POTENTIAL DEPENDENCE OF THE SURFACE TENSION OF IRON-GROUP METALS*

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Information about the double layer at iron and its analogs has been derived from corrosion and adsorption studies [1, 2], work function measurements [3], and differential-capacity measurements [4]. Independent information about the surface of these metals can be obtained by the estance technique.

A special effect occurs when recording the variable surface tension of ferromagnetic electrodes. In a magnetized electrode, the sections of the electrode through which the current passes experience a force in the magnetic field set up by the electrode itself. This leads to an additional deformation of the electrode that is superimposed on the deformation caused by the variation of surface tension. This effect distorts the estance–potential curve, particularly the sections in the vicinity of zero values. It was found that demagnetization of iron-group metals and of a number of their alloys in an alternating magnetic field practically completely eliminates this interference. Demagnetization was carried out prior to the experiments by placing the sample next to the pole of an electromagnet while passing currents with frequencies of 50 to 500 Hz through its windings. The electrodes were sheets measuring $0.5 \times 4 \times 20$ mm. The estance measurements were made by the method of [5].

Many metals interact with redox media. It had been assumed previously, therefore, that the metals as a rule should be protected with a thin galvanic film before any thermal simulation of their surface tension. They were gold-plated.

It was found during the present work that with many practically important metals, thermal simulation can be performed without prior gold-plating and yields the same results as the simulation with gold-plating. These are the metals which in contact with the redox system undergo passivation with the formation of a thin protective, conducting film on the surface. This film transforms the sample to a practically inert electrode reversible relative to the oxidized and reduced forms remaining in the solution. Such is the effect of hexacyanoferrate solution on samples of widely used structural materials: iron, cobalt, nickel, titanium, chromium, vanadium, niobium, molybdenum, tungsten, tantalum, rhenium, and their alloys.

Traces of the modulus of estance $|\partial\gamma/\partial q|$ as function of electrode potential E obtained for iron and nickel in aqueous 0.1 N KOH solution are shown in Figs. 1 and 2; here γ is the surface tension of the solid, q is the surface charge density of the electrode, E is given on the rhe scale in the same solution, and the signs of $\partial\gamma/\partial q$ (which coincide with those of $\partial\gamma/\partial E$) are indicated at the corresponding sections of the $|\partial\gamma/\partial q|$ vs. E curves. The horizontal section in the left-hand part of Fig. 2 is the signal level in thermal simulation of the surface tension in aqueous 0.1 M $K_3Fe(CN)_6$ + 0.1 M $K_4Fe(CN)_6$ solution. Metals having 99.99% purity, twice distilled water, and "specially pure" chemicals were used in the experiments. The electrodes were electropolished: iron in a mixture (1 : 1 by volume) of nitric acid and acetic anhydride, and nickel in a mixture (1 : 3 : 4) of water, sulfuric acid, and glycerol. Oxygen was removed from the solutions by passing helium. The experiments were set up at 20 ± 1°C. The potential scan rate was 24 mV/sec in Fig. 1 and 21 mV/sec in Fig. 2. Polarization to the initial potential lasted 1 min (the interval between the cycles of potential variation).

The potential ranges covered in the experiments of Figs. 1 and 2 include the regions of oxygen (left-hand part of the oscillographic trace) and hydrogen adsorption (right-hand part). In the region of oxygen adsorption the curves display appreciable hysteresis owing to irreversibility of the process. In this respect iron and nickel are similar to the platinum-group metals. However, no similarities exist in the hydrogen region. Platinum, iridium, and rhodium during hydrogen adsorption yield $\partial\gamma/\partial q$ vs. E curves where the forward and return scan are indistinguishable [6]. For iron, nickel, and cobalt, the departure from reversibility is clearly seen in the hydrogen region as well. It is smallest for nickel (Fig. 2).

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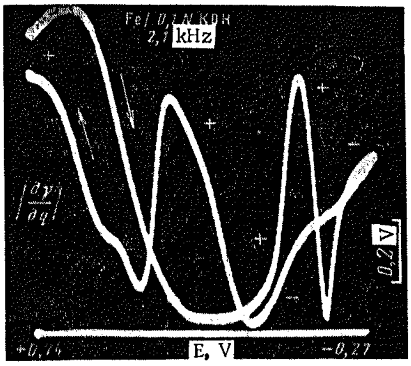

Fig. 1

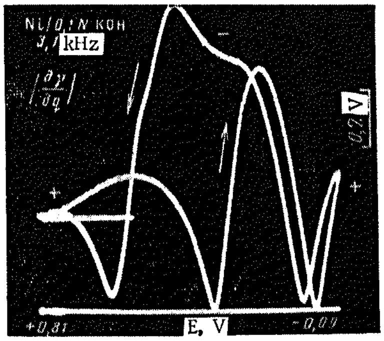

Fig. 2

Fig. 1. Oscillographic estance vs. potential trace recorded at iron in alkaline medium.

Fig. 2. Oscillographic estance vs. potential trace recorded at nickel in alkaline medium.

The oscillographic traces for nickel are W-shaped; $\partial\gamma/\partial q$ changes sign twice. As the potential is made more positive, the first zero transit of $\partial\gamma/\partial q$ occurs almost reversibly and is a direct effect of potential variation. The second zero transit, i.e., the return to positive values, is due to oxygen chemisorption and has no direct relation to potential variation; the increase in surface coverage by oxygen and the associated increase in $\partial\gamma/\partial q$ continue even when the potential is arrested in the oxygen region. For iron the oxidation process is more complicated (it is split up into two stages), but it, too, ends with $\partial\gamma/\partial q$ increasing to high positive values (around 1 V).

The increase of $\partial\gamma/\partial q$ with time at constant potential becomes slower as the amount of chemisorbed oxygen on the metal surface becomes higher. Under these conditions, but now on an oxidized surface, the potential again becomes the decisive factor for $\partial\gamma/\partial q$. At such an oxidized surface, $\partial\gamma/\partial q$ decreases with increasing potential. The slope of the $\partial\gamma/\partial q$ vs. E curve is close to -1 (the same is found for platinum). A linear extrapolation of this section yields $\partial\gamma/\partial q = 0$ for $E \approx 1.4$ V in the case of nickel and for $E \approx 1.7$ V in the case of iron (Figs. 1 and 2).

A certain error (on the order of 0.1 V) is introduced into the recorded value of $\partial\gamma/\partial q$ and into the value found for E by the heat evolved during electrochemical adsorption [7].

The decrease of $\partial\gamma/\partial q$ with increasing E is common for electrodes under the simplest conditions, in particular with electrostatic adsorption of ions. It is equivalent to a monotonic change of electrode charge with potential, and the zero transit of charge corresponds to a single occurrence of a zero value for quantity $\partial\gamma/\partial q$. The observed slope of -1 is characteristic for electrostatic adsorption; under these conditions the zero of estance is close to the potential of zero charge [6]. The similarity between the completely oxidized electrode and an electrode without chemisorption is possible owing to the electronic conductivity of the oxides on metals of the platinum and iron group.

The anomalous positivity of $\partial\gamma/\partial q$ during oxygen chemisorption and the type of potential variation of $\partial\gamma/\partial q$ described above imply, under these conditions, that the electrochemical oxidation of nickel and iron is attended by a strong displacement of the point of zero charge in the positive direction, to the values found above by extrapolation. It had been suggested previously that such a displacement may occur [1]. The values found here are more than 1 V more positive than the zero-charge potential of any polarizable electrode with nonoxidized surface [1]. It follows from the data reported that the metal's own double layer, i.e., the double layer located in the region with electronic conduction, is changing during oxidation of the metal. The observed direction of the displacement implies that the side of the metal's own double layer which is turned outward becomes more negative.

The varying electric field that is applied by varying the electrode potential is concentrated in the electrostatic double layer, i.e., in the electrolyte at the metal surface, and practically does not pass beneath the metal surface. Hence the metal's own double layer has no direct effect on the varying component of surface tension. At fixed potential, however, it determines the charge density on the two sides of the electrostatic double layer, which under these conditions provides the chief contribution to $\partial\gamma/\partial q$.

The formation of dipoles which occurs owing to oxidation is compensated, at fixed electrode potential, by a flow of additional charges to the sides of the electrostatic double layer. When the oxygen dipoles are located between the sides of this layer, then their contribution to varying surface tension due to coulombic interaction is largely neutralized by said additional charges. The strong displacement of the zero-charge point observed here, viz., by more than 1 V, indicates that such neutralization does not occur. This shows, in conjunction with the unit slope of the estance−potential curve, that the chemisorbed oxygen is located outside the electrostatic double layer. A similar conclusion concerning the spatial separation of surface oxide layer and electrostatic double layer had been reached previously by analysis of the estance−potential curves obtained at electrodes of platinum metals [6].

Among the other special features detected by the present method for the iron-group metals, it is conspicuous to note the anomalous negativity of $\partial\gamma/\partial q$ in the region of hydrogen adsorption on iron and cobalt. This can be regarded as an indication that the side of the metal's own double layer which is turned outward becomes more positive during hydrogen adsorption.

LITERATURE CITED

1. A. N. Frumkin, Potentials of Zero Charge [in Russian], Nauka, Moscow (1979), p. 88.
2. B. N. Kabanov, Electrochemistry of Metals and Adsorption [in Russian], Nauka, Moscow (1966).
3. R. Kh. Burshtein, N. A. Shurmovskaya, T. V. Kalish, and L. A. Larin, "The effect of adsorbed gases on the surface properties of metals," Élektrokhimiya, 13, No. 6, 799 (1977).
4. K. V. Rybalka and D. I. Leikis, "Determination of the potential of zero charge of iron," Élektrokhimiya, 11, No. 10, 1619 (1975).
5. A. Ya. Gokhshtein, Soviet Patent No. 658 442; Byull. Izobr., No. 15 (1979).
6. A. Ya. Gokhshtein, The Surface Tension of Solids, and Adsorption [in Russian], Nauka, Moscow (1976), p. 196.
7. A. Ya. Gokhshtein, "Surface tension depression and heat evolution during adsorption," Élektrokhimiya, 16, No. 7, 1080 (1980).

ELECTROCHEMICAL BEHAVIOR OF MOLYBDENUM OXIDE FILMS IN PROPYLENE CARBONATE

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The reduction mechanism of molybdenum oxides in aprotic solutions has been studied previously at porous electrodes. It was suggested in [1, 2] that the process yields $xMoO_3 \cdot yMoO_2 \cdot Li_2O$ and that diffusion of the alkali metal in the solid phase is the rate-determining step in the reduction.

From results obtained when determining the free energy of formation of Mo, W, and V bronzes and comparing them with actually measured cell voltages between the corresponding oxide cathodes and a lithium anode, the conclusion was reached in [3] that reduction yields nonstoichiometric compounds $Li_xV_2O_5$, Li_xWO_3, or Li_xMoO_3. According to data of [4], MoO_3 reacts with at most 1.55 g-eq of lithium, and two new phases result, but their composition has not been given.

It was the aim of the present work to examine the reduction mechanism of thin MoO_3 films in propylene carbonate (PC) as well as the conditions under which the electrode may function reversibly.

Thin molybdenum trioxide films were obtained by anodizing highly pure molybdenum sheet (99.98) at room temperature and a current density of 2.4 mA/cm^2 in the electrolyte suggested in [5], which contains 1 M sodium tartrate, 0.13 M tartaric acid, and 0.01 M sodium carbonate. The films were annealed for 2 h at a temperature of 550°C. The electrodes were stored in a desiccator over P_2O_5. The film thickness was deter-

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