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The Effects of Anions and Cations on Oxygen Reduction and Evolution Reactions on Platinum Electrodes

by

Akiya Kozawa

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-Abstract-

The effects of 10^{-4} -10^{-1} M of various anions and cations added to 1 N H_2SO_4 and 1 M NaOH solutions on oxygen-reduction at pre-anodized and pre-cathodized platinum electrodes were examined by measuring the coulombic efficiency for the formation of hydrogen peroxide (calculated on the basis of $O_2 + H_2O + 2e^- \rightarrow OOH^- + OH^-$). Current-potential curves have also been obtained. In 1 M NaOH, oxygen was reduced to hydrogen peroxide with a coulombic efficiency of almost 100% at the pre-anodized electrode. In the presence of Ba^{++}, Sr^{++}, and Ca^{++} in 1 M NaOH, however, the efficiency decreased to 10-15% with increasing concentration of these ions. In 1 N H_2SO_4, oxygen was reduced principally to water and the coulombic efficiency for hydrogen peroxide formation was only 10-20%. In the presence of Cl^- and Br^- ions this efficiency increased to 50-60%. Current-potential curves indicated that overpotential of the oxygen reduction at the platinum electrodes increased in the presence of Ba^{++}, Sr^{++}, and Ca^{++} ions in 1 M NaOH and Cl^- and Br^- ions in 1 N H_2SO_4. The catalytic activity of the platinum electrodes for hydrogen peroxide decomposition in 1 M NaOH and 1 N H_2SO_4 with and without these anions and cations was also measured. The overpotential for oxygen evolutions on platinum as well as on other electrode surfaces in 1 M NaOH have been found to be increased by 15 to 90 mV when Ba^{++}, Sr^{++}, or Ca^{++} ions are added to the solution. These results are discussed on the basis of the adsorption of cations and anions on the oxide or hydroxide covered electrode surfaces with emphasis on the ion-exchange properties of the oxides.

Evidence for various oxide films and/or adsorbed oxygen on platinum electrodes is summarized. A voltammetric study of a special oxide layer formed on an excessively anodized platinum electrode is also described.

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INTRODUCTION

It has been well recognized in the past ten years that the platinum electrode is not inert and that the surface is electrochemically oxidized and reduced in aqueous solutions (1,2,3,4,55). The electrode surface is covered with an oxide film and/or an adsorbed oxygen layer in a certain potential range and such oxide films play an important role in various electrochemical reactions on the platinum electrodes (5,6,7,8).

Various metal oxides with hydrated surfaces usually exhibit ion-exchange adsorption in aqueous solutions; that is a cation-exchange adsorption in alkaline solutions and an anion-exchange adsorption in acid solutions (9). In earlier work, cation-exchange adsorption on manganese dioxide and silica was studied and the formation of a surface complex as a new adsorption mechanism was proposed by the author (10,11). Since the platinum electrode also is covered with oxide film, cations should be adsorbed in alkaline solutions and anions in acid solutions on the electrode surface at least in some ranges of potential. In view of such an ion-exchange adsorption, an effect of cations and anions added to the electrolyte on oxygen reduction and oxygen evolution reactions at platinum electrodes should be expected. In this paper the effects of anions and cations added to 1 M NaOH or 1 N H_2SO_4 on oxygen reduction and oxygen evolution processes will be described.

The electrochemical reduction of oxygen at platinum electrodes in alkaline and acid solutions has been studied earlier by voltammetry (12-14) and chrono-potentiometry (13,13a,15). The reaction is very much influenced by the surface condition of the platinum electrode. Laitinen and Kolthoff (12) and later Sawyer and Interrante (13) reported that the half-wave potential of oxygen reduction on platinum is independent of the pH of the solution at pre-cathodized electrodes, but changes linearly with a slope of approximately -60 mv per pH unit at pre-xoidized electrodes.

For the mechanism of oxygen reduction, the following three processes are frequently considered (12-15).

$$\text{I:}\quad O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad E^{\circ}_{red} = +\,0.401\text{ V} \qquad [1]$$

$$\text{II:}\quad Pt + 1/2\ O_2 + H_2O \xrightarrow{\text{chemical}} Pt(OH)_2$$

$$Pt(OH)_2 + 2e^- \rightleftharpoons Pt + 2OH^- \qquad E^{\circ}_{red} = 0.155\text{ V}(36) \qquad [2]$$

$$\text{III:}\quad O_2 + H_2O + 2e^- \rightleftharpoons OOH^- + OH^- \qquad E^{\circ}_{red} = -0.05\text{ V}\ (52,53,54) \qquad [3]$$

Reaction III may be followed by either catalytic decomposition

$$\text{IIIa:}\quad OOH^- \xrightarrow{\text{chemical}} 1/2\ O_2 + OH^- \qquad [3a]$$

or electrochemical reduction

$$OOH^- + H_2O + 2e^- \rightleftharpoons 3OH^- \qquad E^{\circ}_{red} = +\,0.85\text{ V}\ (54) \qquad [3b]$$

Although these equations are written for alkaline solution and the E°_{red} values are for alkaline solution, corresponding equations for acid solution can easily be written.

In the first mechanism,* oxygen is reduced directly to OH^- by a four-electron transfer process. This mechanism was supported to some extent by the data obtained by Bockris and Huq (16) in highly purified 0.1-0.001 N H_2SO_4 where a potential corresponding to the overall four-electron process was obtained (see also ref. 16a). These authors pointed out that the exchange current for the reaction was so small that the reversible potential corresponding to reaction [1] could be obtained only in highly purified solutions.

In the second mechanism, the platinum surface is oxidized chemically by dissolved oxygen; then, the platinum hydroxide (or adsorbed oxide) is reduced

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* Reaction [1] is ordinarily considered as an overall reaction. This could be listed as a mechanism under a circumstance in which no particular intermediate is recognized experimentally. Such is quite unlikely, however.

electrochemically (12,15). Comparing the observed half-wave potentials (12,14) with the $E^{o}_{red} = +0.155$ V, this mechanism is acceptable from the standpoint of thermodynamics. The third mechanism was proposed by Berl (17) based on his experiments with carbon electrodes. Later Davies et al. (18) showed by using O^{18} that the bond between the atoms in O_2 is not broken in the electrochemical reduction on carbon. Until last year the principal support for this mechanism on platinum electrodes was a qualitative detection of hydrogen peroxide by Laitinen and Kolthoff (19) and a quantitative determination of hydrogen peroxide by Delahay, who carried out the oxygen reduction experiments in 0.2 N KCl solution (pH 6.9) on various metals and determined hydrogen peroxide in the solution by a polarographic method (20). Recently the author (21) has measured the coulombic efficienty for H_2O_2 formation in O_2 reduction on platinum in acid and alkaline solutions. Of the three mechanisms, only reaction [3] involves hydrogen peroxide as a product. Effects of anions and cations on the formation of hydrogen peroxide in oxygen reduction on platinum have been examined mainly in 1 M NaOH by the author (22). In the present experiments, the coulombic efficiency for hydrogen peroxide formation has been determined in 1 N H_2SO_4 as well as 1 M NaOH with and without added cations and anions.

Oxygen overvoltage was reviewed by Brieter (23). It was demonstrated by means of O^{18}- labeled anions that the oxygen evolution reaction at smooth platinum electrodes involves anions at least in high concentrations (5.8 to 10 N) of $HClO_4$ (24) and H_2SO_4 (25). Hickling and Hill (26) reported that oxygen overvoltage at a smooth platinum electrode increased by 10-60 mv in 1 M KOH and 40-180 mv in 1 N H_2SO_4 in the presence of 0.02 M KF. Erdey-Gruz and Safarik (27) showed that oxygen overvoltage on smooth platinum in 1 N H_2SO_4 increased in the presence of large amounts (0.3-1.0 M) of cations in the following order: $K^+ > Al^{3+} > NH_4^+ > Zn^{2+} > Na^+ > Mg^{2+} > Li^+$. There seems to be no data on the effect of alkaline earth metal cations on oxygen overvoltage in alkaline solution. It will be shown in this paper that oxygen overvoltage in 1 M NaOH increased by

15~90 mv in the presence of 10^{-4}-10^{-2} M of Ba^{++}, Sr^{++}, Ca^{++} on platinum and other metal electrodes.

In the potential range involved in the oxygen reduction and evolution reactions on the platinum electrode, the electrode surface is covered with oxide (or hydroxide) film. Therefore, a knowledge of the surface condition of platinum in terms of oxide film and/or adsorbed oxygen is necessary in order to interpret the experimental results. For this purpose a brief summary on the adsorbed hydrogen, adsorbed oxygen, and oxide films on anodized-and cathodized-platinum electrodes will be given. Some details will be given of an oxide film formed on an excessively anodized platinum electrode in H_2SO_4 solution, since this oxide film has not been described often in the literature.

EXPERIMENTAL

Oxygen reduction experiments were carried out in an ordinary polarographic H-cell with a fritted glass layer in the middle. For coulombic efficiency measurements, 25 ml of 1 M NaOH or 1 N H_2SO_4 solution was put in each arm of the H-cell. A rectangular platinum electrode of 16 or 18 cm^2 apparent surface area was placed as a cathode in the solution of one arm where pure oxygen gas (1 atm) was bubbled through the solution during the experiments and another small platinum electrode (1 cm^2 apparent surface area) was placed in the other arm as an anode. A constant current of 1.0 ma in most of the experiments was passed between the anode and the cathode for a measured time, usually 2 to 20 minutes. A portion of the cathode solution (usually 20.0 ml) was taken out and acidified in the case of 1 M NaOH solution; then the hydrogen peroxide concentration was determined by a spectrophotometric method. The method (21) is based on the formation of a yellow-colored material (28) formed in the reaction between H_2O_2 and $TiCl_4$ reagent. By this method 5 to 100 μg of H_2O_2 in a 30-ml solution could be determined within an error of a few per cent when a 10-cm cell was used in the extinction measurements.

Solutions were prepared from triple-distilled water. Sulfuric acid was purified by distillation twice in a current of air at about 210°C. The 1 M NaOH solution was purified by pre-electrolysis at a platinum cathode under a nitrogen atmosphere for more than 30 hours. Various salt solutions which were added to 1 M NaOH or 1 N H_2SO_4 solutions were prepared from chemicals of analytical reagent grade without further purification. Decomposition of hydrogen peroxide in these purified solutions was negligible for 10 to 20 minutes in the absence of a platinum electrode.

Two types of platinum electrode were used; one was pre-cathodized and the other pre-anodized in 1 M NaOH or 1 N H_2SO_4 depending on the solution used for the oxygen reduction experiments. The cathodic or anodic treatment was carried out for about 20 sec at a current density of 5 ma/cm^2 immediately before use. As will be discussed later, during most of the oxygen reduction experiments the pre-anodized electrode was probably covered with PtO_2-film in both acid and alkaline solutions and the pre-cathodized electrode at least partially with $Pt(OH)_2$ or a similar oxide in 1 N NaOH solutions saturated with oxygen. It is a common experience that the "activity" of platinum electrodes depends on the history and the pre-treatment of the electrodes. In the preliminary experiments, a few electrodes were etched in a hot aqua regia solution or treated in a boiling 6 N HCl solution, or treated anodically and cathodically alternately, and then finally anodized or cathodized as mentioned above immediately before the coulombic efficiency measurements. The efficiencies were not much different among the anodized electrodes, but large differences occurred among the cathodized electrodes particularly in alkaline solutions. The relative effects of added anions and cations, however, were the same among those electrodes. In this paper, therefore, any series of experiments shown in the same table or figure was usually carried out with the same electrode at one time. Furthermore, in the experiments to examine the effect of anions or cations, before and after each experiment the electrode was tested in a standard solution without additives to show that there was no permanent change in the electrode.

Current-potential curves for the oxygen reduction and oxygen evolution processes were measured in the H-cell mentioned earlier by using a polarograph. In these measurements, a small platinum electrode was placed in a solution stirred by O_2 in one arm and a mercurous sulfate plus 1 N H_2SO_4 (+0.667 V vs. N.H.E.) or a mercuric oxide plus 1 M NaOH (+0.115 V vs. N.H.E.) electrode was placed in the other arm of the H-cell. These reference electrodes, which were also used in these experiments as counter electrodes, were not polarized more than a few millivolts even when 50 to 100 μA was drawn. All the potentials in this paper are expressed against N.H.E. All the experiments described in this paper were carried out at room temperature (i.e., 22 ± 1°C).

RESULTS AND DISCUSSION

1. Surface condition of platinum electrodes

a. Anodized and cathodized electrodes: It was shown previously by the author (3,29) and other investigators (2) that current-potential curves of platinum electrodes taken between hydrogen evolution and oxygen evolution potentials in an aqueous solution saturated with inert gas gave a series of peaks due to reduction or formation of adsorbed hydrogen and platinum oxides or adsorbed oxygen. A schematic summary of these curves for an anodized or a cathodized platinum electrode is shown in Figure 1. The original curves were taken in 1 M NaOH (3) with a potential-scanning rate of 2.5 mv/sec. These curves then were shifted to those in a solution of $a_{H^+} = 1$ by assuming that the peaks moved exactly -59 mv per pH unit. The presence of four peaks (a,b,c,d) on the oxidation curve A and four peaks (a',b',c',d') on the reduction curve B indicates that four redox couples A, B, C, and D exist on the surface of platinum electrodes. From the middle of the two conjugated peak potentials (a, a'; b, b'; etc.), approximate standard redox potentials E_A, E_B,

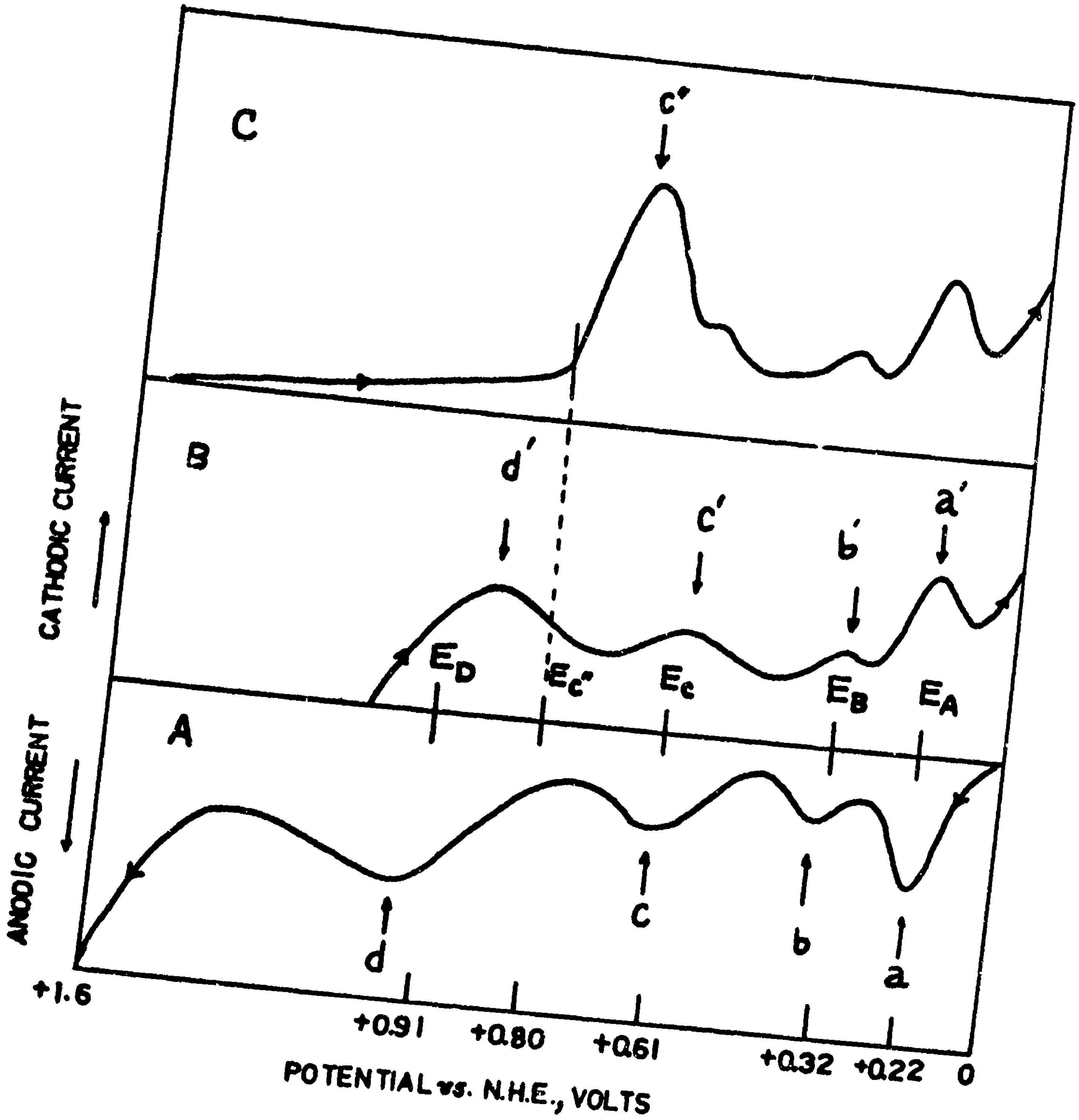

Figure 1. Schematic current-potential curves of platinum electrodes. A: oxidation curve taken at a cathodized electrode from negative to positive potentials, B: reduction curve taken at a cathodized electrode from +1.0 volt to negative potential, C: reduction curve taken at an anodized electrode from positive to negative potentials. Note: data recorded in 1 M NaOH and transposed to $a_{H^+} = 1$ (see text).

E_C, and E_D were obtained and shown on the abscisa. It has been interpreted that the redox couples A and B are two forms of adsorbed hydrogen (3,30-35). The redox couple C was not observed in 1 N H_2SO_4 (2,3) and has not been identified yet. The redox couple D corresponds to adsorbed oxygen and/or platinum hydroxide ($Pt(OH)_2$). On the reduction curve of the anodized electrode (curve C) peak d' was not observed but peak c" appeared at a more cathodic potential than d'. This has been interpreted on the basis that the anodized electrode was covered with $PtO_2 \cdot nH_2O$ and the hydrated platinum dioxide film was reduced directly to Pt at peak c" (3). Principal evidence for this interpretation comes from comparing the potential with the value (36,37) for the following reaction:

$$PtO_2 \cdot nH_2O + 4H^+ + 4e^- \rightleftharpoons Pt + (n+2)H_2O; \ E^\circ_{red} = +0.80 \text{ V} \qquad [4]$$

b. <u>Excessively anodized electrode</u>: A new oxide film, which was not involved in the discussion first presented, was found on the surface of a platinum electrode which was excessively anodized in H_2SO_4. A platinum wire electrode (apparent area: 0.53 cm^2) was polished with fine emery in each case before the anodic treatment. Then it was anodized under various conditions as described in Figures 2, 3, 4, 5, and 6, and the current-potential curves were taken in an N_2-saturated 1 N H_2SO_4 at 25°C starting with +0.87 V and scanning toward negative potentials at 3 mV per sec in the same manner as described previously (3). As shown in Figures 2-6, three peaks (e, f, g) can be seen on these curves. We can see that the peak f remains almost unchanged regardless of the conditions of the anodizing; however, the peak g becomes larger with increasing anodizing time (Figure 2), the temperature of the solution (Figure 3), and the current density (Figure 4) involved in the anodic treatment. The anodic treatment in 1 M NaOH did not show peak g as shown in Figure 5. The peak g appears in the same potential range as that of the peak b which is due to formation of adsorbed hydrogen ($H^+ + e^- \longrightarrow H_{ads}$). As shown in Figure 6, a repeat trial without reanodization shows a normal two peaks for adsorbed hydrogens and a third trial after reanodization (curve C in Figure 6) shows a curve quite similar to the curve C in Figure 1. Therefore, the peak g is not due to

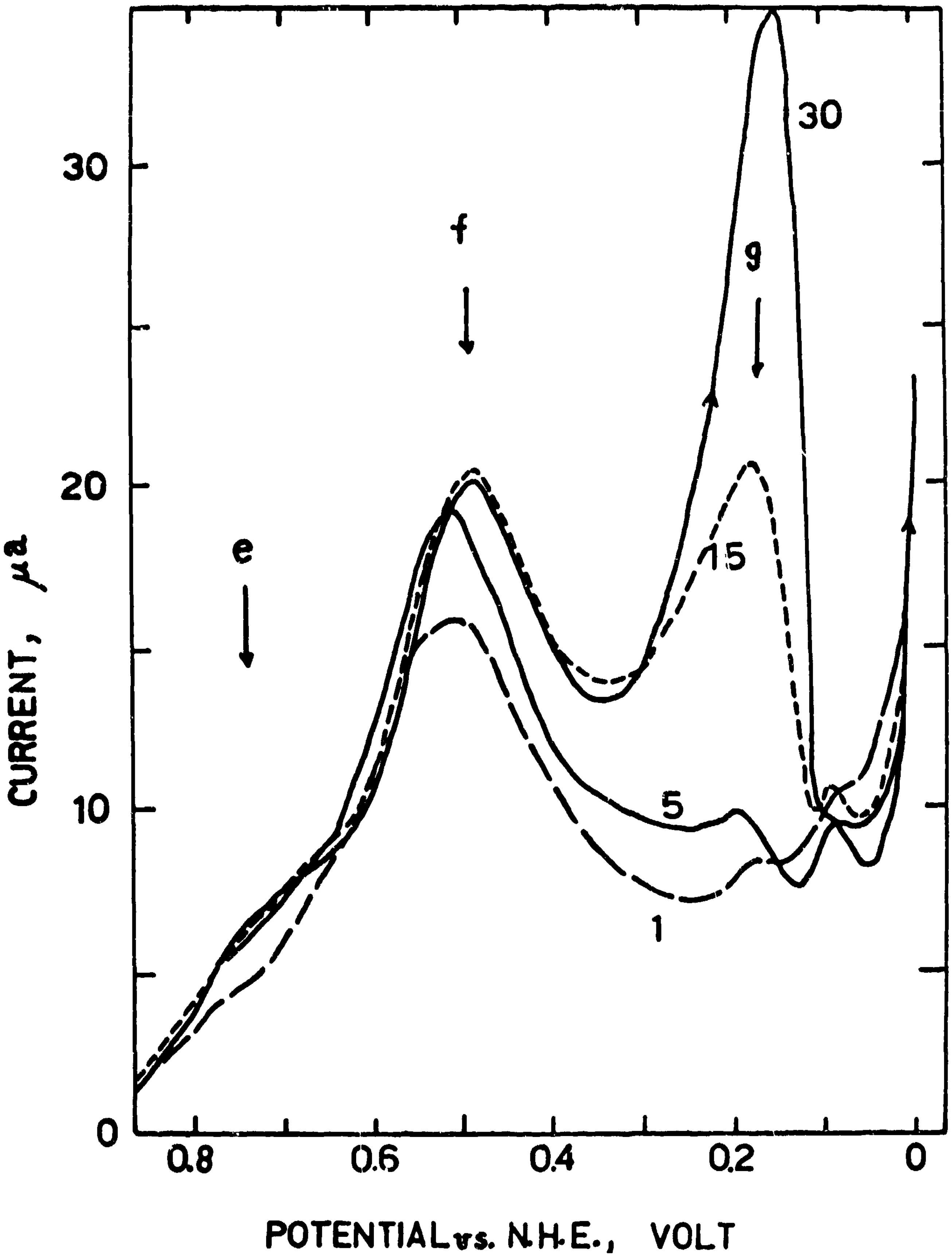

Figure 2. Effect of anodizing time. The anodization was carried out at 100 ma/cm^2 in 1 N H_2SO_4 at 25°C. The numbers 1, 5, 15, and 30 are the anodizing times in minutes.

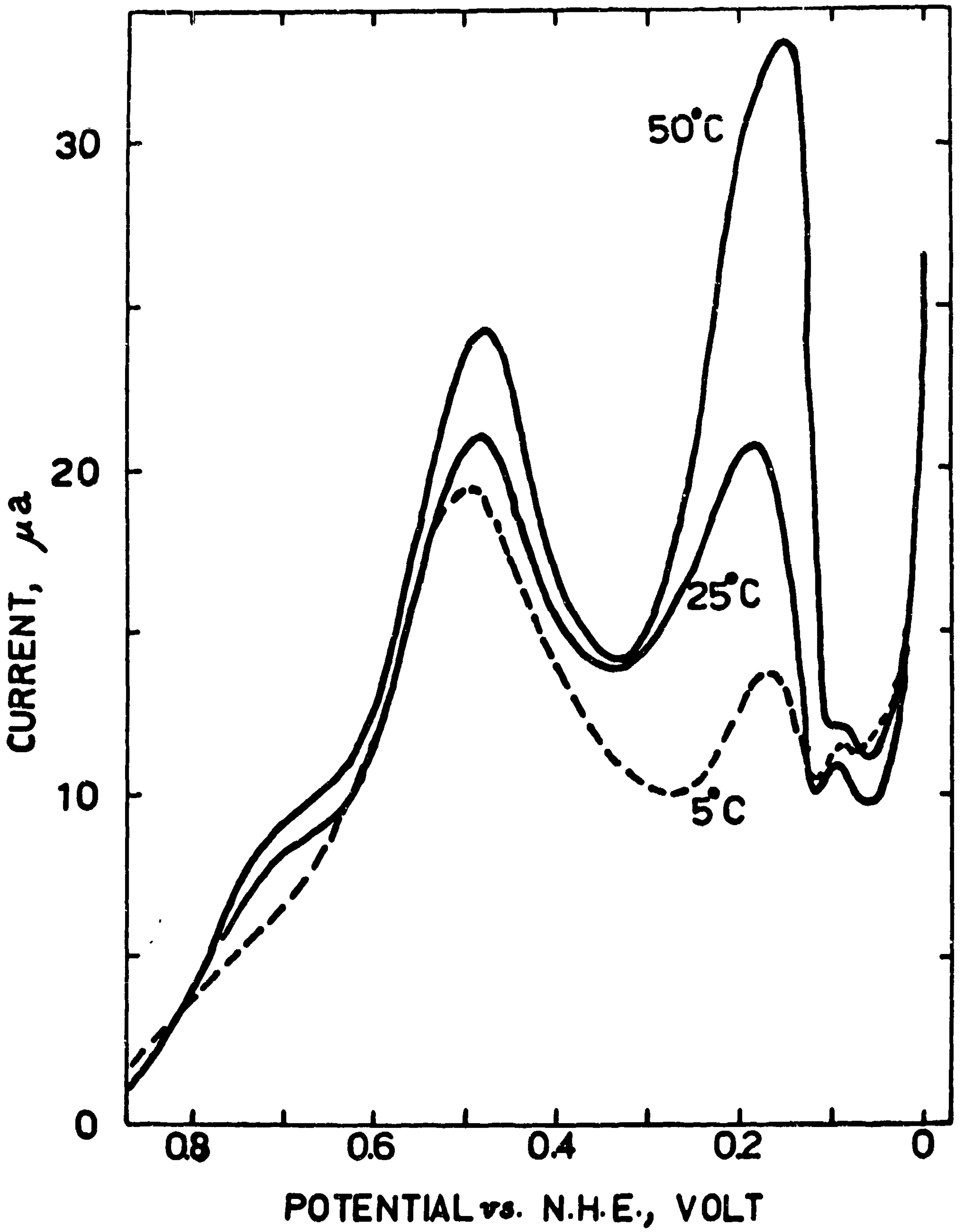

Figure 3. Effect of temperature. The anodization was carried out at 100 ma/cm^2 for 15 min. in 1 N H_2SO_4 at the temperatures indicated.

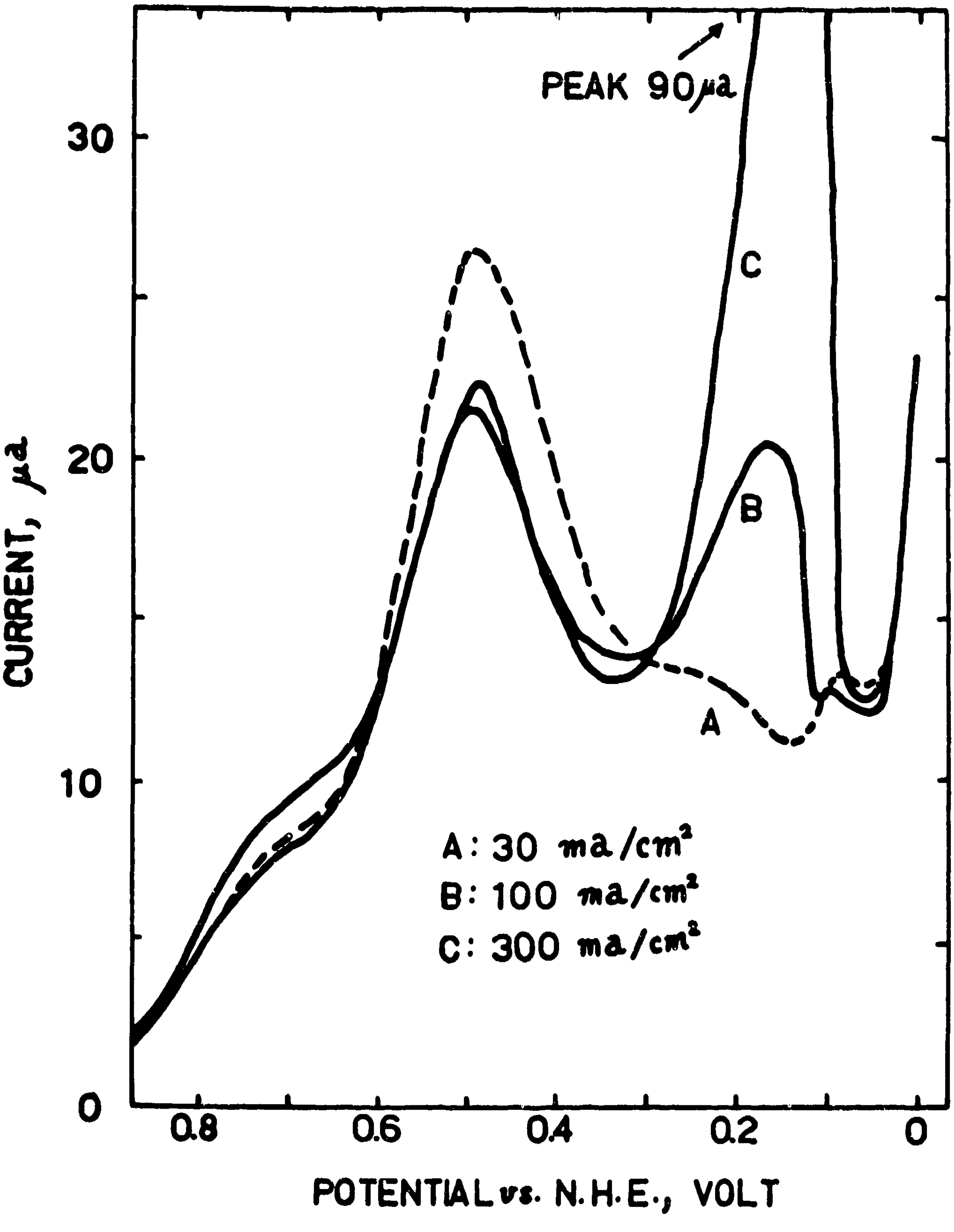

Figure 4. Effect of current density used in anodization. The anodization was carried out at the current densities indicated in 1 N H_2SO_4 for 15 min. at 25°C.

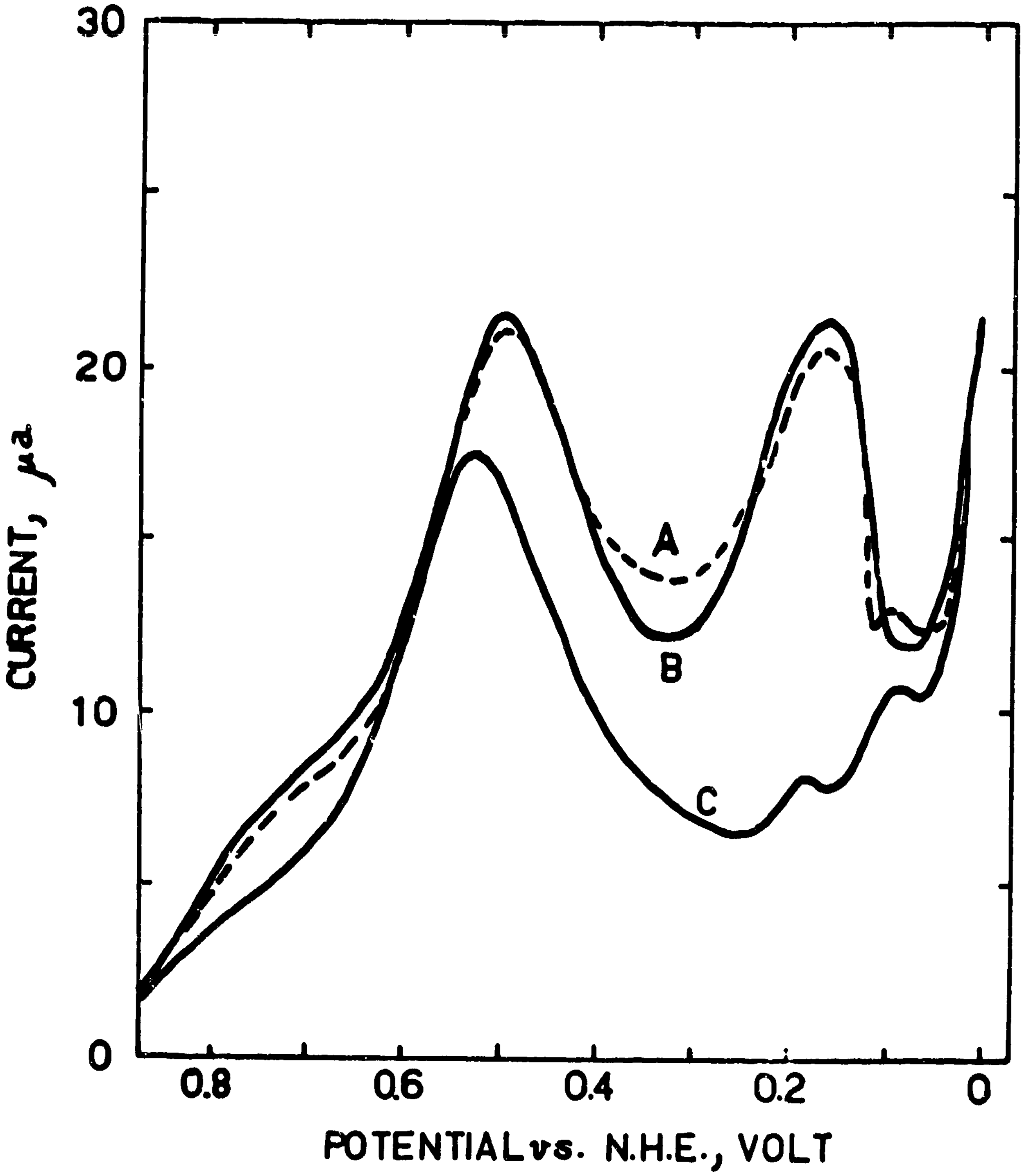

Figure 5. Effect of the electrolyte solution. The anodization was carried out at 100 ma/cm^2 for 15 min. at 25°C in 1 N H_2SO_4, 0.1 N H_2SO_4 and 1 M NaOH for curves A, B, and C, respectively.

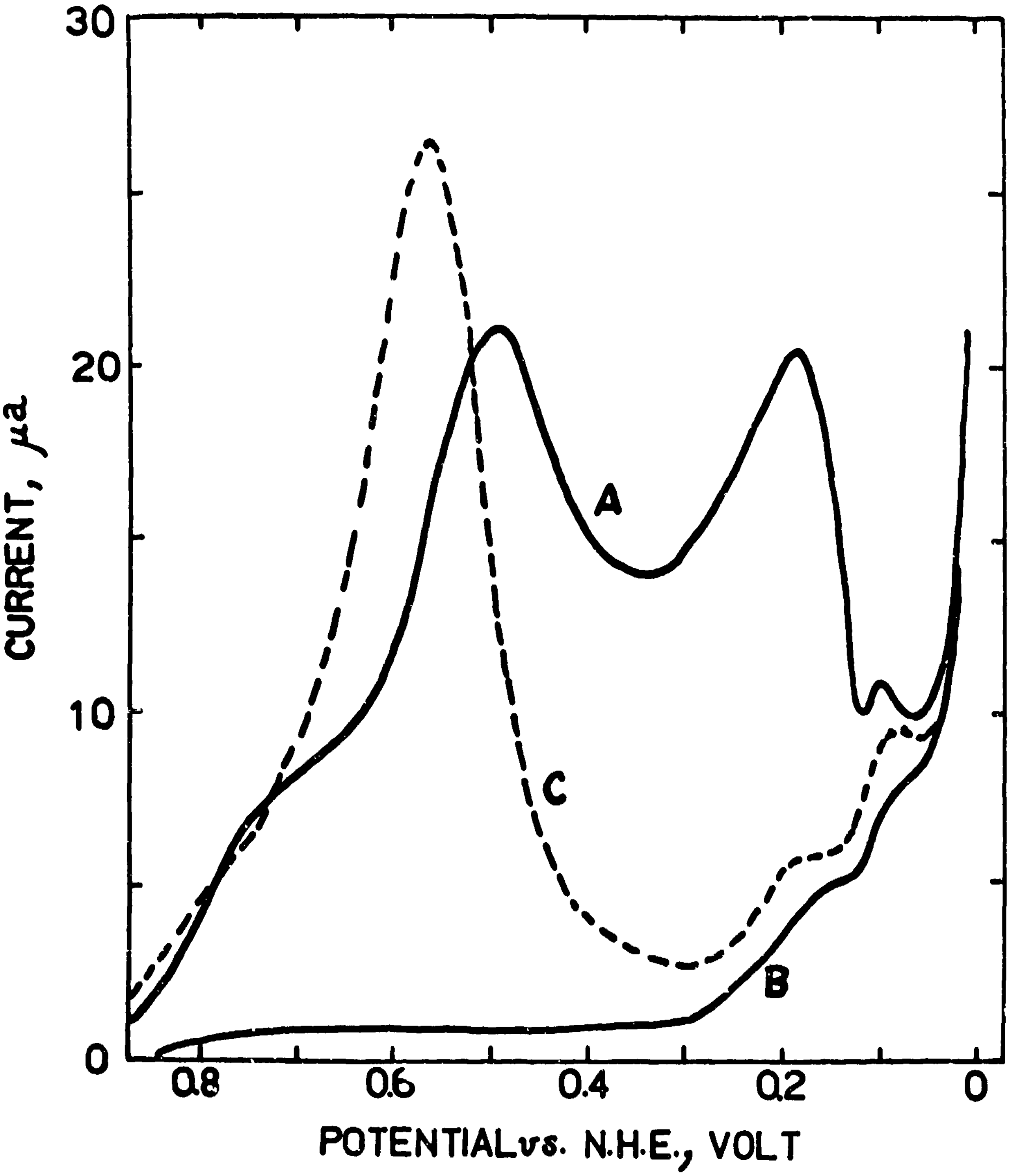

Figure 6. Curves taken consecutively. A: 1st curve after the anodization at 100 ma/cm^2 for 15 min. in 1 N H_2SO_4 at 24°C. B: 2nd curve immediately after the 1st curve. C: taken after the 2nd curve after reanodizing at 100 ma/cm^2 for 1 min. in 1 N H_2SO_4 at 25°C.

an enlarged peak for the peak b, but it seems to be a kind of new oxide which is formed only by excessive anodic treatment at high current density. The peak f reaches a steady state after a few minutes of anodization and does not change on further anodization (Figure 2). The peak f is insensitive to temperature and the current density used in the anodization (Figure 3,4). The peak f appears at a little more cathodic potential than the peak c" (on curve C in Figure 1) which is due to reduction of $PtO_2 \cdot nH_2O$; this might be due to a little more stabilized form of $PtO_2 \cdot nH_2O$.

In an attempt to obtain an x-ray diffraction pattern of the new oxide corresponding to the peak g, a platinum plate with a platinum wire lead was anodized at 300 ma/cm^2 for 100 hours in 1 N H_2SO_4 at 35-45°C. A yellow-colored film appeared after 3 hours of anodization, and the color became thicker with continuing anodization. Several x-ray diffraction patterns were taken during the anodization from time to time and no diffraction peaks were found except those of platinum metal. This might be due to the amorphous nature of the oxide film. This yellow oxide cannot be attributed to any impurity such as Pb^{II} or Mn^{II} which can be deposited as PbO_2 or MnO_2, because the sulfuric acid solution was prepared from highly purified water and distilled sulfuric acid.

This anodic oxide film on platinum also has been studied by Inoue (38) in connection with the platinum foil anodes used in the production of persulfate by electrolysis of a $[H_2SO_4 + (NH_4)_2SO_4]$ solution. A yellow compound which formed on an anodized platinum was described by Ruer (39) as $Pt(OH)_2SO_4 \cdot 3Pt(OH)_4 \cdot PtO_2$. Anodic oxidation of platinum was studied with alternating current superposed on D.C. by Altmann and Busch (40), who found that $PtO_2 \cdot nH_2O$ came off the electrode. Recently Shibata (41) found a large potential step just before the hydrogen evolution in the chrono-potentiogram of a heavily anodized platinum electrode. Probably this corresponds to the peak g in this paper. Oxygen gas containing 15% of ozone by weight has been found by Boer (42) to be produced at very high current densities on a platinum anode in a sulfuric acid solution ($d_{18^\circ C} = 1.065$).

Thus an examination of the literature search indicates that the oxide film corresponding to the peak g shown in Figures 2-6 may not be a new oxide, but is not well recognized or characterized.

c. Effect of Br^-: The effect of bromide ion on the current-potential curves of a platinum electrode taken in 1 N H_2SO_4 saturated with nitrogen is shown in Figure 7. Curve A in this figure corresponds to the formation of an oxide film and/or adsorbed oxygen on the platinum electrode. This process is inhibited in the presence of small amounts of Br^- (curves B, C, and D). The sharp rise of the current in the curves B, C, and D is due to oxidation of Br^- ions. The results in Figure 7 suggest that the Br^- ion is strongly adsorbed on the platinum surface in 1 N H_2SO_4 and inhibits the electrochemical oxidation of the platinum surface.

2. Effects of cations and anions on oxygen reduction

a. Coulombic efficiency: The effects of various cations and anions on the coulombic efficiency for production of hydrogen peroxide were examined at a constant current of 1.0 mA for 10 minutes of electrolysis at a platinum electrode of 16 cm^2. The results for an anodized platinum electrode are shown in Tables 1 and 2 for 1 M NaOH and 1 N H_2SO_4, respectively. The coulombic efficiency values were calculated on the basis of $O_2 + H_2O + 2e^- \rightarrow OOH^- + OH^-$ or $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$. The efficiency values for a cathodized electrode were lower than those (Tables 1 and 2) for an anodized electrode in both acid and alkaline solutions; however, the effects of the addition of the anions and cations were relatively the same. Among the various cations and anions tested, only halide ions in acid solution and alkaline earth metal ions in alkaline solution showed marked effect.

So far as the coulombic efficiency for H_2O_2 production in alkaline solution is concerned, ClO_4^-, NO_3^-, $CO_3^=$, $SO_4^=$, F^-, Cl^-, Br^-, and Zn^{++} had very little effect at concentrations up to 3.3×10^{-2} M (22). The marked effect of

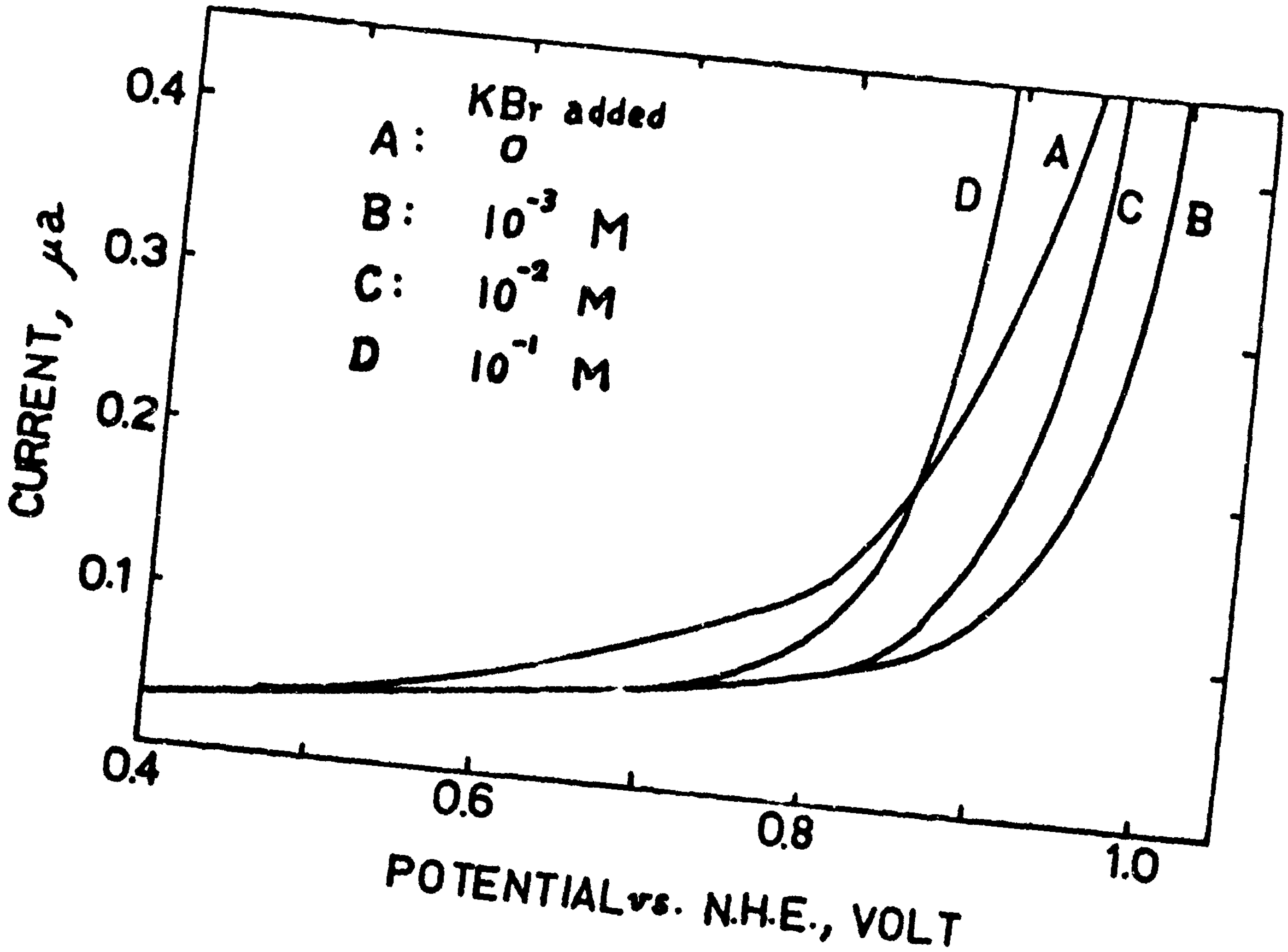

Figure 7. Current-potential curves of a platinum electrode (0.05 cm^2) in nitrogen-saturated unstirred 1 N H_2SO_4. The potential scanning rate was 3 mv/sec.

Table 1. Effect of Cations on the Formation of Hydrogen Peroxide on a Pre-anodized Platinum Cathode in 1 M NaOH

Run No.	Electrolyte	H_2O_2 formed*	Efficiency
1	1 M NaOH	72.0 ± 1.2 μg	68.0%
2	1 M NaOH + 0.001 M $CaCl_2$**	49.5	46.7
3	1 M NaOH + 0.001 M $Sr(ClO_4)_2$	38.4	36.2
4	1 M NaOH + 0.001 M $Ba(ClO_4)_2$	22.4	21.1

* After 10 minutes of electrolysis at a constant current of 1.0 mA at a pre-anodized Pt cathode of 16 cm^2 in a solution of 25 ml.

** A white precipitate [$Ca(OH)_2$] was suspended in the solution.

Table 2. Effect of Anions on the Formation of Hydrogen Peroxide on a Pre-anodized Platinum Cathode in 1 N H_2SO_4

Run No.	Electrolyte	H_2O_2 formed*	Efficiency
5	1 N H_2SO_4	15.0 ± 1.0 μg	14.2%
6	1 N H_2SO_4 + 0.033 M KF	18.7	17.6
7	1 N H_2SO_4 + 0.033 M KCl	32.8	30.5
8	1 N H_2SO_4 + 0.33 M KBr	55.2	52.0
9	1 N HCl	39.2	36.9

* After 10 minutes of electrolysis at a constant current of 1.0 mA at a pre-anodized Pt cathode of 16 cm^2 in a solution of 25 ml.

Ba^{++}, Sr^{++}, and Ca^{++} ions on the efficiency was completely removed by adding EDTA (Na salt of ethylenediamine tetraacetate) to the solution (22).

b. Effect of H_2O_2 decomposition: During the coulombic efficiency measurements, some hydrogen peroxide produced electrochemically may have been decomposed chemically at the electrode as well as in the bulk solution. Platinum is a good catalyst+ for hydrogen peroxide decomposition (43). It is

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\+ The decomposition of peroxide on platinum, however, probably proceeds by an auto oxidation-reduction process involving reactions (3) and (3b). Under these circumstances it is preferable to consider the peroxide as electrochemically reduced. See Technical Report 17 for a discussion of this point.

expected that the longer the electrolysis time the greater would be the amount of decomposition. In an attempt to establish how much hydrogen peroxide was originally formed by the electrochemical process, the efficiencies measured for various electrolysis times were plotted against time as shown in Figure 8. From the efficiency values obtained by extrapolation to zero time, one can see that oxygen is reduced to OOH^- with an apparent coulombic efficiency of 100% in 1 $\underline{M}$ NaOH at an anodized platinum electrode at zero time. In other solutions the extrapolated value for the apparent efficiency is 15-60%, depending on the composition of the solutions. The efficiency values obtained by the extrapolation are shown in Table 3 for various concentrations of Br^- and alkaline earth metal cations in 1 $\underline{N}$ H_2SO_4 and 1 $\underline{M}$ NaOH, respectively. This extrapolation procedure also tends to reduce the effects of the electrochemical reduction of peroxide (reaction 3b) since the rate of the reduction reaction is expected to increase with increasing peroxide concentration.

<u>Table 3</u>. Coulombic Efficiencies for Peroxide Formation Extrapolation to Zero Time.

electrolyte	at pre-anodized Pt	at pre-cathodized Pt
1 $\underline{N}$ H_2SO_4	8.5%	0.0%
1 $\underline{N}$ H_2SO_4 + 10^{-4} $\underline{M}$ Br^-	35.8	39.0
1 $\underline{N}$ H_2SO_4 + 10^{-2} $\underline{M}$ Br^-	51.3	54.5
1 $\underline{N}$ H_2SO_4 + 10^{-1} $\underline{M}$ Br^-	55.7	55.7
1 $\underline{M}$ NaOH	85 - 100*	20 - 45*
1 $\underline{M}$ NaOH + 2 x 10^{-3} $\underline{M}$ Ca^{++}	50 - 65*	15 - 25*
1 $\underline{M}$ NaOH + 2 x 10^{-3} $\underline{M}$ Sr^{++}	40 - 45*	11 - 20*
1 $\underline{M}$ NaOH + 2 x 10^{-3} $\underline{M}$ Ba^{++}	25 - 30*	6 - 15*

* Shows the range of values for three different Pt electrodes.

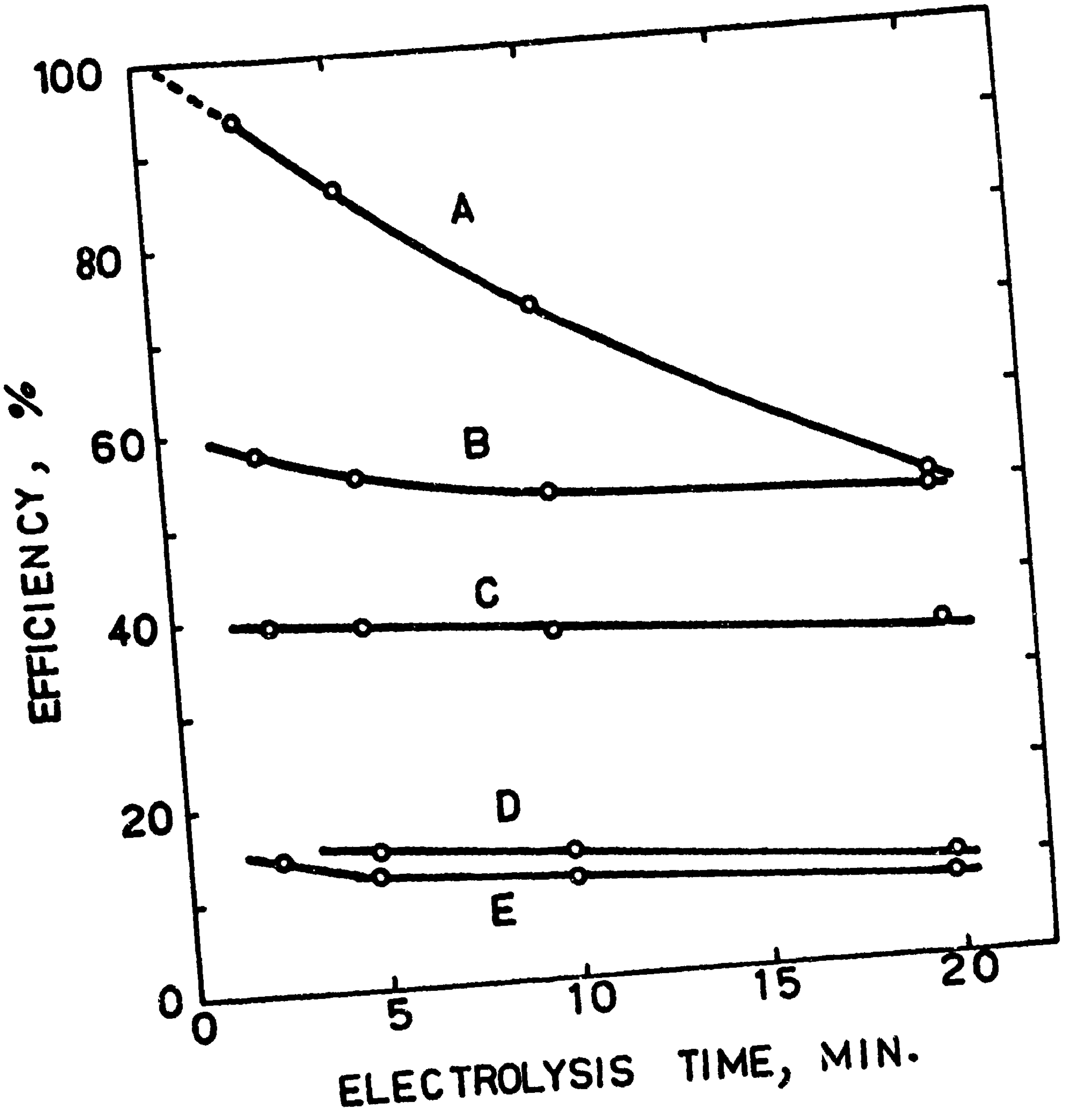

Figure 3. Efficiency of hydrogen peroxide formation at a pre-anodized platinum electrode for various electrolysis times in the following solutions. A: 1 M NaOH, B: 1 N H_2SO_4 + 10^{-2} M KBr, C: 1 N HCl, D: 1 M NaOH + 10^{-2} M $Ba(OH)_2$, E: 1 N H_2SO_4.

The catalytic activity of anodized or cathodized platinum electrodes for the decomposition of hydrogen peroxide was actually measured as follows. Twenty-five ml of 1 N H_2SO_4 solution containing H_2O_2 at a concentration of 92 μg/ml was prepared with and without adding Br^- and placed in the H-cell used in the other experiments. A platinum electrode was dipped into the solution and oxygen gas was bubbled through it in order to stir the solution as in the efficiency measurements. One ml of the soluiton was taken out every 3 min and the hydrogen peroxide concentration was determined spectrophotometrically. The results are shown in Figure 9, from which we can see that the H_2O_2 concentration decreases almost linearly with time except in the presence of KBr (10^{-4}-10^{-1} M). In a pure 1 N H_2SO_4 solution, the decomposition rate is much greater with a cathodized platinum electrode than with an anodized electrode.

The decomposition rates in the H_2SO_4 solutions containing Br^- are very small. Previous investigators have reported that platinum looses its catalytic activity for decomposing H_2O_2 in HCl solution (43,44,45). We may conclude that the coulombic efficiency of less than 100% in 1 N H_2SO_4 containing Br^- is not due to decomposition of hydrogen peroxide, but rather is intrinsic to the electrode system; i.e., in addition to the peroxide producing reaction is a second non-peroxide producing parallel reaction, or the reduction of peroxide according to reaction (3b) proceeds at a substantial rate, or both.

An experiment similar to that of Figure 9 was carried out in 1 M NaOH with and without Ba^{++} ion added. It was found that practically no hydrogen peroxide was decomposed without a platinum electrode in 1 M NaOH, and the decomposition rate was much greater with a cathodized electrode than that with an anodized electrode (21). In the presence of Ba^{++} ion the decomposition rate was greater by about 20% with either a cathodized or an anodized platinum electrode.

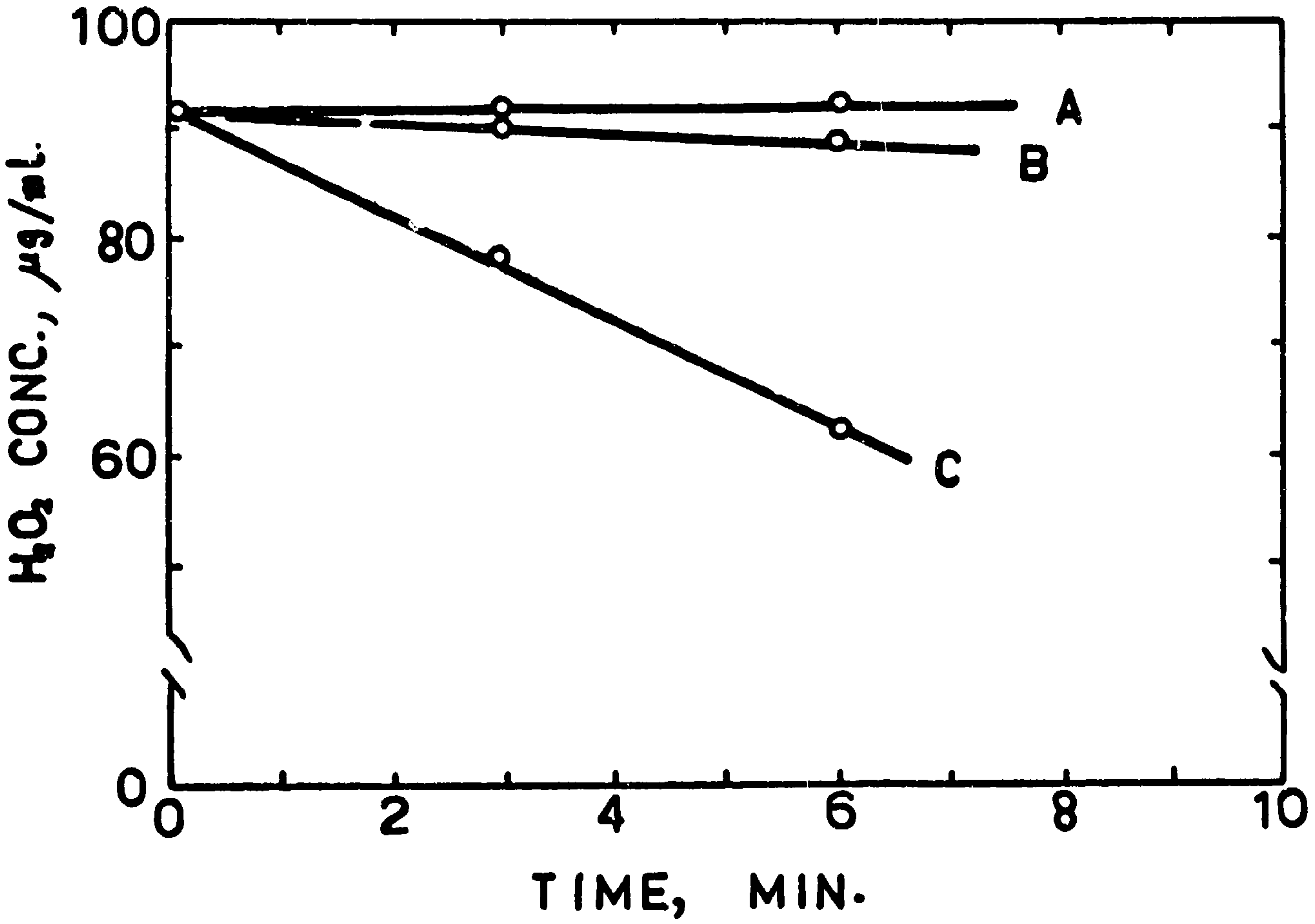

Figure 9. H_2O_2 decomposition in 1 N H_2SO_4 with platinum electrodes. A: represents six experiments with anodized or cathodized electrodes in 1 N H_2SO_4 containing KBr (10^{-4}, 10^{-3}, 10^{-1} M), B: with an anodized electrode in 1 N H_2SO_4, C: with a cathodized electrode in 1 N H_2SO_4.

The method just described, by which electrochemical formation of H_2O_2 was found by extrapolating to zero electrolysis time, has disadvantages. The determination of very small amounts of hydrogen peroxide formed in a short electrolysis time was not accurate; moreover, it was felt that the electrode surface was changing to some extent during the first one or two minutes in the constant current electrolysis, since the potential was changing.

In an attempt to overcome these difficulties the following method was tried with four differently pre-treated platinum electrodes. Both the efficiencies (for 10 minutes of electrolysis at 1.0 mA) and the rates of hydrogen peroxide decomposition in a solution of 120 μg H_2O_2/ml were measured for the four electrodes in 1 M NaOH with and without Ba^{++} added. These results are plotted in the graph shown in Figure 10. The four points on each curve are for anodized, cathodized, aqua regia-treated, and heated (in air at 700°C) platinum electrodes. The points taken in 1 M NaOH fall on one curve (A) and the points taken in 1 M NaOH + 10^{-2} M $Ba(OH)_2$ fall on the other curve (B). The extrapolation of curve A to zero decomposition rate goes to almost 100% efficiency and the extrapolation of curve B does not appear to go to zero. These results imply that the electrode processes for the oxygen reduction in 1 M NaOH with Ba^{++} ions present is different at least to some extent from that in pure 1 M NaOH. If the low efficiency in the presence of Ba^{++} were simply due to a higher rate of hydrogen peroxide decomposition, the data with Ba^{++} present should fall on curve A and the extrapolation to zero decomposition should go to 100% efficiency. We may conclude that oxygen is electrochemically reduced to OOH^- at platinum electrodes in 1 M NaOH, but in the presence of Ba^{++} ions another simultaneous electrochemical process takes place which does not produce hydrogen peroxide, or OOH^- is electrochemically reduced further.

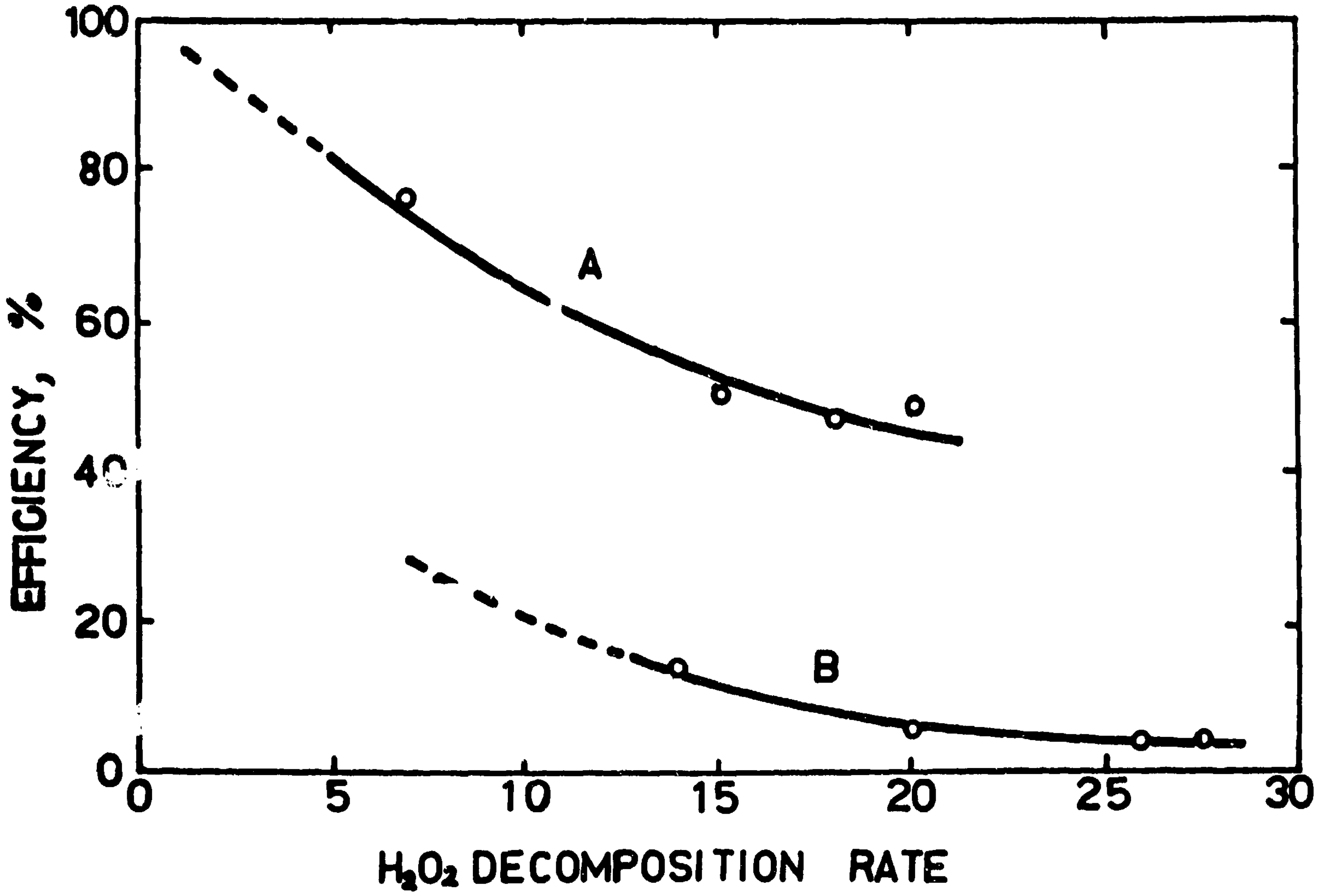

Figure 10. Relation between the efficiency of H_2O_2 formation and H_2O_2 decomposition rate. The efficiency was measured at a constant current of 1 ma for 10 min. and the decomposition rate was expressed in the decrease of H_2O_2 concentration (μg/ml) for the 1st three min. A: in 1 $\underline{M}$ NaOH, B: in 1 $\underline{M}$ NaOH + 10^{-2} $\underline{M}$ Ba($\overline{OH}$)$_2$.

c. Current-potential curves: Current-potential curves of platinum electrodes were recorded in 1 N H_2SO_4 and 1 M NaOH solutions under various conditions with potentials scanning from positive to negative potentials. The results are shown in Figures 11 and 12. The curves C_1 and A_1 in Figure 11 show that the potential where the electrochemical oxygen reduction in a pure 1 N H_2SO_4 solution takes place with an appreciable rate is about 140 mV more cathodic at a pre-anodized electrode than at a pre-cathodized electrode. This was already found by voltammetry (14) and also by chronopotentiometry (7). On addition of bromide ions to the solution, the current-potential curves shift to more cathodic potentials (curves A_2, A_3, C_2, C_3). This means that the overpotential for the oxygen reduction increases in the presence of bromide ions. Small peaks indicated by C" with a small arrow on the curves A_2 and A_3 in Figure 11 are due to the reduction of the oxide film ($PtO_2 \cdot nH_2O$) on the electrode surface. During the coulombic efficiency measurements in 1 N H_2SO_4 (Table 2) with a pre-anodized platinum electrode (18 cm^2 in surface area), the electrode potential was measured and found to change from 0.74 to 0.70 volts vs. N.H.E. during the 10 minutes of electrolysis in pure 1 N H_2SO_4 and from 0.50 to 0.37 V in 1 N H_2SO_4 + 10^{-2} M KBr. Comparing these potential values with those in Figure 11, one may conclude that in the coulombic efficiency measurements (Tables 2 and 3) oxygen reduction was carried out on a PtO_2-covered surface at the pre-anodized electrode in pure 1 N H_2SO_4 and probably on a bromide-adsorbed platinum surface (void of oxide) in the 1 N H_2SO_4-containing bromide.

In alkaline solution, again oxygen is reduced at more anodic potentials at a pre-cathodized electrode than at a pre-anodized electrode as shown by the curves C_1 and A_1 in Figure 12. The overpotential for the oxygen reduction increases when Ba^{++} is added at both pre-anodized and pre-cathodized platinum electrodes. The peaks d' and C" correspond to the reduction of the $Pt(OH)_2$

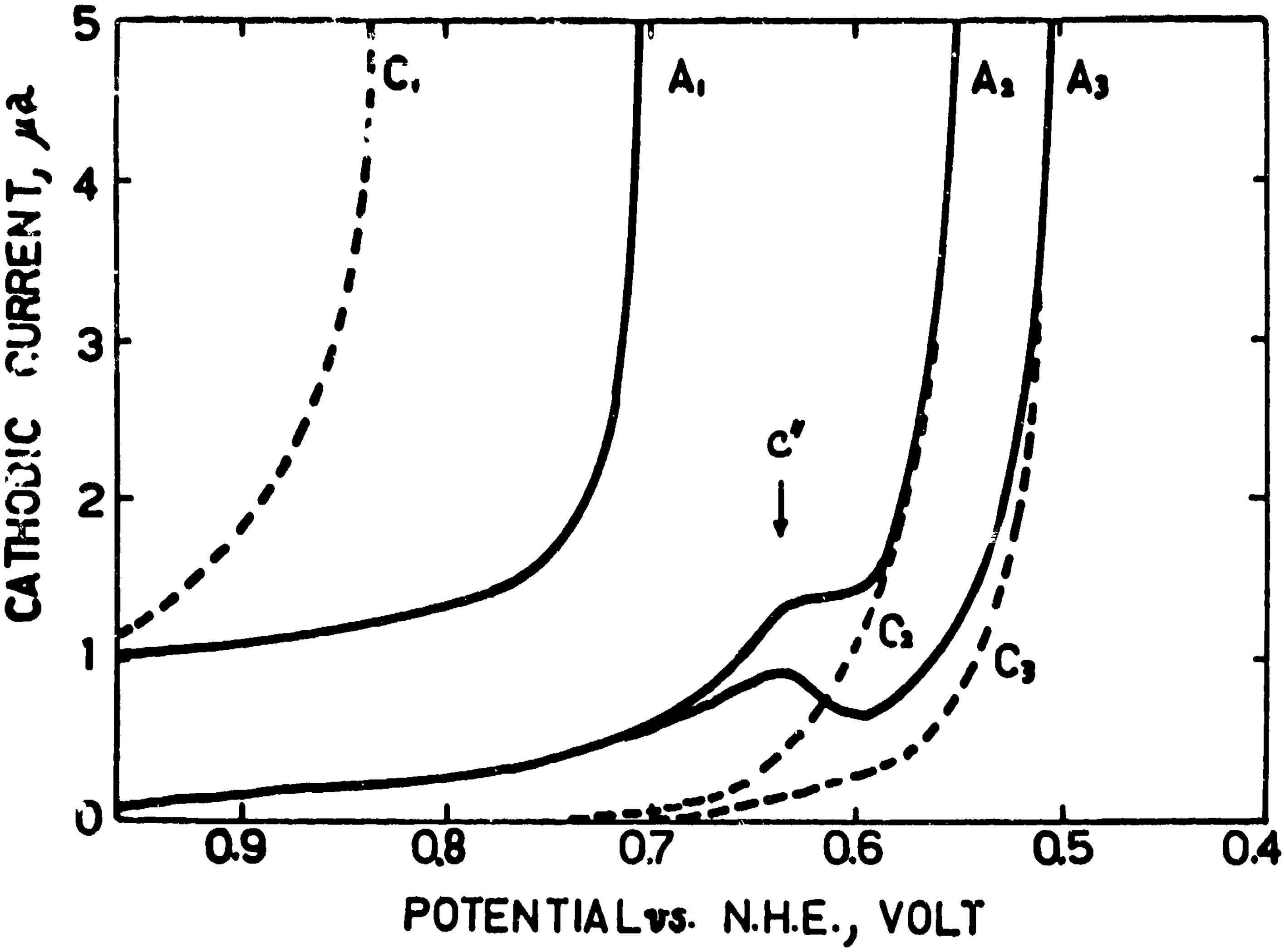

Figure 11. Current-potential curves of pre-anodized and pre-cathodized platinum electrodes (apparent area: 0.05 cm^2) taken in 1 N H_2SO_4 with oxygen gas bubbling. The potential scanning rate was 1.2 mv/sec.

A_1 - pre-anodized Pt in 1 N H_2SO_4
A_2 - pre-anodized Pt in 1 N H_2SO_4 + 10^{-3} M KBr
A_3 - pre-anodized Pt in 1 N H_2SO_4 + 10^{-2} M KBr

C_1 - pre-cathodized Pt in 1 N H_2SO_4
C_2 - pre-cathodized Pt in 1 N H_2SO_4 + 10^{-3} M KBr
C_3 - pre-cathodized Pt in 1 N H_2SO_4 + 10^{-2} M KBr

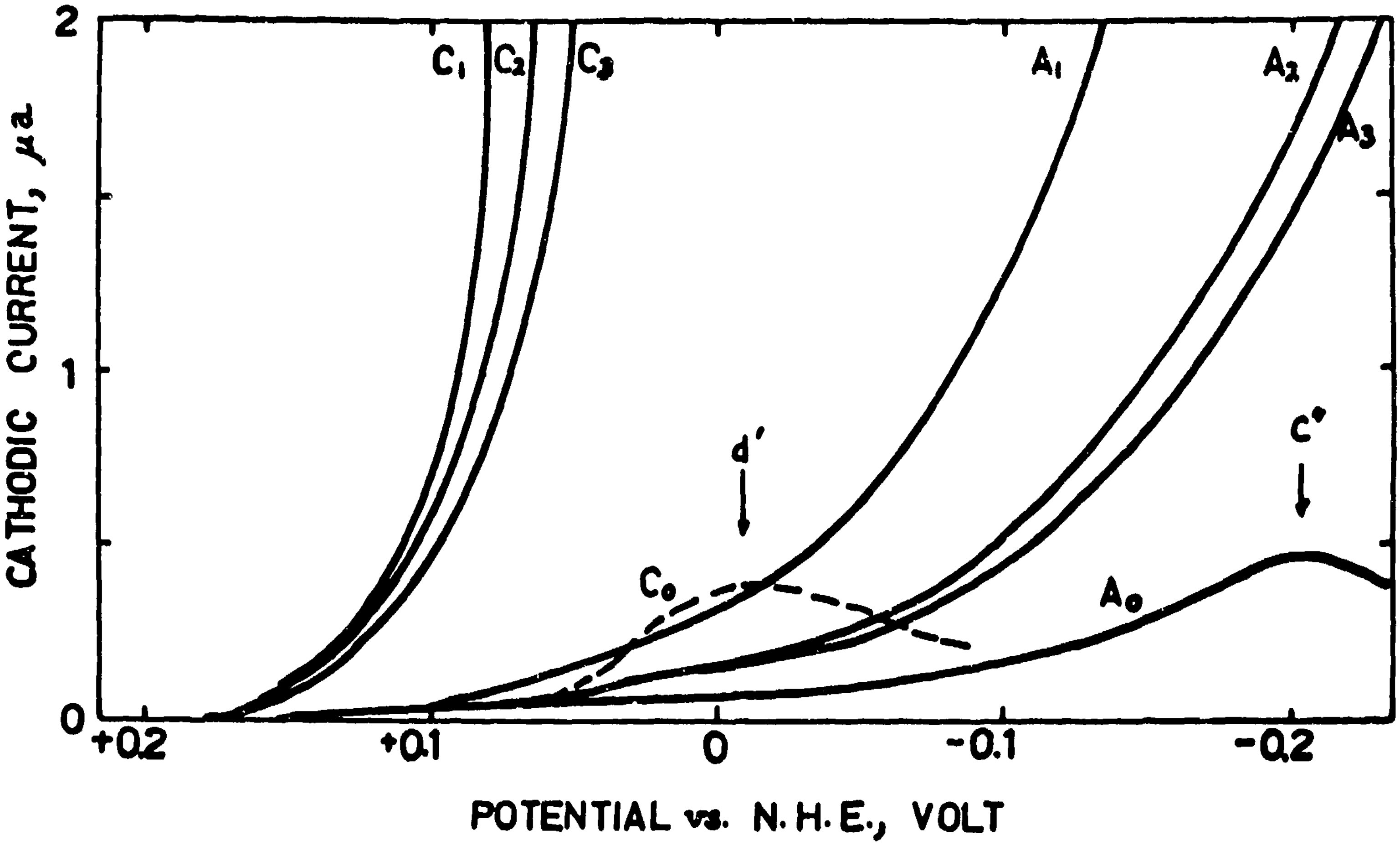

Figure 12. Current-potential curves taken at pre-anodized and pre-cathodized platinum electrodes (apparent area: 0.05 cm^2) in 1 M NaOH. The potential scanning rate was 0.6 mv/sec.

A_0 - taken at a pre-anodized electrode in N_2-saturated 1 M NaOH

A_1 - taken at a pre-anodized electrode in 1 M NaOH with O_2 bubbling

A_2 - taken at a pre-anodized electrode in 1 M NaOH + 4 x 10^{-4} M $BaCl_2$ with O_2 bubbling

A_3 - taken at a pre-anodized electrode in 1 M NaOH + 4 x 10^{-3} M $BaCl_2$ with O_2 bubbling

C_0 - taken at a pre-cathodized electrode in N_2-saturated 1 M NaOH

C_1 - taken at a pre-cathodized electrode in 1 M NaOH with O_2 bubbling

C_2 - taken at a pre-cathodized electrode in 1 M NaOH + 4 x 10^{-4} M $BaCl_2$ with O_2 bubbling

C_3 - taken at a pre-cathodized electrode in 1 M NaOH + 4 x 10^{-3} M $BaCl_2$ with O_2 bubbling.

(or adsorbed oxygen) film and $PtO_2 \cdot nH_2O$ on the electrode surface, respectively. The electrode potentials during the coulombic efficiency measurement in 1 M NaOH (Table 1) were -0.035 V and +0.063 V *vs.* N.H.E. in pure 1 M NaOH for the pre-anodized and the pre-cathodized electrodes, respectively, and -0.015 V and +0.064 V *vs.* N.H.E. in 1 M NaOH + 5 x 10^{-3} M Ba^{++} for the pre-anodized and the pre-cathodized electrodes, respectively. Comparing these potentials to those believed to be associated with the reduction of the oxide films (peak d' and C" in Figure 12), one can conclude that in the coulombic efficiency measurements the oxygen reduction occurred on the PtO_2-covered surface at the pre-anodized electrode and on the $Pt(OH)_2$ (at least in parts)-covered surface at the pre-cathodized electrode in 1 M NaOH, regardless of the presence or absence of Ba^{++} ions.

d. *Influence of pH, current density, and potential:* The coulombic efficiency for hydrogen peroxide production in a neutral solution (pH 7.0) was measured at a pre-anodized electrode. The results given in Table 4 show that the efficiency values (Run No. 1, 2, and 3 in Table 4) fall between the efficiency values in 1 M NaOH and 1 N H_2SO_4 solutions (Tables 1 and 2). The addition of bromide increased the efficiency and the addition of zinc ion decreases it slightly as one can expect from the results obtained on the addition of anions and cations to alkaline and acid solutions.

The coulombic efficiency for the hydrogen peroxide formation was also measured over a wide potential range in 1 M NaOH. The results shown in Figure 13 were obtained by passing a current of 1 to 18 mA with an electrode of 16 cm^2 for 2.5 to 15 min depending on the current. As shown in the Figure, the efficiency values decrease with decreasing electrode potential. The factors contributing to this may be as follows. First, at relatively cathodic potentials, the platinum surface is no longer covered with oxide film, but with adsorbed hydrogen to some extent and the catalytic activity for decomposing hydrogen peroxide may be greater than those at anodic

Table 4. Coulombic Efficiency for H_2O_2 Formation in a Neutral Solution at a Pre-anodized Platinum Electrode.

Run no.	Electrolyte	Electrolysis time	H_2O_2 formed*	Efficiency
1	0.2 M NaAc + HAc (pH 7.0)	5 min	11.6 μg	18.4%
2	" "	10	18.7	17.6
3	" "	15	28.0	17.6
4	" + HAc + 0.03 M KBr	10	46.7	44.0
5	" " + 0.1 M KBr	10	45.5	43.0
6	solution of No. 4 + 0.01 M $ZnSO_4$	10	38.0	35.9
7	" + 0.05 M $ZnSO_4$	10	38.5	36.3

* At a pre-anodized electrode of 18 cm^2 at a constant current of 1.0 mA.

potentials where an oxide film exists on the surface. The decomposition of hydrogen peroxide on platinum has been considered as an electrochemical process (46,47) and therefore should be dependent on the electrode potential. Second, at the most cathodic potential (-0.775 V), 18 mA per 16 cm^2 had to be passed to maintain the potential and this may have exceeded the diffusion limiting current+. Third, some other parallel oxygen-reduction processes and the hydrogen peroxide reduction process may occur to a greater extent at the more cathodic potentials than at the relatively anodic potentials.

At any rate, it should be noted that some hydrogen peroxide formation is certainly taking place on the pre-anodized platinum even at a potential just before the beginning of hydrogen evolution and that Ba^{++} ions added to the 1 M NaOH still produce a small decrease in the H_2O_2 formation, even though the

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\+ The diffusion limiting current may be estimated from the equation $i_L = nf\ Dc/\delta$ where f = faraday, D = diffusion coefficient, c = concentration, and δ = effective thickness of diffusion layer. A value of i_L = 1.0 ma/cm^2 is obtained with the following values: δ = 0.005 cm for the gas-stirred solution, c = 0.8×10^{-6} mole/cm^3, n = 2, and D = 2.7×10^{-5} cm^2 sec^{-1}.

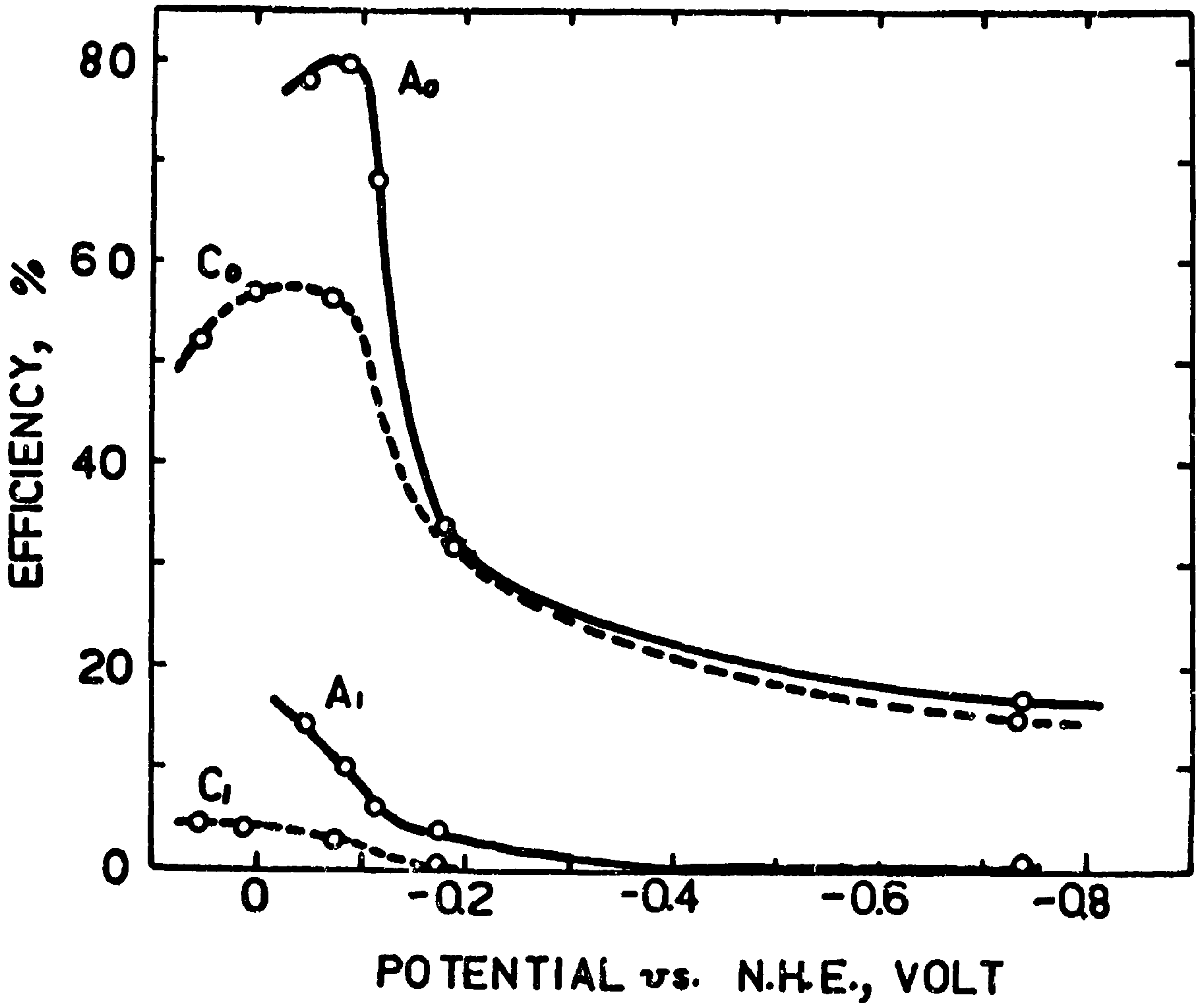


Figure 13. The coulimbic efficiency values for H_2O_2 formation in the oxygen reduction process on platinum electrodes at various potentials in 1 M NaOH.

A_o - in 1 M NaOH at a pre-anodized electrode
A_1 - in 1 M NaOH + 10^{-2} M $Ba(OH)_2$ at a pre-anodized electrode

C_o - in 1 M NaOH at a pre-cathodized electrode
C_1 - in 1 M NaOH + 10^{-2} M $Ba(OH)_2$ at a pre-cathodized electrode.

electrode surface should not be covered with oxide film at this cathodic potential. Further research is necessary to clarify this point.

3. Effects of cations and anions on oxygen evolution

a. Platinum electrodes: Current-potential curves for the oxygen evolution process were recorded for a platinum electrode in 1 M NaCH, scanning from +0.6 V to more anodic direction. The effects of $NaClO_4$, $Sr(ClO_4)_2$, and EDTA added to the solution are shown in Figure 14. The results show that the electrode surface seems to attain a constant state after the first two curves taken successively (curves 1, 3) and the addition of 10^{-2} M $NaClO_4$ (and also KCl in a separate experiment) has very little effect (curves 3, 4). The overpotential for the oxygen-evolution process increases with increasing amounts of $Sr(ClO_4)_2$ (curve 5, 6, 7). The addition of EDTA brings the curve back to the original position, probably because Sr^{++} ions are complexed and no Sr^{++} is adsorbed on the surface.

Among the three alkaline earth ions, the effectiveness of these ions in increasing the over-potential was in the following order: $Ba^{++} < Sr^{++} < Ca^{++}$, when compared at the same concentration. The solubility of $Ca(OH)_2$ is so small in 1 M NaOH, however, that the effect of Ca^{++} was not evaluated properly.

Some question might be raised as to the function of EDTA in the experiments just described. The possibility exists that the EDTA might be electrochemically oxidized on the platinum electrode in 1 M NaOH in addition to forming a complex with Sr^{++} ion. In order to examine this point, 25 ml of an 1 M NaOH + 0.020 M EDTA solution was electrolyzed in an H-cell with a platinum electrode (6.0 cm^2) as the anode at a current density of 1.0 mA/cm^2 for up to 60 min with oxygen-gas stirring. The concentration of the EDTA was determined every 20 min by titrating a 5.0-ml portion of the solution with a standard solution of 0.0100 M $ZnSO_4$ using Eriochrom Black T as an indicator. During the electrolysis the electrode potential rose from an initial value of +0.865 to

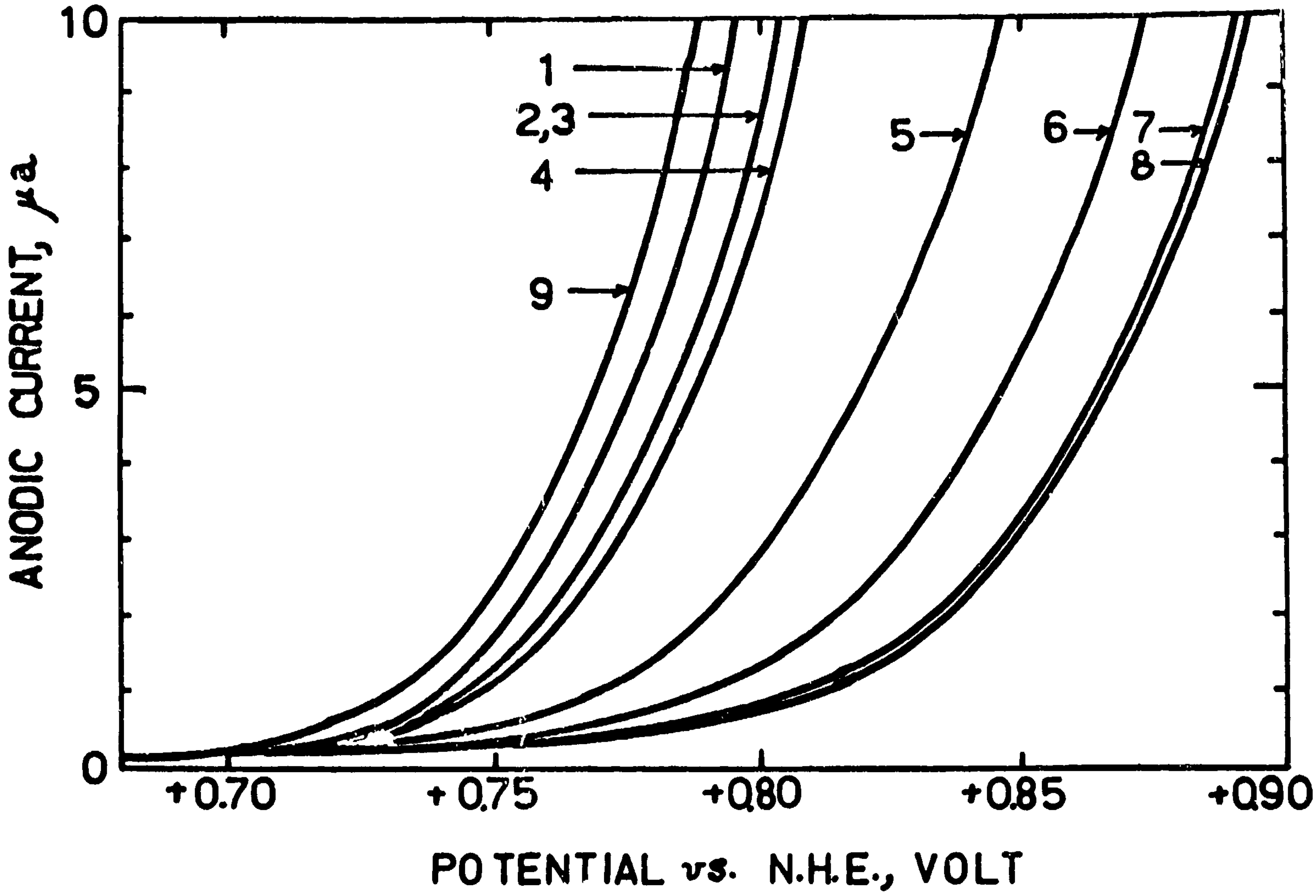


Figure 14. Current-potential curves for a pre-anodized platinum anode (0.13 cm^2 in surface area) for the oxygen evolution process in an O_2 gas-stirred 1 M NaOH solution. The potential scanning rate was 0.6 mv/sec. These curves were taken in the following order.

1. 1st run in 1 M NaOH
2. 2nd run immediately after the 1st run in 1 M NaOH
3. 3rd run immediately after the 2nd run in 1 M NaOH
4. in 1 M NaOH + 10^{-2} M $NaClO_4$ after curve 3
5. in 1 M NaOH + 10^{-2} M $NaClO_4$ + 10^{-4} M $Sr(ClO_4)_2$ after curve 4
6. in 1 M NaOH + 10^{-2} M $NaClO_4$ + 10^{-3} M $Sr(SlO_4)_2$ after curve 5
7. in 1 M NaOH + 10^{-2} M $NaClO_4$ + 10^{-2} M $Sr(ClO_4)_2$ after curve 6
8. repeated in the same condition as curve 7
9. in 1 M NaOH + 10^{-2} M $NaClO_4$ + 10^{-2} M $Sr(ClO_4)_2$ + 2 x 10^{-2} M EDTA.

+1.055 V vs. N.H.E. at the end of the electrolysis. It was found that the concentration of the EDTA solution remained constant within the analytical error even after 60 min. This suggests that EDTA is not oxidized electrochemically under these conditions.

b. Other electrodes: The same experiments as just described for the platinum electrodes were carried out on nickel, palladium, nickel oxide, gold and carbon anodes to establish if the addition of Ba^{++}, Sr^{++}, and Ca^{++} to 1 M NaOH produced similar effects with these electrode surfaces. The results for a nickel electrode are shown in Figure 15; the relative effect of Sr^{++} and EDTA are essentially the same as for a platinum electrode except that oxygen evolution takes place at much lower potentials on nickel than on platinum. Tafel slopes were obtained from these current-potential relations. These results are summarized in Table 5, which shows that the oxygen overpotential increases by 15 to 90 mV in the presence of 5×10^{-3} M $Sr(ClO_4)_2$ depending on the electrode material, and the Tafel slope increases only slightly in most cases when $Sr(ClO_4)_2$ is added to 1 M NaOH.

DISCUSSION

In order to understand the considerable effect of small amounts of anions and cations added to the electrolyte as described in the preceeding sections, we must assume that those ions are adsorbed on the electrode surface. The nature of the adsorption mechanism has to be discussed first.

Various metal oxides with hydrated surfaces generally have an ion-exchange property. The hydroxyl groups which exist on the surface of those metal oxides in aqueous solutions usually dissociate in two ways depending on the pH of the solution (9); i.e.,

$$\vdots M - OH \rightleftharpoons \vdots M^{+} + OH^{-} \text{ (acid)} \qquad [5]$$

$$\vdots M - OH \rightleftharpoons \vdots MO^{-} + H^{+} \text{ (alkaline)} \qquad [6]$$

where $\vdots M$ represents a metal atom on the surface of the oxide. These OH^{-} or H^{+} ions are held near the $\vdots M^{+}$ or $\vdots MO^{-}$, respectively. Therefore, anion

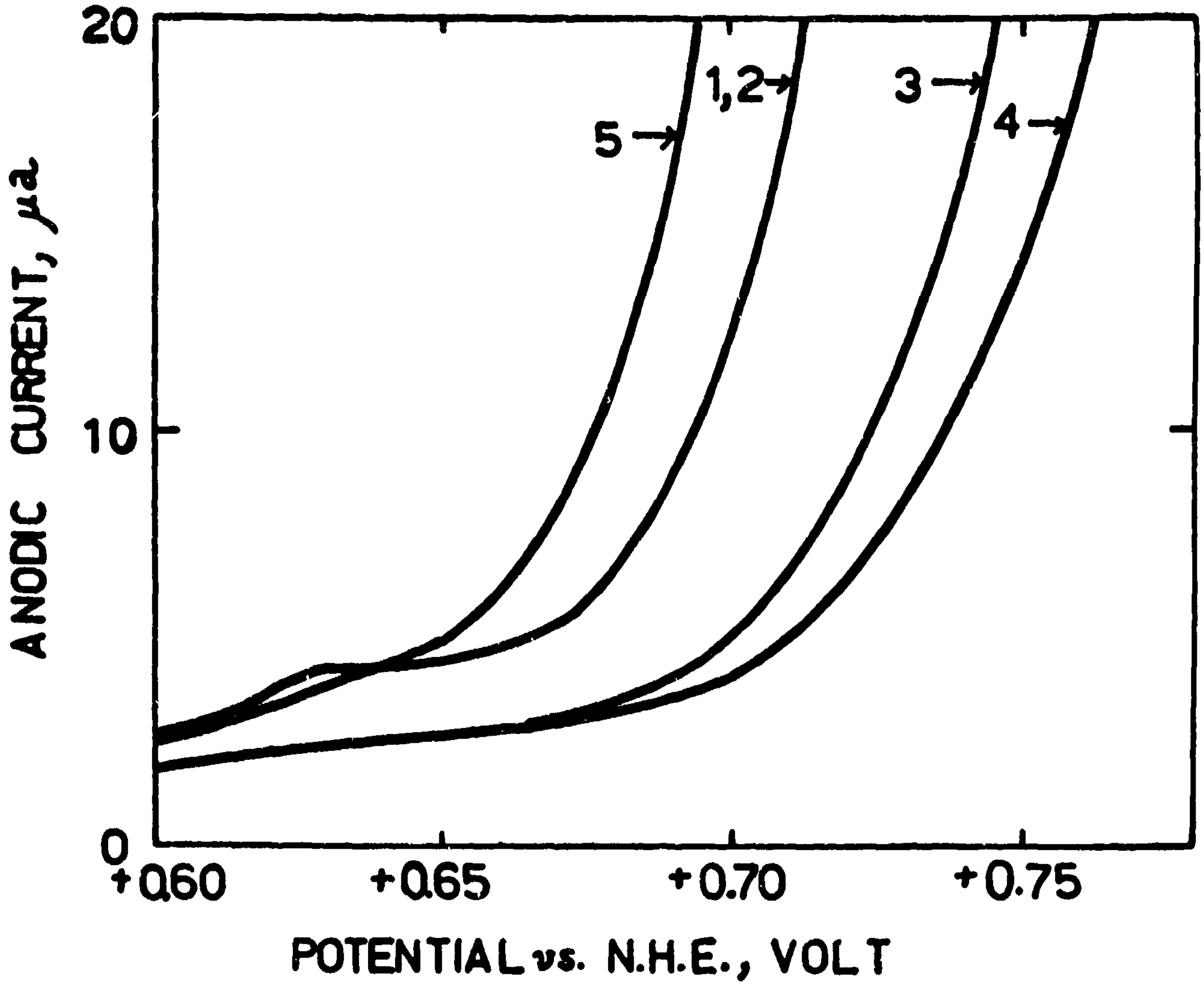


Figure 15. Current-potential curves for a nickel anode (approximately 0.2 cm^2 in surface area) for the oxygen evolution process in an oxygen gas-stirred 1 M NaOH solution taken at 0.6 mv/sec. These curves were taken in the following order.

1. in 1 M NaOH
2. in 1 M NaOH + 10^{-2} M $NaClO_4$
3. in 1 M NaOH + 10^{-2} M $NaClO_4$ + 10^{-3} $Sr(ClO_4)_2$
4. in 1 M NaOH + 10^{-2} M $NaClO_4$ + 5 x 10^{-3} M $Sr(ClO_4)_2$
5. in the same solution as for curve 4 x 10^{-2} M EDTA

Table 5. Influence of Sr^{++} on the Oxygen Overpotential

Electrode	Potential at 0.05 mA/cm^2 (*vs.* N.H.E.)		Potential increase produced by Sr^{++}	Tafel Slopes (mV/decade)	
	1 M NaOH	1 M NaOH + 5 x 10^{-2} M $Sr(ClO_4)_2$		1 M NaOH	1 M NaOH + 5 x 10^{-3} M $Sr(ClO_4)_2$
Ni	0.678 V	0.738 V	60 mV	72	85
Pd	0.754	0.769	15	85	85
Pt	0.785	0.875	90	57	80
NiO*	0.823	0.901	78	54	77
Au	0.858	0.928	70	67	77
carbon**	0.935	0.978	43	105	105

* Prepared by heating a nickel rod at 700°C for 10 min in air.

** Spectroscopic carbon rod.

exchange-adsorptions in acid solutions and cation exchange-adsorptions in alkaline solutions take place as shown in the following equations, respectively:

$$\vdots\, M^{+}\, OH^{-} + Cl^{-} \rightleftharpoons \vdots\, M^{+}\, Cl^{-} + OH^{-} \qquad [7]$$

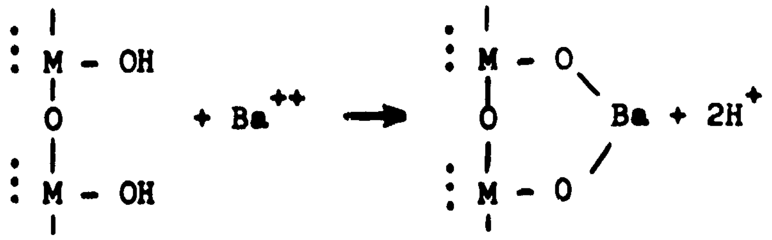
$$\vdots\, M^{-}\, H^{+} + M^{+} \rightleftharpoons \vdots\, MO^{-}\, M^{+} + H^{+} \qquad [8]$$

The platinum electrode is covered with an oxide film over a certain potential range; therefore, anion adsorption in acid solution and cation adsorption in alkaline solution on the electrode surface should be expected.

It has been shown that O_2 is reduced on a PtO_2-covered surface at a pre-anodized electrode and on a surface covered with $Pt(OH)_2$ (or adsorbed oxygen) at a pre-cathodized electrode in 1 M NaOH (Figure 12) and that a small amount of Ba^{++}, Sr^{++}, and Ca^{++} has a considerable effect (Table 1). These cation effects can be understood on the basis of ion-exchange adsorption when the electrode is covered with an oxide or hydroxide layer.

The anion effect on oxygen reduction found in acid solution (Table 2) also can be explained on the basis of anion-exchange adsorption; however, the electrode surface is probably no longer covered with oxide film in the presence of Br^{-} ion during the oxygen reduction (Figure 11). This anion effect in acid and neutral solutions, therefore, must be explained by the specific adsorption of halide ions on the platinum. The effects of such specific adsorption of halide ions on various electrode processes have been described frequently in the literature (48-50).

The author previously suggested (10,11) that the nature of the divalent cation adsorption on the metal oxides was not simple electrostatic attraction but a kind of coordination bonding. Furthermore, the author has proposed that a substantial fraction of the adsorbed divalent cations are involved in surface chelates. For example, with Ba^{++} ions the surface hydroxyl groups may be involved as follows:



[9]

If the adsorption force were just a ordinary electrostatic attraction, Na would be expected to be adsorbed to a far greater extent than Ba^{++} in 1 M NaOH because the concentration of Na^{+} is far greater than that of Ba^{++} and the total molality of the electrolyte is high in the present work (see ref. 51).

It was shown that Ba^{++}, Sr^{++}, and Ca^{++} ions have a marked effect on the oxygen evolution process. This means these positively charged ions must have been adsorbed on the electrode at very positive potentials. This also implies that simple electrostatic attraction between the divalent cation and the electrode surface is not the principal adsorption force and that probably surface complex formation of the type just described is important.

Although the electrochemical reduction of oxygen has been found to be dependent on the surface state of the platinum electrode and the ion adsorption on the platinum electrode, further research is required to establish fully the mechanism for the oxygen reduction.

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