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Noise characterization of surface processes of the Li/organic electrolyte interface

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Abstract

The processes occurring in aprotic electrolyte on a lithium electrode in the steady state conditions and under polarization are studied using the method of electrochemical noise characterization. The evidence of the electrochemical noise measurements on polarized lithium electrodes indicates that the discharge of lithium ions under cathodic polarization, as well as lithium anodic dissolution, is localized under the passive film rather than on its surface. An increase in the polarizing current results in local breakdown of the film; in this case, the electrochemical process emerges on the electrode surface affecting the character of potential fluctuations. The intensity of electrochemical noise significantly increases in the course of cathodic polarization with high currents. The reason is that lithium metal crystals, which are formed under the passive film, perforate the film, and dendrites grow on its surface. The method shows the dependence of electrochemical noise intensity on the nature of the electrolyte and establishes the correlation between the stability of the lithium electrode in the course of cycling and the intensity of fluctuations. This offers an opportunity of using the method of electrochemical noise for screening organic electrolytes for lithium batteries.

1. Introduction

In recent years, increasing attention has been focused on the mechanism of both macro and micro processes on electrodes, which has brought about the use of sensitive techniques. One such method is associated with researching the fluctuating electrochemical phenomena (electrochemical noise), which were systematically studied for the first time more than 30 years ago [1, 2]. A variety of equilibrium and non-equilibrium electrochemical processes was studied using the electrochemical noise method [2–5]. At present, this method is widely used in corrosion studies [6–10]. Non-equilibrium fluctuations of electrode potential of the corroding metal are substantially determined by the electrode surface heterogeneity, in particular, micro- and macro- irregularities depending on the local or general passivity of metal surface and its activation under external influence [11].

We find the idea of applying the electrochemical noise method for studying electrode processes in lithium batteries quite exciting. It is known that the surface of a lithium electrode in aprotic electrolyte is coated with an insulating film which is a result of lithium interaction with the electrolyte [12–15]. This film (solid electrolyte interface – SEI [12, 13] or non-conducting multifunctional layer [15]) possesses the properties of an ion-conducting electrolyte with certain electronic (hole) conductivity. It assures electrode stability over time and simultaneously does not impede the electrochemical processes (anodic dissolution and cathodic deposition of lithium) on the electrode. Thus, it may be said that lithium is in the quasi-passive state.

The corrosion of lithium in the electrolyte occurs due to the presence of SEI ionic and electronic conductivity. This process can be presented as a galvanic cell with a cathode and an anode that are spatially divided and are connected through the solid electrolyte [15]. The anodic process in this cell is the dissolution (corrosion) of lithium, and the cathodic one corresponds to the interaction of lithium ions with the electrolyte components. The generation of electrochemical noise at a non-polarized lithium electrode occurs due to the existence of this cell. The surface passivating film is destroyed in the course of anodic and cathodic polarization resulting in exposure of the active metal surface [14, 15]. Thus the conditions are created for increased lithium surface heterogeneity, which is be accompanied by the appearance of intensive electrochemical noise.

To a certain extent a lithium electrode behaves like a classical semiconductive electrode (e.g. silicon), which under anodic etching shows chaotic potential fluctuations [5].

The aim of this work is to study the character of electrochemical noise of a lithium electrode both in steady state (without polarization) conditions and under application of cathodic or anodic current, i.e. under the real life conditions of the rechargeable battery. Particular attention is given to the dependence of noise phenomena on the nature of the aprotic electrolyte.

2. Experimental details

In this work, the difference between the potentials of two smooth lithium electrodes, the working and the reference ones, is measured. These electrodes are of the same size and made in a similar way. The cell also contained the third lithium electrode, which was used as a counter electrode for the polarization of the working electrode. The electrodes were made by rolling a thin (0.3–0.4 mm) foil of metallic lithium of 99.9% purity (LE-1, OAS "NZKKh", Novosibirsk) on the surface of a fine-mesh (40–60 μm) nickel net of 1×1 cm size, the final electrode thickness being 0.4–0.5 mm.

Three electrolyte systems containing different lithium salts and aprotic organic solvents were used: 1 M $LiClO_4$ solution in 1,3-dioxolane (1), 1 M $LiN(CF_3SO_2)_2$ solution in 1,3-dioxolane (2), 1 M $LiPF_6$ solution in a 1:1 mixture of ethylene carbonate–diethyl carbonate (commercial LP-40 electrolyte, Merck, Germany) (3).

$LiClO_4$ (reagent grade, Russia) was dried in vacuum at 150–180 °C for 5 h; lithium bis-trifluoromethylsulfonyl imide $LiN(CF_3SO_2)_2$ (3 M, USA) was dried in vacuum at 70 °C for 6 h. 1,3-dioxolane (Li-battery grade, Merck, Germany) and LP-40 electrolyte were used as received. Triethylamine (0.1%) was added to the electrolytes containing 1,3-dioxolane, to avoid its polymerization [16] in the course of the experiments.

All manipulations of the lithium electrodes and aprotic electrolytes, assembling the cells and filling the cells with electrolyte were performed in a glove box in an atmosphere of high purity argon dried over P_2O_5. The electrical contacts between the electrodes and the current taps were thoroughly soldered to prevent parasitic ohmic resistances. To minimize the external noise, the cells were placed in a grounded Faraday cage.

The electrochemical measurements were performed using a low-noise universal galvanopotentiostat Solartron 1286 Electrochemical Interface (Schlumberger, UK) with a precision high-resistance (10^{10} Ω) highly sensitive (resolution < 1 μV) digital voltmeter. The electrode potentials were recorded at 1 Hz using a GPIB IEEE-488 interface connected to a personal computer via a bus.

When treating the experimental data, computer fitting of the potential trend of the working electrode in the course of the experiment was used.

3. Results and discussion

In the blank experiments (the measurements with a short-circuit input), it was found that the time-average amplitude of inherent noise of 1286 Electrochemical Interface did not exceed 3 μV.

The steady state of lithium electrodes characterized by a very low and constant level of potential fluctuations was achieved in 5–6 h after immersing the electrodes into the electrolyte solutions. This result agrees well with the observed impedance characteristics of the lithium electrode during ageing in an aprotic organic electrolyte [17].

The state of the lithium electrodes was completely stabilized within 24 h after filling the cell with electrolyte, the potentials of the working and auxiliary electrodes becoming equal. Average amplitudes of potential fluctuations are nearly similar in all electrolytes (4–5 μV) (Figure 1). At the same time, the root-mean-square intensity of the electrode potential fluctuations was higher than the noise intensity of the 1286 Electrochemical Interface. The spectral densities of the lithium

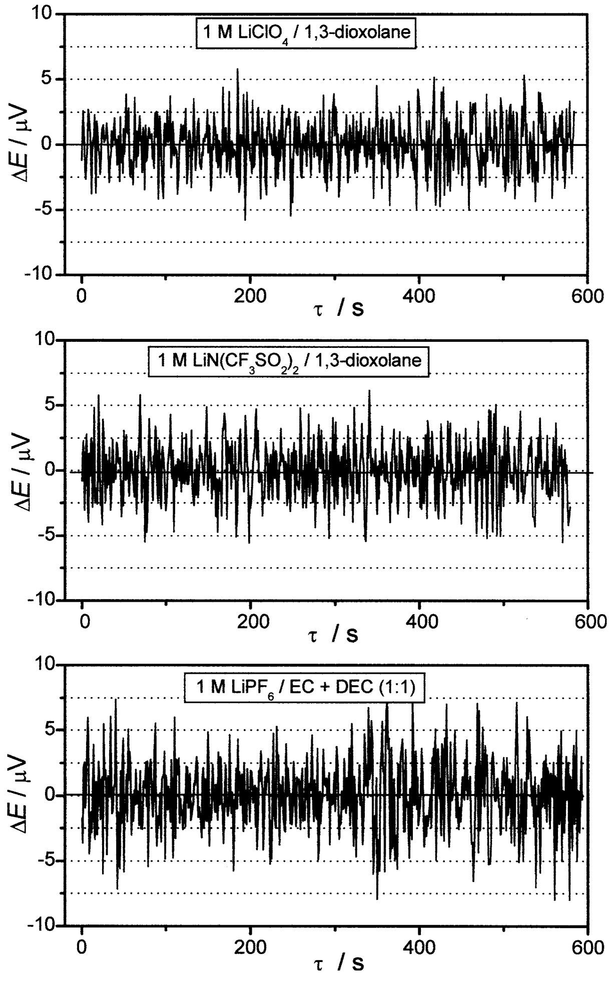

Fig. 1. Electrochemical noise of the lithium electrode in the steady state (at the open-circuit potential) in the different electrolytes: 1 M $LiClO_4$ in 1,3-dioxolane, 1 M $LiN(CF_3SO_2)_2$ in 1,3-dioxolane, 1 M $LiPF_6$ in the 1:1 mixture ethylene carbonate–diethyl carbonate.

electrode potential fluctuations in a frequency band of 0.1–0.5 Hz were ($\mu V^2\ Hz^{-1}$): 8.1 in electrolyte (1), 9.2 in electrolyte (2), and 16.8 in electrolyte (3); the spectral density of the noise observed at the 1286 Electrochemical Interface was 6.9 $\mu V^2\ Hz^{-1}$. The lithium electrode potential fluctuations remained virtually unchanged under prolonged conditioning of the electrodes in the electrolyte, which proved the existence of stable passive film on the lithium surface.

Then the working electrode was alternately anodically and cathodically polarized for a certain time (usually for 20 min). Thereby, the difference between the potentials of the working and reference electrodes and its fluctuations (electrochemical noise) were measured. The nonpolarized standard lithium electrode is a very stable reference electrode with a low noise level, which is comparable to the noise level of the steady state working electrode. Thus, the noise of a foreign reference electrode with its own spectrum of potential fluctuations was eliminated. The lithium surface state varied under polarization. Change in lithium surface leads to some irreproducibility of results. In order to increase the reproducibility, each polarization was performed at intervals of 2–3 h; the number of anodic–cathodic polarization cycles did not exceed 2.

Galvanostatic polarization of the lithium electrode by small currents ($\sim$50 $\mu A\ cm^{-2}$) causes a change in the lithium surface state, which is manifested in a slight increase in the potential fluctuations (Figures 2–4). The noise of anodically and cathodically polarized electrodes is similar in character and intensity, which is a convincing argument in favor of similar localization of anodic and cathodic processes. The fact that lithium anodic dissolution is localized immediately at the lithium/passive film interface is beyond doubt; however, there are different points of view on the localization of lithium cathodic deposition. Along with the concept of lithium deposition at the aforementioned interface, there is an

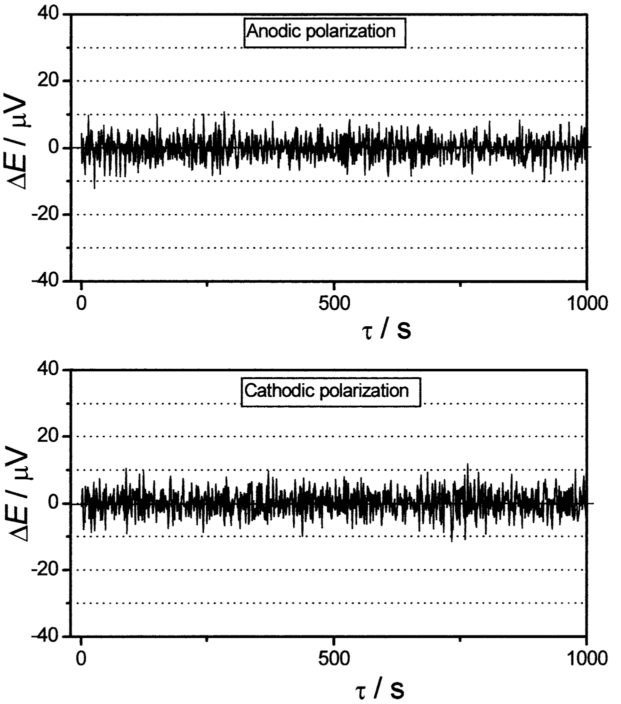

Fig. 2. Electrochemical noise of the lithium electrode under anodic and cathodic polarization with a current of 50 $\mu A\ cm^{-2}$ in 1 M $LiClO_4$ in 1,3-dioxolane.

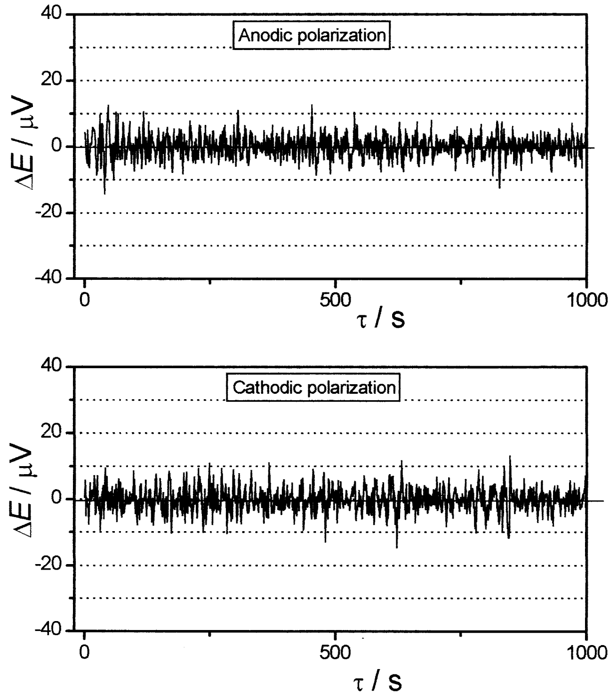

Fig. 3. Electrochemical noise of the lithium electrode under anodic and cathodic polarization with a current of 50 $\mu A\ cm^{-2}$ in 1 M $LiN(CF_3SO_2)_2$ in 1,3-dioxolane.

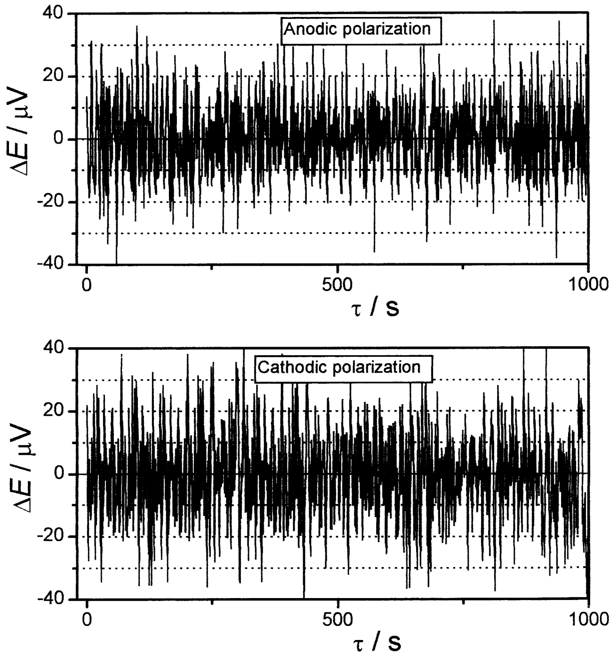

Fig. 4. Electrochemical noise of the lithium electrode under anodic and cathodic polarization with a current of 50 $\mu A\ cm^{-2}$ in 1 M $LiPF_6$ in the mixture (1:1) ethylene carbonate–diethyl carbonate.

opinion that a lithium deposit is formed on the passive film surface or in its bulk [12, 13, 15]. If this were so, potential fluctuations under cathodic and anodic polarization would differ. The results of this study indicate that cathodic lithium deposition (at least, its initial stage) is localized under the passive film. The disturbance, which is caused by polarization with small currents, only intensifies the subfilm corrosion, and the process is not likely to spread beyond the passive film.

Electrode polarization with high currents (1000 μA cm^{-2} which corresponds to the standard electrode load under lithium battery cycling) changes the state of the lithium significantly. This is reflected in the character of the electrochemical fluctuations. Firstly, the noise amplitude increases significantly indicating working electrode activation and destruction of the passive film on its surface (Figure 5).

An additional contribution to the electrochemical noise can be caused by micro bubbles that appear due to the reduction of the electrolyte components during the formation of SEI on the active lithium surface freshly generated in the course of the anodic and cathodic polarization. However, this contribution cannot be high in the case of a smooth lithium electrode with small true surface.

The intensity of potential fluctuations and their character under forced polarization mode depend essentially on the electrolyte composition, i.e. on the nature of the solvent and the lithium-containing salt. In perchlorate electrolyte (1), electrochemical noise of loaded lithium electrodes differs only slightly from that under polarization with small currents. The intensity of potential fluctuations in electrolyte system (2) is considerably stronger; the maximum amplitude of fluctuations was recorded in electrolyte system (3) (Figure 5).

Figure 6 presents the spectra of intensity of electrode potential fluctuations under the cathodic and anodic polarization of the lithium electrode in various electrolytes.

The dynamics of the electrochemical noise of a polarized lithium electrode in aprotic electrolyte can be explained as follows.

Under anodic polarization lithium dissolution takes place under the film, through which metal ions are transferred to the electrolyte, and hollows form under the film. In the case of a sufficiently flexible film, it is pressed against the metal by atmospheric pressure; a more rigid film can crack. In this case, the activated surface area increases and becomes more heterogeneous, resulting in an increase in the noise intensity. In parallel,

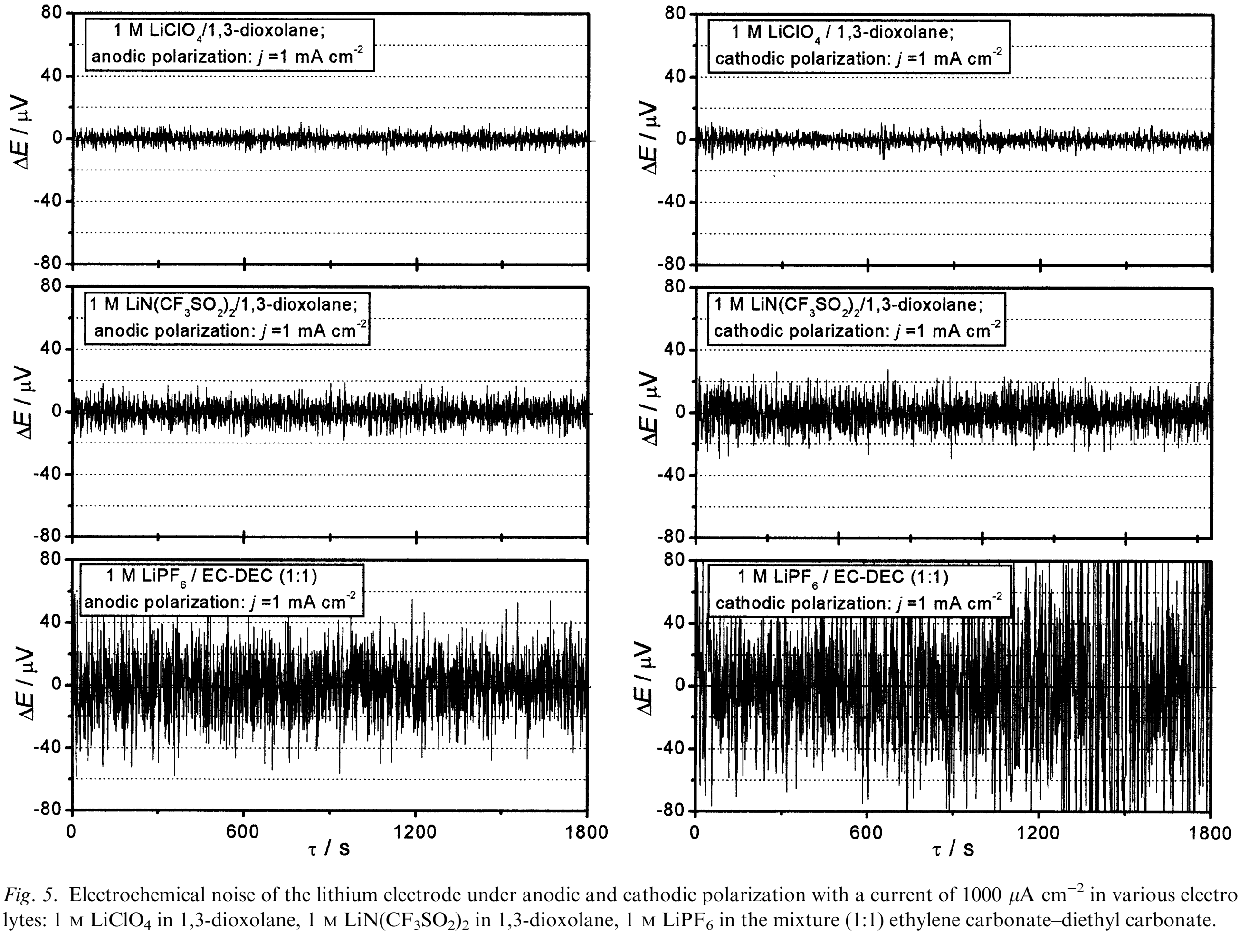

Fig. 5. Electrochemical noise of the lithium electrode under anodic and cathodic polarization with a current of 1000 μA cm^{-2} in various electrolytes: 1 M LiClO$_4$ in 1,3-dioxolane, 1 M LiN(CF$_3$SO$_2$)$_2$ in 1,3-dioxolane, 1 M LiPF$_6$ in the mixture (1:1) ethylene carbonate–diethyl carbonate.

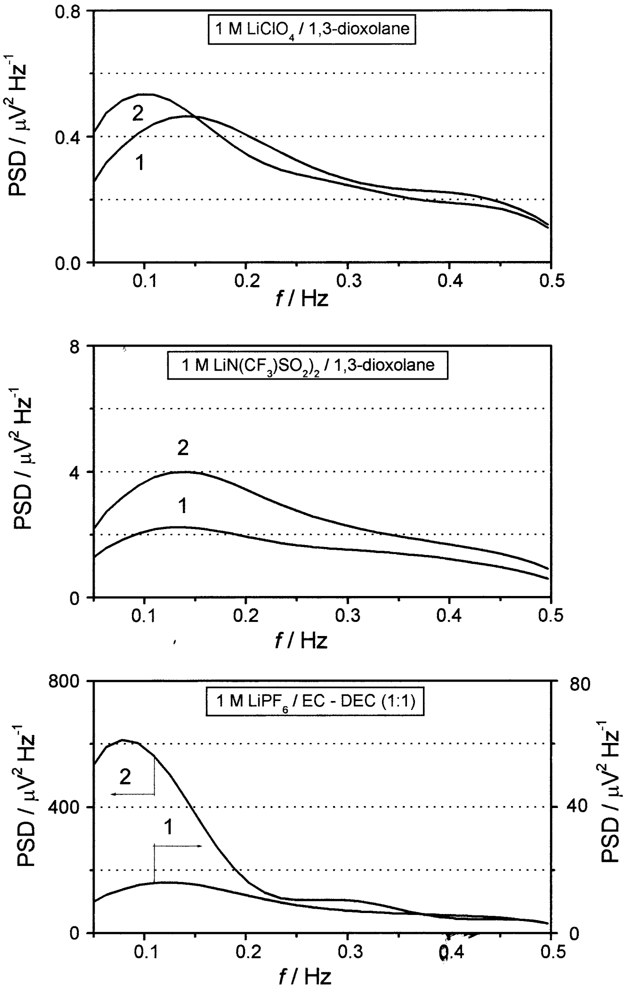

Fig. 6. Spectra densities of electrochemical noise of the lithium electrodes under anodic (1) and cathodic (2) polarization of electrode with a current of 1000 μA cm^{-2} in various electrolytes: 1 M $LiClO_4$ in 1,3-dioxolane, 1 M $LiN(CF_3SO_2)_2$ in 1,3-dioxolane, 1 M $LiPF_6$ in the mixture (1:1) ethylene carbonate–diethyl carbonate.

the exposed surface is passivated, and dynamic equilibrium is achieved. In the case of rapid lithium passivation, the new surface formed in the course of the film cracking is again covered by a surface film, which reduces the surface heterogeneity. In the case of slow passivation, the heterogeneity increases. In the first case, an insignificant intensity of potential fluctuations is recorded, while in the second case, the potential fluctuations are much more intensive.

Under cathodic polarization, lithium deposition on the metal surface proceeds under the passive film. Deposition of a large amount of lithium on the negative electrode is necessarily accompanied by film perforation by growing metal crystals. The freshly formed active lithium surface, as well as in the case of film cracking under the anodic polarization of electrode, causes an increase in electrode heterogeneity and noise intensity. As well as under anodic polarization, in the case of rapid passivation, lithium heterogeneity decreases with time, whereas in the case of slow passivation, lithium heterogeneity does not decrease with time.

According to [18], a lithium surface in the 1 M $LiClO_4 + $ 1,3-dioxolane electrolyte is coated with a thin flexible homogeneous passive film, which is not perforated under cathodic polarization. Lithium, which is deposited on the electrode, is rapidly coated by this film; as a result, dendrite formation on battery charge is hampered, providing high lithium cycling efficiency [19, 20].

The metal passivation rate in the 1 M $LiN(CF_3SO_2)_2$ + 1,3-dioxolane electrolyte containing imide, which is aggressive towards lithium [20], is slightly lower as compared to the perchlorate electrolyte based on 1,3-dioxolane. This makes possible the growth of dendrites on active lithium surface sites. In this case, the electrode surface is more heterogeneous than in the perchlorate electrolyte, as evidenced by an increase in the intensity of potential fluctuations. The study of lithium electrode cycling showed that the dendrite-free service life of a lithium electrode in this electrolyte is 200–300 cycles.

The $LiPF_6$-based alkyl carbonate electrolyte contains a considerable amount of acidic impurities strongly activating the lithium surface. Hence, the dendrite passivation rate decreases and dendrites grow rapidly. Lithium surface heterogeneity increases significantly, i.e. highly active sites are formed along with the passivated metal sites. The experimental results and their explanation are in agreement with data on dendrite formation and on lithium electrode cycling in this electrolyte. The cycling of a lithium electrode in 1 M $LiPF_6$ solution in a mixture of ethylene carbonate and diethyl carbonate is highly unsatisfactory: noticeable dendrites are formed on the electrode even after several charge–discharge cycles.

The variation in the amplitude of potential fluctuations under cathodic polarization of a lithium electrode in the $LiPF_6$-based electrolyte strongly supports the above concept. Prior to imposing the polarization (in the steady state), the amplitude of potential fluctuations was near 4 μV throughout the whole time range (Figure 1); under polarization with a current of 50 μA cm^{-2}, it was 15–25 μV (Figure 4); at a polarization current of 1000 μA cm $^{-2}$, it was initially about 50 μV, gradually increasing to 120–140 μV in 20–25 min and then varying only slightly with time (Figure 7). These data can be

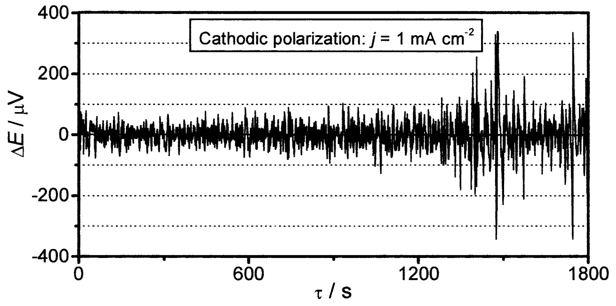

Fig. 7. Electrochemical noise of the lithium electrode under cathodic polarization with a current of 1000 μA cm^{-2} in 1 M $LiPF_6$ in the mixture (1:1) ethylene carbonate–diethyl carbonate.

Table 1. Spectral density of potential fluctuations of cathodically polarized (current density of 1000 μA cm^{-2}) lithium electrodes in various electrolytes and characteristics of lithium electrode stability in the course of cycling

	Electrolyte systems		
	1 M $LiPF_6$ solution in 1:1 mixture of ethylene carbonate–diethyl carbonate	1 M $LiN(CF_3SO_2)_2$ solution in 1,3- dioxolane	1 M $LiC1O_4$ solution in l,3- dioxolane
Root-mean-square spectral density of lithium electrodes potential fluctuations in a frequency band of 0.1–0.5 Hz, $\mu V^2\ Hz^{-1}$	9600	170	25
Lithium electrode stability on cycling; characteristics of dendrite formation	Low, dendrite formation starts after several cycles	Satisfactory, dendrite formation is observed after 200–300 cycles	High, dendrite formation is absent [18]

explained only by dendrite growth on the lithium electrode surface under high cathodic polarization.

Table 1 lists the root-mean-square densities of electrochemical noise in a frequency band of 0.1–0.5 Hz under cathodic polarization for 30 min; these were obtained by the Fast Fourier Transformation method. The Table also contains the electrode stability parameters on electrode cycling in various electrolytes. A correlation is clearly seen between the intensity of potential fluctuations under cathodic polarization and electrode stability in the course of cycling: the higher the noise intensity, the poorer the cycling (due to the formation of dendrites). On this basis, a method for determining the suitability of organic electrolyte for rechargeable lithium batteries with negative electrode of metal lithium can be developed and elaborated.

4. Conclusion

Using the method of electrochemical noise, the processes occurring on a lithium electrode in steady state conditions and under polarization were studied in several aprotic organic electrolytes, which differ in the nature of the solvent and of the electrolyte salts. The analysis of noise characteristics support the concept of electrochemical processes localization under the passive film, both under anodic and cathodic polarization. The film is not broken at low currents. An increase in current causes film destruction; the electrochemical process emerges on the electrode surface affecting the character of potential fluctuations. The intensity of these fluctuations depends on the nature of the electrolyte. A correlation between fluctuation intensity and lithium electrode stability in the course of cycling is established. It is found that a low electrochemical noise intensity is typical of systems with a high lithium cycling efficiency and the absence of dendrite formation. This makes it possible to use the method of electrochemical noise determination for screening organic electrolytes for rechargeable lithium batteries.

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