CHARGING OF ELASTICALLY DEFORMED ELECTRODE

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UDC 541.1

In electrostatic adsorption the double electric layer at the electrode–solution boundary with certain metals is the same at potentials φ, equally distant from the zero charge point φ_0 [1]. The increase in the full charge Q of the electrode, divided by the increase in area Ω of the boundary under a small elastic deformation, would give the charge density $q = Q/\Omega$, if the deformation had no effect on φ_0. However, there is such an effect and $q = q(u)$, where u is the relative change in area, $1 + u = \Omega/\Omega_0$, Ω_0 is the initial value of Ω, and $u < 0.001$. Therefore,

$$Q'_{\Omega} = q + (1 + u)\, q'_{u}, \quad \varphi = \text{const.} \tag{1}$$

The term with $q'_u = \partial q/\partial u$ takes account of the change in q resulting from the deformation. For $u = 0$, $Q'_{\Omega} = q + q'_u$. In chemisorption, conformity is established between the individual atoms of the electrode and the particles adsorbed from the solution. At low deformations the number of electrode atoms facing the solution does not change. With a certain degree of chemisorption, therefore, $Q'_{\Omega} = 0$ and (at $u = 0$) $q'_u = -q$. Similarly, when Q = constant, an increase in Ω is accompanied by an increase in φ, and $\varphi'_u = [q + (1 + u)\, q'_u]/C$, with Q = constant, where C is the specific capacity of the electrode (at the frequency of the determination).

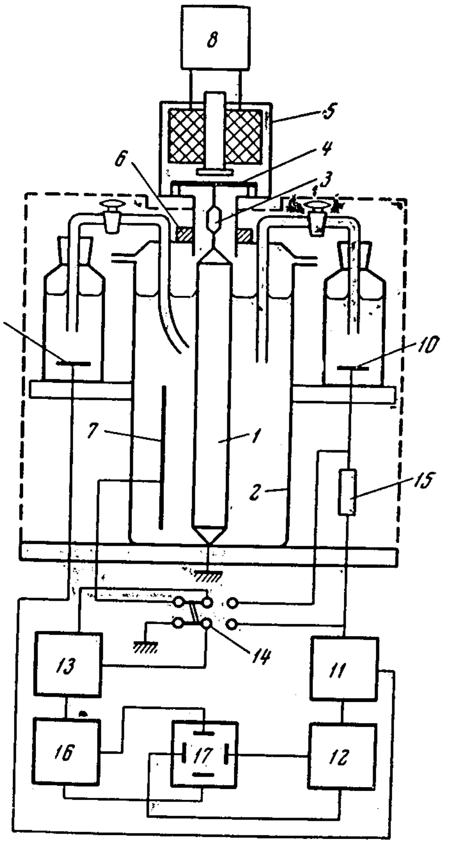

Fig. 1. Apparatus for investigating the charging of elastically deformed electrode and block circuit. 1) Electrode consisting of a stretched strip; 2) vessel; 3) insulating link; 4) diaphragm; 5) vibrator; 6) micrometer screw for preliminary extension of electrode; 7) auxiliary electrode; 8) alternating voltage generator; 9) reference electrode; 10) auxiliary electrode; 11) voltage compensator; 12) linear voltage generator; 13) selective amplifier; 14) selector switch for Q = constant and φ = constant conditions; 15) load resistance; 16) rectifier; 17) recorder.

Institute of Electrochemistry, Academy of Sciences of the USSR. (Presented by Academician A. N. Frumkin on February 12, 1969.) Translated from Doklady Akademii Nauk SSSR, Vol. 187, No. 3, pp. 601-604, July, 1969. Original article submitted February 11, 1967.

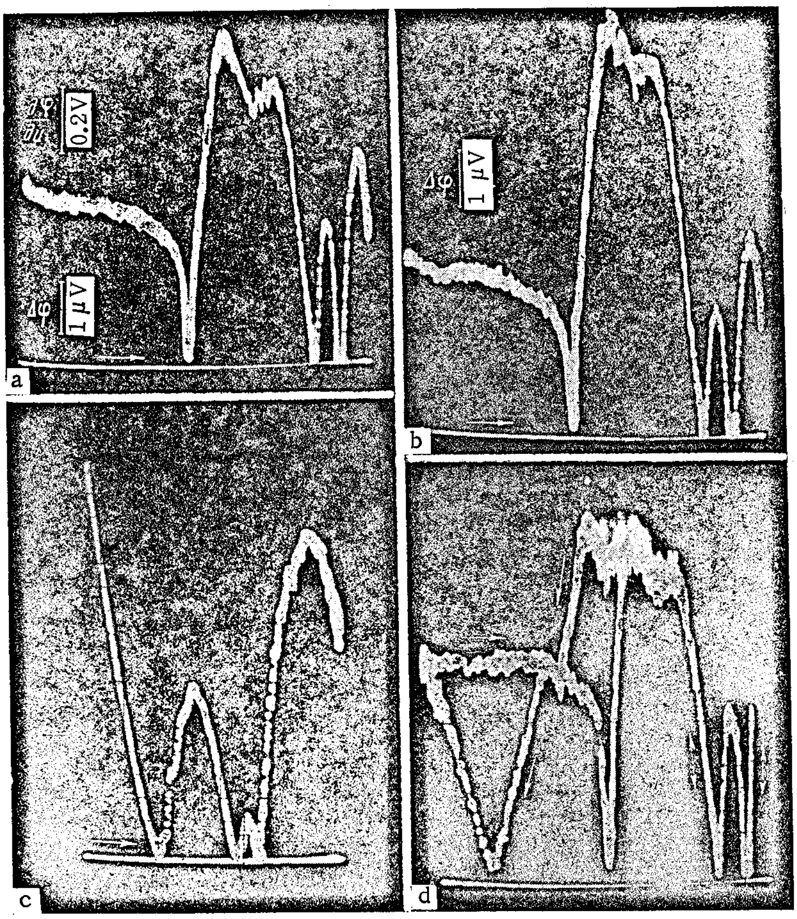

Fig. 2. Oscillograms of amplitude of potential $\Delta\varphi$ for periodically elongated electrode against mean potential φ_m at Q = constant, for platinum in 1 N sulfuric acid; ν = 38 Hz; the electrode was a 1×11.5 cm strip of foil 10 μ thick; $\Delta p = 20$ kgf/cm^2; φ_m with reference to normal hydrogen electrode; scanning time 7 min; temperature 20°C; a) and b) φ_m changes (from left to right) from + 1.40 to −0.04 V, τ_0 = 3 min, p_0 increased from 120 kgf/cm^2 (b) to 350 kgf/cm^2 (a); c) φ_m changes from +0.32 to − 0.04 V, p_0 = 100 kgf/cm^2; d) φ_m changes from +1.45 to +0.05 V and back, p_0 = 400 kgf/cm^2, τ_0 = c min.

In the present work (Fig. 1) a stretched strip of foil was used as the electrode. On the constant tensile strength p_0 was superimposed a small periodic stress, $p = p_0 + \Delta p \sin \omega t + \ldots$, where Δ denotes amplitude, t is time, $\omega = 2\pi\nu$, and ν is frequency. The $\Delta\varphi$ value was measured under conditions where Q = constant, for which the time constant of the electrode was established at two orders of magnitude longer than the vibrational period. The vibrator for the periodic stretching of the electrode (Fig. 1) operated on higher harmonics; the fundamental frequency of attraction of the diaphragm to the core of the electromagnet was twice as high as the frequency of the current in the vibrator winding. This avoided pickup at a measurement frequency equal to the elongation frequency, and the sensitivity threshold with respect to $\Delta\varphi$ was shifted to 10^{-7} V. The dependence of $\Delta\varphi$ on the mean potential of the electrode φ_m was recorded on an oscillograph.

The $\Delta\varphi$, φ_m oscillogram obtained by this method for a smooth platinum electrode in sulfuric acid (Fig. 2) reproduces in all its details the $\Delta\gamma$, φ_m oscillogram (γ is surface tension) obtained earlier [2] for the same system with constant Δq and Ω values (Fig. 3), where the platinum specimens were different. On both the $\Delta\varphi$, φ_m and $\Delta\gamma$, φ_m oscillograms, beginning with considerable anodic potentials, the recorded signal passes through zero near +0.7 V (oxygen zero, its φ value depends on the length τ_0 of the delay at the initial φ value), again at +0.2 V, and twice near +0.1 V on the normal hydrogen electrode scale. On passing through zero the signal changes phase by π. On both oscillograms the two zeros near +0.1 V emerge as a result of preliminary anodic polarization from the

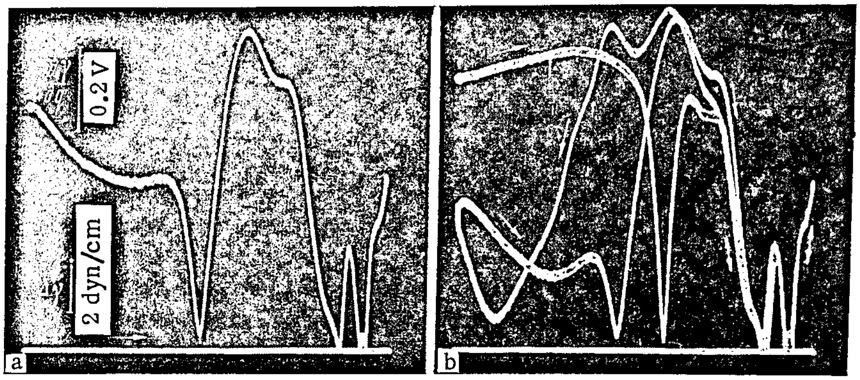

Fig. 3. Oscillograms of amplitude of surface tension $\Delta\gamma$ against mean potential φ_m for platinum in 2 N sulfuric acid; ν = 990 Hz; the electrode (above the meniscus) was a × 4 × 0.35 mm plate; the amplitude of the applied current was 0.01 A/cm^2; the scanning time 20 sec; temperature 20°C; a) φ_m changes from +1.40 to +0.02 V on normal hydrogen electrode scale, τ_0 = 15 sec; b) φ_m changes from +1.40 to +0.02 V and back, and again from +1.40 to + 0.02 V; preliminary treatment of 10 sec at +1.8 V, τ_0 = 10 min.

minimum corresponding to the rise in pseudocapacity at +0.1 V. (The reasons for this effect require further investigation.) The reverse form of the two curves is also identical.

The correspondence of these two curves is not only interesting because they were obtained by independent methods. The variable components of the various physical quantities — charge Q and surface tension of solid electrode γ — repeat each other. Replacement of ΔQ at φ = constant by $\Delta\varphi$ at Q = constant does not affect the nature of the method, since these values are related, and $\Delta Q = C\Delta\varphi$ for any investigated subject. In the experiments of Figs. 2 and 3, the fluctuations in φ and γ are generated by small fluctuations of constant amplitude in u and q. Therefore, $\Delta\varphi$ and $\Delta\gamma$ are equivalent to φ'_u and γ'_q. The scales calculated for these values (both in volts) are shown in Figs. 2 and 3. Experiment thus indicates that φ'_u and γ'_q coincide.

Calculation also leads to the same result. Development for the full differential of the free enthalpy gives, at constant temperature and pressure:

$$\text{a) } (\gamma'_\varphi)_\Omega; \quad \text{b) } (\gamma'_Q)_\Omega = (\varphi'_\Omega)_Q; \quad \text{at} \quad u = 0 \ (\gamma'_q)_\Omega = (\varphi'_u)_Q;$$
$$\text{d) } (\widetilde{\gamma}'_\varphi)_{\widetilde{\Omega}} = -(O'_{\widetilde{\Omega}})_\varphi; \quad \text{d) } (\widetilde{\gamma}'_Q)_{\widetilde{\Omega}} = (\varphi'_{\widetilde{\Omega}})_Q; \quad \text{at} \quad \widetilde{u} = 0 \ (\widetilde{\gamma}'_{\widetilde{q}})_{\widetilde{\Omega}} = (\varphi'_{\widetilde{u}})_Q; \tag{2}$$

γ, Ω, u, and q with the wavy lines relate to a surface with large-scale roughness, and the same symbols without the wavy lines relate to the plane which averages this surface. In the latter case, they are directly commensurate. The surface tension method for solid electrodes [2] and the method of charging under elastic deformation give the left and right sides of Eqs. (2a) and (2b) respectively. An accurate comparison of the results can be made without taking the roughness into account. For this purpose it is necessary to measure γ'_q and φ'_u on the same specimen.

What does such a comparison achieve? Firstly, it confirms the fact that the electrode fluctuations are actually caused by fluctuations in surface tension. Secondly, it allows the side effects, which are different for the two methods, to be determined. The correspondence between the electrical and mechanical quantities is not always reversible. At low frequencies (38 Hz) the thermal effect does not distort the $\Delta\varphi$, φ_m curve. The correspondence of the $\Delta\gamma$ and $\Delta\varphi$ zeros therefore confirms the conclusion [2, 4] about the small quantity of heat liberated during adsorption of H$^+$ ions on platinum (less than 1 kcal/F).

Combination of Eq. (1) with Eq. (2) and similar operations for the adsorption of particles with chemical potentiall μ density Γ give, for solids at u = 0:

$$\text{a) } \gamma'_\varphi = -q - q'_u; \quad \text{b) } \gamma'_\mu = -\Gamma - \Gamma'_u \tag{3}$$

in place of the Lippman equation $\gamma'_{\varphi} = -q$, which is valid for liquids. The $\Delta\gamma$ value is determined from the formula $\gamma = f/\Lambda\,(1 - \sigma)$ or $\gamma = \lambda A Y/\Lambda\,(1 - \sigma)$, where f is the force which balances the relative elongation of the electrode λ caused by γ; A and Λ are the cross-sectional area and perimeter; σ is the Poisson coefficient; $Y = Y(u)$ is the elasticity modulus of the electrode [4]. For a plane $\Delta u = \Delta p(1 - \sigma)/Y$. For a surface with a roughness factor of α, $\Delta\tilde{u} = \xi(\alpha)\Delta u$ and $\xi(\alpha) = 1 + [(1 + u)/\alpha]\alpha'_u$; when $u = 0$,

$$\xi(\alpha) = 1 + \alpha'_u/\alpha. \tag{4}$$

For small values of $\alpha - 1$, $\xi(\alpha) = (1 + \alpha^2)/2\alpha^2$ is approximately true. The value of ξ decreases with increase in α and can become negative under certain conditions. The elongation of the solid is then accompanied on the other hand by a reduction of its surface owing to the smoothing out of the roughness. Similarly $\tilde{\gamma} = \eta(\alpha)\gamma$, where $\eta(\alpha) = 1/\alpha\,\xi(\alpha)$. Calculation by means of the functions of the effect of elasticity theory also gives $\gamma/\tilde{\gamma} = d\tilde{\Omega}/d\Omega$. The $d\tilde{\Omega}/d\Omega$ ratio corresponds to deformation by a force applied, like γ, to the contour of the averaging plane and can be measured, for example, by stretching a specimen in the form of a strip or rod.

The closeness of the γ'_{φ} zeros to the φ_0 points ($q = 0$), found with solid thallium, cadmium, lead, and a series of other metals [2], shows that when $n = 0$ here $|q'_u| \ll |q|$. This can be checked by measuring Q'_{Ω} and φ'_u at various u values. On platinum an increase in the u value from 0 to 1.2×10^{-4} (slope) leads to a reversible increase of $|\varphi'_u|$ in the hydrogen region (Fig. 2a and b). Since $q + q'_u$ is commensurate with q, and $u < 10^{-3}$, the variation of $q + q'_u$ with u practically coincides with the variation of q'_u. The amplitude of the second harmonic φ, caused by the nonlinearity of u(p), changes with φ_m in the same way as $\Delta\varphi$.

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