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Final Report

FURTHER DEVELOPMENT OF A BIOCIDE GENERATION
AND
WATER SYSTEM PASSIFICATION SYSTEM

Contract No. NAS 9-12998

April 18, 1975

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Final Report

FURTHER DEVELOPMENT OF A BIOCIDE GENERATION AND WATER SYSTEM PASSIFICATION SYSTEM

Abstract

The research presented herein consists of further development and testing of the previously demonstrated scheme of electrochemically generating iodine *in situ* in a potable water metallic storage system. The degree of concurrent corrosion protection and of metallic ion buildup was determined. A working metal bellows system was evaluated and tested for the buildup of metallic ions comparable to that reported in the current research spacecraft potable water specifications. This effort resulted in the assembly and testing of an integrated system which may be used to maintain the potability of water which is passively stored in metallic containers for extended periods of time.

Experiments have been conducted in solutions containing from less than 1 ppm to 500 ppm. The optimum concentration of iodine is in the range of 6-10 ppm. The higher concentrations (>20 ppm) are slightly more agressive than the recommended optimum concentrations.

Introduction

The purpose of this effort was to further develop and test an integrated concept for the preservation of the chemical and microbiological quality of a spacecraft potable water system during long-term storage in metallic containers.

Corrosion and the associated production of potentially toxic metallic cations in potable water systems will continue as a potential problem in all potable water spacecraft systems. Further, it will be a continuing requirement that a continuous biocidal agent level in spacecraft potable water be maintained. The latter of these currently requires mechanical addition of the agent. This requires excessive crew time and effort. The former obviously must be limited from the system mechanical integrity aspect as well as the human physiological (toxicological) standpoint. The work presented herein clearly demonstrates the feasibility of eliminating both of these problems.

The further eleucidation of galvanostatic and potentiostatic behavior of stainless steels was initiated in the early stages of the following program for the purpose of supplementing previous work and existing documentation so that it could be readily reduced to practice for aerospace applications. The data should also be useful in predicting the probability of serious galvanic effect when dissimilar metals are in contact in the presence of a "service-related" electrolyte such as potassium iodide and/or iodine type species. This final report describes in detail how the study was conducted and the apparatus used.

Experimental

A. Initial Potentials

The preliminary procedure and apparatus for measuring the initial electrode potentials was by the use of two half-cells. The reference electrode was saturated calomel electrode (SCE). The working electrodes (anode) were composed of the various stainless steels (17 cm^2) and a platinum gauze was used as the counter electrode (cathode). Various supporting electrolytes were used for calibration. The half-cells were internally connected by a saturated potassium chloride solution. The half-cell configuration is shown in Fig. 1. All measurements were made using a wide range, potentiostat acid galvanostat. A hydrogen half-cell was used in the preliminary work for reference purposes only.

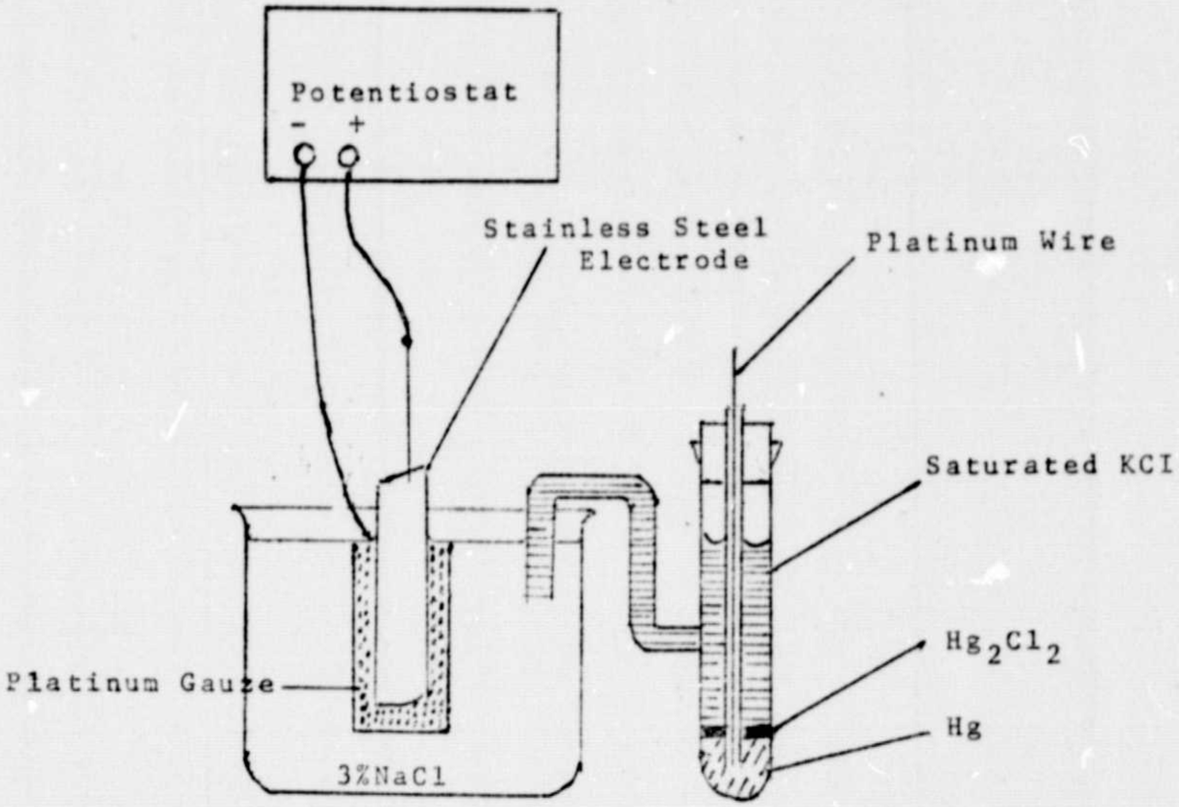
Measurements of the initial potentials of silver, gold, and platinum were in good agreement with known, published values for these materials.

It was established that neither the surface area of the metal being tested nor the interelectrode distance appreciably affected the results as long as a planar electrode was used. Liquid junction potentials added an additional EMF to the circuit. Appropriate corrections were made wherever a liquid junction constituted a part of the cell. The solution resistance and total capacitance was measured by means of an impedance badge.

B. Anodic Polarization Studies

Measurements were made in a conventional type

Figure 1.


Potentiostat
-
+
Stainless Steel Electrode
Platinum Wire
Saturated KCI
Hg_2Cl_2
Hg
Platinum Gauze
3%NaCl

electrolyte cell. Stirring was provided by a stirrer in a side compartment so that diffusion was the rate controlling step in the oxidation process. The solution was deaerated by bubbling purified nitrogen or argon through the cell until the current was comparable to that of charging current (non-faradaic--corresponding approximately 0.1 microampere). Known quantities of oxygen were also added to the iodide solutions to determine their overall effect on the passivity of the stainless steel. A large area platinum wire gauze, as well as 316 and 321 stainless steels, were used as the working electrodes and Pt was used as the cathode to avoid the possibility of anodic dissolution in slightly anodic, iodide containing electrolytes. The stainless electrodes were also used to study the effect and role of alloying elements such as Cr, Ni, Mn, Mo, etc. on the generation of iodine as well as effect on the passivity of the stainless steel electrodes.

The electrodes were fabricated from type 304, 316, 321, and 347 stainless steels. They were washed and degreased with acetone and benzene, followed by activation in a $1N \cdot H_2SO_4$ solution. All solutions were made up with deionized water that was distilled twice in glass (conductivity 10^{-6} $ohm^{-1}cm^{-1}$). The concentration of potassium iodide was varied from a few parts per million to several thousand parts per million. The pH was adjusted with NaOH and H_2SO_4. Buffer solutions consisting of boric acid salts were used in some experiments. Prior to the addition of the potassium iodide and/or iodine, the solutions were pre-electrolyzed with dual platinum electrodes at 10 milliamperes for 48 hours.

The potentials were measured versus a saturated calomel electrode (SCE) using a Research Potentiostat. Direct current was supplied by a Kepco regulator power supply operating to 600 volts and controlled by a set of resistors.

Specimen Preparation

All stainless steels were cleaned, vapor honed, and polished, followed by rinsing in distilled water immediately before testing. Values for passivated stainless steel-type alloys were obtained after immersion of the alloy in a 50 percent by weight sulfur acid solution for 30 minutes, followed by a distilled water rinse.

The stainless steels were passivated in an oxygen free borate buffer solution (pH = 8.4) for several hours.

Test Conditions

All tests were conducted at ambient temperatures (30°C) in [illegible] 3-percent sodium chloride solution adjusted to pH 6.[illegible]-7.2. The solution was exposed to air but not artifically aerated or agitated. The immersion time in the supporting electrolyte varied from 10 minutes to one hour, depending upon the time required to reach a sensibly constant value of potential.

All of the stainless steel-type alloys studied failed to produce usable consistent values when tested over a 10 minute period. For this reason, it was decided that a study of longer immersion time vs potential be made for all of the materials to establish a state of equilibrium. The purpose of this study was to try to relate electrode potentials more closely to actual service conditions.

Each of the materials was mounted in a 250-milliliter beaker. The beaker was then filled to 1/2 inch from the top with a 3-percent salt solution. All beakers and reservoirs were interconnected by salt bridges. Each specimen was then connected to the numbered terminal module for ease of reference. By inserting the leads from the potentiometer into the proper sockets, the potential between any two electrodes in the system could be measured. Most preliminary measurements, however, were made with silver as the reference electrode.

All measurements in this study were relative to the silver electrode as zero. This procedure was adopted because the EMF of silver is zero and comparisons of a silver electrode with a calomel electrode yielded consistent values for a three month period. Table I gives the active region and regions of passivity for the various types of stainless steels.

TABLE I.

Type	Condition	Form	Potential, volts Initial	 Aged	Effective Potential Range, volts
304	Annealed	Rod	-0.40 Active +31 Passive	-	--
316	Annealed	Rod	-0.36 Active +10.20 Passive	+.22	+.21 to +.28
321	Annealed	Rod	-0.38 +0.27	-	0.26 to +.08
347	Annealed	Rod	-0.42 +0.18	-	-0.27 to +.02

The effective potential ranges may be considered as a useful service related value for design purposes for a brine solution having a rather high ionic strength. The regions of passivity and activity may be observed to be approximately the same in this type of environment. This data has no direct correlation with that of an iodine type species but is given to demonstrate the relative narrow regions of passivity for a brine solution. On the other hand, iodine type solutions have been shown to remain over a wide range of potentials.

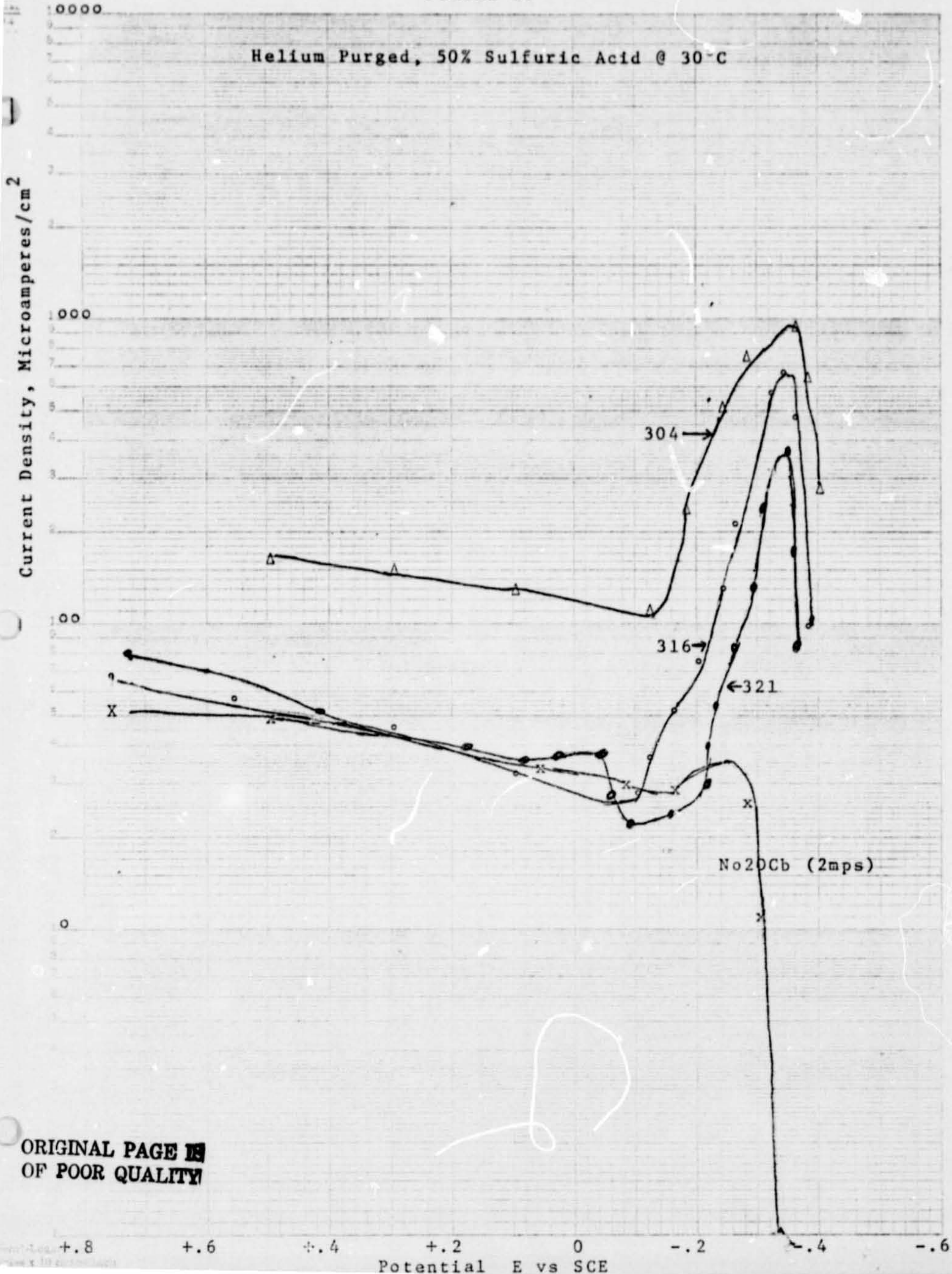
Polarization Data

Figure 2 shows the anodic polarization data for several stainless steels in 50% sulfuric acid. The more noble (positive) corrosion potentials of the No. 20 Collumbrum (b) alloy and its low critical anodic current density indicate that it will be the most resistant to sulfuric acid. Likewise, Type 321 followed by Type 316 would be expected to be superior to Type 304. The corrosion rates as determined by a Corrosometer, along with loss in weight is also given for the various stainless alloys and collumbrum alloy. There is a good correlation between the electrochemical polarization studies, weight loss, and corrosion test data as well as known service performance. Metals susceptible to pitting usually do so when they are passive over almost, but not quite all, of their surface. This situation exists as we move from passive to the transpassive region. As a general rule, the more positive the potential at which breakdown of passivity occurs, the greater the pitting resistance.

The beneficial effect of a more noble pitting potential is borne out by other laboratory tests and service experience. For example, Types 321 and 316 stainless steel will resist pitting in some iodide environments that pit Type 304. Likewise, Type 347 is somewhat superior to Type 430 or 434 stainless steel.

The effect of many environment and material changes on corrosion therefore can be effectively studied with anodic polarization diagrams.

FIGURE 2.


Helium Purged, 50% Sulfuric Acid @ 30°C
Current Density, Microamperes/cm2
10000
1000
100
10
304
316
321
No20Cb (2mps)
X
+.8
+.6
+.4
+.2
0
-.2
-.4
-.6
Potential E vs SCE

Results

When the 316 and 321 stainless steels were subjected to anodic current deviation ranging from 10 to 50 microamperes per square centimeters, a steady oxygen evolution potential was maintained as long as the current was applied (approximately 6 hours) for iodide concentrations (pH 1-6) of less than 1000 ppm. The stainless electrodes were observed to behave differently in acidic solutions when the potassium iodide concentration was increased to 1500 ppm and greater. At current densities (anodic) greater than 10 microamperes per square centimeter a maximum appears in the current--time curve (Fig. 3) This maximum was found to be dependent on the iodide concentration. Despite continued flow of anodic current, the potential was found to decay to more active values (dotted line). Fig. 4 shows anodic polarization curves of 321 stainless steel at various pH values with and without oxygen present. Each point represents the maximum observed potential regardless of whether a steady state had been achieved. The current density was found to increase by approximately one order of magnitude when the stainless steel was polarized in an acid solution (pH 0.3) was saturated with oxygen (approximately 8.3 ppm) (Figure 5) Increasing the pH to 0.7 caused the curve to be displaced slightly to more anodic potential. The hump in the curve for the more anodic solution is presumably due to chromium dissolution at the lower current densities and due to oxygen saturation and evolution at the higher current densities.

In the present case, some corrosion of the 321 stainless steel was noted in the high current density regions in solution with 1000 ppm of KI and more. At these high potentials iodine evolution is possible thermodynamically and probably does occur simultaneously with O_2 evolution. Attack of the electrode

FIGURE 3.

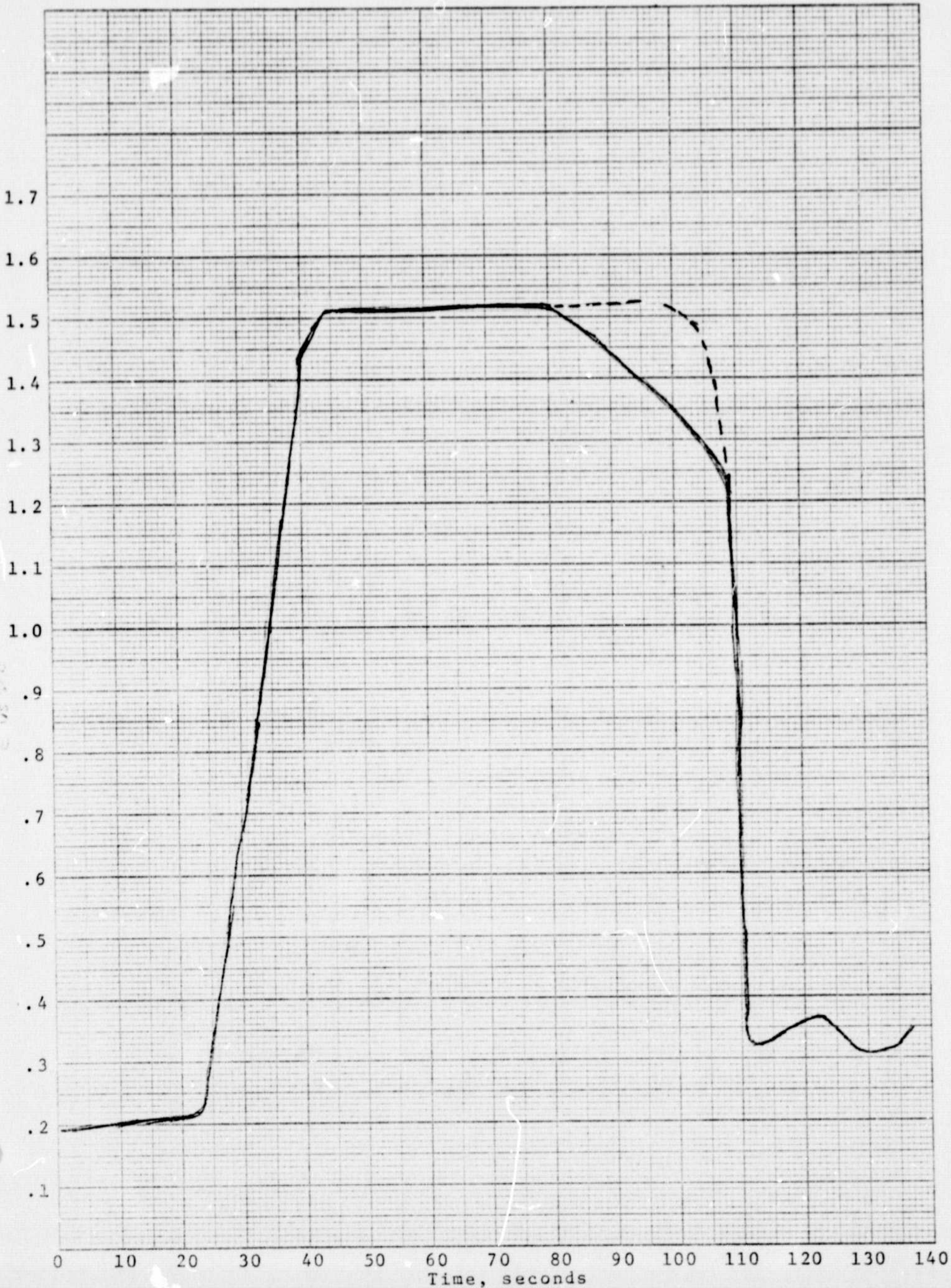

1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time, seconds

FIGURE 4.

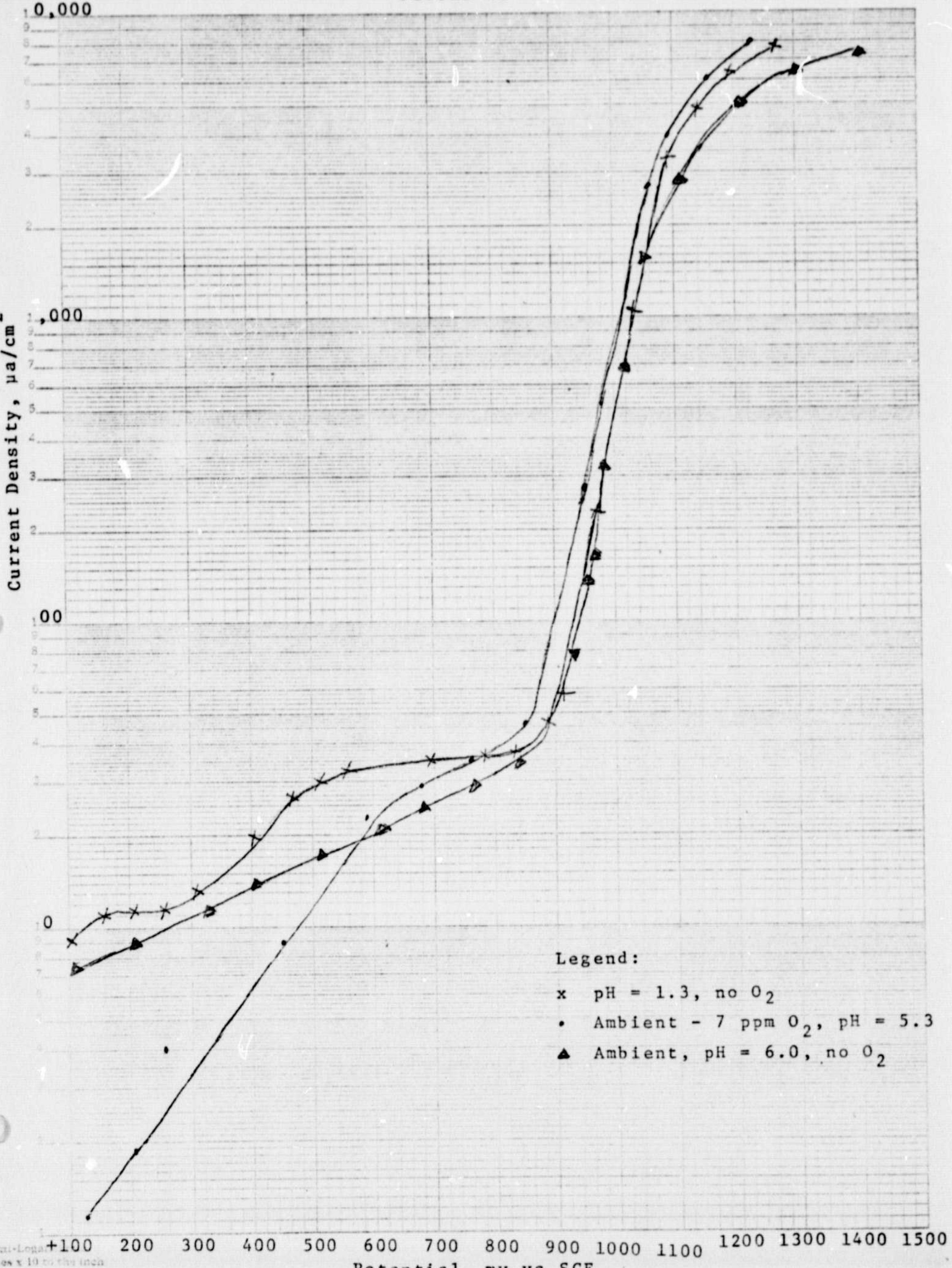
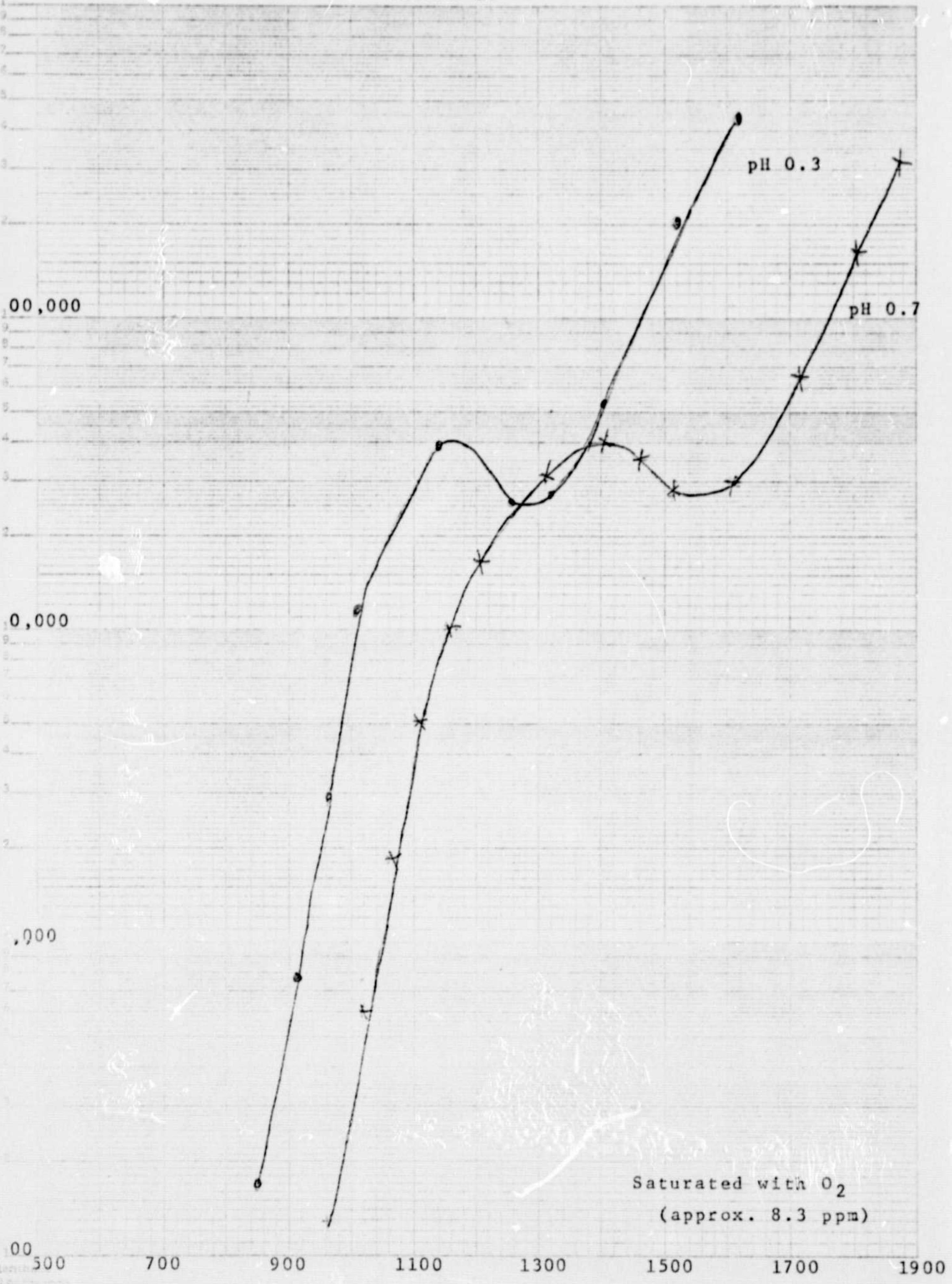

10,000
1,000
100
10
1
Current Density, μa/cm²
+100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Potential, mv vs SCE
Legend:
x pH = 1.3, no O₂
• Ambient - 7 ppm O₂, pH = 5.3
▲ Ambient, pH = 6.0, no O₂

FIGURE 5.



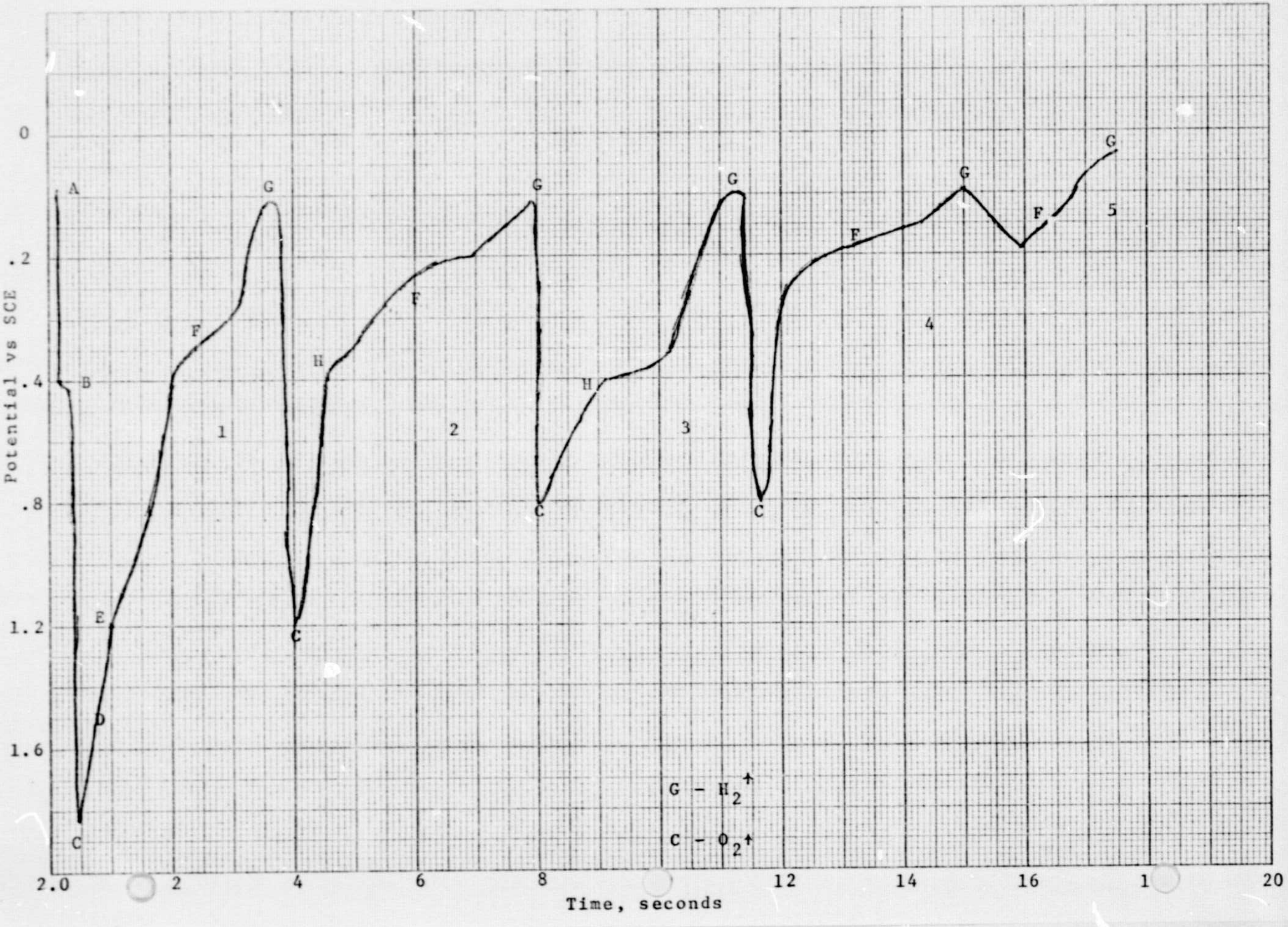
Saturated with O_2
(approx. 8.3 ppm)

by atomic iodine would account for the corrosion observed. The shift in the jump toward higher current densities seen in Fig. 5 is undoubtedly due to the increased acidity of the solutions; however, they both maintain approximately the same slope and configuration.

No pitting was observed in basic solutions of >8.

Fig. 6 shows typical time potential traces (vs SCE) for anodic passivation and its forced decay under small cathodic current densities in solution of various pH. Starting from the steady state open circuit potential (A) of section 1, anodic polarization at current densities of 10 ma/cm^2 forced the potential through that for anodic dissolution (B) to that of oxygen evolution (C). Reversing the polarity at (C) by substituting cathodic current densities on the order of 100 microamperes/(cm^2) forced the electrode potential to decay back to active values. The initial forced valve was through (D) which is the instantaneous over-voltage decay. Following (D) the exact mode of decay was interrelated with the pH. The next observed step was (E), which was the over-voltage due to high concentration polarization which was induced by continued passage of current. This decay step was found to be a function of the applied current density as well as the stirring rate (convection control) and the hydrogen ion concentration (pH). Following (E), step (F) was observed where the pH was <5; in step (H) at a pH of >9, or a mixture of the two was found at intermediate values. At constant pH the rate of decay of steps (F) and (H) was found to be a function of the cathodic current density. Following these steps, the potentials then passed uniformly to the hydrogen evolution potential (G).

FIGURE 6.


Potential vs SCE
0
.2
.4
.8
1.2
1.6
2.0
Time, seconds
2
4
6
8
12
14
16
1
20
A
B
C
D
E
F
G
H
1
2
3
4
5
G - H_2↑
C - O_2↑

Further Experiments on the Anodic Production of Iodine

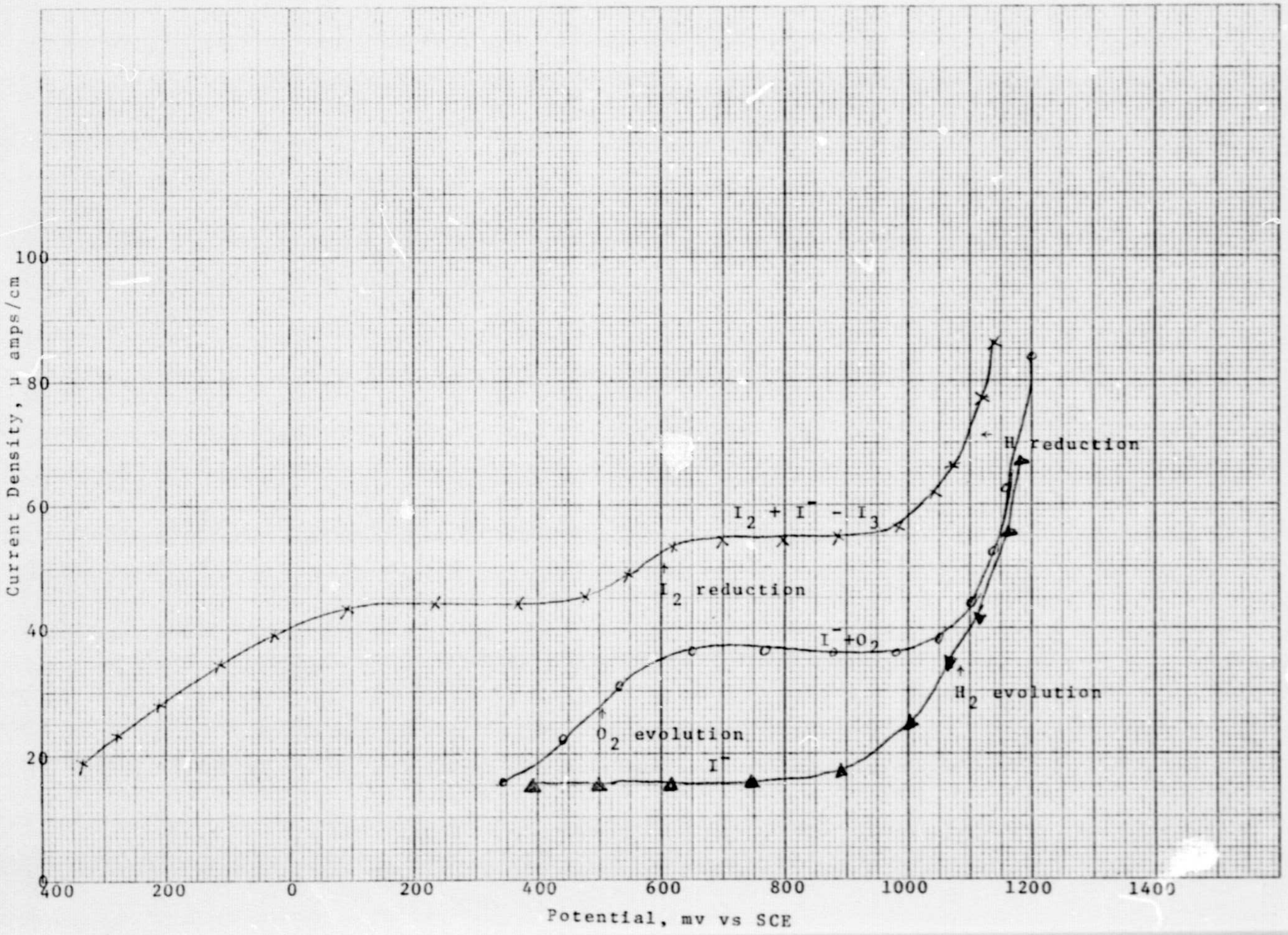
A specially constructed electrochemical cell was prepared in the form of an H cell, separated into two compartments by a fritted disc salt bridge. One compartment was filled with potassium iodide solution and a platinum electrode inserted in the iodide compartment and a 321 stainless steel electrode in the other compartment. The two cells were then connected to a source of DC potential and a very small background current was observed (<1 μa). With the application of an input signal across the electrodes, iodine may be observed to be generated at the platinum electrode and diffuse across the membrane (fritted disc) cuasing current to flow in the electrochemical cell. The increased current is fed back to the generating electrode so that iodine once formed cannot escape. The composition of the generating electrode can be made of precisely the same material (e.g., 316 or 321 stainless steel) to obtain anodically deposited iodine.

Experiments were also performed wherein two stainless steel electrodes were separated by a fritted disc and the electrolyte solution allowed to flow at a constant rate. The current in the external circuit was found to be directly proportaional to the generating current and the fluid flow.

Cathodic Polarization Studies

The cathodic polarization behavior of Type 321 stainless steel is given in Fig. 7. The potential of the polarized Type 321 stainless steel was measured with respect to that of another stainless counter electrode (also Type 321) which was in close proximity of the working electrode. The potentials were therefore measured with respect to the redox potential of the iodine--iodide couple. It is evident from Fig. 7 that the cathodic polarization takes place in the region of a positive 400 millivolts to a negative 400 millivolts. Since iodine reduction probably occurs in the region of -400 mv to -660 millivolts, this greatly diminishes the extent of polarization. The hydrogen reduction wave was observed to start in the region of -1000 mv vs. the saturated calomel electrode. It is interesting to note that the hydrogen reduction wave is shifted to slightly more positive potentials than that observed for the iodide containing solution which contains no reducible species other than that of oxygen. This shift in potential is probably due to the presence of some adsorbed iodine in the electrode surface which may act as a depolarizer in the hydrogen reduction.

FIGURE 7.


Current Density, μ amps/cm
100
80
60
40
20
0
400
200
0
200
400
600
800
1000
1200
1400
Potential, mv vs SCE
$I_2 + I^- - I_3$
I_2 reduction
H reduction
$I^- + O_2$
H_2 evolution
O_2 evolution
I^-

Cylindrical Electrode Experiments

Cylindrical electrodes of the Type 316 and 321 stainless steels were constructed to establish the rate of oxide formation with and without the presence of iodide solution. The stainless electrodes were then cathodically reduced to establish the current potential plot. Figure 8 shows the polarization curves of the Type 316 and 321 to be essentially the same when the oxide is allowed to form for 12 hours at a potential of +0.40 volts vs SCE and with the subsequent addition of 500 ppm of I^-. The anodic polarization was carried out to a potential of +1.4 volts and found to increase to a current density of 350 micro-amperes per square centimeter.

Figure 9 shows the anodic and cathodic polarization curves of Type 316 stainless steel. Iodine was observed to be liberated in the region of +0.90 volts vs SCE prior to the evolution of oxygen. The current potential plot was re-established after the oxygen evolution step and the iodine evolution found to be shifted to slightly more negative potentials ($\sim$+0.85v).

The cathodic reduction step was found to correspond to +0.10 volts before O_2 evolution and -0.11 volts after the oxygen evolution.

3 Hour Cathodic Reduction
in 1:1 $H_3BO_3:Na_2B_4O_7$ pH 8.4

FIGURE 8.

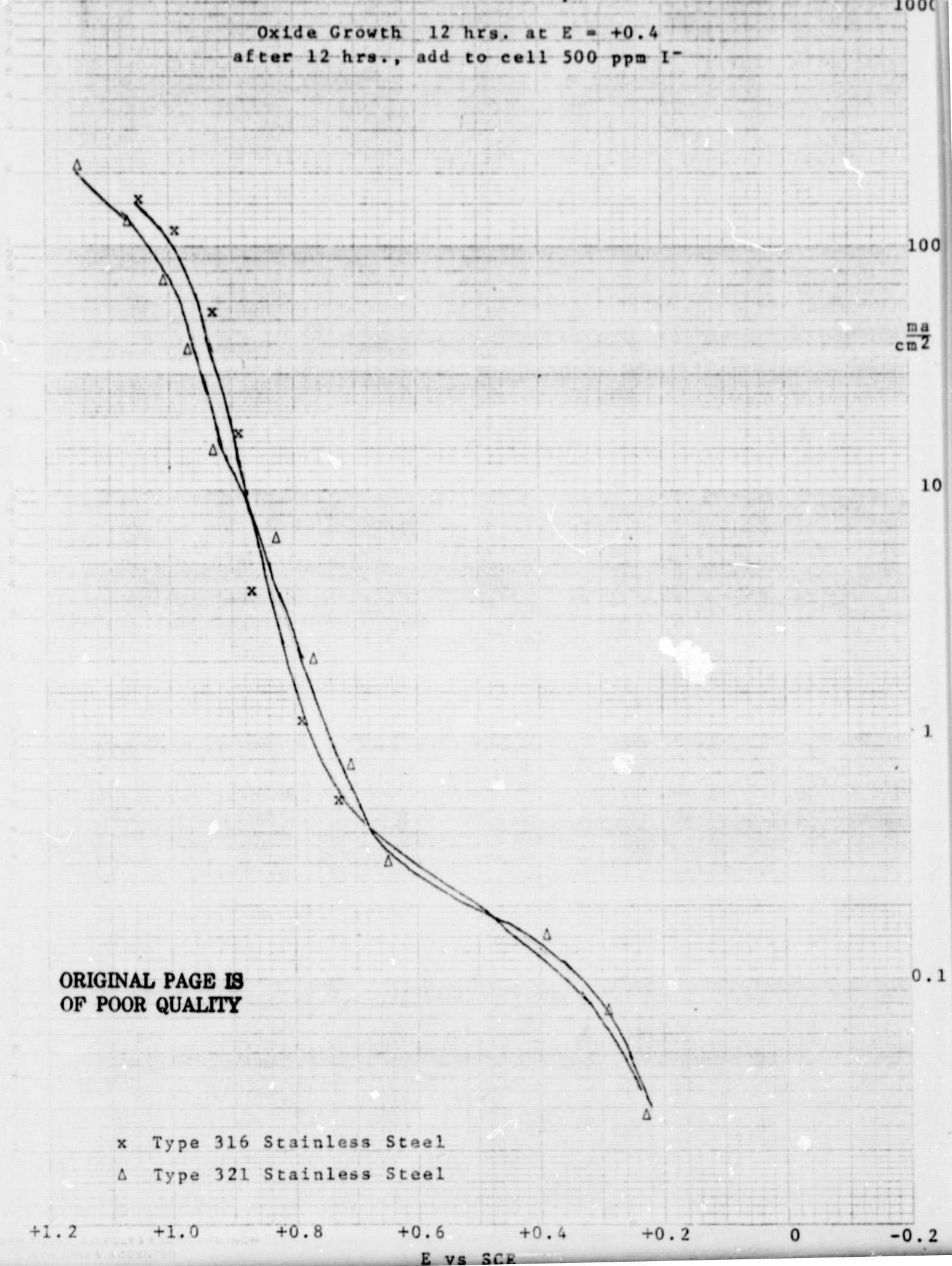


FIGURE 9.

Type 321 Stainless Steel

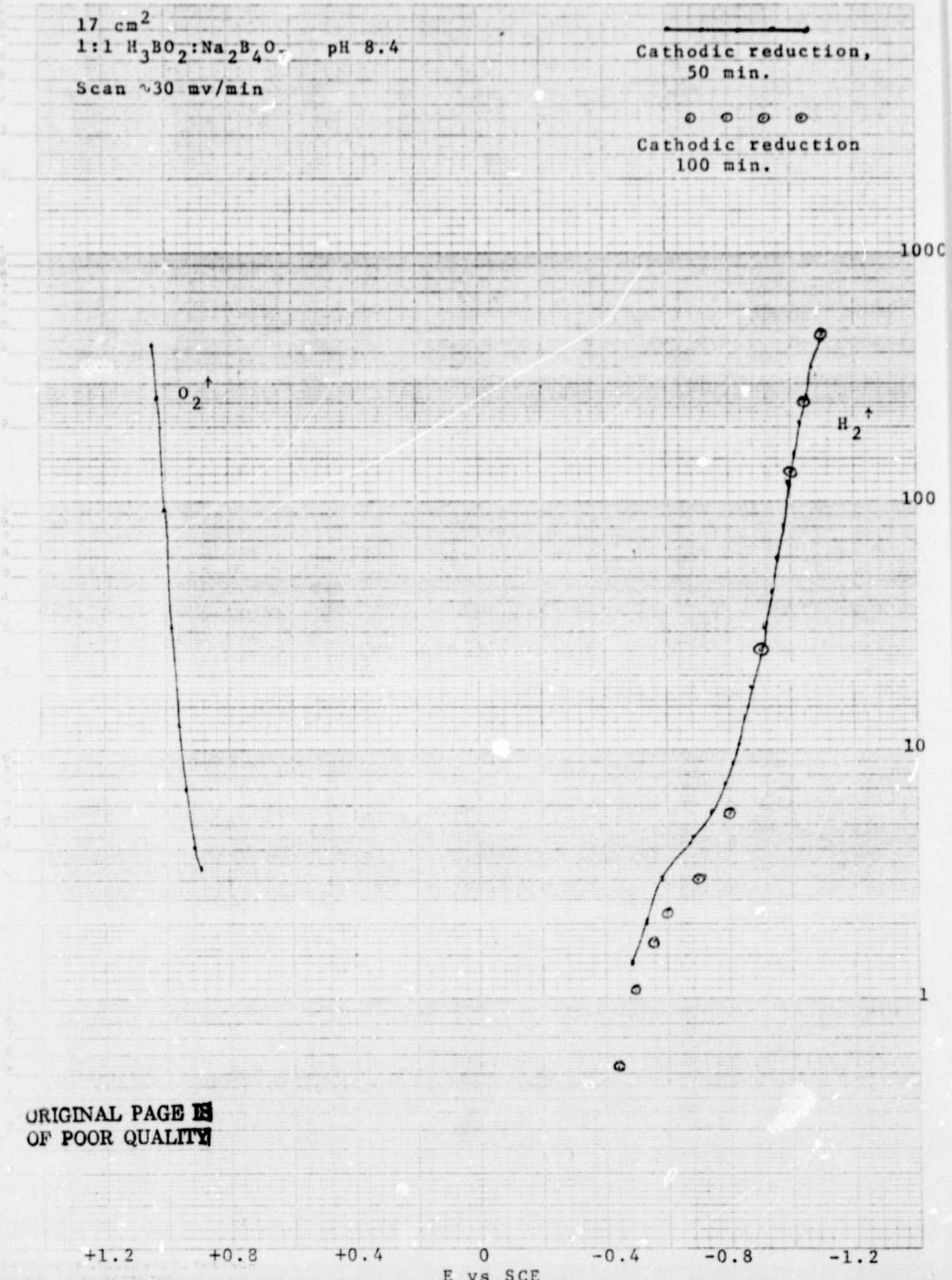


Fig. 9 shows the oxygen and hydrogen evolution curves of the boric acid-borate buffer solution. The oxygen is liberated in the region of potential of +1.0 volts when the hydrogen reduction occurs at a potential of approximately -0.90 volts.

When the oxide is grown for 100 minutes at a potential of E = +0.20 volts and with the subsequent addition of 100 ppm iodide ion, the current potential plot takes the form shown in Figure 10 .

Figure 11 gives the polarization curves when fifty parts per million of iodine is added to 100 ppm of iodide. The values given were corrected for the change in impedance due to the electrolyte composition. The anodic oxidation reaction was observed to be essentially reversible, as is demonstrated by the reduction wave shown in the region +0.1 volts vs SCE.

Figure 12 shows the anodic and cathodic polarization curves that were re-established after the oxygen evolution. The curves may be observed to be shifted to more anodic potentials.

FIGURE 10.

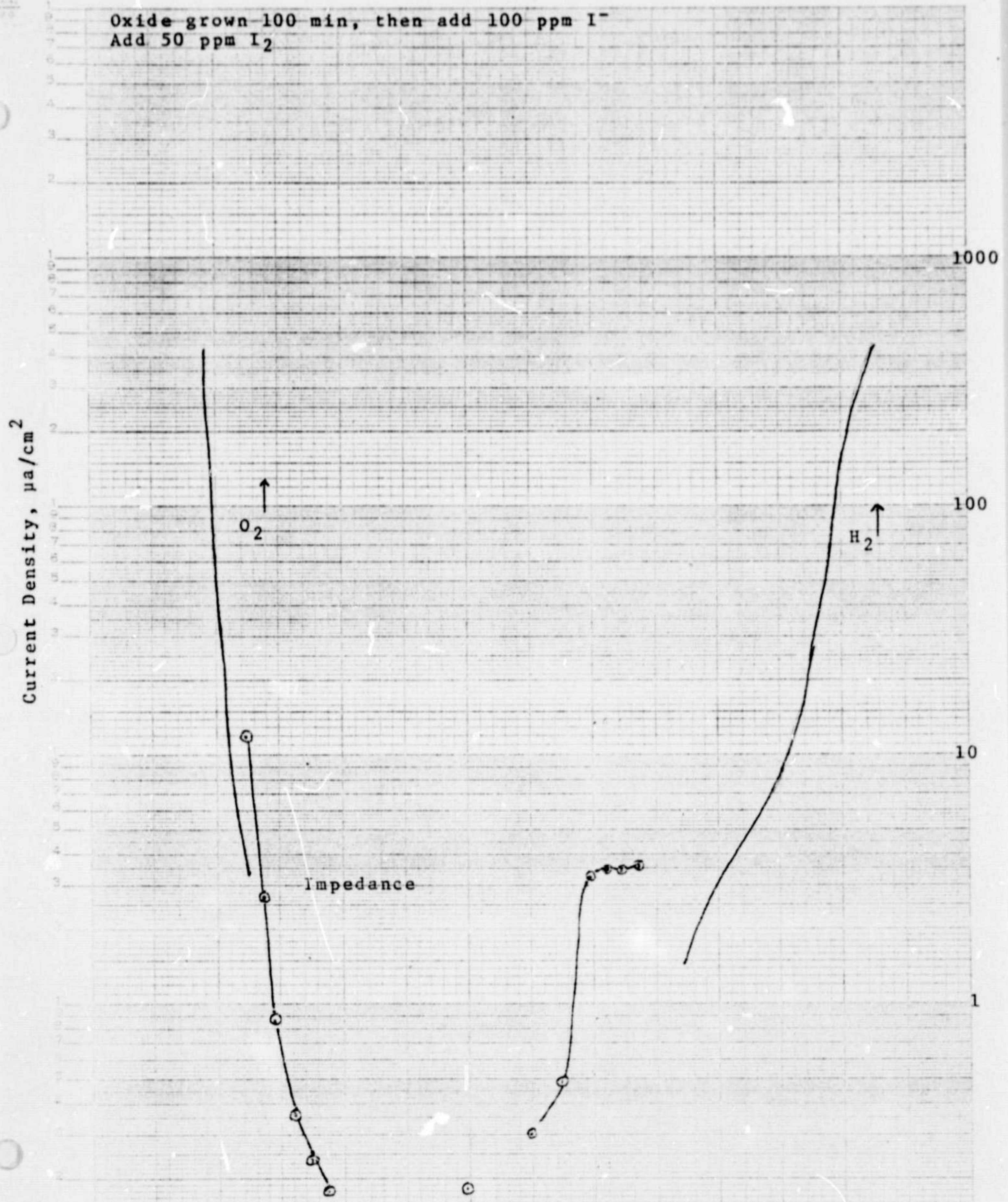

Oxide grown-100 min, then add 100 ppm I⁻
Add 50 ppm I2
Current Density, μa/cm²
1000
100
10
1
O2
H2
Impedance
+1.2
+0.8
+0.4
0
-0.4
-0.8
-1.0
E vs SCE

FIGURE 11.

Type 321 Stainless Steel

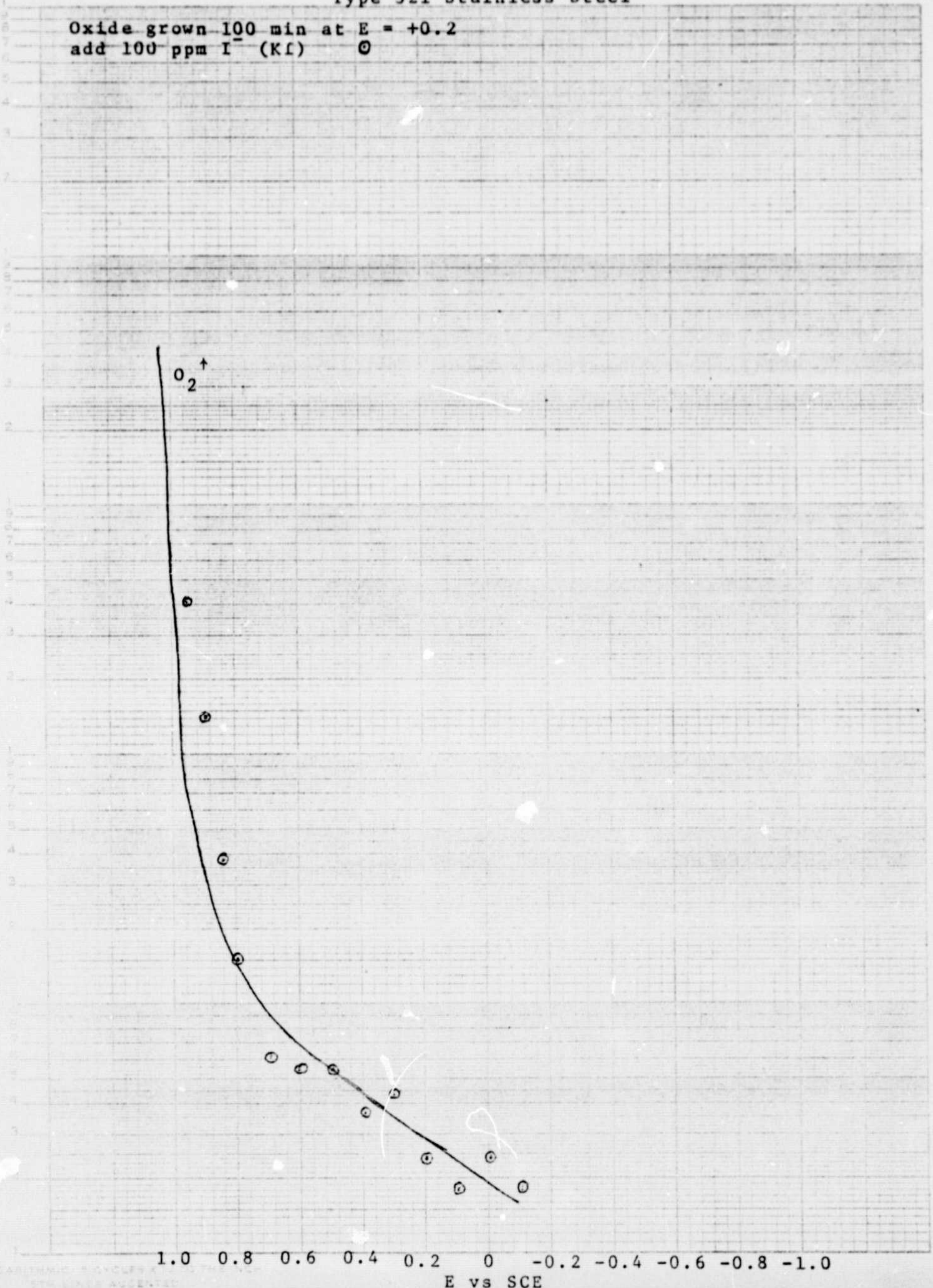
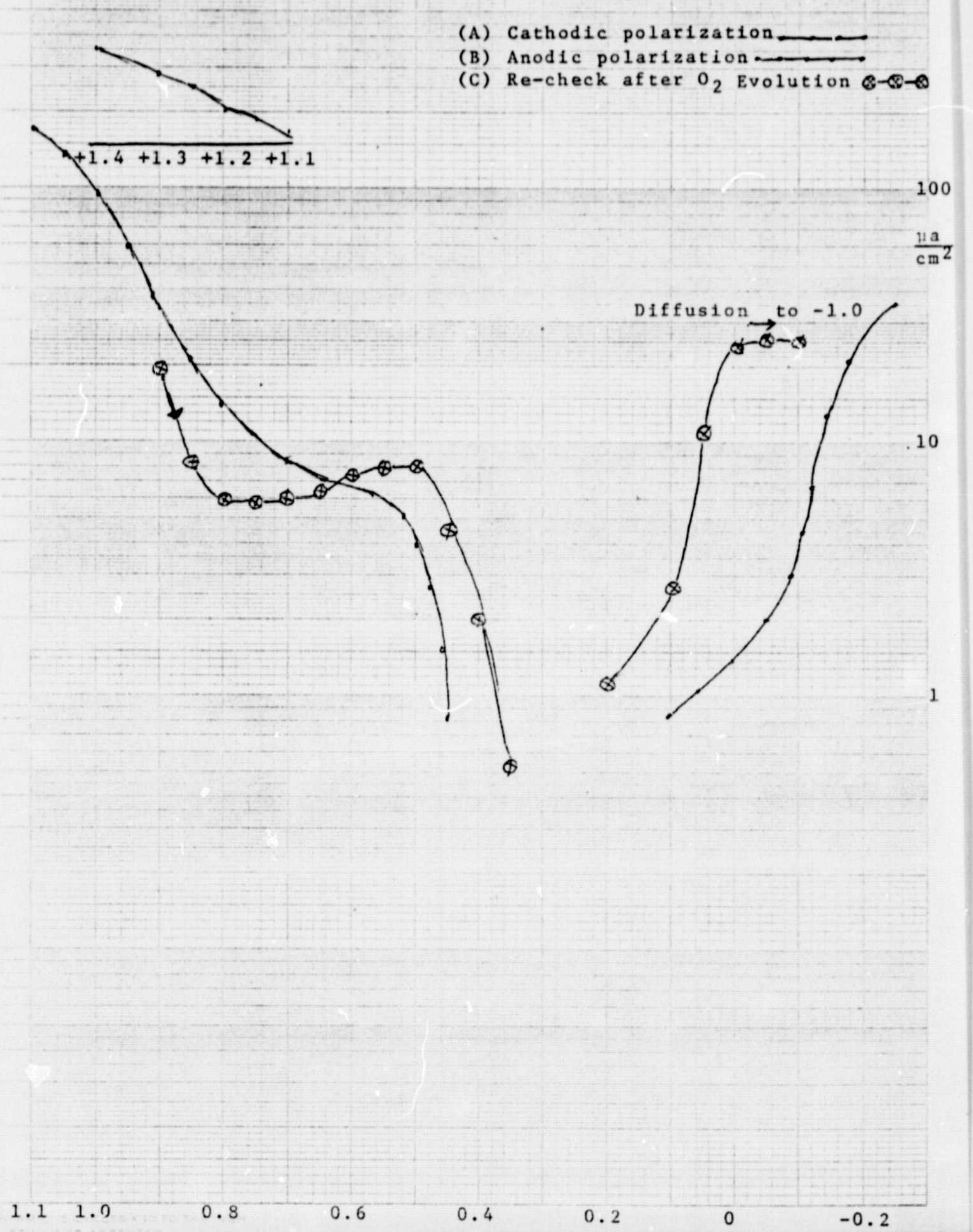


FIGURE 12.

Type 316 Stainless Cylindrical Electrode

A = 17 cm^2

500 ppm I^- + 250 ppm I_2



Corrosion Rate Measurements

Corrosion rate measurements of Type 316, 321 and 347 stainless steels have indicated that <u>active</u> corrosion does not occur in an iodine containing environment provided the concentration does not exceed 50 ppm of I_2 or I_3^-. The corrosion rates, as determined with a Corrosometer, for the stainless steels are as follows:

Type	Corrosion Rate
316	.014 mpy
321	.011 mpy
341	.029 mpy
304	.076 mpy

An active corrosion process would be expected to give a corrosion rate of greater than 0.5 mpy in the regions of cathodic potentials ranging from -0.30 to 0.50 volts.

No severe pitting was observed in any of the stainless steels when a concentration of less than 50 ppm was used in the electrochemical cell.

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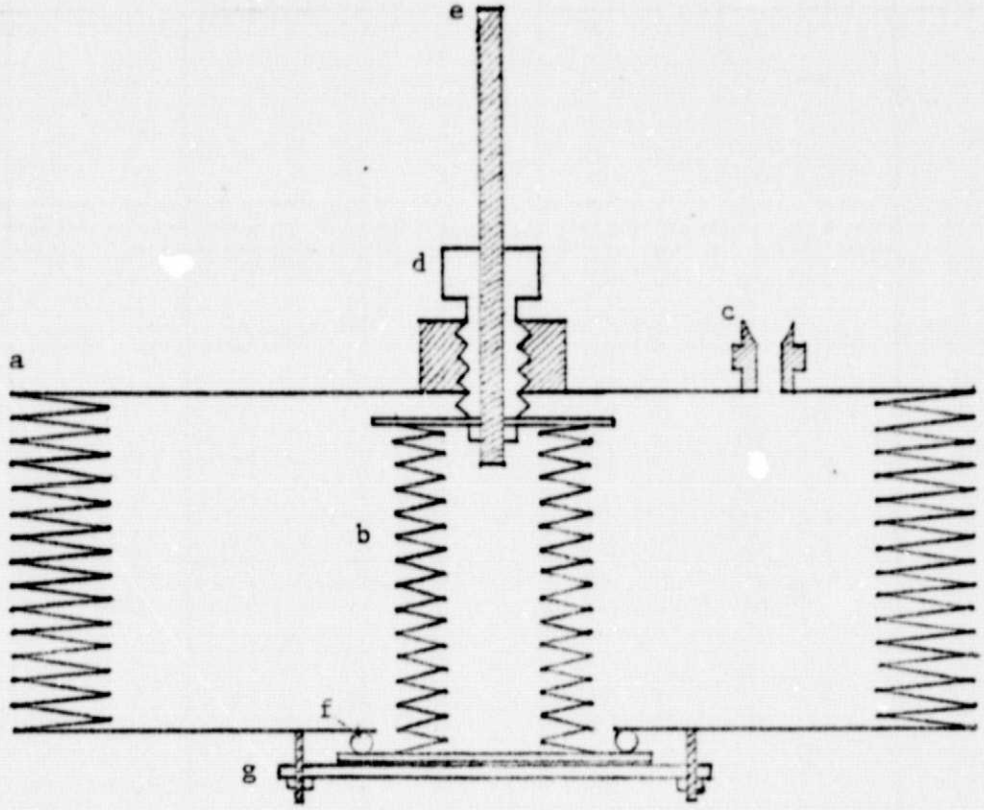
No severe pitting was observed in any of the stainless steels when a concentration of less than 50 ppm was used in the electrochemical cell.

Prototype Metal Bellows Electrochemical Cell

A working model of a stainless steel metal bellows electrochemical cell was constructed to demonstrate the feasibility of metal bellows as the working anode and a self contained counter cathode. The metal bellows configuration was designed to expand and contract to maintain a constant electrode distance, as well as provide a maximum surface area relationship. Figure 13 shows a schematic of the metal bellows cell configuration used. A saturated calomel reference electrode was introduced external to the bellows. The electrochemical cell was first evacuated to remove air and subsequently filled with deionized water containing potassium iodide. Electrochemical measurements were then made on the bellows at various degrees of expansion.

FIGURE 13.

Metal Bellows Electrochemical Cell



Description:

a) Stainless steel (316) anode

b) Stainless steel (347) cathode

c) Port for reference electrode (SCE)

d) Teflon insulator

e) Stainless steel cathode connecting rod

f) Teflon "O" ring

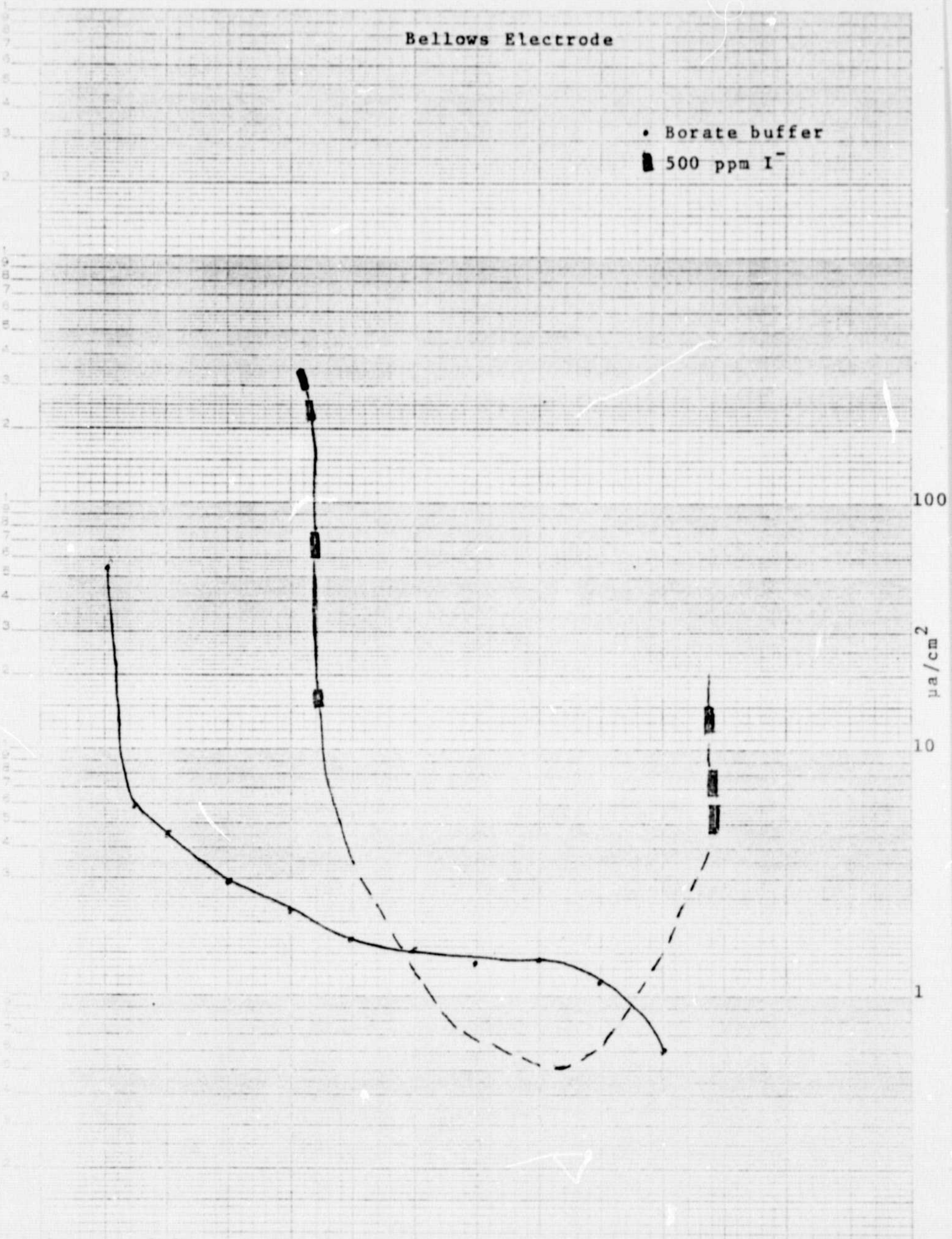
g) Phenolic insulator

Electrochemical Polarization of Metal Bellows

A passive film was first deposited on the stainless metal bellows using a deaerated borate buffer solution (pH = 8.4). Approximately 20 hours were required for the preparation of a stable passive layer. Figure 14 shows the potential vs current density plot for the passive film. The current may be observed to increase sharply in the region of +0.88 volts vs SCE. Following passivation of the metal bellows system, a 500 ppm potassium iodide solution was introduced into the metal bellows and allowed to equilibrate for 24 hours. The current was found to osciallate by approximately 10%, which is common when stainless steels are used as the passivating electrode and are immersed in the same solution (Figure 14).

The current density was found to increase sharply in the region of +0.52 to +0.58 volts, which corresponds to the anodic oxidation of KI for the production of triiodide ion. When the electrodes are polarized in a cathodic direction, the current sharply decreases to a current density of less than 1 $\mu a/cm^2$. At +0.2 volts and again in the region of -0.1 volts, the current density increases. The dotted line portion of the graph is somewhat ill defined, probably because of the depassivating character of the stainless steel in this region of potential. This increase in current is due to the reduced iodide species. The current oscillation in the cathodic region was also found to be of the order of ±10%.

FIGURE 14.



Bellows Electrode
• Borate buffer
▮ 500 ppm I⁻
100
10
1
μa/cm²
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4

Discussion

The region of optimum anodic potentials ranges from +0.70 volts to +1.0 volts vs SCE. In the region of potential there is a linear relationship with current. At potentials more positive than +1.0 volts, oxygen is produced which decreases the polarization rate. Frequently it has been found that adsorption of oxygen, or some oxygen containing species, is a precusor to oxygen evolution. Therefore, it seems reasonable to assume that the initial effect of the anodic current is a conversion of adsorbed water depoles into a layer of chemisorbed oxygen containing species as the hypoiodite, iodates, periodates, etc. This assumption is supported by our observation that in driving the electrode potential to the point of oxygen evolution is approximately one microcoulomb. In the iodide containing solutions, a second electrode process is possible which tends to set the potential at more active values. This process is dependent on the iodide ion concentration and on the time during which the electrode has been on open circuit prior to anodic polarization. Chemisorption of the iodine species leads to the removal of the passive layer at the electrode surface which may cause potential decay to more active values. Then the adsorption competes with the anodic current, which attempts to restore passivity when the potential of the electrode is outside the regions of 0.70 to 1.0 volts.

Depending upon the pH, some mixed iodine containing species are probably found in the region of 0.95 to 1.10 volts (e.g. OI^-, IO_3^-, $IO_5^{=}$, $HIO_5^{=}$, HIO_4) due to a methathetical reaction of I_2 and/or as I_3^- in combination with oxygen. All of these compounds are effective biocides and should not appreciably alter the water quality and biocidal activity. In the region of +1.15 to +1.30 volts vs SCE, chromium is produced but does not appear to cause any severe general or pitting corrosion due to breakdown of the stainless steels.

Cyclic voltammetry may be used to pulse the electrodes in a cathodic or anodic direction. The steels may also be kept in a passive state in the cathodic regions of polarization (-0.30 to -0.40 volts); however, it is desirable not to polarize the electrodes at more negative values since the iodide reduction wave occurs at approximately -0.50 volts, followed by hydrogen reduction in the region of -0.60 volts vs the SCE.

The anodic oxidation of potassium iodide may be used effectively to produce sufficient amounts of iodine using the stainless steel metal bellows electrochemical system. The water is totally potable and free from microbal attack. Some of the iodine produced at the anode migrates to the cathode and is subsequently reduced in the cathodic process. Since the rate of diffusion to the cathode is slow compared to the anode oxidation step, an excess of iodine is readily maintained in solution. The kinetics of adsorption of iodine to the stainless steel surface is also not rate determining.

Spectroscopic Evidence or Adsorption and/or Reaction of Iodine Species

Some large initial efforts were observed in the passivation phenomena by the iodine. This initial effect is attributed to a temporary change associated with sorption of a suitable species onto the clean stainless steel surface. It is generally agreed that permanent passivity stems from a thin insoluble film of a compound of the metal, but it is suggested that it forms by migration of the metal ion into the assay displayed by the adsorbed species. It was postulated that the more nearly a complete sorbed monolayer forms before metal ion migration, the more likely is the formation of a defect-free compound film. The thickness of such films should be self-limiting kinetically and should provide long lived passivity because they offer minimum opportunity for meeting of the reactive iodine species.

Experiments were performed studying this interfacial phenomena using Photoelectron Spectroscopy (ESCA). Both types 316 and 321 stainless steels were found to give a complete molecular iodine compound which was intimately bound to the stainless substrates. The molecular iodine species appear to be somewhat crystalline in nature with well defined grain boundary paths and increased lattice permeability. This crystalline character causes temporary losses in passivity; however, a coherent relatively impermeable film could be regenerated by reapplying a positive potential (+0.9 to +1.1 v) for the further generation of iodine type compounds. The effect of the solution species either on actuation or on passivation are associated with permeation of the "non-porous" films or with adsorption competition, which apparently aids in the regeneration of the sorption initiated film.

Electrochemical Action of Iodine on Steel

Iodine and/or iodides readily dissolve in water and act as a charge transfer complex in solution. The following reaction takes place:

$Fe \rightarrow Fe^{++} + 2e$

$I_2 + 2e \rightarrow 2I^-$

As the iodide ion concentration increases, the solubility of iodine increases because of the formation of the triiodide (I_3^-) complex.

The reaction at the steel surface after extended periods of time becomes

$Fe \rightarrow Fe^{++} + 2e$

$I_3^- + 2e \rightarrow 3I^-$

The corrosion rate accelerates as the concentration of iodide ions and hence of I_3^- complex, increases.

Since iodine forms a host of different compounds in aqeous solution, a list of probable reactions and electrode potentials is given in the following section.

Equilibrium Diagrams

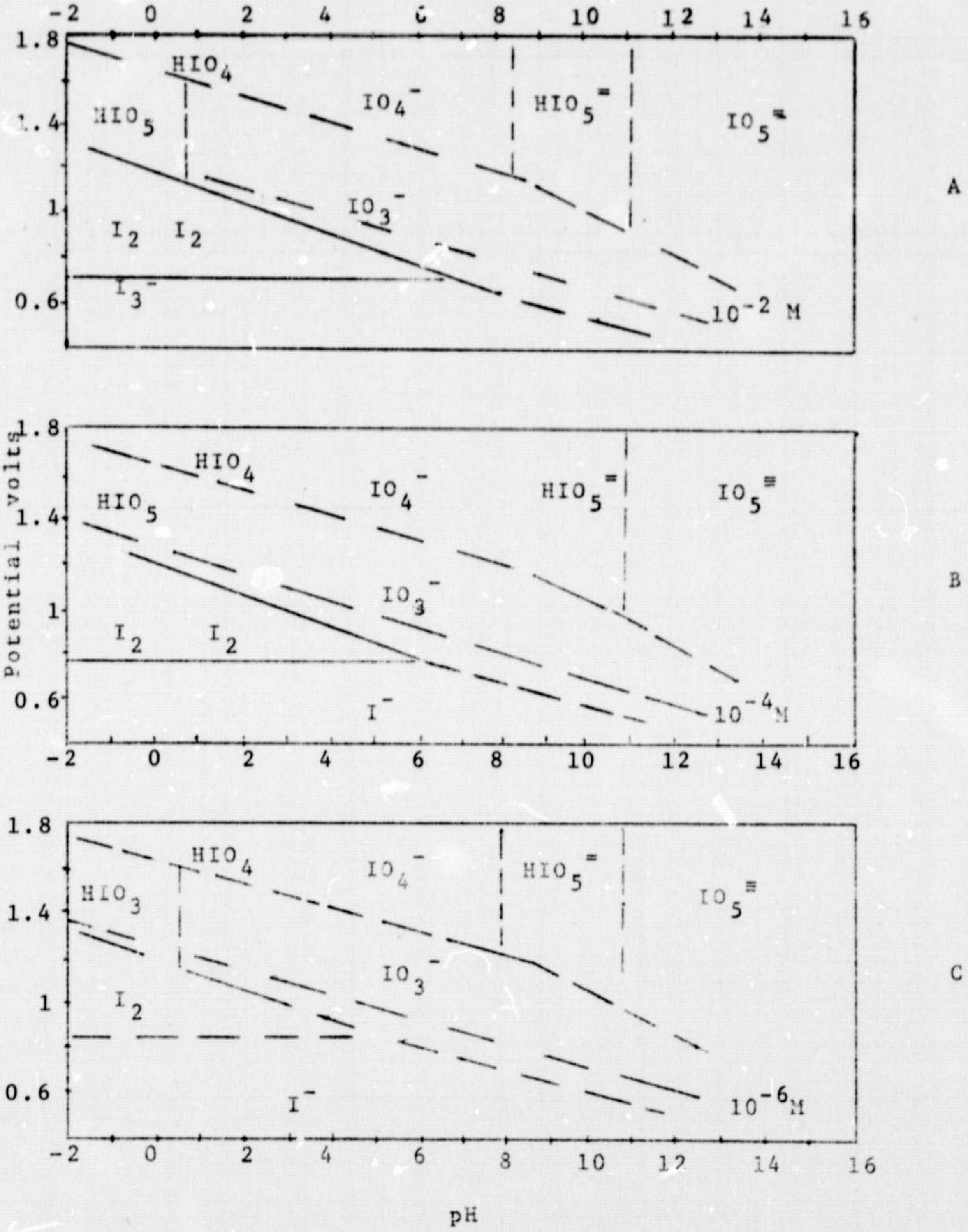
Using the various equilibrium formula given in the previous section, the potential pH diagrams have been constructed to establish the regions of thermodynamic stability for the iodine-water system at 25°C. The domain of relative predominance is given for a variety of different iodine species. Iodine ion may be observed to be stable all along the pH scale. The oxidation of iodides at potentials more positive than +0.4 volts leads to the formation of iodates, accompanied in media by the intermediate formation of iodine and possibly triiodide (I_3^-) and hypoiodite derivatives as I^+. Further oxidation can lead to the formation of periodic acid and periodates. Iodine may be observed to be stable in the trangular region shown on the left. Iodine is therefore stable in slightly oxidizing acid solutions. It reacts in alkaline solution to give iodate and iodide according to the following reactions:

$$\begin{array}{l} I_2 + 6H_2O \rightarrow IO_3^- + 12H^+ + 10e \\ 5I_2 + 10e \rightarrow 10I \\ \hline 3I_2 + 3H_2O \quad 10IO_3 + 5I^- + 6H^+ \end{array}$$

Iodic acid (HIO_3) and the iodates (IO_3^-) may be observed to be stable in water. The hypoiodores ion (OI^-) are unstable and do not appear on the diagram. (Figure 15)

FIGURE 15.

Potential pH Equilibrium Diagram for the Iodine-water System @ 25°C



A = 10^{-2}M B = 10^{-4}M C = 10^{-6}M

Probable Electrochemical Reactions of Iodine Containing Compounds

$3I^- = I_3^- + 2e$

$2I^- = I_2 + 2e$

$I^- = I^+ + 2e$

$I^- + H_2O = HIO + H^+ + 2e$

$I^- + 3H_2O = HIO_3 + 5H^+ + 6e$

$I^- + 3H_2O = IO_3^- + 6H^+ + 6e$

$I_3^- = 3I^+ + 4e$

$I_2 = 2I^+ + 2e$

$I_2 + 2H_2O = 2HIO + 2H^+ + 2e$

$IO^- + 2H_2O = IO_3 + 4H^+ + 4e$

$IO^- + 4H_2O = IO_5^{=} + 8H^+ + 6e$

$IO_3^- + H_2O = HIO_4 + H^+ + 2e$

$I_3^- + 3H_2O = 3HIO + 3H^+ + 4e$

$2I_3^- = 3I_2 + 2e \qquad Eo = .534 - .059 \log I_3^-$

$2I^- = I_2 + 2e \qquad Eo = .5355 - .059 \log I^-$

$I_2 + 2H_2O = 2IO^- + 4H^+ + 2e \qquad Eo = 2.09 - .1182\ pH + .0591 \log (IO^-)$

Other Iodine Couples

$\frac{I^-}{I_3^-}$	Eo = .532 = .0591 log C
$\frac{I^-}{I^2}$	Eo = .621 - .0295 log C
$\frac{I^-}{IO^-}$	Eo = 1.313 - .0591 pH
$\frac{I^-}{HIO_3}$	Eo = 1.077 - .0493 pH
$\frac{I_3^-}{IO_3^-}$	Eo = 1.154 - .0665 pH + .0074 log C
$\frac{I^-}{IO_4^-}$	Eo = 1.227 = .0591 pH
$\frac{I^-}{HIO_5^=}$	Eo = 1.288 - .0665 pH
$\frac{I_3^-}{I_2}$	Eo = .782 + .0295 log C
$\frac{I_3^-}{I^+}$	Eo = 1.149 + .0295 log C
$\frac{I_2}{IO^-}$	Eo = 2.005 - .1182 pH + .0295 log C
$\frac{HIO}{IO_3^-}$	Eo = 1.134 - .0739 pH
$\frac{HIO_3}{IO_3^=}$ & I_2	pH = 0.8
$\frac{I_3^- \text{ \& } I_2}{I_2}$	Eo = .714
$\frac{I_2}{IO_3^-}$	Eo = 1.195 - .0709 pH + .0118 log C

Recommendations

It is obvious that more work is desirable to supplement these data. The evaluation of corrosion effects by subjecting couples to actual environmental conditions would be a valuable backup. For example, studies made under dynamic conditions such as a flowing electrolyte would represent more realistically certain environmental conditions to which the hardware can be subjected.

It would be desirable to isolate the counter electrode from the working metal bellows anode. By the isolation of this electrode one could present the diffusion of the reduced species to the anode when a cathodic potential is applied. It would also be desirable to use an uxillary electrode that requires passivation. Electrodes as graphite or carbon should be effective, and are recommended, for this purpose. Platinum or rhodium metals have also been shown to be effective non-corrosive materials and should also be extremely effective as auxillary or counter electrodes. It is, however, recommended that they be isolated from the working anode. The service related values of potentials and current densities presented herein should reflect the behavior of the stainless steels under actual field use, and may be used for design purposes.

Every effort should be made to avoid the use of dissimilar metallic couples, and it is recommended that the potential difference not exceed more than 100-150 volts maximum.

Conversion coatings such as chromate and phosphates should not be used. The stainless surface may be passivated with buffer solutions as borates (pH = 8.4); however, it is not recommended that the borates be used as supporting electrolytes in the potable water system. They should only be used to render the stainless steel passive. Type 316 or 321 stainless steels are the recommended materials of construction for the iodide-iodine containing potable water metal bellows systems.

Conclusions

1. The measured initial potentials for 304, 316, 321 and 347 stainless steels were found to have an average deviation of less than 5 percent in a brine solution.

2. In general, the stainless-type materials tested exhibited an oscillating range in potential between their active and passive states while aging.

3. The cause of the variations in the potential values of alloys and metals in the iodide, iodine containing electrolytes may be ascribed to the following:
   a. Probable changes in the surface properties of the metal which arise from corrosion products and surface reactions of the alloying constituents. In the case of the active form of stainless steel-type materials, the metal becomes less anodic (+) with time because of oxide-film formation. The passive form becomes more anodic with time because of probable attack by the iodide ion (electrolyte) on the slightly porous passive surface.
   b. Changes in the electrolyte because of corrosion products. In general, any change in the electrolyte (e.g. I^- to I_3^-) used in the aging study could be responsible for observed potential variations. This could result in the reference electrode and working electrode existing in dissimilar environments with consequent liquid junction potential artifacts.
   c. Mixed potential effects resulting from inhomogeneous alloys.
   d. Porous surfaces that allow the electrolyte to affect the basis metal.

4. The service related potentials for most pure metals were usually very close to the initial potentials; the active metals tending to become more active and the passive, or noble metals, tending to become more passive.

5. Types 316, 321, and 347 stainless steels have been shown to be relatively non-corrosive (<0.03 mpy) in an iodine containing environment (<50 ppm).

6. Iodine depletion rates are approximately the same in Type 316 and Type 321, and slightly higher in Type 347 stainless steels.

7. Anodic polarization offers some advantage in helping the stainless steels remain effectively passive in the presence of low concentrations of iodine (<50 ppm). Cathodic protection does not appear to offer any advantages in protecting the stainless steels.

8. Iodine and/or triiodide may be effectively produced anodically on various stainless steels. The concentration may be made to vary from 1 to 500 ppm depending upon the amount of iodide used.

9. Photoelectron spectroscopy has demonstrated that the electroactive species is a mixed iodide complex resembling iron iodide (FeI_2).

10. Anodic potentials ranging from +0.7 to +.90 volts may be used to effectively generate iodine as well as keep the stainless steel in the passive state.

11. The electrodes may be periodically pulsed with cathodic potentials (-0.3 to -0.4); however, it is not necessary to cathodically protect the surface on a continuous basis.

12. The system should be kept free of dissolved oxygen, since its oxidation wave is very near that of the oxidation of iodide ion.

13. A multimetal system as Type 316, 321, and 347 have been shown to be feasible systems for spacecraft application.

14. The temperature of the water should be kept below 100°F because of the volatile nature of the iodine as well as increasing the probability of affecting thermal degradation of the iodine.

15. It is not desirable to keep the solution agitated or continuously stirred since the rate controlling step may be changed from a diffusion controlled process to a convection controlled system. Convection also enhances the rate of adsorption of electroactive species.

16. The metal bellows electrode system may be effectively passivated with a borate buffer solution.

17. Iodine may be produced in a metal bellows electrode configuration; however, the region of potential is shifted to slightly less anodic values (+0.55 to +0.58 volts). The cathodic reduction of the idoine occurs at approximately the same value (i.e., -0.10 volts vs SCE).

18. The presence of oxygen shits the cathodic reduction of iodine from a -0.10 volts to a +0.10 volts vs SCE. The presence of oxygen also causes the electrode to become deactivated.

19. A specially constructed research potentiostat capable of delivering approximately 500 milliamperes was found to be desirable in making polarization measurements.

20. Metallic ions such as chromium, nickel, iron, cobalt, molybdenum, copper, and mercury are not generated in sufficient quantitites to alter the potability of the water system as set forth in the specifications.