Dynamics of Electrochemical Noise of the Lithium Electrode in Aprotic Organic Electrolytes

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Abstract—Processes that occur on the lithium electrode under open-circuit conditions and when polarized cathodically and anodically are studied by means of the electrochemical-noise method. The study is carried out in such aprotic organic electrolytes as 1 M solution of $LiClO_4$ in 1,3-dioxolane; 1 M solution of $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate; and 1 M solution of $LiN(CF_3SO_2)_2$ in 1,3-dioxolane. An analysis of the noise characteristics of the polarized electrode confirms that the electrochemical process is localized under the passivating film. Potential fluctuations of the electrode polarized at high current densities depend on the electrolyte nature. The amplitude of the electrochemical noise is maximum in the electrolyte system 1 M $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate. The fluctuation intensity is found to correlate with the electrode stability when cycled. This fact suggests that the method can be used for express assessment of organic electrolytes intended for lithium batteries.

Key words: electrochemical noise, lithium electrode, lithium battery, dendrite formation, organic electrolyte

INTRODUCTION

At the current stage in the development of theoretical and applied electrochemistry, the study and understanding of the mechanism of electrode processes on both macro and micro levels command a far greater attention of the researchers. Along with the perfecting of traditional procedures and techniques by applying modern instruments and computers, of particular importance becomes the use of fine investigation methods. One of such methods involves studying the fluctuation electrochemical phenomena (electrochemical noise). Systematic research in this direction, begun more than 30 years ago [1, 2], proved to be very creative and the electrochemical-noise method appeared to have been instrumental in exploring quite a number of diverse equilibrium and nonequilibrium electrochemical processes [2–5].

Special place among such processes is occupied by corrosion processes. As was pointed out in the 1970s, it would make much sense to examine noise phenomena in the corrosion processes [3, 4]. Nowadays the noise diagnostics method is extensively used in corrosion investigations of metals. The reason for such an extensive application is that the nonequilibrium fluctuations of the electrode potential are much dependent on the heterogeneity of its surface, in particular, on macro and micro irregularities, the latter being dependent on the local or overall passivation of the electrode surface and its activation resulting from external perturbations [6]. The electrochemical-noise method proved useful for studying processes of uniform, pitting, and cavity corrosion, the passivation of various metals and their depassivation by chemical (insertion of activating agents, for example chlorides, into electrolyte) and electrochemical (anodic and cathodic polarization) means [7–10]. The method has been productive enough for assaying the tendency of lead grids in lead–acid batteries to intergranular corrosion [11]. Of late the electrochemical-noise method was suggested for estimating the level of charge and overcharge of diverse power sources (in particular, lithium-ion and metal hydride batteries) [12].

We thought the electrochemical-noise method exceedingly appealing for studying electrode processes in lithium batteries. The lithium electrode surface in an aprotic electrolyte is always covered by a passivating film, which is the product of interaction of lithium with its surround and the electrolyte [13–15]. This film possesses properties of an ion-conducting solid electrolyte with a share of electron (hole) conduction. It is responsible for the time stability of the electrode and makes no impact on the electrochemical processes occurring at the electrode—anodic dissolution and cathodic deposition. Hence, it is logical to speak of a quasi-passive state of the lithium electrode and its noise characteristics. The behavior of the lithium electrode resembles that of classic semiconductors, say, silicon: when anodically etched, these exhibit chaotic fluctuations of the potential [5]. Resorting to the approaches that are adopted in corrosion studies performed by the electrochemical-noise method, we expected to garner additional information about the electrode processes in real lithium batteries in conditions of their operation and

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expand our knowledge concerning the operation mechanism.

The aim of this work is to examine electrochemical noise on the lithium electrode under steady-state conditions (nonpolarized) and upon applying perturbations (cathodic and anodic polarization), which is characteristic of operation of real batteries. Particular attention was paid to dependence of noise phenomena on the nature of aprotic organic electrolytes.

EXPERIMENTAL

Thus, we resorted in our work to the approaches that are adopted in corrosion studies performed by the electrochemical-noise method [8–10, 16, 17]. Specifically, we measured fluctuations of potential between two parallel smooth metallic plates of identical size and pretreatment character. Initially, the working electrode in lithium batteries is a smooth plate, which utterly satisfies demands to an object for noise investigations.

The electrochemical cell of glass contained organic electrolyte and three lithium electrodes—working, auxiliary, and standard (reference)—of identical size. To prepare electrodes, a thin (0.3–0.4 mm) layer metallic lithium LE-1 (OAO NZKhK, Novosibirsk) was rolled on the surface a fine (aperture size 40–60 μm) nickel mesh 1 by 1 cm in area. The thickness of such an electrode was 0.4–0.5 mm. For the electrolytes we selected several systems used in lithium batteries, namely, 1 M solutions of lithium perchlorate $LiClO_4$ in 1,3-dioxolane (E1); lithium bis(trifluoromethylsulfonyl)imide $LiN(CF_3SO_2)_2$, in 1,3-dioxolane (E2); and lithium hexafluorophosphate $LiPF_6$, in an equivolume mixture of ethylene carbonate and diethyl carbonate (commercial electrolyte LP-40, Merck) (E3). Lithium perchlorate (reagent grade, Russia) was dried in a vacuum at 150–180°C for five hours. Lithium bis(trifluoromethylsulfonyl)imide was dried in a vacuum at 70°C for six hours. The LP-40 electrolyte and 1,3-dioxolane (Merck, both) were used as received. To prevent 1,3-dioxolane from polymerization, 0.1% of triethylamine were added into electrolytes on its basis [18]. The electrodes and electrolytes were prepared and the cells assembled and filled with electrolytes in a glove box filled with high-purity argon dried over P_2O_5. To remove parasitic ohmic resistances, electric contacts between electrodes and current leads were carefully soldered. The external electric pick-up was reduced in the course of measurements by enclosing the cell in a Faraday cage.

Twenty four hours after filling the cell with electrolyte, the state of lithium electrodes would stabilize. The leveling-out of the potentials of the working and auxiliary electrodes evidenced that. Then we alternately performed anodic polarization (AP) and cathodic polarization (CP) of the working electrode, which took some 20 min. In the course of polarization we would measure the potential difference between the working and standard electrodes and its fluctuations, i.e. electrochemical noise proper. Nonpolarized standard lithium electrode is a very stable reference electrode with a low intrinsic noise, which is commensurate with the noise of the electrode under study in a steady state. In this way we excluded a noise generator from any foreign reference electrode with its own potential fluctuation spectrum, which could have been impossible to account for. To reduce the irreproducibility of results connected with the change in the lithium surface state upon applying a current, every next polarization was done 2-3 h after the previous one. The overall number of AP and CP cycles usually did not exceed two.

To perform electrochemical measurements, we used low-noise multifunctional potentiostat–galvanostat 1286 Electrochemical Interface (Solartron Instruments). The latter was equipped by a precision voltmeter with a large input resistance (10 Gohm) and high sensitivity (potential was measured to an accuracy of 1 μV). The electrode potentials were read discretely (at 1 Hz) with use made of an in-built interface IEEE-488 connected to a computer via an interface bus. A program for the registration and preliminary processing of obtained results had been designed.[1]

A special program was designed for processing experimental results. Graphical constructions were performed by package Microcal Origin 6.1. The peculiarity of mathematical and graphical processing of the obtained results consisted of that the electrochemical noise had to be estimated in the time and frequency domains under the conditions where, due to the action of the polarizing current, the electrode potential smoothly varied with an amplitude that considerably exceeded the noise constituents of interest to us. Hence the introduction of a computer-aided fitting, which allowed for the potential tendency during experiment.

According to fundamental properties of the Fourier transforms, these slowly varying quantities manifest themselves chiefly at the lowest frequencies and infiltrate middle- and high-frequency ranges attenuated thousandfold. However, due a tremendous difference in the initial amplitudes, the low-frequency signals exceeded the high-frequency electrochemical noise manifold even when attenuated. As a result it would have been wrong to evaluate the noise power using a direct Fourier transform.

To alleviate the situation, it was necessary to compensate the slowly varying signals with a large amplitude before the Fourier transform stage. This was realized by dividing experimental data into small groups (64 points each). The data of each group were expanded into the Taylor series and coefficients of a few polynomials of the lowest order were calculated using the least squares method. Thereafter the polynomials were subtracted out of the initial data.

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[1] The program was designed by V.M. Mazin and improved by Yu.Yu. Volodin†.

The mathematical aspect of the treatment of results with consideration of criteria for the determination of polynomials of the highest order, which must be compensated with the aid of the above procedure, is comprehensively described in [19].

A major part of the Fourier image of polynomials of lower orders occurs at the lowest frequencies of the Fourier transform. However, low-frequency constituents of electrochemical noise also occur at these frequencies. When calculating the polynomial coefficients, the contribution of each individual constituent cannot be distinguished. That is why the compensated noise spectra exhibit hollows at the lowest frequencies, which distort the spectra. To eliminate this phenomenon, we had to calculate the power at frequencies above 0.1 Hz, where the effect of polynomials of 3rd order and higher is not that severe.

RESULTS AND DISCUSSION

As established in blank experiments (measurements with the input short-circuited), the average amplitude of the noise generated by the potentiostat–galvanostat did not exceed 3 µV.

The lithium electrodes reached a steady state, in which the potential fluctuations were very low and steady, soon after being immersed in the electrolytes. The average amplitude of fluctuations of nonpolarized electrodes in all the electrolytes was virtually identical (3–5 µV), while the power spectral density (PSD) of the noise generated by the electrodes exceeded the instrument's PSD (6.9 μV^2/Hz). At 0.1–0.5 Hz, the root-mean-square PSD of fluctuations of the lithium electrode was 8.2, 9.9, and 16.8 μV^2/Hz in electrolytes E1, E2, and E3. The fluctuation intensity of electrodes kept for a long time (up to five days) under open-circuit conditions (OCC) remained practically invariant, indicating that a stable passive film covered the lithium surface.

Polarizing lithium electrodes at low currents (~50 µA/cm^2) slightly alters the lithium surface state, which manifests itself in a marginal increase of the potential fluctuation amplitude (Table 1). The character and intensity of the noise generated by cathodically and anodically polarized electrodes are very similar (Fig. 1). The results obtained in electrolytes E1 and E3 are analogous. This fact very convincingly argues in favor of identical localization of anodic and cathodic processes under the passivating film, the electrolyte nature notwithstanding. While the localization of anodic dissolution of lithium, which occurs at the lithium/passivating film interface, causes no doubt, there is no consensus on the cathodic deposition of lithium. The notion that the lithium deposition occurs at the interface just mentioned coexists with the viewpoint that it occurs on the passivating film or inside it [13, 14]. Should the cathodic process have proceeded in this manner, the potential fluctuations during cathodic and anodic polar-

Table 1. Average amplitudes ΔE_{mid} of fluctuations of lithium electrode potential

Electrode state	j, µA/cm^2	ΔE_{mid}, µV		
		E1	E2	E3
OCC	–	3	3.5	4
AP	50	5	5	16
CP	50	6	6	19
AP	1000	7	10	30
CP	1000	8	15	50–130

ization would have been different. The results we obtained (identical character and intensity of electrochemical noise during cathodic and anodic polarization) indicate that during the cathodic polarization (at least at its initial stage) the lithium deposition occurs under the film. When polarizing at low currents, the perturbation itself causes no substantial influence—only the process of under-film corrosion accelerates somewhat, but this process probably does not expand beyond the film.

At high polarization currents (1000–1200 µA/cm^2, which is a standard electrode current when cycling lithium batteries), the lithium surface state substantially alters, which manifests itself in a qualitative change of the potential fluctuations, mainly in a sharp rise of their amplitude (Table 1). This points to activation of the
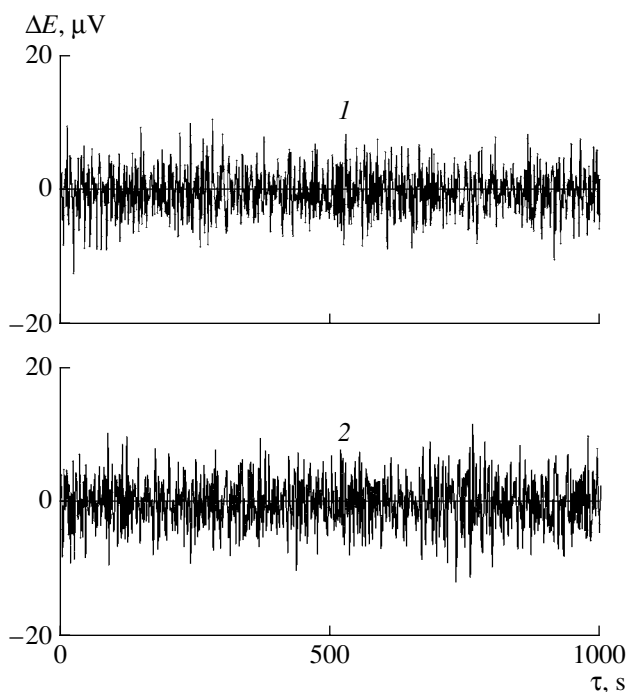

Fig. 1. Electrochemical noise of lithium electrode polarized (*1*) anodically and (*2*) cathodically at 50 µA/cm^2 in E2.

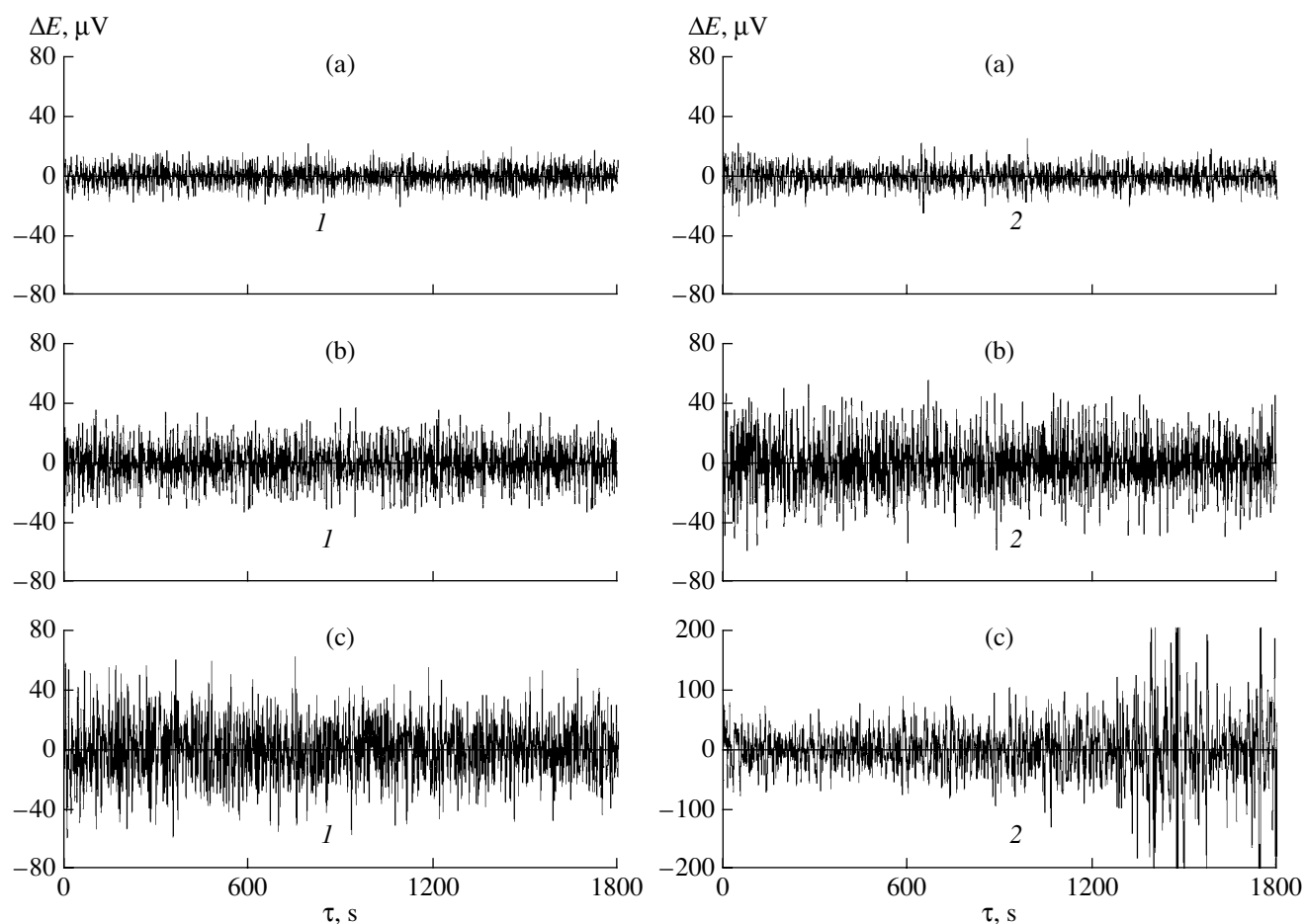**Fig. 2.** Electrochemical noise of lithium electrode polarized (*1*) anodically and (*2*) cathodically at 1000 μA/cm^2 in (a) E1, (b) E2, and (c) E3.

working electrode and destruction of the passivating film on its surface. At such currents, the character and intensity of fluctuations severely depend on the electrolyte composition—on the nature of the solvent and lithium-containing salt (Fig. 2, Table 1). In electrolyte E1, electrochemical noise of lithium electrodes at high and low polarization currents is nearly the same; in E2, fluctuations at high currents are perceptible higher; and the maximum fluctuation amplitude was registered in electrolyte E3. An analysis of noise characteristics suggests that passivation and activation processes proceed differently in different electrolytes.

The frequency spectra of the noise generated by lithium electrodes polarized cathodically and anodically, obtained using a fast Fourier transform, yield very convincing information about the noise. Figure 3 presents such spectra obtained at 1000 μA/cm^2. We clearly distinguish the difference between PSD in different electrolytes. In electrolyte E1, the PSD is low and practically identical for cathodic and anodic polarization. In E2, the PSD is ~5 times that in E1 and PSD for cathodic polarization is larger than that for anodic one by 30–40%. The spectra for E3 discernibly alter: the fluctuations are more intensive and the PSD for cathodic polarization sharply increases.

Table 2 presents root-mean-square values of PSD of fluctuations at 0.1–0.5 Hz for a lithium electrode in a steady state and polarized at 50 and 1000 μA/cm^2.

To explain the dynamics of the noise of a polarized lithium electrode in an aprotic electrolyte it makes sense to consider properties of the passivating film,

Table 2. Root-mean-square value of PSD of lithium electrode potential fluctuations at 0.1–0.5 Hz

Electrode state	j, μA/cm^2	PSD, μV^2/Hz		
		E1	E2	E3
OCC	–	8	10	16
AP	50	16	19	260
CP	50	18	24	530
AP	1000	23	107	590
CP	1000	27	169	9600

which can undergo destruction under polarization [15]. The resultant primary surface of lithium turns more active, leading to statistical heterogeneity of the surface and higher potential fluctuations. A similar phenomenon is characteristic of various corrosion processes [10, 16], in which fluctuations of the electrode potential of metal rise under the action of activating agents.

The activation of the lithium electrode occurs simultaneously with the passivation of the naked surface. In the case of fast passivation of lithium, the active surface of lithium, which turned naked due to the film cracking, undergoes intensive passivation, which on the whole decreases its heterogeneity. In the case of slow passivation, the heterogeneity rises with time. Obviously, potential fluctuations in the former case must be insignificant and, in the latter, far larger.

It should be remembered that the rate of deposition and formation of lithium crystals during cathodic polarization is higher, which leads to the growth of dendrites. These dramatically reduce the lifetime of lithium batteries.

The thin elastic homogeneous passivating film that covers the lithium surface in electrolyte E1 is not perforated by cathodic polarization [20]. The film rapidly covers lithium which is being deposited on the electrode, hampering the formation of dendrites when charging a battery. This in turn provides for a long cycle life of lithium [21, 22].

The lithium passivation rate in electrolyte E2 containing imide, which is very hostile toward lithium [22], is somewhat lower than that in E1 and, possibly, dendrites can grow on the active areas of the lithium surface. The lithium surface heterogeneity in E2 exceeds that in E1, which follows from larger potential fluctuations (Fig. 2). Cycling a lithium electrode in E2 showed that the dendrite-less cycle life is 200–300 cycles.[2]

Electrolyte E3 contains a noticeable amount of acid impurities, which facilitate intensive activation of the lithium surface accompanied by a rapid growth of dendrites, whose passivation rate is low. The result is a severe heterogeneity of the electrode surface, i.e. the presence of high-activity areas along with passivated ones. The phenomenology of the observed phenomenon and its explanation well conform to the results of a study of the dendrite formation and cycle life of a lithium electrode in E3. The cycle life in E3 is absolutely unsatisfactory: dendrites are discernible after a few charge–discharge cycles.

Comparing average values of PSD for electrodes polarized cathodically at 1000 $\mu A/cm^2$ (Table 2) and cycling characteristics in different electrolytes reveals a clear-cut correlation between the root-mean-square value of PSD and the cycle life. Specifically, the higher the noise intensity, the higher tendency to the formation of dendrites. This provides a basis for the development

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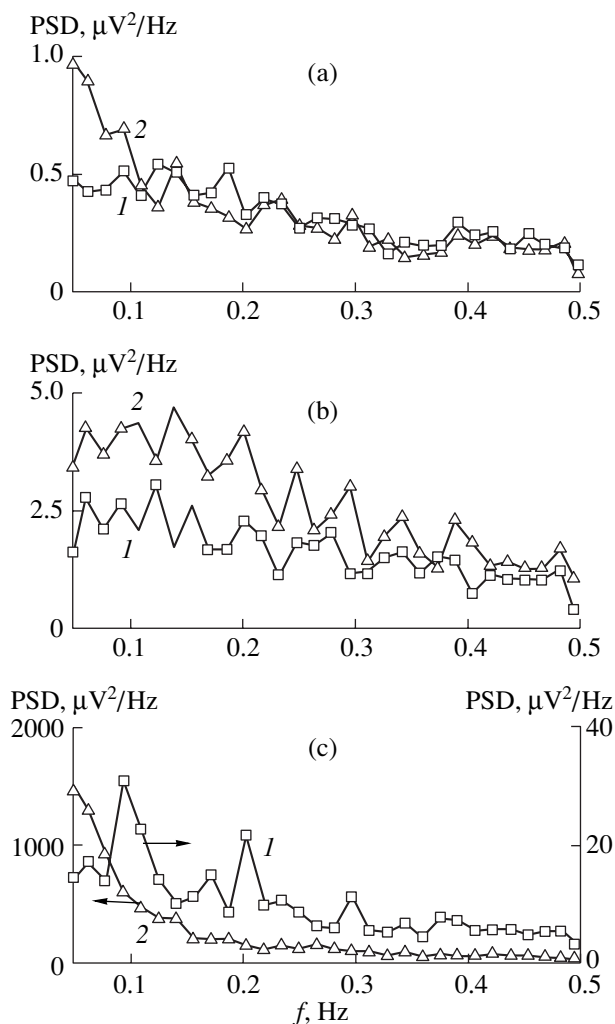[2] The cycling in electrolytes E2 and E3 was done in FIE RAS by O.Yu. Grigor'eva.

Fig. 3. Values of PSD for lithium electrode polarized (*1*) anodically and (*2*) cathodically at 1000 $\mu A/cm^2$ in (a) E1, (b) E2, and (c) E3.

of an express method, which would make it possible to determine whether some organic electrolyte can be used in lithium batteries or not.

CONCLUSIONS

Processes, which occur on a lithium electrode under open-circuit conditions (in a steady state) and when polarized, were studied by the electrochemical-noise method in some aprotic organic electrolytes with different solvents and electrolyte salts. An analysis of the noise characteristics confirmed the viewpoint that the electrochemical process is localized under the passivating film during both cathodic and anodic polarization. The film remains intact at small values of the polarizing current, but increasing the latter demolishes the film and the electrochemical process exits on its surface, affecting the potential fluctuations, whose intensity depends on the electrolyte nature. The fluctuation

intensity correlates with the stability of the cycled lithium electrode. A low electrochemical noise is characteristic of systems with a high stability of lithium cycling in the absence of the dendrite formation. The correlation permits the development of an express method for evaluating the applicability of organic electrolytes in lithium batteries, which would not involve prolonged cycling.

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