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1962

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Abstract

Full Text

PHYSICAL CHEMISTRY

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KINETIC HINDRANCES TO THE FORMATION OF A NEW PHASE DURING THE CATHODIC REDUCTION OF OXIDES OF CERTAIN METALS

(Presented by Academician A. N. Frumkin, 24 VII 1961)

Kinetic hindrances to the formation of a new phase in the process of electrocrystallization of metals from solutions of their salts are well known ([1]). In the electrodeposition of metals on foreign electrodes, these hindrances manifest themselves as sharp polarization peaks at the initial moments of the process. Similar phenomena should also be observed in the case of cathodic reduction of sparingly soluble metal oxides that are free of the final reaction product. During cathodic reduction in alkalis of mercuric oxide, as noted in the work of P. D. Lukovtsev ([2]), and of silver suboxide (Dirks and Werkam ([3])), increased polarization is indeed observed at the initial moment of the process. However, the authors cited associate this phenomenon with the high resistance of the oxides, which accordingly leads to large ohmic losses at the electrodes; these losses disappear when reaction products appear—droplets of mercury or silver crystallites.

To clarify the nature of the indicated polarization peak, we carried out oscillographic recording of changes in the potentials of mercuric-oxide and silver-oxide electrodes at the beginning of cathodic reduction, and determined the dependence of the magnitude of the drop in polarization on the strength of the current passed.

In the case of mercuric-oxide electrodes, the specimens were prepared by pressing red mercuric oxide of "ch.d.a." grade, mixed with thermally enriched graphite (with an ash content of 0.1%), into steel nickel-plated cups. The tests were conducted in concentrated solutions of caustic potassium (5-10 *N*) with an addition of zinc oxide. Metallic zinc was used as the auxiliary electrode. Constancy of the current in the circuit was ensured by inserting into it a high-voltage mercuric-oxide battery. The measurements were carried out by oscillographic recording of the change in the potential of the mercuric-oxide electrode relative to a zinc reference electrode. An MPO-2 type oscillograph was used; the potential difference under study was fed to the oscillograph through a direct-current amplifier with an amplification factor of 1,000,000.

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Fig. 1. Oscillograms of the change in potential of a mercuric-oxide electrode at the moment the current is switched on: *a*—2 mA/cm^2, *b*—8 mA/cm^2, *v*—32 mA/cm^2, *g*—80 mA/cm^2, *d*—200 mA/cm^2

Figure 1: Fig. 1. Oscillograms of the change in potential of a mercuric-oxide electrode at the moment the current is switched on: *a*—2 mA/cm^2, *b*—8 mA/cm^2, *v*—32 mA/cm^2, *g*—80 mA/cm^2, *d*—200 mA/cm^2

The form of the oscillograms obtained is shown in Fig. 1. The oscillograms reveal, at the initial stage of discharge, a characteristic polarization "peak." The nature of this peak can be clarified if one considers the magnitude of the difference $\Delta\varphi$ between the polarization at the peak and the steady value of the polarization. The dependence of $\Delta\varphi$ on current density is shown in Fig. 2; from it one can see that the value of $\Delta\varphi$ increases strongly with increasing current in the region of small currents and changes practically not at all in the region of large currents. The values of $\Delta\varphi$ obtained do not change when the concentration of caustic potassium is varied (the tests were carried out with solutions in the interval 5-10 *N*), when red mercuric oxide is replaced by considerably more finely dispersed yellow mercuric oxide, when considerably coarser-grained elemental graphite is used instead of thermally enriched graphite, and also when the porosity of the electrodes is increased.

These facts, in particular the course of the curve $\Delta\varphi$ versus i, are difficult to explain on the assumption that the drop in polarization is associated with a decrease in ohmic losses at the electrode. If this assumption were correct, one would rather expect a linear dependence of $\Delta\varphi$ on i.

A number of facts are also at variance with this assumption, indicating that the electrochemical stage of reduction of mercuric oxide proceeds through the solution (4).

The increased polarization observed experimentally at the beginning of cathodic reduction of mercuric oxide should be explained by difficulties in the formation of a new phase—droplets of metallic mercury; the value $\Delta\varphi$ should in this case be regarded as the overvoltage required for the formation of these droplets. Qualitatively, this assumption agrees well with the facts cited above. In addition, the very course of the curve $\Delta\varphi$ versus i, and the absolute value of the limiting value of $\Delta\varphi$ at high currents—0.16 V—are in good agreement with the data of Erdey-Grúz and Wick, who directly measured the overvoltage in the formation of mercury droplets on graphite from solutions of mercuric nitrate (5). The limiting value of the overvoltage obtained by them was 0.2 V. In their experiments it was reached at considerably lower currents than in our case, since they used electrodes with a correspondingly smaller true surface area. Better agreement of the limiting value of $\Delta\varphi$ is difficult to expect if one takes into account the differences, in the cases considered, in diffusion difficulties.

Fig. 1. Oscillograms of the change in potential of a mercuric-oxide electrode

at the moment the current is switched on: a–2 mA/cm^2, b–8 mA/cm^2, v–32 mA/cm^2, g–80 mA/cm^2, d–200 mA/cm^2.

The statistical treatment (5) shows that the overvoltage $\Delta\varphi$ in the formation of mercury droplets is related to the current density by the equation

$$\ln i = a + b\frac{1}{(\Delta\varphi)^2},$$

where a and b are constants depending on the surface tension, the magnitude of the true surface area, and the temperature. The qualitative course of the dependence of $\Delta\varphi$ on i, obtained experimentally, fully corresponds to the indicated equation. The data obtained on the independence of the overvoltage under consideration from the type of mercuric oxide and graphite and from the porosity of the electrode are in exactly the same agreement with it. Upon prolonged residence in alkali of partially discharged mercuric-oxide electrodes and their subsequent discharge, an initial polarization peak is again observed. This fact can be explained by the mercury droplets formed during the preliminary discharge, in the course of the electrode' s residence in alkali, coalescing into larger drops and, moreover, by their being partially covered with an oxide film. The initial stage of cathodic reduction of electrodes made of silver suboxide Ag_2O was studied by a procedure completely coinciding with that used for mercuric-oxide electrodes. The specimens were prepared from a mixture of "chemically pure" silver suboxide and thermally enriched graphite. The oscillograms of switching on for silver-suboxide electrodes have the same appearance as for mercuric-oxide electrodes (see Fig. 2). In the case of silver suboxide, the initial polarization peak should be associated with difficulties in the formation of a new phase, and not with a decrease in ohmic losses owing to the formation of reaction products with good conductivity.

In connection with the consideration of the nature of the initial polarization peak, cases of cathodic reduction of oxides are of special interest when,

it occurs not up to the metallic phase, but up to a lower oxide with poor conductivity, and when the indicated polarization peaks are nevertheless observed. Such cases include manganese dioxide.

The cathodic reduction of manganese dioxide in neutral and alkaline electrolytes proceeds according to the equation:

$$MnO_2 + H_2O + e^- \rightarrow MnO(OH) + OH^-.$$

As P. D. Lukovtsev showed, this reaction proceeds through the solid phase and is accompanied by the formation of a phase of variable composition, including tetravalent and trivalent manganese (^{2}). This explains the gradual drop in the e.m.f. of manganese-zinc cells as their degree of discharge increases.

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Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 2. Dependence of $\Delta\varphi$ on i for mercuric oxide (1) and silver suboxide electrodes (2)

Fig. 3. Voltage–time curves for different types of manganese dioxide: 1 —sample No. 1, 2 —sample No. 2, 3 —sample No. 3

In the studies of Lukovtsev and in other works on the cathodic polarization of manganese dioxide (^{2}), no increased polarization was observed at the beginning of discharge. As a more detailed examination shows, in all these works either natural manganese dioxide was used, or artificial preparations obtained by oxidation of divalent manganese. The electrochemical properties of manganese dioxide depend strongly on the type of crystalline modification used, as well as on the method of its preparation. Since the cathodic reduction of manganese dioxide proceeds through the solid phase, one may suppose that, in the case of using dioxide samples not inclined to form solid solutions with compounds of trivalent manganese, difficulties should arise at the beginning of formation of the new phase during discharge of the electrodes.

In order to detect such cases, samples of manganese dioxide obtained by decomposition of potassium permanganate were tested. If potassium permanganate is treated with concentrated sulfuric or nitric acid, it decomposes with formation of manganese dioxide and oxygen (^{6}). As X-ray diffraction patterns show, the structure of the product formed when sulfuric acid is used (sample No. 1) corresponds to the α-modification, and when nitric acid is used (sample No. 2) to the γ-modification of manganese dioxide (^{6}). In addition to these samples, for comparison manganese dioxide obtained by electrolytic oxidation of manganese sulfate (sample No. 3) was tested.

The electrodes for the tests were prepared in the form of tablets by pressing manganese dioxide mixed with acetylene black, ammonium chloride, and electrolyte solution. An aqueous solution of ammonium chloride and zinc chloride was used as the electrolyte. Sheet zinc of Ts-O grade served as the auxiliary electrode. The tested electrodes were cathodically polarized with a current of 150 μA/cm^2. Since under these conditions

zinc electrodes are practically not polarized, the potentials of the electrodes under test were measured directly relative to the auxiliary electrode, i.e., by the cell voltage.

Figure 3 presents voltage–time curves for the three above-mentioned types of manganese dioxide. As can be seen from Fig. 3, in the case of samples obtained by decomposition of permanganate (samples No. 1 and No. 2), a voltage minimum is indeed observed on the initial portion of the curve, whereas on the curve for sample No. 3 it is absent. In addition, the first curves differ from the latter by a considerably greater constancy of voltage (after the minimum), which confirms the assumption that the types of dioxide under consideration have a lesser tendency to form phases of variable composition than is the case for other types of manganese dioxide.

It is interesting to note that the X-ray diffraction patterns of sample No. 3 indicate that this type of manganese dioxide also corresponds, in its crystal structure, to the γ-modification. However, the fundamental difference between the discharge curves of this type of dioxide and of the sample obtained by decomposition of nitric-acid permanganate indicates that there are certain differences between their structures that are not detected by phase X-ray analysis.

When comparing the two cases of difficulty in the formation of a new phase discussed above—during the cathodic reduction of mercuric oxide and silver suboxide, on the one hand, and manganese dioxide, on the other—the difference in the rates of the processes is striking. If in the first case the difficulties disappear within seconds, then in the second case this occurs over a time of the order of 100 hours. This difference is naturally explained by the fact that, whereas on mercuric oxide and silver oxide the cathodic process proceeds through solution, on manganese dioxide, as already noted above, it proceeds through the solid phase, and therefore a much longer time is required here for the formation of crystals of the new phase.

All-Union Scientific Research Institute
of Current Sources

Received
24 VII 1961

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