



ELSEVIER

Journal of Power Sources 54 (1995) 525–527

JOURNAL OF
POWER
SOURCES

Photoelectrochemical currents and noises on a lithium electrode

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Abstract

The spectra of a photoelectrochemical current on a lithium electrode in γ -butyrolactone, propylene carbonate, dimethylsulfoxide solution with LiClO_4 and LiBF_4 were investigated. The threshold energy of electron photoemission E_{th} from lithium to the oxide film were compared; we obtained, as a result, that $E_{\text{th}} = 1.3\text{--}1.4$ eV for the different electrolytes. The value of the intensity of the electric field in the oxide film under stationary conditions was $1 \times 10^7\text{--}3 \times 10^7$ V/m. It was found that, under a strong illumination of electrode by sunlight radiation, the value of the photo-electromotive force and the electrochemical noise increases. By the analysis of the kinetics of this photoeffect and noise we concluded that the migration of photogenerated carriers through the oxide film is a limiting stage of its transfer process. The velocity constant of this reaction was $K_s = 1 \times 10^2\text{--}2 \times 10^2$ s⁻¹.

Keywords: Electrodes; Lithium

1. Introduction

An investigation of the photoeffects on metal electrodes, covered by a thin passivating film, allows to determine the characteristics of the charge migration process through the oxide film and also to find the mechanism of a charge transfer through the interface [1,2]. The noises of this electrochemical system characterise its disequilibrium process, for example, the oxidizing and passivation of electrodes [3–5].

The noise method gives enough perspectives for the investigation of many processes in the field of electrochemical kinetics [6]. In this work, the spectra of photoelectrochemical currents and noises on a lithium electrode in organic solvents (γ -butyrolactone, propylene carbonate and dimethylsulfoxide) with LiClO_4 and LiBF_4 were investigated in order to obtain information on the processes of a photostimulated charge transfer in the system: lithium oxide/electrolyte.

2. Experimental

The organic solvents (γ -butyrolactone, propylene carbonate and dimethylsulfoxide) were distilled in an atmosphere of dry argon under a static pressure 15 to

18 mmHg. The water concentration in the electrolytes was less than 0.008%. The inorganic substances were subjected to vacuum drying under 160 to 180 °C. We also used lithium (EO mark, concentration of electroactive pollution <0.01%). The potential of working lithium electrode was measured relatively additional Li-electrode.

The spectra of photoelectrochemical currents were measured by the monochromator MDR-2 on various diffraction lattices; the spectral resolution was 1 nm. A xenon lamp DKSSh-500 was used as the radiation source. A photocurrent was measured by the light beam modulation method with a mechanical modulator under the frequency $f = 15\text{--}400$ Hz, using a standard scheme of synchronous detection. The sensitivity of this research photocurrent equipment was 10^{-12} A. The experimental equipment for the noise measurement was described in Ref. [7]. It was characterized by the equivalent noise resistance R_{eq} , reduced by an internal resistance pre-amplifier of noise: $R_{\text{eq}} = 1.3$ k Ω m under $f = 1$ kHz and $R_{\text{eq}} = 7$ k Ω m under $f = 20$ Hz. The internal resistance of pre-amplifier of noise was about 2 M Ω .

3. Results and discussion

It was found, that a photoeffect on the lithium electrode was observed in the energy region of $h\nu >$

1.1 eV (Fig. 1). Under $h\nu > 1.6$ eV the amplitude of the photocurrent essentially increased to the short waves region of the spectra, whereas in the long waves spectrum region the amplitude of the photocurrent was small and weakly depended on the energy $h\nu$. The amplitude of the photocurrent increased according to the increasing negative potential on lithium.

In order to identify the types of phototransmissions on the lithium electrode under negative potentials we draw the relation I_{ph} from $h\nu$, which was typical for the electron photoemission from a metal to a polar environment [1,2,8]. As it was shown in Fig. 1 this relation is linear in the region $1.6 < h\nu < 2.4$ eV.

The value of the photocurrent for p- and s-light polarization under different angles of the light, θ , did not vary in the whole investigated spectrum region. In addition, the equation $I_{ph} = I_{ph}^{max} \cos\theta$ fitted. The weak relation of the photocurrent with the polarization vector is non-typical for a photoemission process. However, we can explain this relation by a strong scattering of the wave's vector of emitted electrons on a rough lithium surface, which always takes place in experimental conditions. Such explanation has been suggested in Ref. [9], when the photoemission process of 'hot' hole on a golden electrode was studied.

The value of threshold energy of the electron photoemission $E_{th} = 1.3\text{--}1.4$ eV was obtained for all the investigated solvents from an extrapolation of the linear relation $I_{ph}^{0.4}(h\nu)$ to the zero value of the photocurrent (Fig. 1). At that time, the existence of small residual photoeffects in a long-wave spectrum region if energy of a light quantum lower than the threshold energy of photoemission (Fig. 1), has indicated that another process of photogeneration of charge carriers takes also place, for example, a photoexcitation of charge carriers in the oxide film.

This model suggests the existence of an intermediate stage of the charge transfer from the oxide to the electrolyte. Photoemitted electrons, getting into the oxide film, can be thermolyzed there and can take part in the transfer of an ion–electron current through the

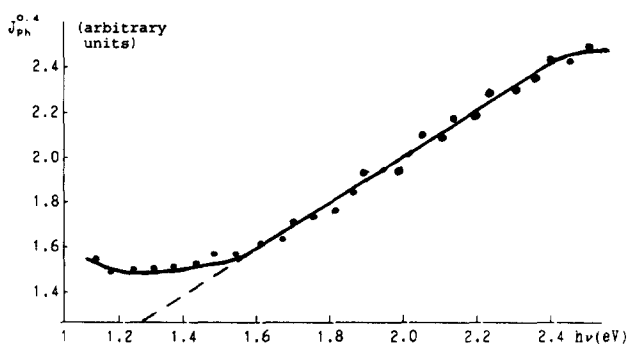


Fig. 1. Photocurrent $I_{ph}^{0.4}$ from the energy of light quantum on a lithium electrode in γ -butyrolactone with 0.5 M LiClO_4 ; $\Delta E = -0.035$ V; non-polarized light.

oxide film. The data shown in Fig. 2 give also evidence of the existence of an intermediate stage of photoelectrochemical processes.

The long (10–20 min) of the photoeffect relaxation was observed after step polarization with a duration of 1–3 s in the anodic as well as the cathodic region $|\Delta E| = |E - E_{st}| = 100\text{--}150$ mV (where E_{st} is the stationary potential of the lithium electrode). These factors testify the influence of ion–electron processes in the oxide film on the photoeffect observed. The relation $I_{ph}(\Delta E)$ is given in Fig. 2. It was shown that the electrical field takes place in the oxide film on lithium under a stationary potential, E_{st} , and that this electrical field has divided photogenerated charge carriers and caused therefore the photoeffects.

It is evident from the relation $I_{ph}(E)$ that this field promotes negative charge to be moved to the oxide film/electrolyte interface. The intensity value of this field in stationary conditions was $10^7\text{--}3 \times 10^7$ V/m, as estimated, in different solvents.

From the noise measurements, we calculated the coefficient of fluctuation noise $\gamma(f)$ [6]:

$$\gamma(f) = -(i_2/2eI\Delta f) \quad (1)$$

where i is the value of noise current, measured in frequency strip, Δf , near basic frequency. I the value of dark electrochemical current, and e the charge of an electron.

It was concluded, that the value $\gamma(f)$ was greater than the value of fluctuation noise ($\gamma(f) = 1$) (Figs. 2 and 3) and proportional to current I , that is typical for modulation noises [3,7]. The frequency relation $\gamma(f)$ in the region $f = 10\text{--}180$ Hz was in accordance to the correlation $\gamma(f) = f^{-n}$, (Fig. 3), where $n = 1.2 \pm 0.1$. At that time, the value $\gamma(f)$ for the lithium electrode increased unmonotonously during the time the oxide film being formed and it increased also by increasing the light power on the electrode. The deviation of the potential ΔE on ± 50 mV caused to an essential increase in noise and correlated with an increasing

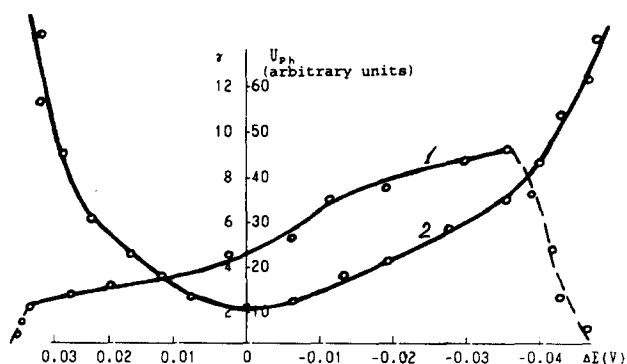


Fig. 2. Relation of (1) photovoltage U_{ph} and (2) coefficient of fluctuation noise from the potential ΔE on lithium in γ -butyrolactone with 0.5 M LiClO_4 ; frequency, $f = 20$ Hz.

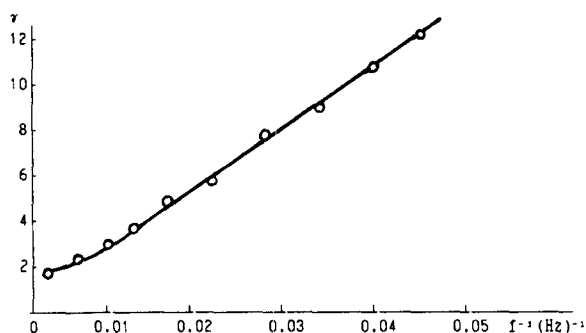


Fig. 3. Frequency relation of the coefficient of fluctuation noise, γ , on lithium in propylene carbonate with 0.25 M LiBF_4 .

photocurrent relaxation (Fig. 2). It was found that strong lighting of a freshly prepared electrode ($P=4\text{--}6 \text{ kW/m}^2$) in the visible region intensified the velocity of the oxide film formation and exercised an essential influence on the kinetics of the photoeffect. In addition, the increase in photo-electromotive force on the electrode was in accordance with the increase in the electrochemical noise. After intensive lighting, stationary characteristics of noise, dark conductivity and photoeffect on the lithium-electrode was achieved after 1 to 2 h when the lithium electrode came in contact with the electrolyte, but if there was not lighting, this time was longer.

In this way, the obtained data showed that the process of migration of photogenerated charge carriers in the system lithium oxide/electrolyte displayed photoeffect relaxation and noise. The cause of photocurrent relaxation is, most likely, the structural changes of lithium

oxide film that affected the mobility and quantity of the charge carriers. Based on these data we may conclude that the migration of the charge carriers through the oxide film is a limiting stage in the photo-electrochemical process. We found the velocity constant of this stage, K_s , under stationary conditions after a long relaxation time of photo-electromotive force and noise by the analysis of frequency relation of E_{ph} under modulation of the light beam by a mechanical modulator, $K_s=0.01\text{--}0.02 \text{ s}^{-1}$ for different electrolytes. The correlation between low-frequency noise and photoeffect on lithium electrode shows, as we noted, that these methods are promising for the investigation of the processes of charge transfer through the oxide film under various stages of its formation.

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