PHYSICAL CHEMISTRY

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1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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DETERMINATION OF THE POTENTIAL OF ZERO CHARGE OF LEAD DIOXIDE ELECTRODES BY THE METHOD OF HARDNESS MEASUREMENT

(Presented by Academician P. A. Rehbinder, 18 VII 1956)

In the works of P. A. Rehbinder and E. K. Venstrem ([1]-[3]) it was shown that the electrocapillary curve for the decrease in the strength of a solid metal as a function of the potential jump at the metal—electrolyte boundary is completely analogous to the classical electrocapillary curve for the decrease of the surface tension of a liquid metal. Later E. K. Venstrem, V. I. Likhtman, and P. A. Rehbinder ([4]), using lead as an example, showed that when hardness is measured by the pendulum method under conditions of sufficiently strong deformation and dispersion of the metal, a normal curve with a maximum is obtained; whereas under conditions of measuring the limiting friction between the pendulum support and the metal, the curve has a minimum. However, independently of this, the extremal points of the curves always lie at the potential of zero charge.

The use of such methods makes it possible to determine directly the potential of zero charge of a solid metal in concentrated solutions, which is impossible or very difficult to do by other methods (such as, for example, the method of measuring the capacity of the double layer, or the adsorption method).

We have applied the method of hardness measurement to the determination of the potential of zero charge of electrodes made of PbO_2. Such a direct determination of the potential of zero charge in a concentrated solution is especially interesting in the case of a PbO_2 electrode used in the lead accumulator: as I. G. Kiseleva and B. N. Kabanov ([5]) have shown, irreversible adsorption of sulfuric acid occurs on this electrode, changing the electrochemical properties of the electrode (in particular, the oxygen overvoltage changes). As a result of such adsorption, a change in the potential of zero charge upon passing from dilute solutions to concentrated ones is also highly probable.

To solve the problem posed, we carried out measurements in 0.1 N and 8 N H_2SO_4. The measurements in dilute acid were carried out by us in order to compare the results obtained with data obtained by other methods.

The measurements showed that a PbO_2 deposit obtained by anodic oxidation of lead in H_2SO_4 (analogously to the way this is done in the manufacture of surface plates for a lead accumulator) possesses physical properties sufficient for

Fig. 1. Curves of the dependence of hardness on potential for electrodes of PbO_2 in H_2SO_4. A –in 0.1 N H_2SO_4; B –in 8 N H_2SO_4

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carrying out hardness measurements by the pendulum method with dispersion of the surface. The curve of the dependence of hardness on potential has a well-defined maximum. The PbO_2 deposit studied was obtained by prolonged (over several days) anodic oxidation of metallic lead in the same solution in which the measurements were made. Fig. 1 presents curves obtained

on the PbO_2 electrode. As is seen from the figure, the maximum of the curve in 0.1 N H_2SO_4 lies at a potential of ~1.9 V (N.H.E.). We believe that this value corresponds to the potential of zero charge. It should be noted that, by the method of measuring the double-layer capacitance and by the adsorption method, B. N. Kabanov, I. G. Kiseleva, and D. I. Leikis ([6]) obtained a value of the potential of zero charge of 1.8 V (N.H.E.) in 0.01 N and 0.1 N H_2SO_4. The difference of only ~0.1 V between the results obtained by different methods is evidence of the applicability of these methods to electrochemical deposits—such as PbO_2—especially if one takes into account that, in the case of metallic electrodes, the difference between results obtained by different methods reaches values of 0.2-0.3 V (for example, Tl, Cd, etc.) ([7]-[9]).

Fig. 1. Curves of the dependence of hardness on potential for electrodes of PbO_2 in H_2SO_4. **A** –in 0.1 N H_2SO_4; **B** –in 8 N H_2SO_4

As is seen from Fig. 1, the maximum of curve **B**, obtained in 8 N H_2SO_4, lies at a potential of 1.7 V, i.e., 0.2 V more negative than in 0.1 N H_2SO_4. The shift of the potential of zero charge upon a change in the H_2SO_4 concentration is qualitatively consistent with ideas concerning the surface-active properties of the anion of sulfuric acid ([5], [10], [11]). As is known, specifically adsorbing anions shift the maximum of the electrocapillary curve on mercury to the negative side. Apparently, in a concentrated solution of sulfuric acid, more acid anions are specifically adsorbed on the surface than in a dilute solution, which causes the indicated shift of the potential.

When considering curve **A** in Fig. 1, attention is drawn to the asymmetry of the curve, expressed in a sharper decrease in hardness with potential in the region of positive surface charges than in the region of negative charges. In the main, this effect, as is known from the theory of electrocapillary phenomena, is due to the fact that a positive surface charge promotes the adsorption of specifically active anions. This phenomenon, apparently, can be related to the results obtained when measuring the double-layer capacitance on the same electrode ([6]). At potentials above 1.9 V, a sharp increase in the double-layer capacitance was observed, which was tentatively explained by an increase in the true surface due to a change in the crystalline structure of the surface. It may be assumed that the sharp decrease in hardness and the increase in capacitance are partly a consequence of surface dispersion caused by adsorption ([12], [13]) of sulfuric acid anions. Such an assumption agrees with the fact that a deposit obtained in a concentrated solution (8 N H_2SO_4) and, naturally, adsorbing more acid, has a reduced hardness–i.e., is more readily dispersed (cf. Fig. 1: curve **A** lies considerably above curve **B**). In the case of the concentrated solution (curve **B**) there is no noticeable asymmetry. This is probably connected with the fact that the total amount of specifically adsorbed acid anions in the concentrated solution is so large even in the region of negative surface charges* that it changes little upon transition into the region of positive charges. In other words, sulfuric acid molecules are partially adsorbed.

Thus it has been shown that the method of measuring hardness can be applied to the determination of the potentials of zero charge of oxide electrodes. By this method one can measure the dependence of the potential of zero charge on the concentration of the electrolyte.

* Possibly in connection with the simultaneous adsorption of cations.

In conclusion, we consider it a pleasant duty to express our gratitude to Prof. B. N. Kabanov for valuable advice that contributed to the completion of the work.

Received
21 VI 1956

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Note: Figure translations are in progress. See original paper for figures.