KINETIC HINDRANCES IN THE FORMATION OF A NEW PHASE DURING THE CATHODE REDUCTION OF CERTAIN METAL OXIDES

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The kinetic hindrances in the formation of the new phase during the electrocrystallization of metals from salt solutions are widely known [1]. In the electrodeposition of metals on electrodes of another sort, these hindrances show up as sharp polarization peaks at the start of the reaction. Similar phenomena should also be observed in the cathode reduction of difficultly soluble metallic oxides, which are free of the end product of the reaction. In the alkaline cathode reduction of mercuric oxide, as was noted in a paper by P. D. Lukovtsev, [2], and of silver oxide (Dirkse and Werkema [3]), an increase in polarization is actually observed at the start of the reaction. However, the authors mentioned relate this phenomenon to the large resistance of the oxides, which causes large ohmic losses at the electrodes, these later disappearing when the reaction products are formed, mercury droplets in one case, or silver crystallites in the other. In order to discover the nature of the polarization peak, we have made oscillographic measurements of the potentials of an oxide-mercury and of an oxide-silver electrode at the start of cathode reduction, and the relationship has been found between the magnitude of the polarization drop and the strength of the current being passed.

With the oxide-mercury electrodes, the samples were prepared by pressing "analytically pure" grade red oxide of mercury, mixed with thermally enriched graphite (ash content 0.1%), into nickel plated steel cups. The experiments were made in concentrated solutions of caustic potash (5-10 N) with zinc oxide added. Metallic zinc was used as the auxiliary electrode. The current in the circuit was kept constant by connecting in a high-voltage oxide-mercury battery. The measurements were made by taking an oscillograph record of the change in potential of the oxide-mercury electrode relative to the zinc comparison electrode. A type MPO-2 oscillograph was used, and the potential difference being studied was fed to the oscillograph through a D.C. amplifier with an amplification of 1,000,000.

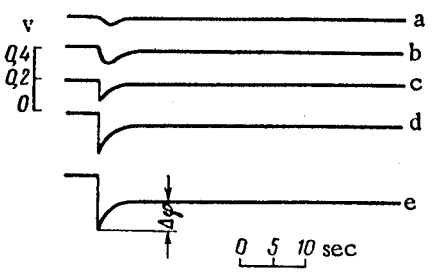


Fig. 1. Oscillograms of the change in potential of an oxide-mercury electrode at the moment the current is turned on: a) 2 ma/cm^2; b) 8 ma/cm^2; c) 32 ma/cm^2; d) 80 ma/cm^2; e) 200 ma/cm^2.

The appearance of the oscillograms obtained is shown in Fig. 1. The oscillograms catch the characteristic polarization "peak" at the initial stage of discharge. The nature of the peak may be discovered, if we consider the magnitude of the difference $\Delta\varphi$ between the polarization at the peak and the stable value of polarization. The curve $\Delta\varphi$ as a function of current density is shown in Fig. 2, from which it is seen that the magnitude of $\Delta\varphi$ increases greatly as the current is increased in the small current region, and remains practically unchanged in the high current region. The values of $\Delta\varphi$ found do not change when the caustic potash concentration is changed (the experiments were made with solutions in the range 5-10 N), nor when the red oxide of mercury is replaced by the considerably more finely disperse yellow oxide of mercury, nor if considerably more coarsely disperse elementary graphite is used in place of thermally enriched graphite, nor if the porosity of the electrodes is increased.

These facts, and in particular the form of the curve $\Delta\varphi$ against i are difficult to explain, if we go on the assumption that the polarization drop is a matter of reduction in the ohmic losses at the electrode. If this assumption were true, we would be more likely to expect a linear relationship between $\Delta\varphi$ and i.

This assumption is also contradicted by a number of facts, which give evidence to the effect that the electrochemical stage of the reduction of mercuric oxide occurs through the solution [4].

The increased polarization which is observed experimentally at the start of cathode reduction of mercuric oxide must be explained in terms of hindrances to the formation of the new phase, in this case droplets of metallic mercury, and the value $\Delta\varphi$ must here be considered as the value of overvoltage required to form the droplets. Qualitatively, this assumption is in good agreement with the facts given above. In addition, the form of the curve of $\Delta\varphi$ against i itself, and the absolute magnitude of the limiting value of $\Delta\varphi$ at high currents, namely 0.16 v, are in good agreement with the data of Erdey-Gruz and Wick, who made direct measurements of the overvoltage in the formation of mercury droplets on graphite from solutions of mercury nitrate [5]. The limiting overvoltage which they found was equal to 0.2 v. This value was reached in their experiments at considerably lower currents than in our case, since they used electrodes with a correspondingly less intrinsic surface. Any better agreement in the limiting value of $\Delta\varphi$ is scarcely to be expected, if we consider the differences in the diffusional hindrances of the cases being discussed.

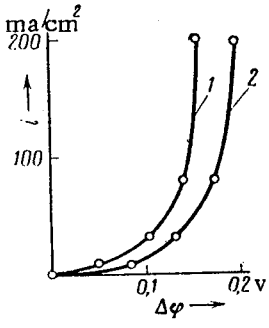


Fig. 2. $\Delta\varphi$ as a function of i for mercury oxide (1), and silver oxide electrode (2).

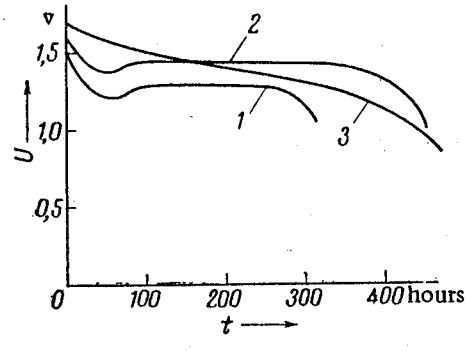


Fig. 3. Potential–time curves for various types of manganese dioxide: 1) Sample No. 1; 2) sample No. 2; 3) sample No. 3.

A 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 value of the intrinsic surface, and the temperature. The qualitative form of the curve of $\Delta\varphi$ against i, obtained experimentally, fits this equation completely. It is also in exact agreement with the data showing that the overvoltage in question is independent of the type of mercuric oxide or graphite, and is independent of the porosity of the electrode. If the partially discharged oxide-mercury electrodes are kept in the alkali for a long time, and are then charged up again, an initial polarization peak is observed. This fact may be explained by saying that the mercury droplets, formed during previous discharge while the electrode was being kept in the alkali, coalesce into larger drops, and, in addition, by saying that they are partly covered by an oxide film. The study of the initial stage of the cathode reduction of electrodes made of silver oxide, Ag_2O, was made by exactly the same method as was used with oxide-mercury electrodes. The samples were prepared from a mixture of "pure" grade silver oxide and thermally enriched graphite. The transient oscillograms for the silver oxide electrodes have the same form as for the mercury oxide electrodes (see Fig. 2). In the case of silver oxide, the initial polarization peak must be connected with hindrances to the formation of the new phase, and not with a reduction in ohmic losses resulting from the appearance of reaction products having good conductivity.

In connection with any discussion of the nature of the initial polarization peak, particular interest is presented by the cathode reduction of oxides, where the reduction occurs not to a metallic phase, but to a lower oxide with poor conductivity, but where, nevertheless, the polarization peaks are observed. Manganese dioxide is one of these cases.

Cathode reduction of manganese dioxide in neutral or alkaline electrolytes proceeds according to the equation

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

As P. D. Lukovtsev has shown, this reaction goes through the solid phase, and is accompanied by the formation of a phase of variable composition, which includes quadri- and trivalent manganese [2]. This explains the gradual drop off in e.m.f. of manganese-zinc cells as the degree of discharge is increased. In Lukovtsev's studies and other papers on the cathode polarization of manganese dioxide [2], no increase in polarization is observed at the start of discharge. As is shown by a more detailed consideration, all these workers used either natural manganese dioxide, or artificial forms, prepared by oxidizing bivalent manganese. The electrochemical properties of manganese dioxide are strongly dependent on the type of crystalline modification used, as well as on the method of preparation. Since the cathode reduction of manganese dioxide goes through the solid phase, it may be assumed that if samples of the dioxide are used, which are not inclined to form solid solutions with compounds of quadrivalent manganese, hindrances can arise at the start of formation of the new phase during the discharge of the electrodes. To the end of observing cases of this sort, tests were made on manganese dioxide samples, prepared by decomposing potassium permanganate. If potassium permanganate is treated with concentrated sulfuric or nitric acid, it decomposes to form manganese dioxide and oxygen [6]. As the x-ray diagrams show, the structure of the product formed using sulfuric acid (sample No. 1) corresponds with the α-modification, while using nitric acid (sample No. 2) gives the γ-modification of manganese dioxide [6]. In addition to these samples, a comparison test was made on manganese dioxide prepared by the electrolytic oxidation of manganese sulfate (sample No. 3).

The test electrodes were prepared in the form of tablets, pressed from manganese dioxide mixed with acetylene black, ammonium chloride, and a solution of an electrolyte. The electrolyte used was an aqueous solution of ammonium chloride and zinc chloride. The auxiliary electrode was Ts-0 grade sheet zinc. The test electrodes were given a cathode polarization by a current of 150 $\mu a/cm^2$. Since, under these conditions, the zinc electrodes undergo practically no polarization, the potentials of the test electrodes were measured directly with respect to the auxiliary electrode, i.e., from the voltage of the cells.

Figure 3 gives potential–time curves for the three types of manganese dioxide mentioned above. As may be seen from Fig. 3, the samples prepared by decomposing permanganate (samples No. 1 and No. 2) actually show a voltage minimum in the initial part of the curve, while it is absent from the curve of sample No. 3. In addition, the first curves differ from the last one in that they show a considerably more constant voltage (after the minimum), which confirms the assumption that the types of manganese dioxide under consideration are less inclined to form phases of variable composition, than is the case with the other types of manganese dioxide.

It is interesting to note that the x-ray diagrams of sample No. 3 give evidence for the fact that this type of manganese dioxide also corresponds in its crystal structure with the γ-modification. However, the thoroughgoing difference between the discharge curves of this type of dioxide and the sample prepared by decomposition of permanganate with nitric acid, gives evidence for the fact that there is some difference in structure between them which is not caught by the x-ray phase analysis.

In comparing the two different cases of hindrance to the formation of the new phase,—in the cathode reduction of mercuric oxide and silver oxide on the one hand, and of manganese dioxide on the other—what strikes the eye is the difference in rate of the processes. Whereas, in the first case, the hindrances disappear in the course of seconds, in the second case this takes time of the order of 100 hours. This difference is naturally to be explained by the fact that, whereas on mercuric oxide and silver oxide the cathode process goes through the solution, on manganese dioxide, as has already been mentioned above, it goes through the solid phase, in view of which a considerably longer time is required to form the crystallites of the new phase.

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