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Effect of oxygen adsorption on the laser-induced thermal jump of potential on a smooth polycrystalline platinum electrode

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It has been shown for the first time that the laser-induced thermal jump of potential on a platinum electrode is sensitive to the form of oxygen adsorption.

Barker[1] was the first to find that the irradiation of an electrode with a light pulse generates a jump in the electrode potential (ΔE) caused by heating of the metal with absorbed radiation. More recently, considerable progress was reached in the understanding of both the structure of the electrochemical double layer (DL) and the thermoelectric effects at the electrode/electrolyte interface.[2,3] The thermal jump (TJ) technique was used to estimate the zero-charge potentials of different Au and Pt faces in single-crystal electrodes.[4,5] However, the potential range studied was limited by potentials of the start of oxygen adsorption. Here, we describe the effect of oxygen adsorption on the TJ and the shape of the ΔE–time plot on a smooth polycrystalline platinum electrode (pc-Pt) in the potential range of oxygen adsorption.

The measurements were carried out in a three-electrode cell similar to that described elsewhere.[2] The end face of a polished pc-Pt wire 0.5 mm in diameter sealed in a glass capillary was used as the working electrode. The true surface area determined by hydrogen adsorption[6] amounted to 3×10^{-3} cm^2. A platinum mesh was used as the auxiliary electrode and a saturated calomel electrode was used as the reference electrode.

The working electrode was irradiated with a laser through an optical window in the upper cell part. An ILGI-503 nitrogen laser (wavelength $\lambda = 337$ nm, pulse length $t_0 = 15$ ns, recurrence frequency $f = 100$ Hz) was used as the main source of irradiation. The irradiation intensity at the electrode (L) was ~320 kW cm^{-2}. Reference experiments were carried out using an excimer laser with $\lambda = 590$ nm and $t_0 = 20$ ns. The absence of photoemission for the range of anodic potentials studied follows from the fact that the signal shape is the same for both lasers with considerably different wavelengths; furthermore, the low radiation intensity allows us to disregard the nonlinear photoeffect and the electrode modification.[7,8] ΔE was amplified with a broadband amplifier ($\Delta f = 40$ MHz) and fed to the input of a computer-controlled LA-n10M4 digital oscilloscope. As a rule, the signal accumulation was based on 512 pulses. Electrochemical measurements were carried out with an IPC-compact potentiogalvanostat developed at the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry (Moscow). Solutions were prepared from twice-distilled water, special purity H_2SO_4 and twice-distilled MeOH of chemically pure grade. All potentials refer to the reversible hydrogen electrode in the same solution.

The electrode was first anodically-cathodically activated (10–20 cycles) in the potential range 0.050–1.50 V at a potential sweep rate of 100 mV s^{-1}; then, accumulation of adsorbed oxygen was performed by means of a cathodic or anodic pretreatment. In the former case, the electrode was kept for 5 min at a potential of 0.050 V, while in the latter case, at 1.50 V (5 min); after that, the required potential was set and the TJ was measured after 5 min. The surface coverage with adsorbed oxygen (θ_O) at a given potential was determined in separate experiments using cathodic potentiodynamic pulses.[9]

In the experiments with methanol, $E = 1.5$ V was set for 5 min in order to accumulate a monolayer of O_{ads} in a 0.5 M H_2SO_4 + 0.01 M MeOH solution. The circuit was then interrupted and the temperature response was recorded during the potential decay caused by the reaction of O_{ads} with MeOH.[9]

An estimate of the maximum electrode heating temperature by the formula[2]

$$\Delta T_m = \frac{L(1-R)}{\sqrt{\pi k c \rho} - \sqrt{\pi k_1 c_1 \rho_1}}\sqrt{t_0}, \qquad (1)$$

where k, c, ρ and k_1, c_1, ρ_1 are the thermal conductivity, thermal capacity and specific density of the metal and solution, respectively, gives $\Delta T_m \approx 7$ K for the reflection index of pc-Pt equal to $R = 0.5$.[10]

The course of galvanostatic curves of O_{ads} electroreduction in 0.5 M H_2SO_4[11] does not change upon the laser irradiation of the electrode. Likewise, no effect of laser-induced heating on the rate of O_{ads} removal *via* the reaction with MeOH was observed. Hence, important conclusions can be made that there is no noticeable change in the state of O_{ads} due to pulsed laser heating of the electrode surface under the conditions used and that it is principally possible to use laser pulses with the specified intensity as probing pulses in order to assess the amounts and forms of oxygen adsorption on a pc-Pt surface.

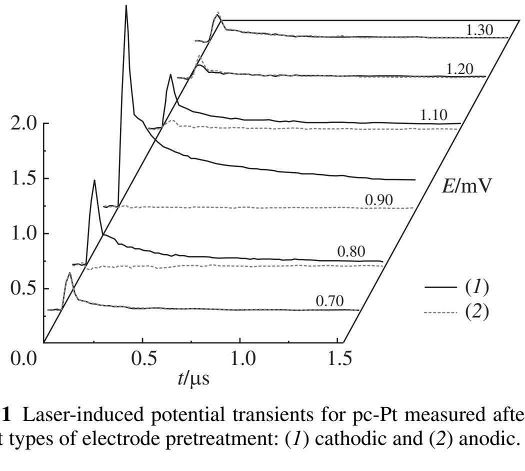

Figure 1 Laser-induced potential transients for pc-Pt measured after two different types of electrode pretreatment: (*1*) cathodic and (*2*) anodic.

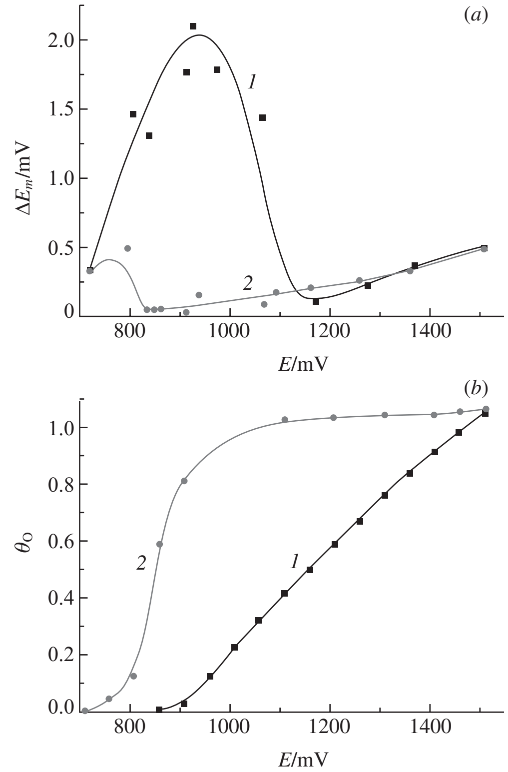

Figure 2 Dependence of (*a*) the temperature jump of potential ΔE_m and (*b*) surface coverage with adsorbed oxygen on potential obtained for different electrode pretreatments: (*1*) cathodic and (*2*) anodic.

Typical $\Delta E(t, E)$ plots obtained by heating of the electrode surface with a laser pulse are presented in Figure 1. The cathodic and anodic curves (at $E < 0.75$ and $E > 1.10$ V, respectively) are characterised by a signal build-up to ΔE_m during a laser pulse, followed by a decay with asymptotic behaviour close to $t^{-0.5}$, which agrees qualitatively with published data.[5] The ΔE_m–E plots for 0.5 M H_2SO_4 are shown in Figure 2(*a*). Figure 2(*b*) shows the θ_O–E plots for the cathodic (curve *1*) and anodic (curve *2*) pretreatments.

It has been shown[2] that the major contribution to the heating-induced signal is made by the change in the DL potential due to the temperature dependence of its capacitance and structure under coulostatic conditions:[†]

$$\Delta E_m \approx \left(\frac{\partial \Delta E}{\partial T}\right)_q \Delta T_m, \tag{2}$$

where $(\partial \Delta E/\partial T)_q$ is the temperature factor of the potential drop in the DL defined as:

$$\left(\frac{\partial \Delta E}{\partial T}\right)_q = -\left(\frac{\partial \Delta S}{\partial q}\right)_T, \tag{3}$$

where ΔS is the interface formation entropy equal to the difference between the entropies of the components in the state where they have formed the interface and where they exist in the bulk of the adjacent phases.

It is known[6,12,13] that the observed hysteresis of $\theta_O(E)$ in case of the adsorption–desorption of O_{ads} [Figure 2(*b*)] appears due to the predominantly irreversible character of oxygen adsorption on platinum. Cyclic potentiodynamic curves recorded at a small potential sweep rate (0.020 V s^{-1}) on a smooth platinum electrode (Figure 3) show that, at reversal potentials $E_A < 0.90$ V, the peaks of O_{ads} adsorption and desorption are almost not shifted relative to each other (curves *1*–*4*). However, at $E_A > 0.90$ V (curves *5*–*7*), the O_{ads} reduction potentials become considerably more negative than adsorption potentials, which suggests that oxygen adsorption becomes irreversible as the upper potential sweep limit is increased. Hence, oxygen is adsorbed on pc-Pt rather reversibly at the initial stage, as was assumed previously.[12] According to Petrii *et al.*,[14] the surface of a Pt/Pt electrode in 0.01 M H_2SO_4 behaves as an equilibrium system up to $E \sim 0.95$ V. According to the thermodynamic theory of a hydrogen electrode, reversibly adsorbed oxygen species (OH_{ads} or O_{ads})[12,15] contribute considerably to the total charge of the hydrogen electrode.[16] On the other hand, the variation in the amount of irreversibly adsorbed oxygen with potential affects the total charge only through relatively small changes in the adsorption of background ions (in our system, HSO_4^-/SO_4^{2-}). According to equation (3), this should result in different thermal factors of the potential drop in the DL $(\partial \Delta E/\partial T)_q$ at low θ_O depending on the conditions of O_{ads} accumulation. In fact, the course of the ΔE_m–E plots in the potential range 0.75–1.10 V [Figure 2(*a*)] differs considerably for the cathodic and anodic electrode pretreatments. One may speak of a selective sensitivity of the TJ to the surface coverage with O_{ads} that manifests itself as a considerable change in ΔE_m at the initial (reversible) stage of oxygen adsorption on pc-Pt.

The proximity of curves *1* and *2* in Figure 2(*a*) to the abscissa axis and to each other at $\theta_O > 0.5$ suggests that ΔE_m is little sensitive to the surface coverage with irreversibly adsorbed oxygen, irrespective of the method of its accumulation. At $\theta_O > 0.5$, oxygen is mainly chemisorbed as Pt–O.[12,15] Note that the abrupt decrease in ΔE_m in curve *1*, Figure 2(*a*), corresponds to potentials close to 1.10 V, where the form of irreversible oxygen adsorption is assumed to change (from Pt–OH to Pt–O[12] or from Pt_2–O to Pt–O[15]).

If methanol is present in solution, a reaction of MeOH with adsorbed oxygen starts after one monolayer of O_{ads} is accumulated on the platinum surface and the circuit is disconnected. As a result, the surface coverage with oxygen decreases and the electrode potential shifts in the cathodic direction.[9] The ΔE_m–E plot obtained in a 0.01 M MeOH + 0.5 M H_2SO_4 solution during such a potential decay is demonstrated in Figure 4 (curve *2*). It also shows a curve *1* recorded after anodic pretreatment in a sulfuric acid solution containing no MeOH. It is evident that curves *1* and *2* almost coincide. Unfortunately, at medium O_{ads} coverages (θ_O = 0.8–0.2), *E* changes so quickly[9] that averaging over a small number of pulses has to be used, hence the measured ΔE_m values have a large scatter. For this reason, the TJ data obtained during the decrease in the potential of an oxidized electrode under open-circuit conditions in the presence of methanol in solution[9] are limited to the potential range that corresponds to high degrees of surface coverage with O_{ads}

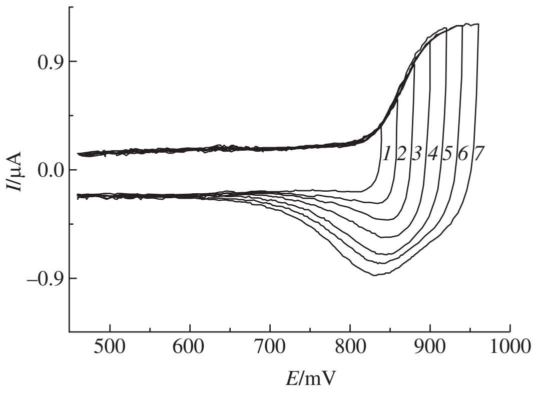

Figure 3 Cyclic potentiodynamic curves recorded in 0.5 M H_2SO_4 at different potentials E_A of reversal from anodic to cathodic potential sweep. E_A/mV: (*1*) 840, (*2*) 860, (*3*) 880, (*4*) 900, (*5*) 920, (*6*) 940 and (*7*) 960.

[†] The potential drop between the DL boundary and the solution bulk[3] is not considered in this paper.

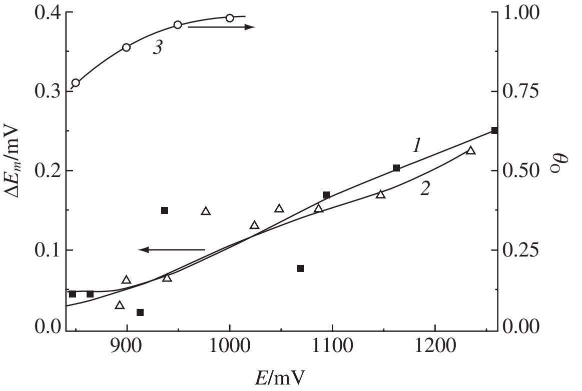

Figure 4 Dependence of the temperature jump of potential ΔE_m on the electrode potential measured in the following solutions: (*1*) 0.5 M H_2SO_4 (anodic pretreatment), (*2*) 0.1 M MeOH + 0.5 M H_2SO_4 (see the text), (*3*) the region of θ_O *vs.* potential plot observed during the potential decrease in a methanol-containing solution.[9]

(curve *3* in Figure 4). A mechanism of the reaction of MeOH with O_{ads} on a pc-Pt electrode under open-circuit conditions was suggested,[9] according to which a direct reaction of O_{ads} with MeOH molecules from solution bulk occurs at high θ_O values. The absence of noticeable methanol chemisorption on sites that are becoming free from O_{ads} has been shown experimentally. Under these conditions, one should expect that the characteristics of the adsorption layer of oxygen should not depend on the presence of methanol in the solution; this is confirmed by the data on TJ presented in Figure 4.

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