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THE ELECTROCHEMICAL BEHAVIOUR OF OXYGEN AND HYDROGEN PEROXIDE ON SILVER ELECTRODES*

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Abstract—The reduction of oxygen and the reduction and oxidation of hydrogen peroxide at silver electrodes is examined, with special reference to the side reactions involving the metal and its corrosion products.

Résumé—On a étudié la réduction de l'oxygène ainsi que la réduction et l'oxidation de H_2O_2 sur des électrodes d'argent; on a tenu compte, en particulier, des réactions secondaires, auxquelles participent le métal et ses produits de corrosion.

Zusammenfassung—Die Reduktion von Sauerstoff sowie die Reduktion und Oxydation von Wasserstoffperoxyd an Silberelektroden wurde untersucht. Spezielle Beachtung schenkte man Nebenreaktionen, an denen das Metall und seine Korrosionsprodukte beteiligt sind.

1. INTRODUCTION

THE electrochemical processes concerning oxygen and hydrogen peroxide on various electrodes including silver have been studied by several authors, especially the cathodic reduction of oxygen.

Tomashoff[1] obtained cathodic polarization curves of oxygen on silver for various degrees of agitation of the solution. Delahay[2] studied the process of oxygen reduction on various metals in neutral solution and considered the contribution of the two processes (a) $O_2 \rightarrow H_2O_2$ and (b) $O_2 \rightarrow H_2O$ to the total current for the oxygen reduction. In the case of silver, the two processes occur simultaneously: at high current densities corresponding to the most negative tension values (-1 V on the hydrogen scale), process (b) overcomes process (a).

Kresilschikov *et al.*[3] obtained similar polarization curves and concluded that the reduction of molecular oxygen takes place at low current density and the reduction of atomic adsorbed oxygen takes place at high current density. In both cases the reduction occurs through intermediate stages.

The cathodic reduction of oxygen on the silver electrode was also considered by Bianchi[4] who obtained polarization curves for solutions of various pH and observed that the tension of the process of oxygen reduction was almost independent of the pH.

In the study of the electrochemical processes of oxygen and hydrogen peroxide on silver electrodes we consider the possibility of interference by the processes of reduction or oxidation of the silver compounds. In the case of graphite[5] and platinum[6] we observed that the electrochemical processes of the system H_2O–H_2O_2–O_2 occurred at the same time as those concerned with the electrode metal itself.

The general electrochemical behaviour of silver was studied by Delahay *et al.*,[7] who collected the thermodynamic data for silver and its compounds in a potential/pH diagram.

The electrochemical processes of formation of silver oxides were studied by several authors[8] on account of the importance of these processes in the field of the dry batteries.

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We have obtained anodic and cathodic polarization curves on silver electrodes in solutions of various pH. The electrochemical processes concerning oxygen and hydrogen peroxide and those concerning silver compounds were examined. The processes concerning silver compounds may be:

(a) $Ag \rightarrow Ag^+$; anodic dissolution of the electrode.

(b) $Ag^+ \rightarrow Ag$; cathodic deposition of silver from Ag^+ ions produced by the corrosion of the electrode.

(c) Anodic formation of silver oxides.

(d) Cathodic reduction of silver oxides present on the electrode.

2. EXPERIMENTAL TECHNIQUE

The experimental work was performed by means of a cell already described.[9] In the cell, filled with the required solution, O_2 or N_2 was made to bubble. When N_2 was bubbled, the solution was previously deaerated with the same nitrogen. The electrode, a disk of 99·99 per cent silver (diameter 20 mm), was ground with quartz powder and washed in distilled water before each experiment.

The solutions were prepared with pure 'for analysis' Merck products of composition:

acid:	0·5 M	H_2SO_4.		
neutral:	0·5 M	H_3BO_3,	0·5 M	Na_2SO_4.
alkaline:	0·1 M	NaOH,	0·5 M	Na_2SO_4.

The pH of the neutral solutions was adjusted by the addition of small quantities of NaOH. To the solutions was added the quantity of H_2O_2 (Perhydrol Merck) needed to obtain the required concentration. The gases were pure commercial O_2 (with traces of N_2 and rare gases) or high purity N_2 (99·999 per cent). The flow rate of the gas was of 150 cm^3/min.

All experiments were carried out in an air thermostat at 25 ± 0·1°C.

The polarizing current circuit consisted of a 150 V battery with resistances in series. Measurements were made with a precision potentiometer (Leeds and Northrup, Model K 3) and a high impedance electronic voltmeter (Philips, Model 6010). A saturated Ag/AgCl electrode was used; all the tension values are reported on the hydrogen scale by adding 0·196 V to the experimental values without correction for the liquid junction.

The experimental procedure consisted first in the measurement of the static tension and then, after the closure of the polarizing current circuit, in the measurement of the value of the tension. The current density values were increased one after the other and the corresponding values of the tension were measured, the polarizing current circuit being opened between two measurements. The polarization curve for increasing current density values was so obtained; when the maximum value was reached ($\simeq$5 mA/cm^2) with the same procedure the polarization curve at decreasing current density values was obtained.

The variation of the electrode tension with time was also studied by means of a recording potentiometer (Leeds and Northrup, Model Speedomax) operated by a high impedence voltmeter (Keithley, Model 610 A).

3. EXPERIMENTAL RESULTS

Figures 1–6 show the polarization curves. The broken line in each Figure corresponds to the value of the reversible tension of the indicated process of OH^--ion or H^+-ion discharge, at the pH of the experiment, and Table 1 shows values of the static tension in our experimental conditions for acid solutions.

The values become more positive (maximum value observed 0·5 V) when the agitation of the solution is increased or when the electrode remains longer in the solution.

TABLE 1. STATIC TENSIONS OF Ag ELECTRODE IN 0·5 M H_2SO_4,

Gas	H_2O_2 concentration (M)	Static tension (E_H) (V)
N_2	10^{-4}	0·32
N_2	10^{-3}	0·32
N_2	10^{-2}	0·39
N_2	10^{-1}	0·41
O_2	—	0·35

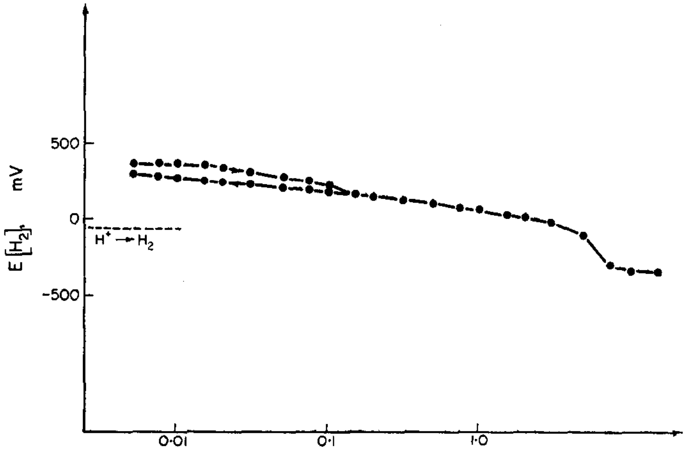

FIG. 1. Cathodic polarization curve for the reduction of H_2O_2 on silver. Acid solution. 10^{-2} M H_2O_2

Figure 1 shows the cathodic polarization curve in acid solution containing H_2O_2. Fig. 2 shows the cathodic polarization curve in acid solution with O_2 bubbling. The curves have a general common shape: a first step is shown at a noble tension, which does not reappear when the curve is plotted by decreasing current density values; it represents the deposition of silver from Ag^+ dissolved from the electrode, present in the solution at the beginning of the experiment Ag^+ is not reformed during the short time elapsing between the beginning and the end of an experiment. The first step of the polarization curve is the less evident if the electrode is in the solution, before the measurements, for a shorter time.

Figures 1 and 2 show a second step at less noble tensions, corresponding to the reduction of H_2O_2 (Fig. 1) or of O_2 (Fig. 2). It may be seen that in the cases of the

0·01 M H_2O_2 solution and in the case of solution in which oxygen bubbles the slope is 0·12 ($2RT/F$).

At the highest current densities the curves show the step corresponding to hydrogen evolution.

At silver anodes, in acid solutions the only process is the dissolution $Ag \rightarrow Ag^+$. The tension value is higher than under cathodic conditions (0·50 V) owing to the greater concentration of Ag^+ ions present in the layer of solution next to the electrode.

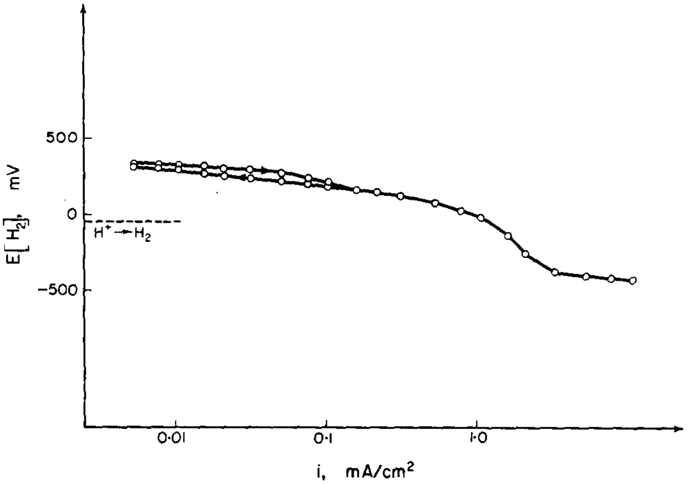

FIG. 2. Cathodic polarization curve for the reduction of O_2 on silver. Acid solution. Gas: O_2

TABLE 2. STATIC TENSIONS OF Ag ELECTRODE IN 0·5 M H_3BO_3, 0·5 M Na_2SO_4 (pH 7)

Gas	H_2O_2 concentration (M)	Static tension, (E_H) (V)
N_2	10^{-4}	0·30
N_2	10^{-3}	0·56
N_2	10^{-2}	0·61
N_2	10^{-1}	0·62
O_2	—	0·35

At the end of the experiment the electrode was corroded, but the high current density leading to the formation of AgO[10] was not reached. Table 2 shows the values of the static tension in neutral solution. It can be seen that the tensions are nobler for the more concentrated H_2O_2 solutions, in which preliminary experiments demonstrated that silver is corroded. The corrosion continues until the concentration of the Ag^+ ions reaches the value of about 10^{-3} M. The static tension is nearly coincident with that of silver in 10^{-3} M Ag^+ solution.

When O_2 is bubbling in the solution (Fig. 3) the cathodic curve is similar to that of the acid solution (Fig. 2). On the contrary the case of the more concentrated H_2O_2 solutions is different (Fig. 3); the electrode is corroded and the process $Ag^+ \rightarrow Ag$

occurs at a tension of about 0·6 V owing to the increased quantity of Ag^+ in the solution. The process is indicated also in the decreasing current density curve; hence the corrosion of the electrode is sufficient to maintain the Ag^+ concentration in the solution. Thus the process $Ag^+ \rightarrow Ag$ conceals the process of H_2O_2 reduction; however the corresponding step appears at the high current densities and H_2O_2 reduction is seen to occur at the same tension as in acid solutions.

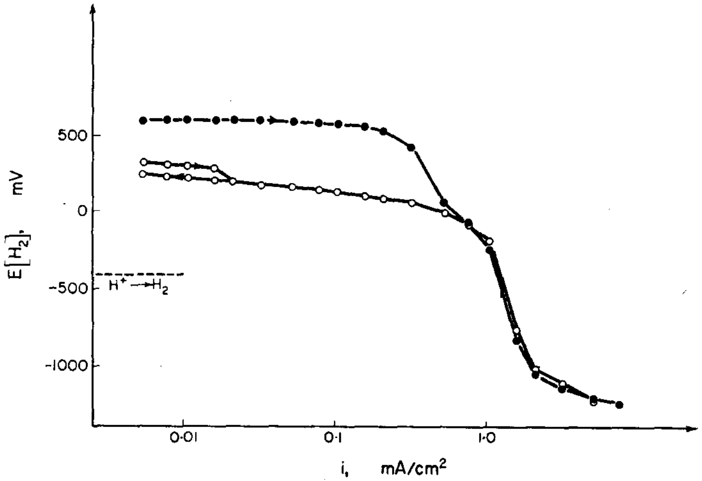

Fig. 3. Cathodic polarization curves for the reduction of O_2 and H_2O_2 on silver. Neutral solution. ● 10^{-2} M H_2O_2. ○ Gas: O_2.

Table 3. Static tensions of Ag electrode in 0·1 M NaOH and 0·5 M Na_2SO_4.

Gas	H_2O_2 concentration (M)	Static tension, (E_H) (V)
N_2	10^{-4}	0·19
N_2	10^{-3}	0·19
N_2	10^{-2}	0·19
N_2	10^{-1}	0·19
O_2	—	0·28

In alkaline solutions the cathodic curves never indicate Ag^+ reduction; we observe only H_2O_2 or O_2 reduction and hydrogen evolution.

Table 3 shows the static tension in alkaline solution; the value depends on whether or not the solutions contain hydrogen peroxide.

We conclude that when the solution contains H_2O_2 the electrode is bare, while in the other cases it is covered with an oxide film, for it is known that hydrogen peroxide reduces silver oxide.[11] In the absence of H_2O_2, the film of silver oxide determines the value of the static tension, but it does not interfere with the process of oxygen reduction, presumably because it is quickly destroyed when the first cathodic current passes on the electrode. The polarization curves are similar to those obtained with other electrodes such as bare platinum.[6] The silver electrode thus behaves in alkaline solutions as an inert electrode for the cathodic processes of H_2O_2 and O_2 reduction.

It may be observed that the process of oxygen reduction differs from the process of H_2O_2 reduction (Fig. 4) as regards the slope of the polarization curves. The slope is about 0·06 (*RT*/*F*) in the case of oxygen and exceedingly low in the case of hydrogen peroxide.

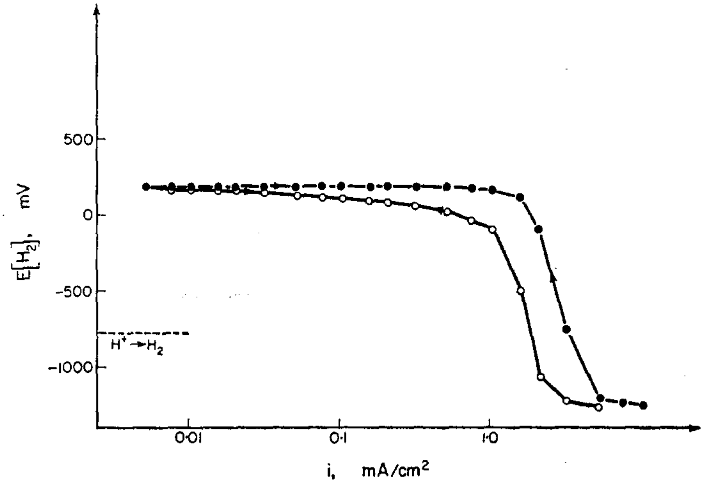

FIG. 4. Cathodic polarization curves for the reduction of O_2 and H_2O_2 on silver. Alkaline solution. ● 10^{-2} M H_2O_2. ● Gas: O_2.

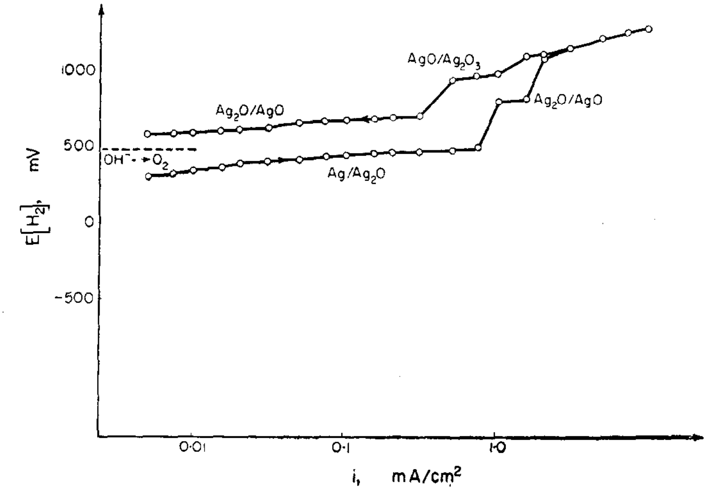

FIG. 5. Anodic polarization curve for the formation of silver oxides on silver. Alkaline solution. Gas: O_2

The anodic behaviour in alkaline solution is quite different from that in acid and neutral solutions. The polarization curves show several steps corresponding to the formation of the various silver oxides, as indicated. In Fig. 5 the decreasing current density curves do not show a step corresponding to $Ag \rightarrow Ag_2O$ because the oxide AgO is stable in this condition and the tension for $Ag_2O \rightarrow AgO$ is nobler than that for $Ag \rightarrow Ag_2O$.

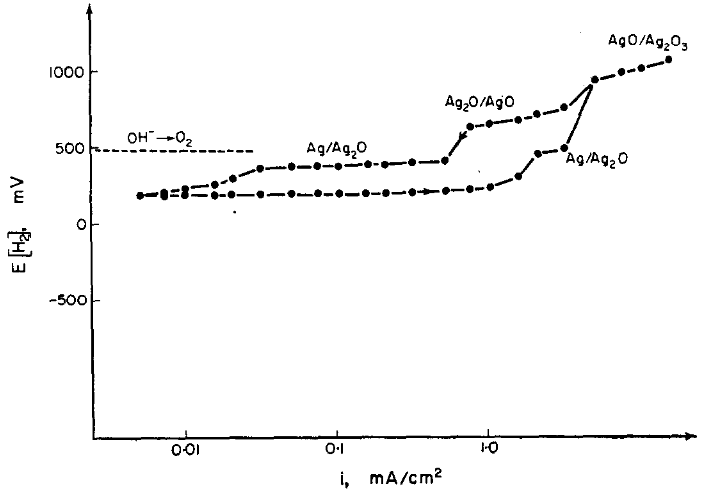

Fig. 6.—Anodic polarization curve for the oxidation of H_2O_2 on silver. Alkaline solution. Gas: O_2

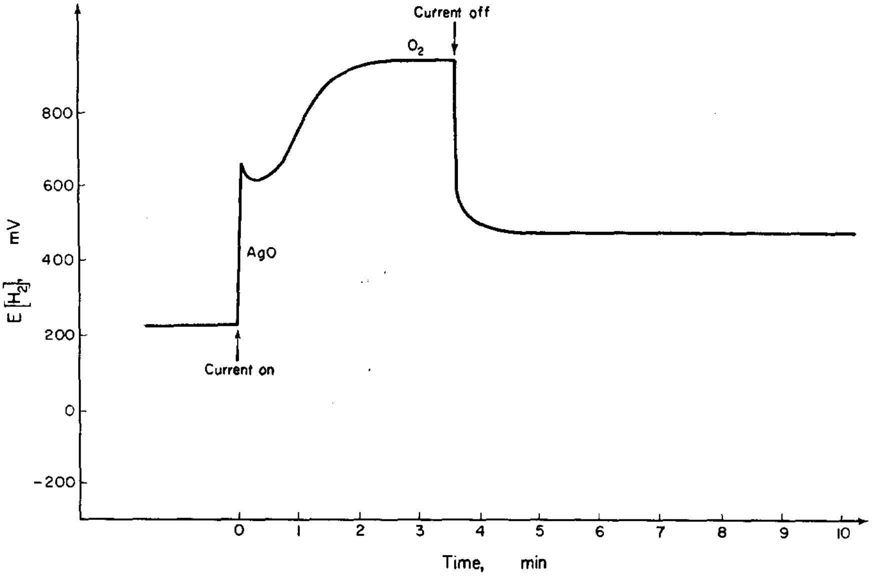

Fig. 7.—Variation of the tension of the silver electrode with time. ($i = 3$ mA/cm²). Alkaline solution. Gas: O_2

When the solution contains H_2O_2 the curve shows at first the step corresponding to H_2O_2 oxidation (Fig. 6); the process occurs at the same tension as on the platinum electrode. The decreasing current density curve indicates both Ag → Ag_2O and H_2O_2 oxidation. In fact, H_2O_2 reduces AgO and Ag_2O; at the end of the experiment the electrode is bare.

Figure 7 shows the variation of the tension with time in alkaline solution without hydrogen peroxide: it may be observed that at the closure of the polarizing circuit ($i = 3$ mA/cm²) the tension increases rapidly, shows a peak, and then increases to a stable value. The first step corresponds to the formation of AgO on the electrode and the stable value corresponds to the evolution of oxygen. Hickling and Taylor[8] think the peak may be due to the formation of an oxide higher than AgO that decomposes to this substance; Jones *et al.*[8] think it may be due to the difficulty of nucleation of AgO. An analogous tension peak was observed in the cathodic process $Pb^{2+} \rightarrow Pb$ by Piontelli and Guerci[12], who also interpreted it as caused by the difficulty of nucleation of lead.

When the polarization circuit is opened, the tension drops (Fig. 7) to the value corresponding to Ag_2O/AgO and remains constant.

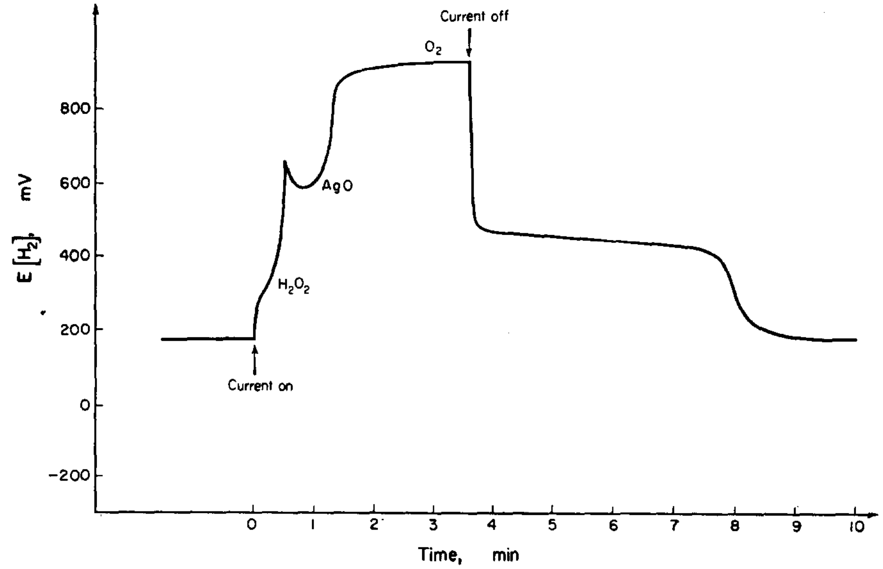

FIG. 8.—Variation of the tension of the silver electrode with time in presence of hydrogen peroxide. ($i = 3$ mA/cm^2).
Alkaline solution. 10^{-2} M H_2O_2

When the solution contains 10^{-2} M H_2O_2, the curve of Fig. 8 is obtained. We observe AgO formation and O_2 evolution and also, before the tension peak, H_2O_2 oxidation. When the polarizing circuit is opened, the tension drops at first to the value corresponding to Ag_2O/AgO and then falls to another constant value, to the initial static tension of H_2O_2/O_2. This second tension drop demonstrates the destruction of silver oxides by H_2O_2.

4. CONCLUSIONS

1. *Acid solution*

In acid solution the reduction of O_2 and that of H_2O_2 occur on silver in the same way. The tension of the processes is about 0·15 V (E_H) and the slope of the cathodic polarization curve is $2RT/F$. The disturbing process $Ag^+ \rightarrow Ag$ occurs only at low current densities.

At silver anodes the process $Ag \rightarrow Ag^+$ takes place rather than the anodic processes of the system H_2O–H_2O_2–O_2.

2. *Neutral solution*

In neutral solution the reduction of O_2 and that of H_2O_2 occurs in the same way as in acid solutions. The tension is still 0·15 V and the slope $2RT/F$. The process $Ag \rightarrow Ag^+$ in this case also takes precedence over the processes of the system H_2O–H_2O_2–O_2. In constrast to acid solution, in neutral solution containing H_2O_2 the cathodic process $Ag \rightarrow Ag$ plays an important role; it occurs at a tension higher (0·6 V) than in acid solution and partly hides the process of H_2O_2 reduction.

In neutral solutions containing H_2O_2 corrosion of the electrode is observed so that the solution is continually furnished with Ag^+ ions. The corrosion stops when the tension of the electrode reaches the value of about 0·6 V. This value is the same as of that of the process of H_2O_2 oxidation to oxygen.

H_2O_2 decomposes on metals by an electrochemical mechanism, (a) a cathodic reaction $H_2O_2 \rightarrow H_2O$ determining the rate of the decomposition; many authors consider radicals such as OH, HO_2 to be intermediates (b) an anodic reaction $H_2O_2 \rightarrow O_2$.

There is no direct experimental evidence of the tension of the process (a). The tension of process (b) is 0·6 V in neutral solution as calculated[13] from thermodynamic data for the reaction

$$HO_2^- + OH^- - 2e \rightarrow H_2O + O_2.$$

In presence of silver the reaction $Ag \rightarrow Ag^+$ is concurrent with reaction (b) until the tension of the former process is lower than the tension of the latter; thus $Ag \rightarrow Ag^+$ occurs, i.e. the electrode is corroded, until the concentration of Ag^+ is about 10^{-3} M giving a tension of about 0·6 V.

In acid solution the mechanism of decomposition does not occur and also the corrosion of the electrode is hindered.

3. *Alkaline solution*

In alkaline solution reduction of O_2 occurs at 0·18 V and the slope of the cathodic curve is RT/F.

In presence of H_2O_2, the oxide film covering the electrode is destroyed, and reduction of H_2O_2 occurs on a bare electrode. The tension is 0·18 V and the slope of the cathodic polarization curve is very low.

The coincidence of the tension for the reduction of H_2O_2 with the tension for the process $H_2O_2 \rightarrow O_2$ may be referred to the fact that H_2O_2 is readily decomposed in alkaline solutions, the cathodic process being an apparent reduction of H_2O_2. The decomposition of H_2O_2 leads to the consequent reduction of the oxygen produced according to $O_2 + H_2O + 2e \rightarrow OH^- + HO_2^-$.

Process involving silver do not interfere with the cathodic reduction of H_2O_2 and O_2 in alkaline solutions. At silver anodes, the formation of the silver oxides occurs, but does not interfere with H_2O_2 oxidation because of the lower value of the tension of this process, which occurs at 0·18 V according to the above mentioned equilibrium.

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DISCUSSION

N. Ibl.—Avez-vous étudié la variation, en fonction des conditions d'électrolyse, du palier observé sur les courbes potentiel-temps obtenues à courant constant? Est-il possible d'évaluer à partir des longueurs de ces paliers par exemple l'épaisseur des couches d'oxyde formées et pourriez-vous éventuellement nous donner une idee de l'épaisseur de ces couches dans les conditions de vos très intéressantes expériences.

G. BIANCHI.—Sur la base de la courbe de la Fig. 7 nous avons calculé la quantité d'électricité débitée entre la fermeture du circuit et le commencement du dégagement d'oxygène. La valeur, calculée pour 1 cm^2 de surface d'électrode, est de 0,4 C à peu près. On a donc la formation de $\frac{0{,}4 \times 247{,}76}{2 \times 96{\cdot}500} = 5{,}1 \times 10^{-4}$ g de AgO; ce qui correspond à une couche d'oxyde de 0,7 μ environ. Des valeurs semblables ont été obtenues avec des densités de courant comprises entre 1 et 5 mA/cm^2.

M. LEWARTOWICZ.—(1) Quelle était la composition des solutions alcalines dans vos expériences?

(2) Avec-vous étudié des solutions fortement alcalines? Nous avons observé récemment des courbes de polarisation très semblables aux votres sur l'argent dans KOH 4N et nous avons constaté qu'en présence d'oxygène cette électrode pouvait servir d'électrode de référence.

(3) Comment expliquez-vous le fait que H_2O_2 formé cathodiquement à partir de O_2 ne détruit pas chimiquement l'oxyde d'argent dans les solutions alcalines?

G. BIANCHI.—(1) La composition des solutions alcalines était NaOH O, 1 M, Na_2SO_4 0,5 M.

(2) Nous n'avons pas étudié de solutions fortement alcalines en considération du fait que les mesures ont été faites avec une cellule en verre de forme compliquée et avec des rodages qui pouvaient être endommagés par ces solutions. Nous sommes d'accord avec vous sur le fait que l'electrode d'argent en solution alcaline peut servir d'électrode de référence.

(3) Si l'électrode est recouverte d'oxyde, pendant la polarisation cathodique on a toujours d'abord la réduction de l'oxyde, qui se produit à une tension plus noble. Ensuite, à une tension plus cathodique, se produit la réduction de O_2 avec formation de H_2O_2 sur l'électrode nue.

C. CAPEL-BOUTE.—Avec-vous fait des études semblables sur le Pd? L'oxyde de Pd pourrait-il être réduit par l'eau oxygenée comme l'oxyde d'argent?

G. BIANCHI.—Nous n'avons pas fait d'éxpériences sur le Pd mais il est fort possible que son comportement soit assez semblable à celui de l'argent.

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