since the slowed down stage can appear the charge transfer over through the film [2]. By means of the galvanostatic method on anode polarizing curves of lithium electrode in propylene carbonate, dymethylsulphoxide and tetrahydrofuran solutions [3] the limiting currents are observed, their dependence on time of endurance of the electrode in the electrolyte assumes stipulation by condition of the electrode surface.

At the present time it has been practically established that exponential current dependence on overstrain at polarization of the lithium electrode displays not the separation border characteristic (Tafel dependence), but the exponential characteristic of charge transfer through the surface film in the fields of the considerable intensity [3]. At the big film thicknesses or small polarization values such dependence passes into the Ohm's law [3].

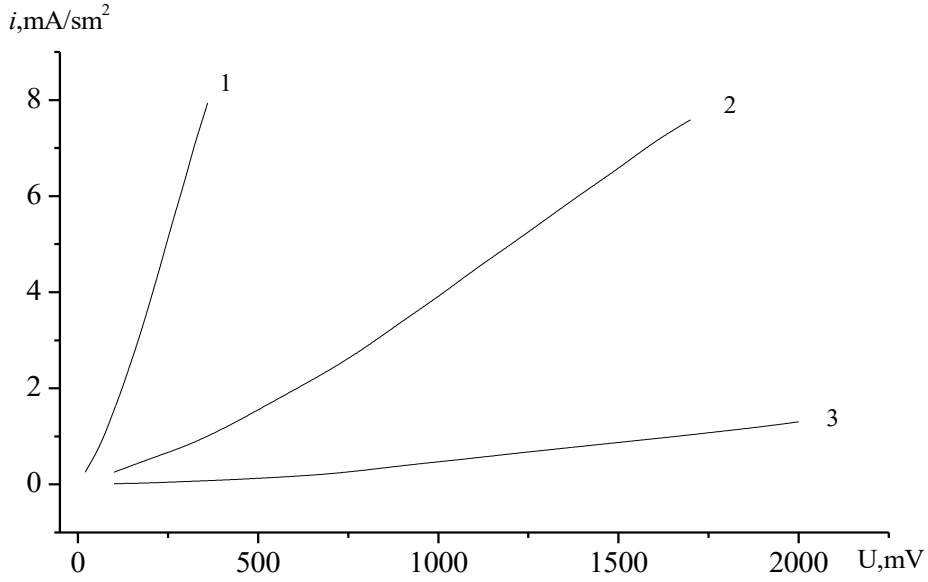
Frequently the volt-ampere characteristic on the lithium electrode represents the proportional dependence between the square of overstrain and the current that is caused by injection into the film of additional charge carriers and corresponds to the current limited with the spatial charge [4-6]. At the

monopolar injection into the non-drip dielectric the running current should be proportional to U^2 and inversely proportional to the cube of thickness of the layer in which carriers [7] are injected.

2. RESULTS AND DISCUSSION

For revealing of laws of charge transfer in the lithium corrosion films the polarizing curves in the solutions of lithium bromide and iodide in the mix of pyridine and nitromethane were obtained. The polarizing curves were taken at the various speeds of sweep after the various release time of the lithium electrode in the electrolyte. The registered curves in all cases look like the non-monotonously increasing dependence.

At the figure 1 the anode polarizing curves obtained after the various time of the electrode exposition in the solution are presented. According to this figure it is visible that at increase of the exposition time the curve inclination angle diminishes, and accordingly, the speed of the electrode reaction for the same overtension also decreases. It is connected with growth of the film thickness on the lithium the expense of corrosion.



The exposition time: 1 – 60 sec, 2 – 200 sec, 3 – 300 sec

Figure 1 – The anode polarizing curves for the lithium electrode in the LiBr-solution in the pyridine-nitromethane mix (Py-NM) at the various exposition periods.

During our experiment it was noticed, that the kind of a polarizing curve very strongly depends on speed of change of potential. Probably the electrode polarization causes the change of the film condition or its separate sites. Among the possible reasons of the change of the film condition is the conductivity change. If to consider, that the film thickness is 0.5 microns and more, and the power failure in it makes an order 1 V, so the electric field intensity in the film or on its separate sites can reach values 10^4 - 10^5 V/cm. The presence of the fields having so high intensity forces us to analyze the polarizing characteristics for the presence in them the injection of additional current carriers into

the film, or the presence of the ionizing processes. According to it, obtained experimental data were processed for the purpose of finding in them of the listed dependences.

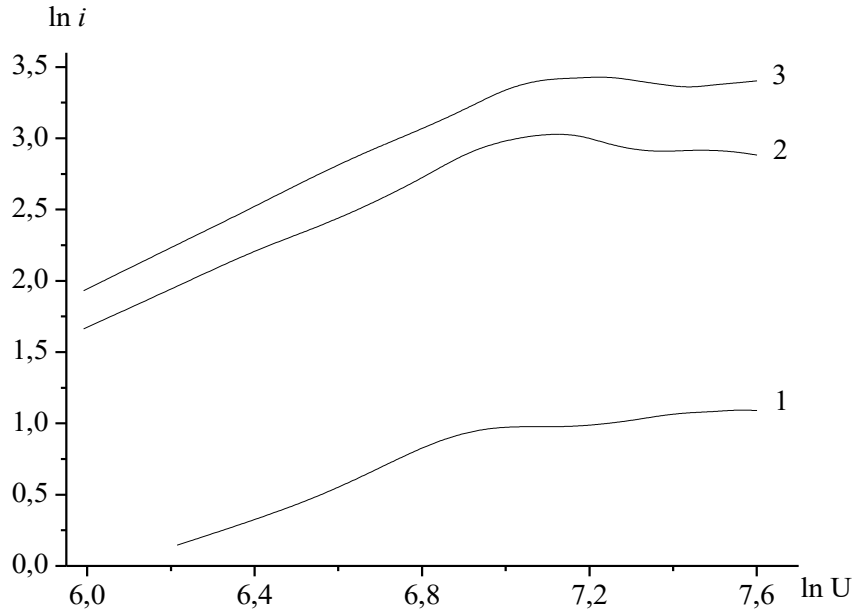
For this purpose the polarizing curves were represented in co-ordinates *lni-lnU, lni-U* displaying the current limited with the spatial charge and the transfer of the particles into the high intensity field.

At the figures 2-3 the polarizing curves are presented at various periods of potential sweep in co-ordinates *lni-lnU:* On the polarizing curves in these co-ordinates practically everywhere there are extensive enough rectilinear sites. The value of the inclination angle for these curves which should be theoretically equal 2.0, for solutions LiBr as a rule a little bit more low and fluctuates in the range from 1.4 – 1.7. For LiI this value is close to 2.0 and sometimes exceeds it, reaching values 2.5 – 3.0. The abnormal high value of the inclination angles under messages available in the literature is possible referred to a current of traps filling.

In the lithium corrosion film having a complex structure and being polycrystalline, the formation of such traps is quite proved. Iodide-ion influence, in comparison with a bromide-ion, is shown in a kind of more disordering because of its big radius.

The increase of the potential sweep speed leads to increase of a linear site extent in *lni - lnU* co-ordinates and to the approximation of the inclination angle value to 2.0.

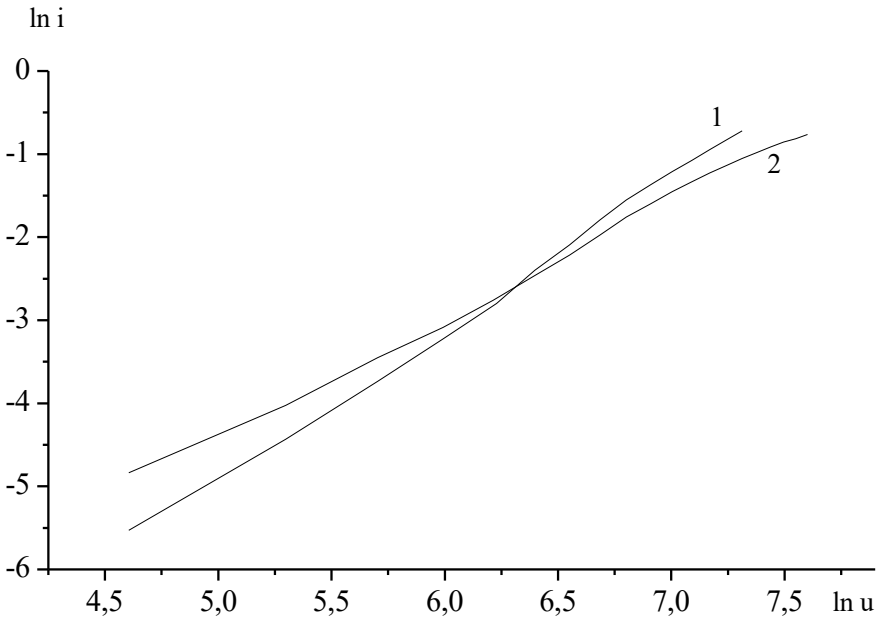
At the small sweep speeds the area of linear dependence in co-ordinates *lni - lnU* essentially decreases and in the limit disappears absolutely. It testifies that in parallel to the process of injection of additional charges into the film there is a charge transfer passing by means of other mechanism characterized with big relaxation time. In this case at small sweep periods it is necessary to expect the display of other laws, than current restriction by a spatial charge.



1 – 80 mV/s, 2 – 200 mV/s, 3 – 400 mV/s

Figure 2 – The cathodic polarizing curves for the lithium electrode in the LiI solution in the pyridine-nitromethane mix (Py-NM) at the various sweep speed

On the curves in co-ordinates *lni-U* the linear sites start to be shown at reduction of potential sweep speed (figure 4). Most accurately it is looked through for the iodide lithium solutions. There is an assumption, that the exponential dependence i from *U,* characterizing the charge into the high intensity field as well as a current limited with a spatial charge, are shown in the obtained curves not in the pure state because of the presence of the mixed characteristic of the film and the layer of the electrolyte solution. In particular, the electrolyte resistance is added to the film resistance. In this connection the attempt of excluding the electrolyte resistance from the general chain resistance was undertaken. For this purpose by means of use of the 1000 Hz frequency impulses we defined the power failure in the electrolyte and deducted this value from the general intensity.



1 – 80 mV/s, 2 – 240 mV/s

Figure 3 – The cathodic polarizing curves for the lithium electrode in the LiBr solution in the pyridine-nitromethane mix (Py-NM) at the various sweep speed

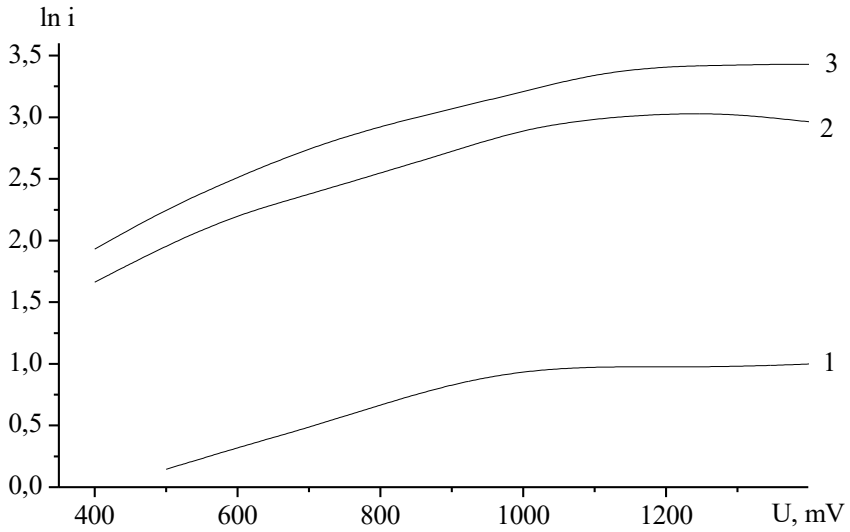
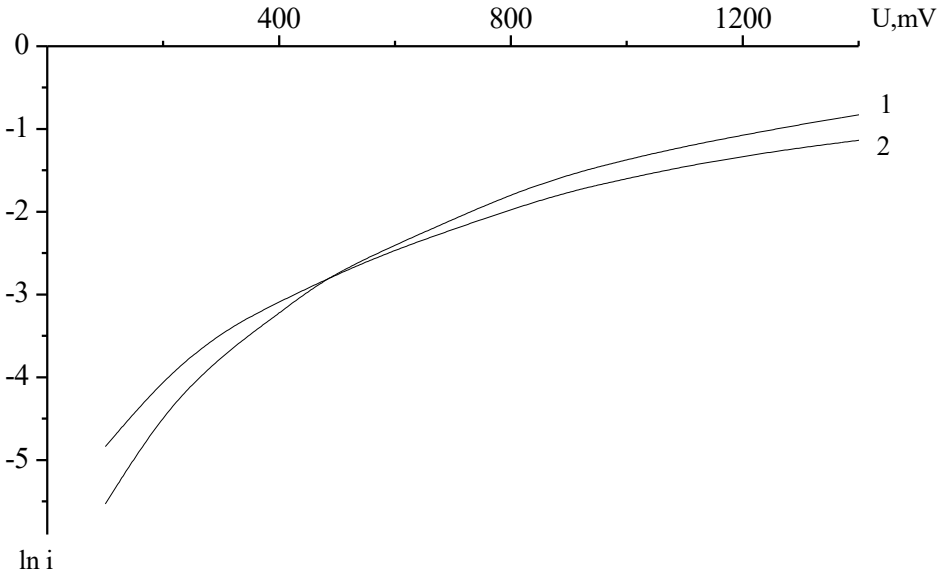


Figure 4 – The cathodic polarizing curves for the lithium electrode in the LiI solution in the pyridine-nitromethane mix (Py-NM) at the different sweep speed

At the figure 5-6 it is available to see the curves obtained in the solutions of lithium bromide. They were obtained without and with the compensation of the intensity failure in the solution.



1 – with the compensation of the intensity failure in the solution; 2 – without the compensation

Figure 5 – The cathodic polarizing curves for the lithium electrode in the LiBr solution in the pyridine-nitromethane mix (Py-NM)

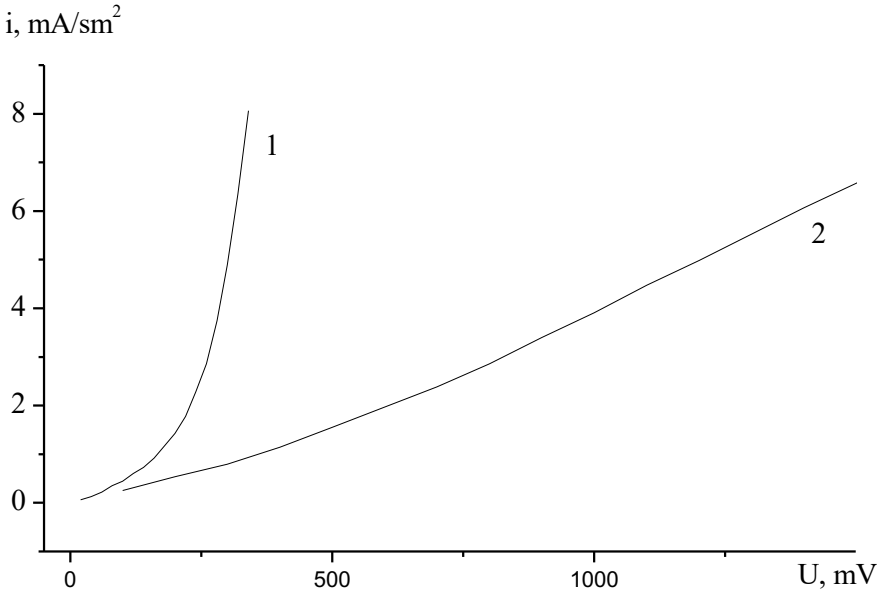


Figure 6 – The anodic polarizing curves for the lithium electrode in the LiBr solution in the pyridine-nitromethane mix (Py-NM) at the various volume of the polarizing current

At the figure 7 the same curves in co-ordinates $ln\,i - U$ are presented. Apparently, the curves with indemnification of an ohmic intensity failure in the solution very well keep within linear dependence at small potential sweep speeds.

It is quite probable, that there is a double injection into the film from its both sites, and then at small speeds of the potential imposing the condition in the film volume is closer to the equilibrium for the account of the recombination of the two-sites-injected current carriers. Generally some stationary condition for streams of injected particles is established, which is defined including by the current size. The acknowledgement to that is the overstrain dependence on time at the polarization by the current of constant force (figure 8) when the effective resistance of the film decreases in time to the certain value. After the deenergizing of the polarizing current the system reverts to the original state after 3-5 minutes.

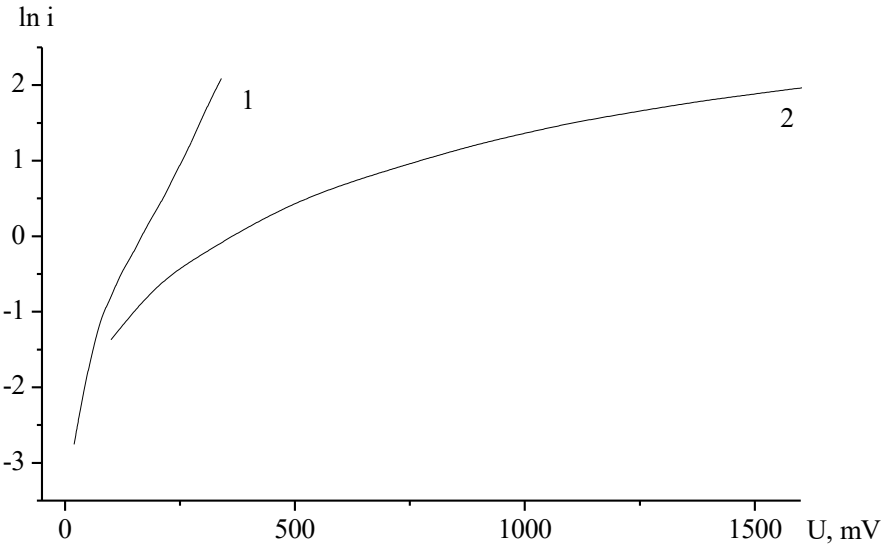
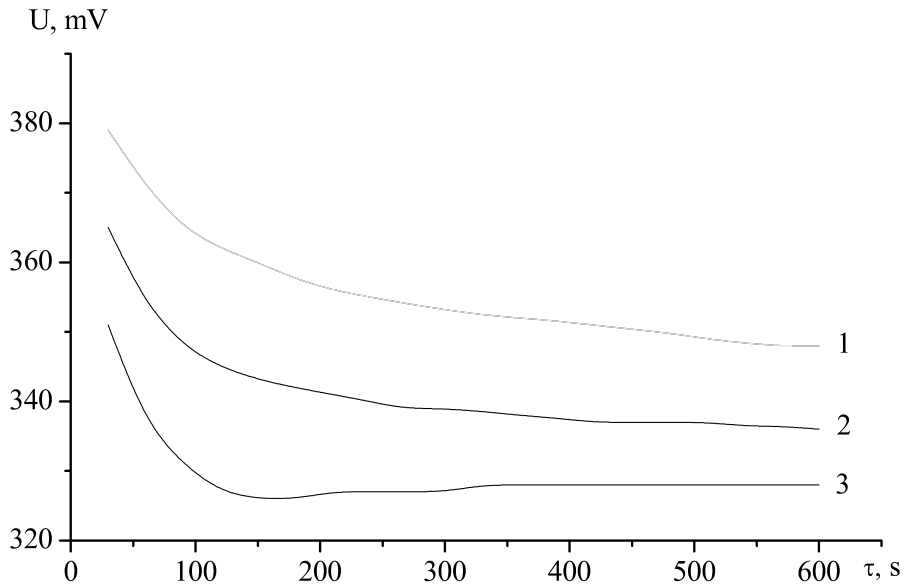


Figure 7 – The anodic polarizing curves for the lithium electrode in the LiBr solution in the pyridine-nitromethane mix (Py-NM) at the various volume of the polarizing current



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