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Technical note

CATHODIC REDUCTION OF OXYGEN AND HYDROGEN PEROXIDE
ON PLATINUM, PALLADIUM AND IRIIDIUM SMOOTH ELECTRODES

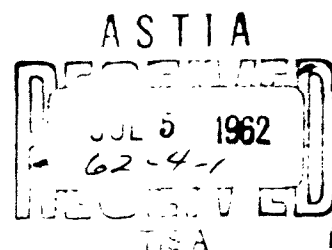
by

G. Bianchi, F. Mazza and T. Mussini

University of Milano (Italy)

Laboratory of Electrochemistry and Metallurgy

December 1961



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ABSTRACT

Polarization curves in acid, neutral and alkaline solutions have been drawn by potentiostatic method, for oxygen and hydrogen peroxide reduction processes and for hydrogen peroxide oxidation process, on Platinum, Iridium and Palladium electrodes.

These curves could be classified as follows : those whose slopes are 0.030 to 0.12, and those with slopes higher than 0.12. The former can be explained through already proposed mechanisms (addition of one electron or one atom of hydrogen to an adsorbed oxygen molecule; or addition of one electron to a HO_2 adsorbed radical) which mechanisms imply that the adsorption process is so quick as not to result kinetically determining. The latter involve a slow oxygen or HO_2 radicals adsorption which becomes kinetically determining first of all for Iridium in both acid and neutral solutions. For Palladium in H_2SO_4 solution and for Platinum in HCl solution the oxygen adsorption process is very slow essentially due to the complexing action of the solution with resulting formation of surface complexes which engage the metal atoms, thus preventing or reducing the formation of adsorbed oxide.

1. INTRODUCTION

Platinum has been used longer than other metals in researches on electrochemical behaviour of oxygen and hydrogen peroxide, both in the form of smooth plate and of platinum black.

These researches concern :

a) - Catalytic decomposition of hydrogen peroxide solutions, that is, according to GERISCHER's conclusions (1), an electrochemical process resulting from partial cathodic and anodic processes of reduction of hydrogen peroxide to water and of oxidation of hydrogen peroxide to oxygen. BIANCHI and his co-workers (2) have shown that decomposition of hydrogen peroxide in the case of acid solutions involves the adsorbed oxides of the metal.

b) - Anodic evolution of oxygen from hydrogen peroxide solutions and "depolarizing" action on anodic processes. These researches are owed to RIUS and OCON, RIUS and GUILLEN, HICKLING and WILSON, GINER, and BIANCHI and co-workers (3).

c) - Oxygen cathodic reduction process, which is strictly connected to hydrogen peroxide decomposition and reduction processes.

Besides HOAR's researches (4) and ROITER and JAMPOLSKAJA's (4) mention must be made of the researches carried out by TOMASHOV, KRASIL'SHCHIKOV and ANDREIEVA, BIANCHI and RIVOLTA, BOCKRIS and OLDFIELD, GERISCHER, WINKELMANN, BIANCHI and CAPRIOGLIO, KRASIL'SHCHIKOV (4).

Researches on Pd and Ir are very few. Catalytic action of these metals on decomposition of hydrogen peroxide acid solutions has been considered by BIANCHI and co-workers (5), who here again have confirmed the intervention of the oxides.

Oxygen reduction on palladium has been glimpsed upon by BAIN (6); the case of iridium has been considered by BAIN (6) and by

GARRISON and LILLY (7).

In the case of platinum the various workers have confirmed that for oxygen cathodic reduction, polarization curves have $0.11 + 0.12$ slope in the case of acid solutions, and $0.036 + 0.045$ in the case of alkaline solutions (8).

These results have not been confirmed by KRASIL'SHCHIKOV and ANDREIEVA (9) in the case of platinum. By operating at extremely low current densities (ranging about 1 micro A/sqcm), they have checked a 0.59 slope in polarization curves, in both alkaline and acid solutions.

Hydrogen peroxide cathodic reduction has been examined only for platinum by GERISCHER (10) and WINKELMANN (11).

As it is well known, it runs over more negative potentials than theoretical potentials (1.77 Volts in acid solution and 0.88 Volts in alkaline solution).

Hydrogen peroxide cathodic reduction occurs at potentials which are very close to those observed for oxygen cathodic reduction (12).

Electrochemical reduction processes of oxygen and hydrogen peroxide may interfere in reduction processes of the oxides adsorbed on the electrode surface. For these latter processes the electrochemical conditions of formation and reduction and the chemical stability conditions in contact with hydrogen peroxide solutions must be considered.

As far as platinum oxides are concerned, mention can be made of the researches made by HICKLING, VETTER and BERNDT, GINER, LAITINEN and ENKE, NAGEL and DIETZ, WILL and KNORR (13). As it has already been shown by BIANCHI and CAPRIOGLIO (14), the potential for oxygen and hydrogen peroxide cathodic reductions in acid solutions is very close (about 0.8 V, NHS) to the one for the

system Pt-PtO.

The formation and reduction of oxygen adsorbed on iridium have been considered by KNORR and by BÖLD and BREITER (15).

As far as iridium oxides are concerned, only LATIMER's (16) theoretical data are available. For palladium oxides HICKLING and VRJOSEK's (17) experimental data are available.

As far as the chemical behaviour of oxides is concerned, it is known that ~~water~~^{H₂O₂} strongly reduces Pt(OH)₂ (18) and it reduces with less strength Pd(OH)₂ (19).

No data for iridium oxides are available.

2. - EXPERIMENTAL

The research which is matter of this report was carried out by drawing polarization curves, concerning the electrode metals next cited, by means of a potentiostat and a polarization cell already described (20).

99,9% Iridium (Degussa), Platinum -10% Iridium, Platinum -20% Iridium, 99,9% Platinum (Johnson and Matthey), 99,9% Palladium (Johnson and Matthey) electrodes were considered. During the above polarization experiments the following solutions were employed, all of them prepared with reagent-grade Merck products:

Acid solutions : H₂SO₄ 0.5M

Neutral solutions : Na₂SO₄ 0.5M, H₃BO₃ 0.5M and NaOH to adjust pH at value 7.

Alkaline solutions : Na OH 0.1M and Na₂SO₄ 0.5M

Hydrogen peroxide was added to the solutions so prepared until the required concentrations were reached. Gases employed to saturate and stir the above solutions during the measurements

were 99.5% oxygen (with small traces of N_2 and rare gases), or hyperpure nitrogen (99,999%) : these gases bubbled through the solution in the cell at a rate of 150 cc/min. As reference electrode a saturated-silver-chloride electrode was used : its own potential value (+0.196 V) then was added to the read potentials to convert them into the normal hydrogen scale; no corrections were tried for liquid junction potentials.

All the potentials indicated in the text and on the figures are intended as referred to the normal hydrogen scale (NHS).

All the experiments were carried out with the aid of an air-thermostat, at a temperature of $25 \pm 0,1^\circ \text{C}$.

3. - EXPERIMENTAL RESULTS

In alkaline solutions, cathodic reduction of oxygen occurs without remarkable overvoltages at potentials which are very close to those of the process $O_2 + 2H^+ + 2e \longrightarrow H_2O_2$, and the resulting hydrogen peroxide decomposes catalytically so that only some traces can be determined in the solution ($\ll 10^{-4} \text{M}$). The process runs in a similar way ($b=0,060$) on Platinum (Figure 1) and Palladium (Figure 2). In the case of Iridium (Figure 3) polarization curve has a stronger slope ($b=0,12$), although the same static potential and the same limiting current are observed.

If the solution contains hydrogen peroxide (10^{-2}M) a cathodic process and an anodic process are observed to which similar limiting currents and potentials are corresponding, still very close to the theoretical ones corresponding to the above reaction, considered in terms of oxidation of hydrogen peroxide to oxygen.

Figure 4 shows the anodic and the cathodic polarization curve for Platinum; and Figure 5 shows the very similar ones for Palladium.

Figure 6 shows the curves for Iridium, which although starting from the same static potentials and showing the same limiting currents, are divided into two parts. The first part is up to 0.5 micro A/cm^2 , comparable to the curves for Platinum and Palladium ($b = 0.020$), and the next part with a greater slope ($b = 0.060$).

In the case of neutral solutions, the cathodic reduction occurs for oxygen at a potential of about 500 mV (NHS) and is affected by intermediate overvoltages in the case of Platinum (Figure 7), Palladium (Figure 8) and Iridium (Figure 9). In the case of Palladium the slope is 0.060, while for Platinum the slope, initially similar to the one for Palladium, tends to increase with higher current densities. The slope is very greater for Iridium ($b = 0.16$).

The cathodic reduction and the anodic oxidation of hydrogen peroxide occurs at potentials close to 500 mV (NHS) as it is shown by the cathodic and the anodic polarization curve for Platinum (Fig. 10), Palladium (Fig. 11) and Iridium (Fig. 12). Still in this case cathodic overvoltages are small for Palladium ($b = 0.020$), medium for Platinum ($b = 0.030$) and very high for Iridium ($b = 0.42$). Anodic overvoltages are of the same order ($b = 0.020$ to 0.060) for the three metals.

In the case of acid solutions, the oxygen cathodic reduction clearly depends on the fact whether working with sulphuric or hydrochloric acid solutions, as Figure 13 shows. Polarization curves with Platinum electrode are little sloping with sulphuric acid solutions ($b = 0.060$) and the limiting currents are clearly observed. With hydrochloric acid solutions, the curves are strongly sloping ($b = 0.180$) and gradually join with the part to which the development of hydrogen is corresponding. The same thing happens with solutions containing hydrogen peroxide (Fig. 14).

The cathodic curve in a sulphuric acid solution (A) has a particular trend and clearly shows the limiting current, always keeping above

the curve obtained with an hydrochloric acid solution, which curve (B) is strongly sloping and gradually connecting with the hydrogen discharge. The anodic curve (C) has been determined only in sulphuric acid solution ($b = 0.080$) and shows the same limiting current as the cathodic curve.

Figure 15 shows the cathodic polarization curves for oxygen reduction on Iridium in a sulphuric and in an hydrochloric acid solution. It is observed that with Iridium the difference disappears which had been observed with Platinum, and polarization curve is however still very sloping ($b = 0.28$) and connected with the part corresponding to the hydrogen cathodic discharge.

In the case of solutions containing hydrogen peroxide (Fig. 16) the cathodic curves both in sulphuric and in hydrochloric acid solutions remind those for Platinum, although a better nobility for Iridium in the cathodic process with sulphuric acid solutions is only kept for very small current densities. In sulphuric solutions, the anodic curve offers a characteristic hysteresis : the slope in the first part of the curve ($b = 0.050$) is comparable to the one for Platinum. In the case of Pt 90-Ir 10 alloys (Figures 17-18) and Pt 80-Ir 20 alloys (Figures 19-20), the same differences are observed between sulphuric and hydrochloric acid solutions, as those already observed for pure Platinum. In the case of Palladium it is impossible to work in hydrochloric acid solutions, because of the electrode corrosion. Oxygen cathodic reduction in a sulphuric acid solution goes according to the curve shown on Figure 21, being strongly sloping and gradually connected with the part corresponding to the hydrogen discharge. Figure 22 shows the anodic curve ($b = 0.060$) and the cathodic curve ($b = 0.24$), comparable to those obtained for Platinum in a sulphuric solution of hydrogen peroxide.

T A B L E I

Slope of polarization curves
for $0.01 < i < 1 \text{ mA/cm}^2$, at 25°C

			Platinum	Palladium	Iridium
Acid solutions	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic	0.060	0.24	0.28
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ anodic	0.080	0.060	0.050
	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic	0.030/0.45	0.24	0.040/0.34
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic	0.180	-	0.28
Neutral solutions	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic	0.24	-	0.34
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic	0.060	0.060	0.16
	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ anodic	0.060	0.060	0.040
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic	0.030	0.030	0.42
Alkaline solutions	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic	0.060	0.060	0.12
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ anodic	0.030	0.020	0.030
	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic	0.020	0.030	0.060
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$ cathodic			

T A B L E II

Static potentials at 25°C

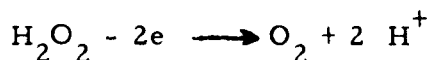
			Platinum	Palladium	Iridium
Acid solutions	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$	0.92 V	0.77 V	0.90 V
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$	0.79 V	0.78 V	0.85 V
	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$	0.72 V	-	0.86 V
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$	0.88 V	-	0.88 V
Neutral solutions	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$	0.51 V	0.52 V	0.52 V
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$	0.44 V	0.47 V	0.46 V
Alkaline solutions	$\left\{ \begin{array}{l} \text{H}_2\text{SO}_4 \\ \text{HCl} \end{array} \right.$	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$	0.20 V	0.21 V	0.23 V
		$\left\{ \begin{array}{l} \text{O}_2 \\ \text{H}_2\text{O}_2 \end{array} \right.$	0.10 V	0.11 V	0.15 V

4. - DISCUSSION

On considering Table 1 and Table 2, showing the experimental results with Platinum, Palladium and Iridium, it is apparent that polarization curve slope for oxygen cathodic reduction on Platinum is 0.060 in sulphuric acid solutions, for the field of current densities examined in this work.

The same result is obtained for Platinum in alkaline and neutral solutions, thus confirming Krasilshchikov's results already cited (4). Different results are obtained for Palladium in sulphuric acid solution and Platinum in hydrochloric acid solution. In both cases polarization curves have a high slope (0.18 + 0.24), thus implying a different mechanism for the oxygen cathodic reduction. In the case of Iridium, polarization curves for oxygen cathodic reduction in acid solution have a very high slope (0.28), and this higher slope is also observed in neutral (0.16) and in alkaline solutions (0.12).

As far as hydrogen peroxide solutions are concerned, due account is to be taken of the fact that hydrogen peroxide, particularly in alkaline solutions, undergoes a decomposition and the potential recorded on polarization curves is a mixed potential, resulting from the cathodic reduction process of hydrogen peroxide to water, and from the anodic oxidation process of hydrogen peroxide to oxygen. The mixed potential of the hydrogen peroxide solutions is very close to the reversible potential for the process



showing that the decomposition process is controlled by the hydrogen peroxide reduction cathodic process.

In other words, all the cathodically reducible hydrogen peroxide is spent in the decomposition process and then the cathodic external

polarizing current cannot correspond to the hydrogen peroxide cathodic reduction.

Cathodic and anodic polarization curves have a low slope ($0.030 + 0.020$) in both neutral and alkaline solutions, but the cathodic curve must be attributed to the reduction process of the oxygen which develops in the hydrogen peroxide decomposition.

In the sulphuric acid solutions where such decomposition is much smaller, there is less oxygen available for the cathodic process and the polarization curve slope on platinum is kept small only for limited values of current density (Fig. 14, A).

In the case of Palladium, for which polarization curve for oxygen cathodic reduction is strongly sloping (Fig. 21), even the cathodic curve for hydrogen peroxide solutions is very sloping (Fig. 22, B). This is also true for platinum in hydrochloric acid solutions (Fig. 13, B and 14, B).

As far as anodic behaviour is concerned, Iridium is analogous to Platinum and Palladium, except for the lower values of the limiting currents in acid solutions, which values were attributed, in a previous paper (21), to the lower reactivity of Iridium oxide with hydrogen peroxide solutions.

As far as the cathodic behaviour is concerned, polarization curve slopes are always higher, even in the alkaline solution themselves. As one single exception, there is a part in the curve at low current densities for solutions of hydrogen peroxide in sulphuric acid (Fig. 16, A).

In a hydrochloric acid solution, the behaviour of Iridium is analogous to Platinum, and to Gold in sulphuric solution (23).

Polarization curves obtained with Platinum, Palladium and Iridium can be divided into two main classes :

Those whose slopes are between 0.040 and 0.12, and those with slopes higher than 0.12.

The former can be explained through one of the mechanisms already described (addition of one electron or one atom of hydrogen to a molecule of adsorbed oxygen; or the addition of one electron to a HO_2 adsorbed radical), which mechanisms imply that the adsorption process is so quick as not to result kinetically significant. This is the case of Platinum in acid (H_2SO_4), neutral and alkaline solutions, of Palladium in neutral and alkaline solutions, and Iridium in alkaline solutions.

When the adsorption process is slow, as soon as it becomes kinetically significant, the interdependence of the potential and the current density will result through the coverage of the metal surface with adsorbed oxygen, and will involve a slope in the polarization curve that is generally high.

This is the case of Iridium for which it is to be concluded that oxygen adsorption processes are slow, in both acid and neutral solutions. For Palladium in sulphuric acid solutions and for Platinum in hydrochloric acid solutions the conclusion should be that the oxygen adsorption process is very slow, due to the complexing action of the solution and to the resulting formation of surface complexes which engage the atoms of the metal, thus preventing or reducing the formation of adsorbed oxide.

When, during the cathodic polarization, the surface coverage by adsorbed oxygen is nullified (22), the covering begins with atomic hydrogen and the cathodic process results from the discharge of hydrogen adsorbed atoms which combine with the oxygen dissolved in the solution (depolarization).

If the oxygen adsorption process is very slow - case of Iridium - the hydrogen discharge potential is reached before the limiting current for the reduction of oxygen, and the polarization curve joins with the part corresponding to the hydrogen discharge.

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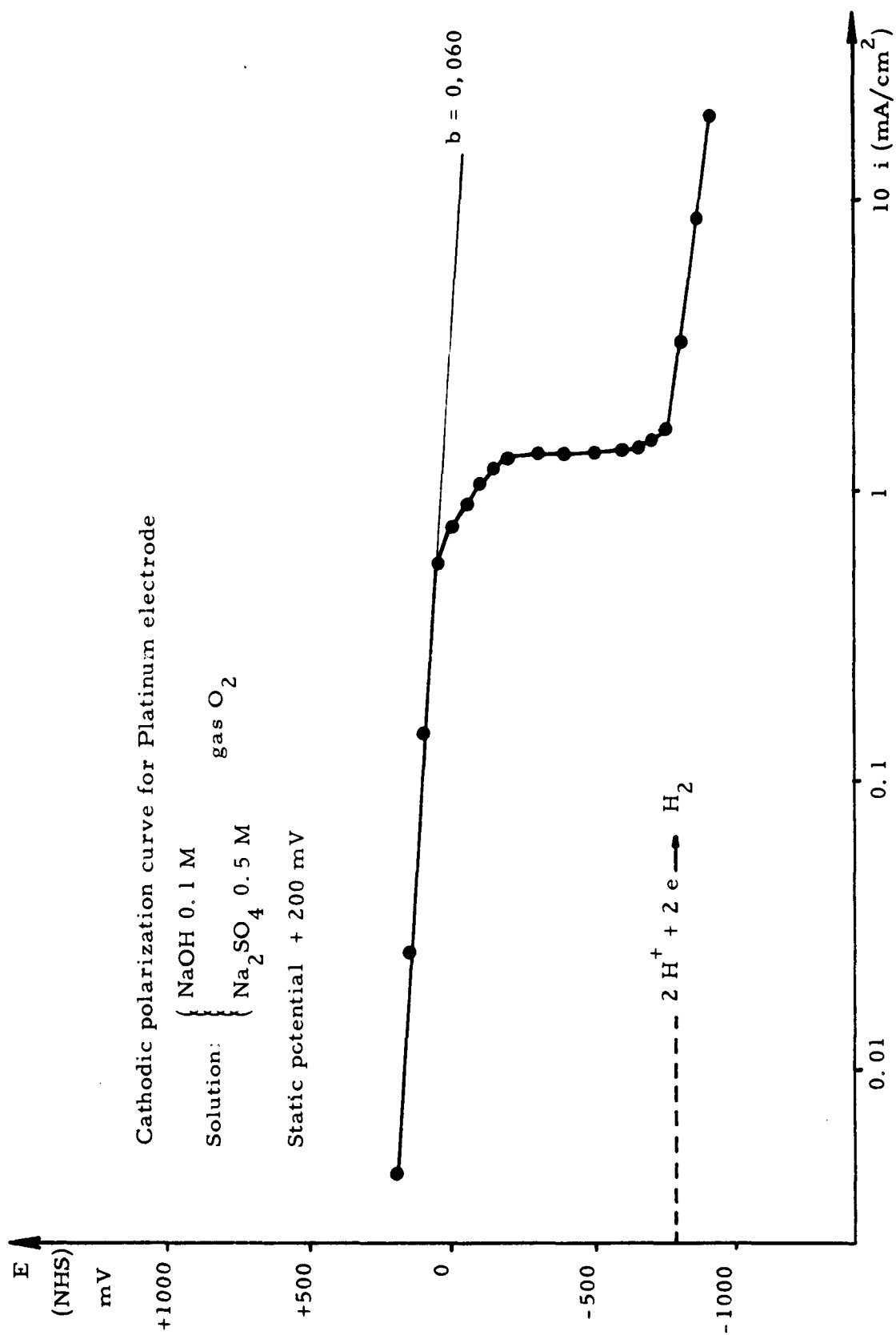


Fig. 1

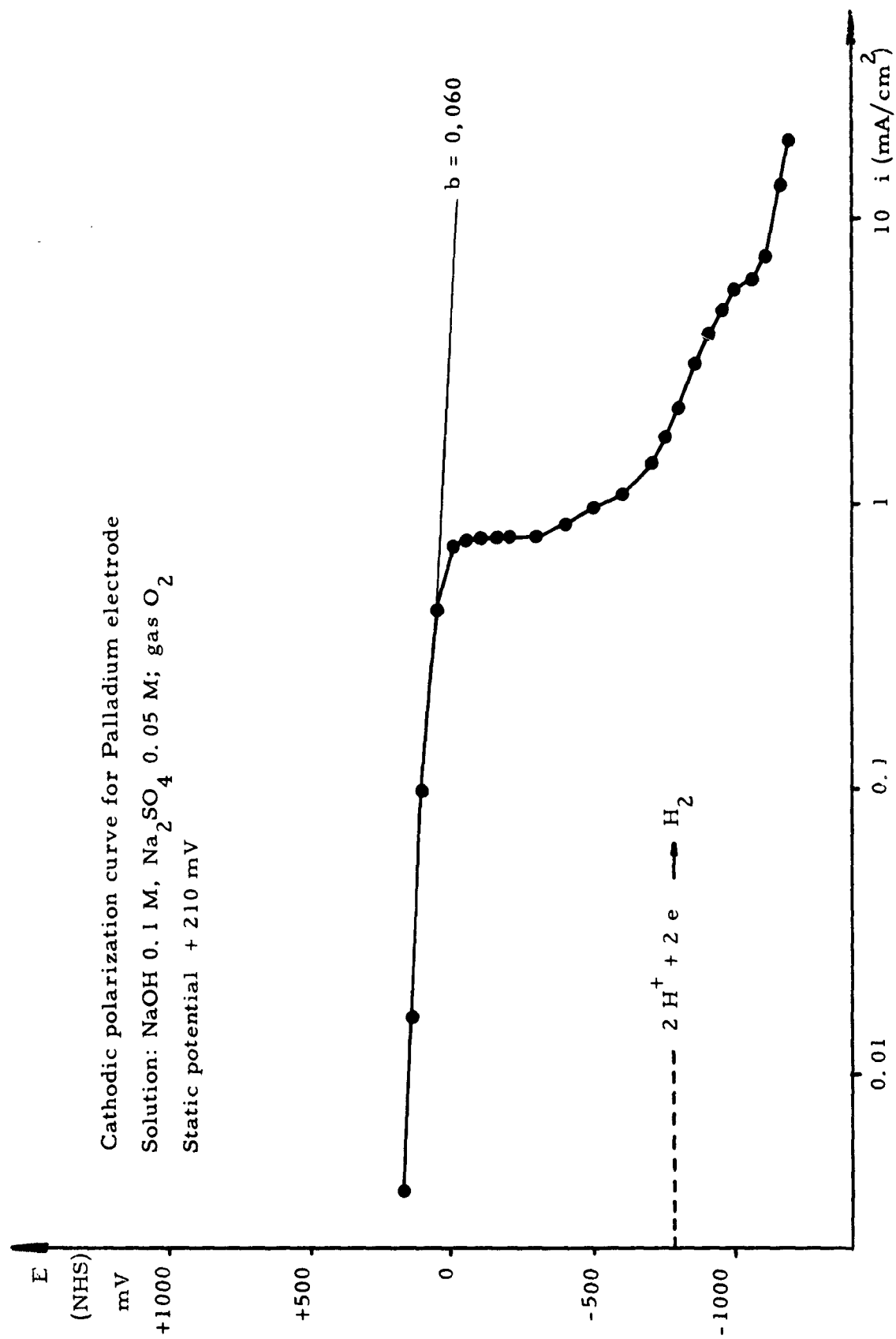


Fig.2

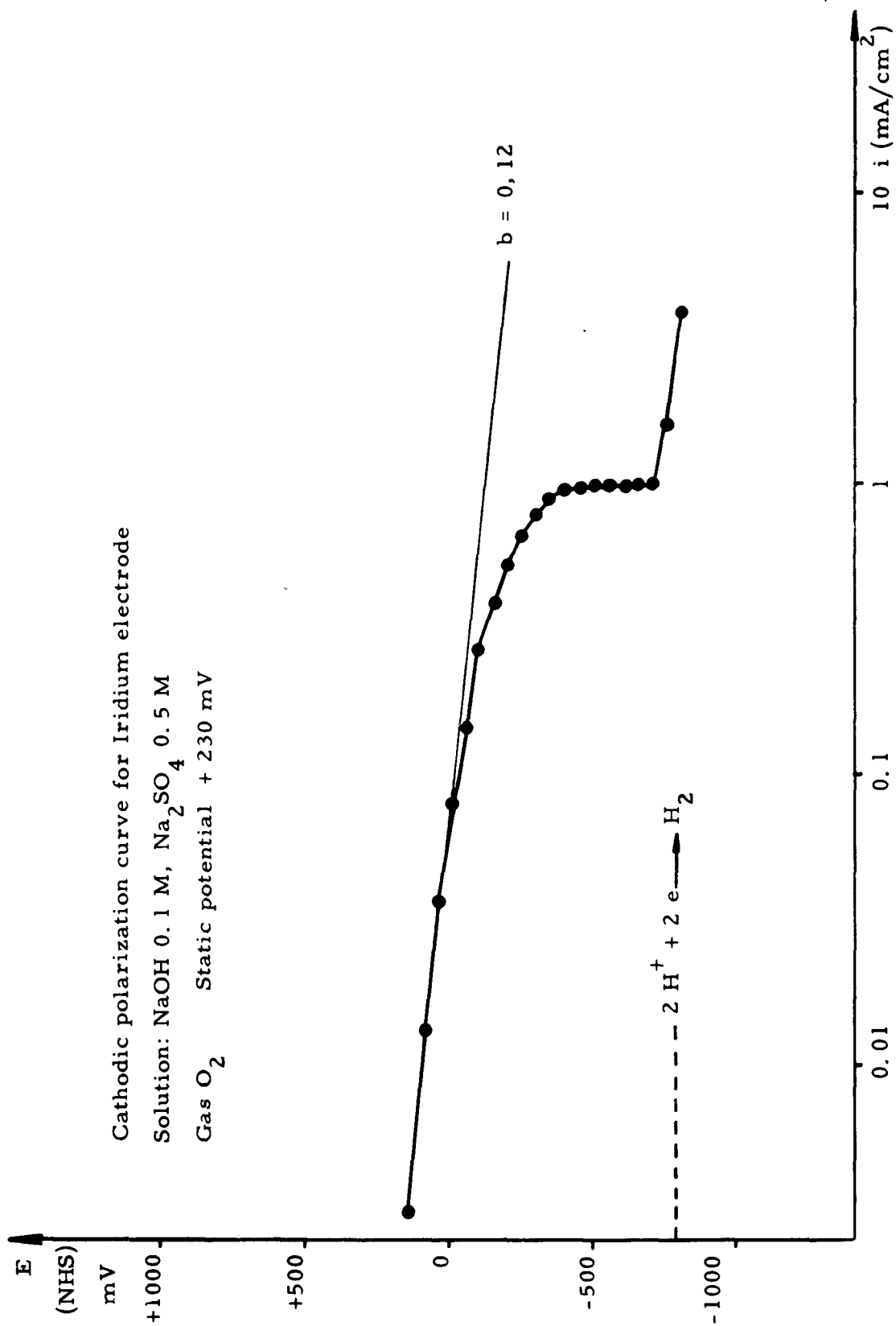


Fig. 3

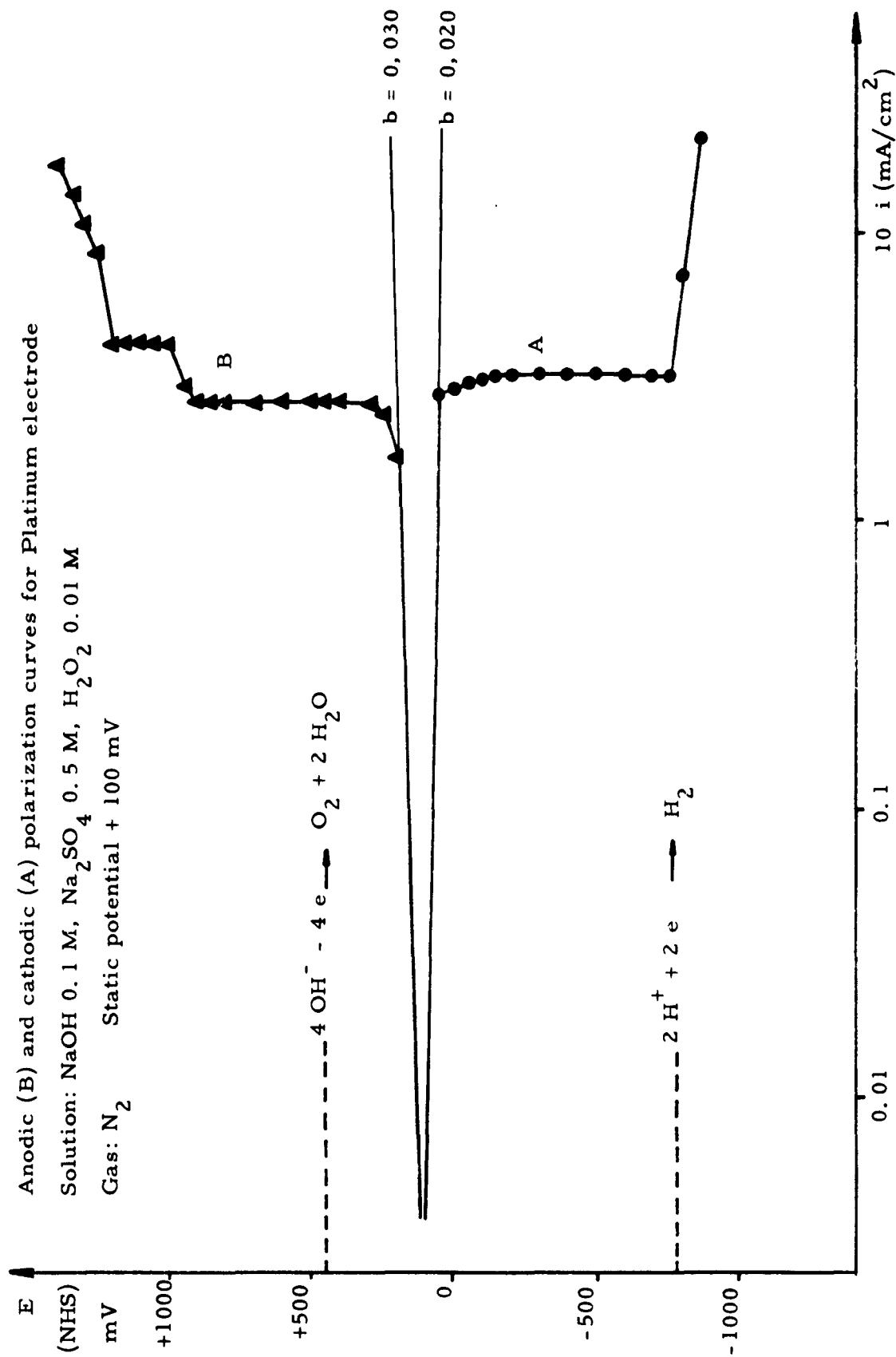


Fig. 4

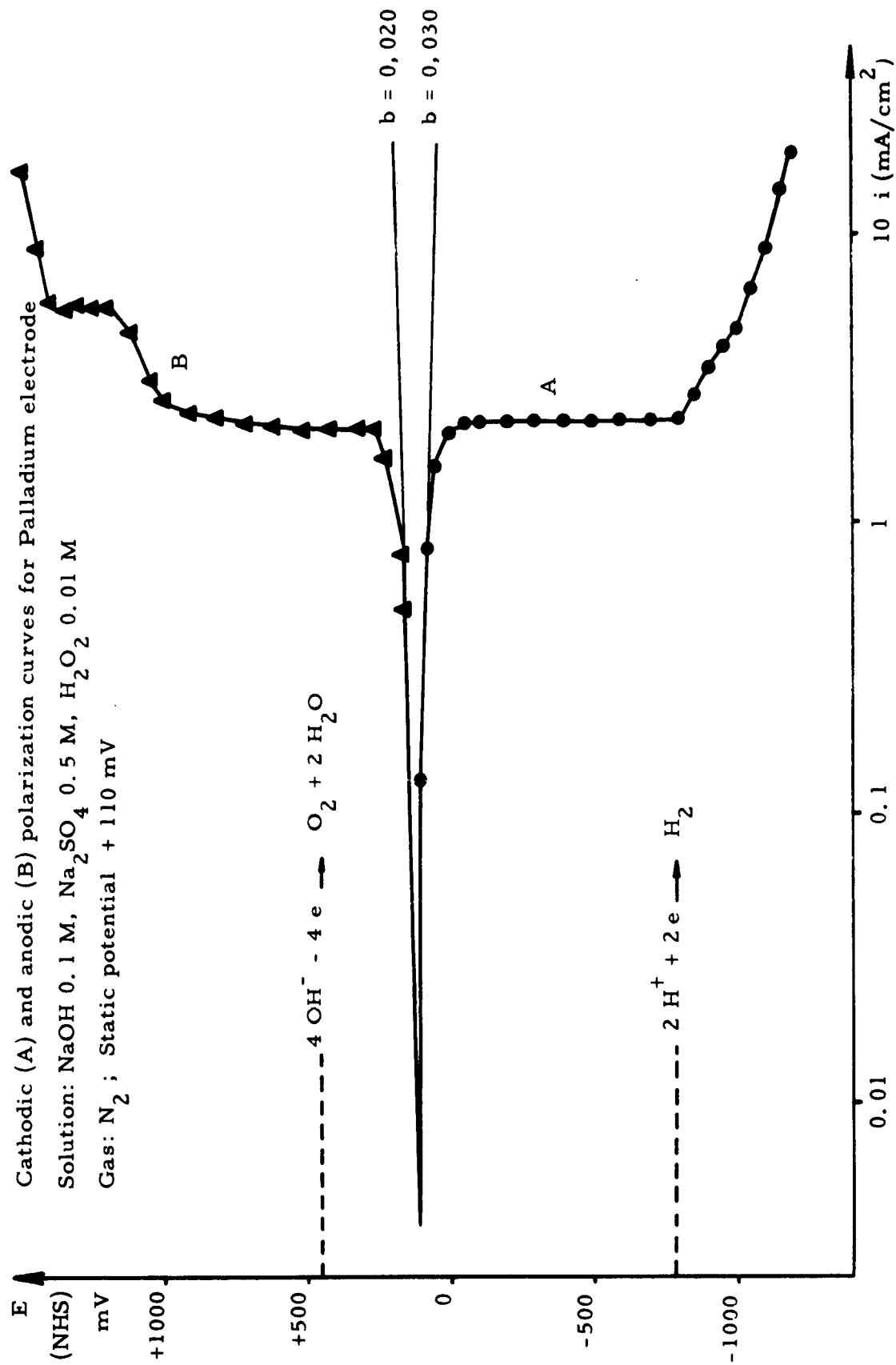


Fig. 5

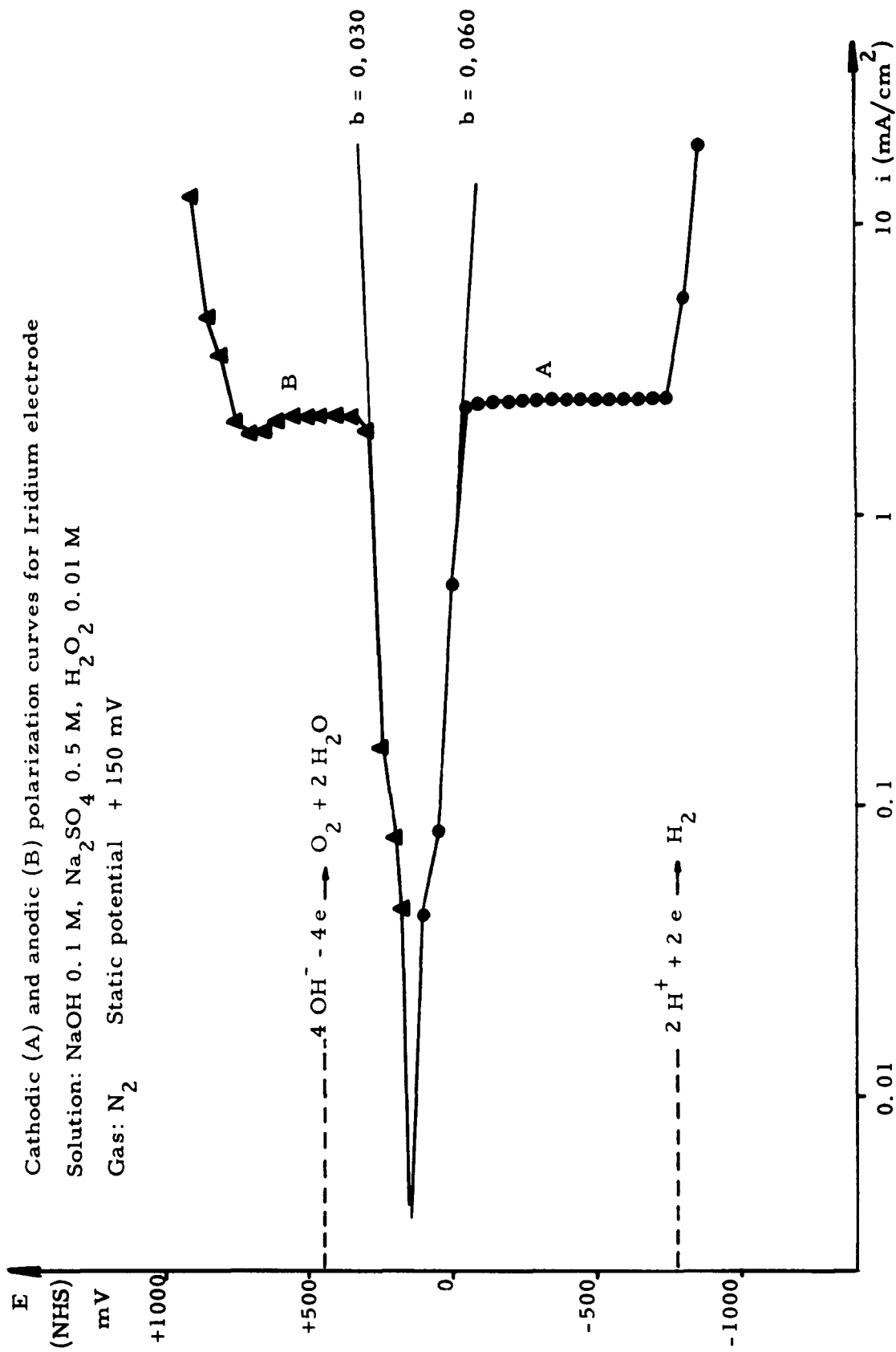


Fig. 6

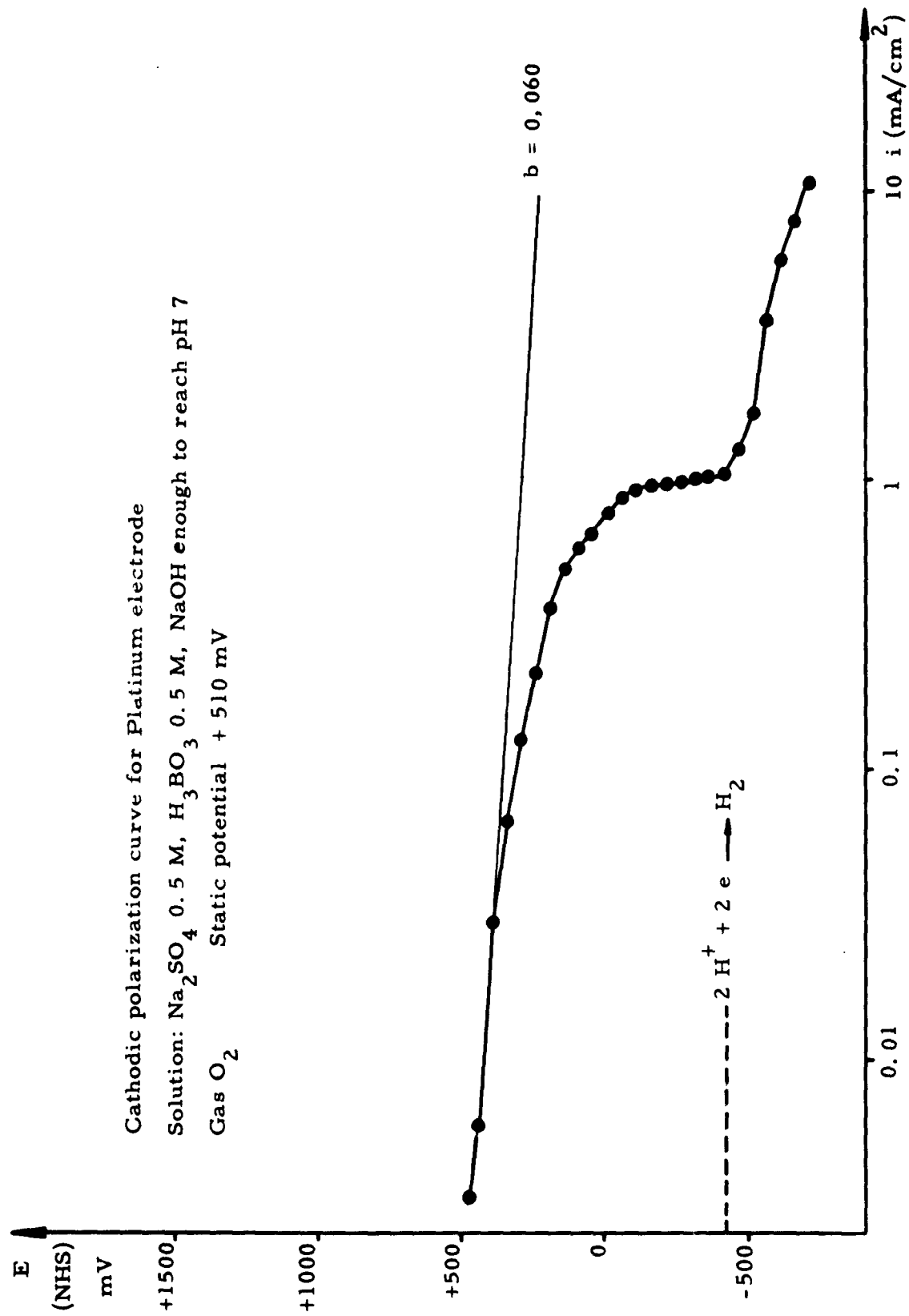


Fig. 7

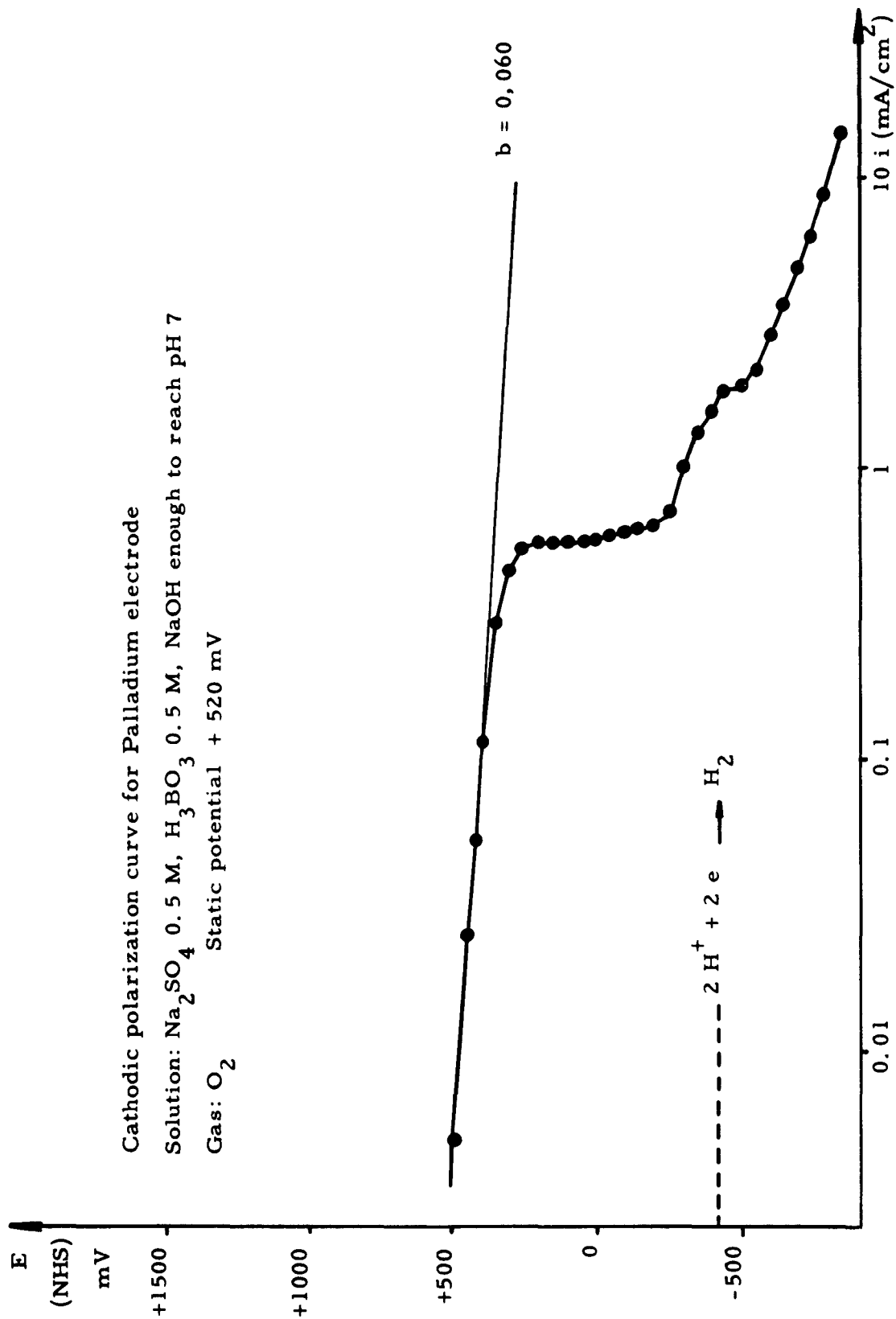


Fig. 8

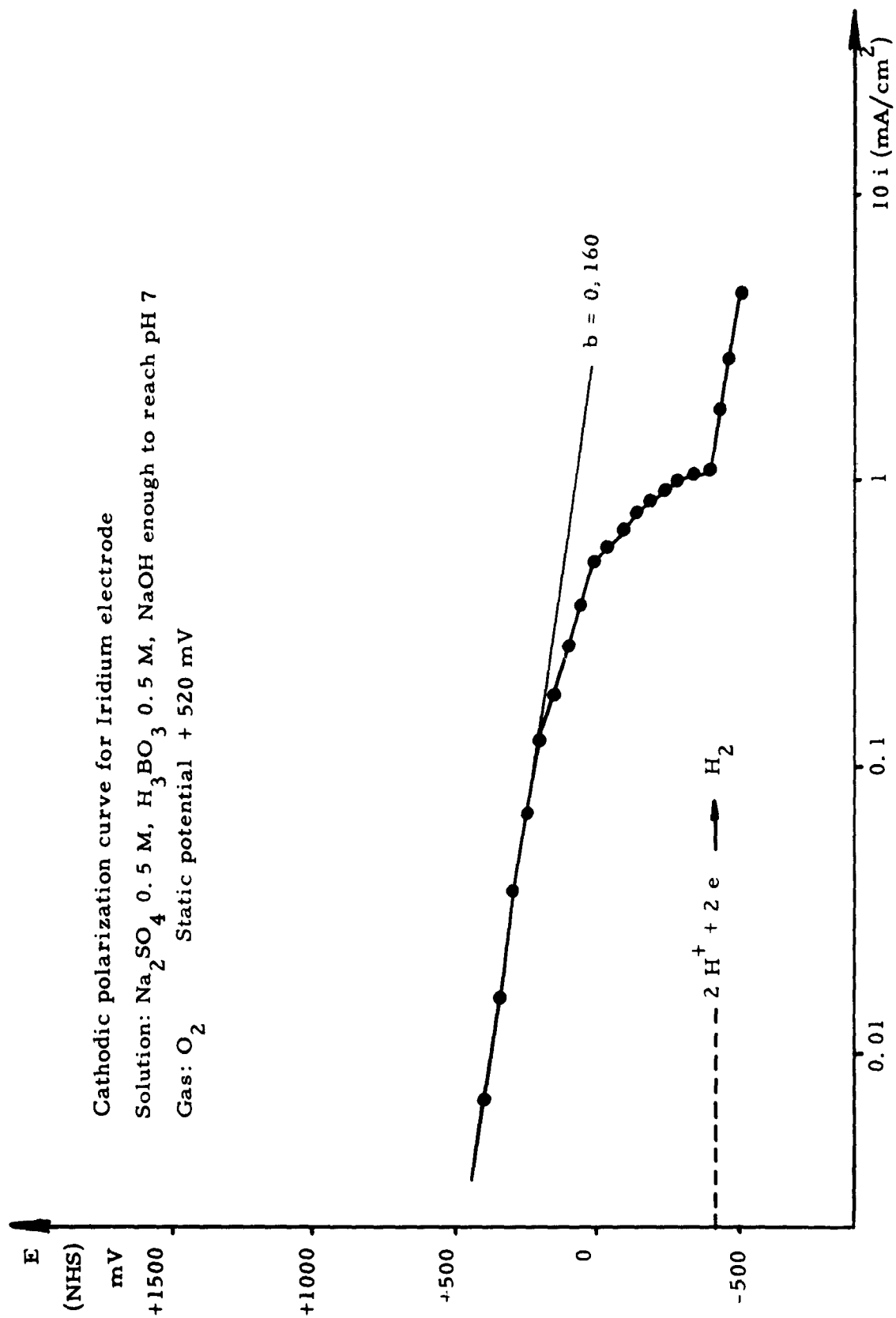


Fig. 9

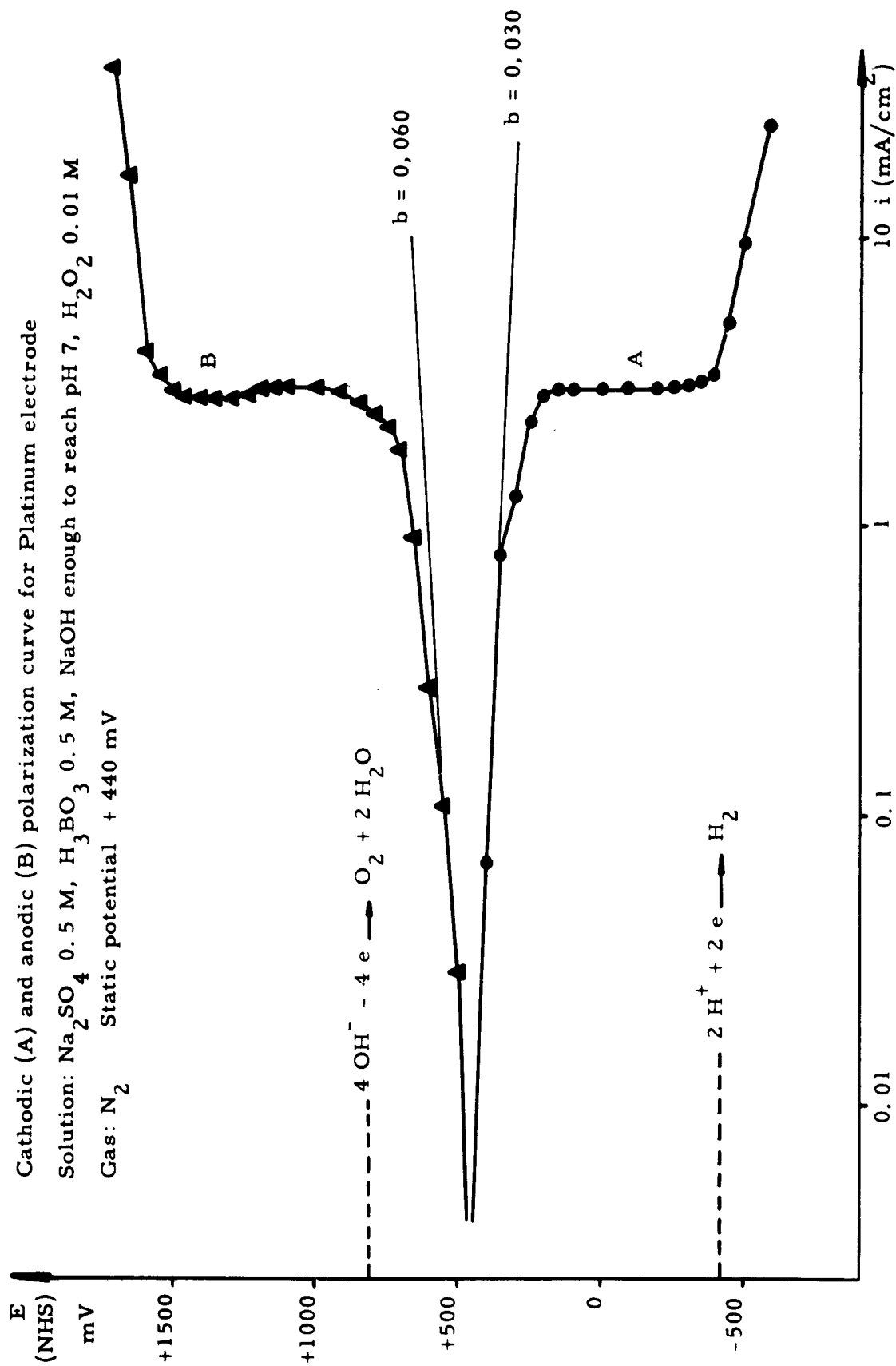


Fig. 10

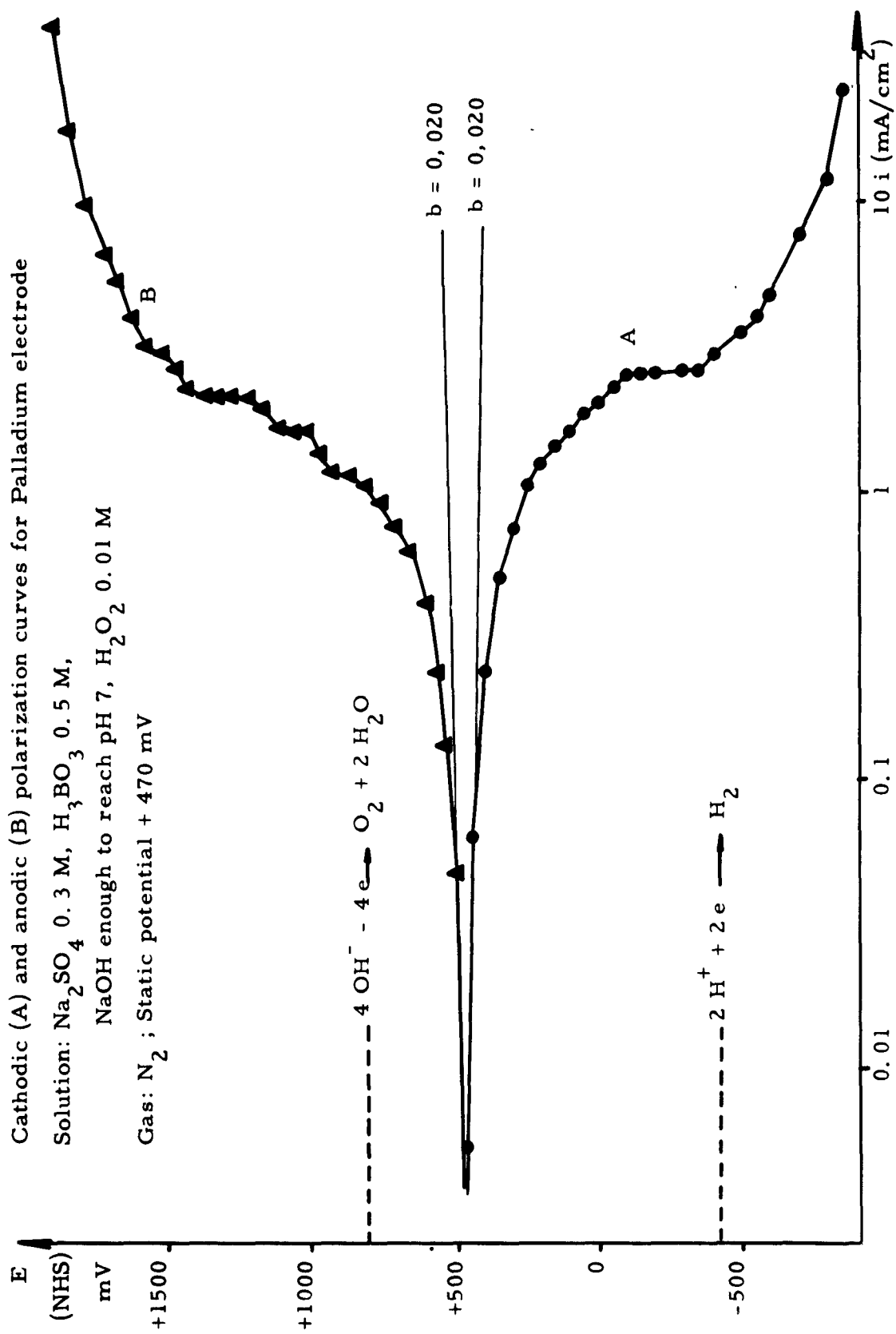


Fig. 11

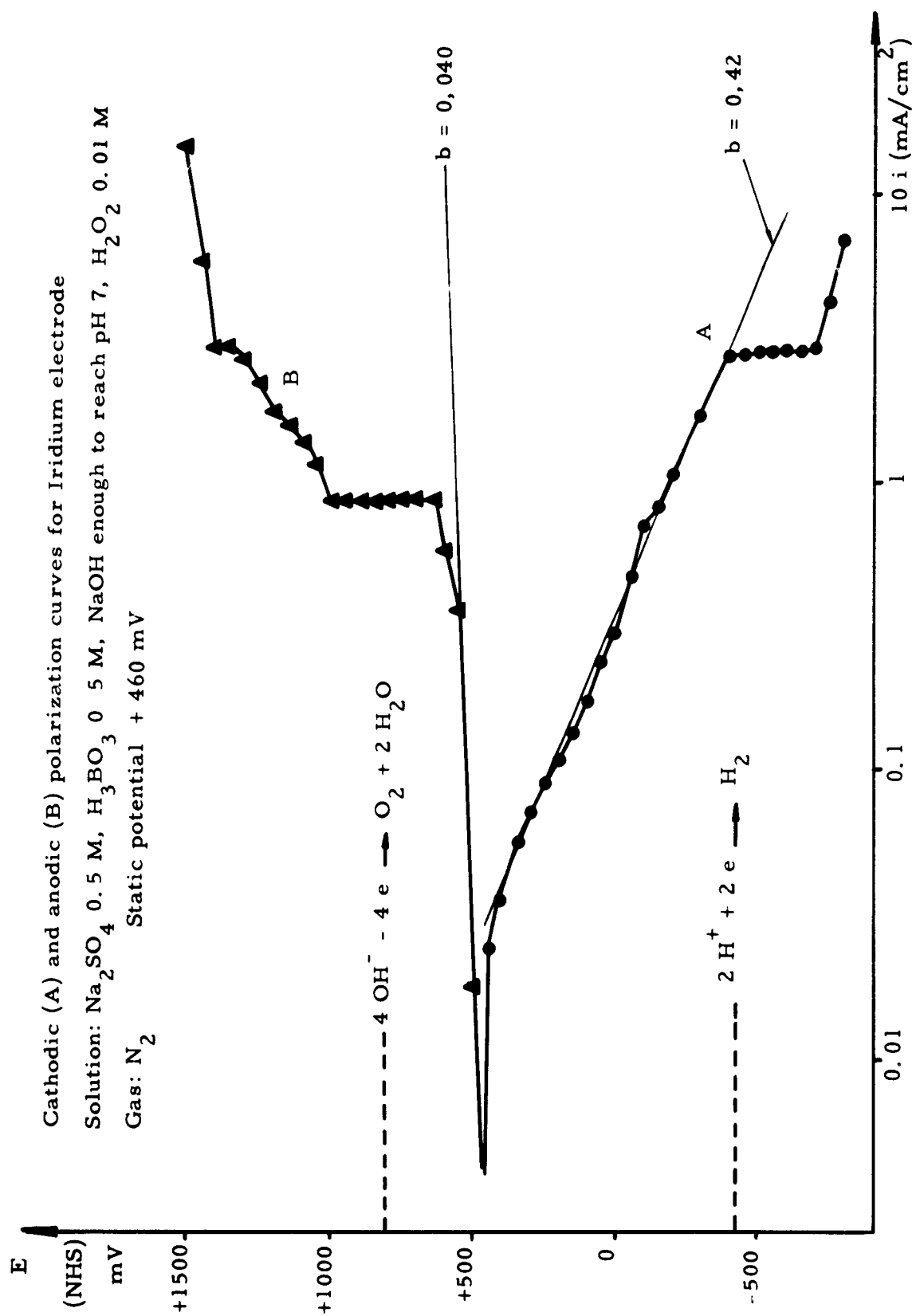


Fig. 12

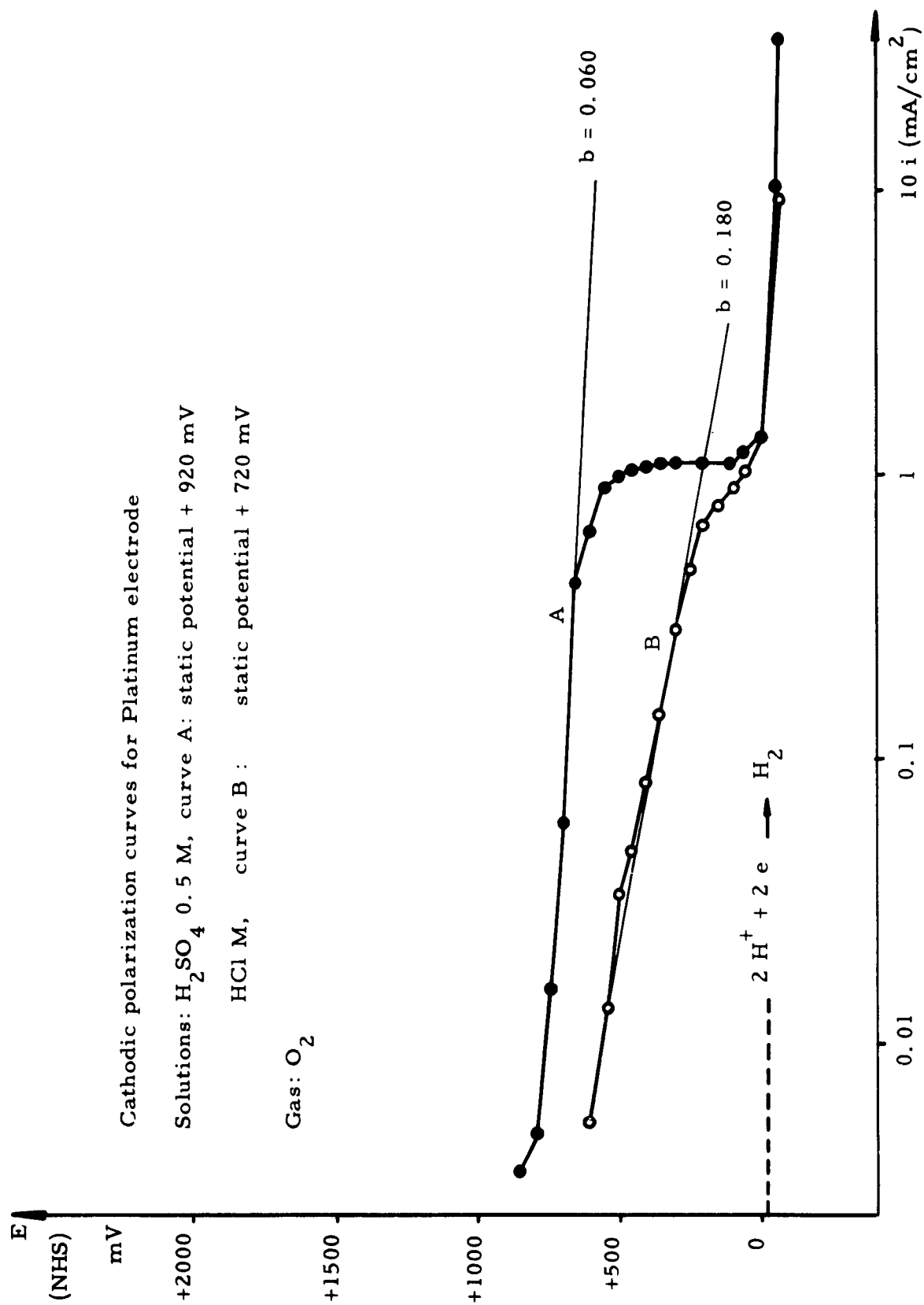


Fig. 13

Platinum electrode

- A : cathodic polarization curve - solution: H_2SO_4 0.5 M, H_2O_2 0.01 M; gas N_2
 B : cathodic polarization curve - solution: HCl 1 M, H_2O_2 0.01 M; gas N_2
 C : anodic polarization curve - solution: H_2SO_4 0.5 M, H_2O_2 0.01 M, gas N_2

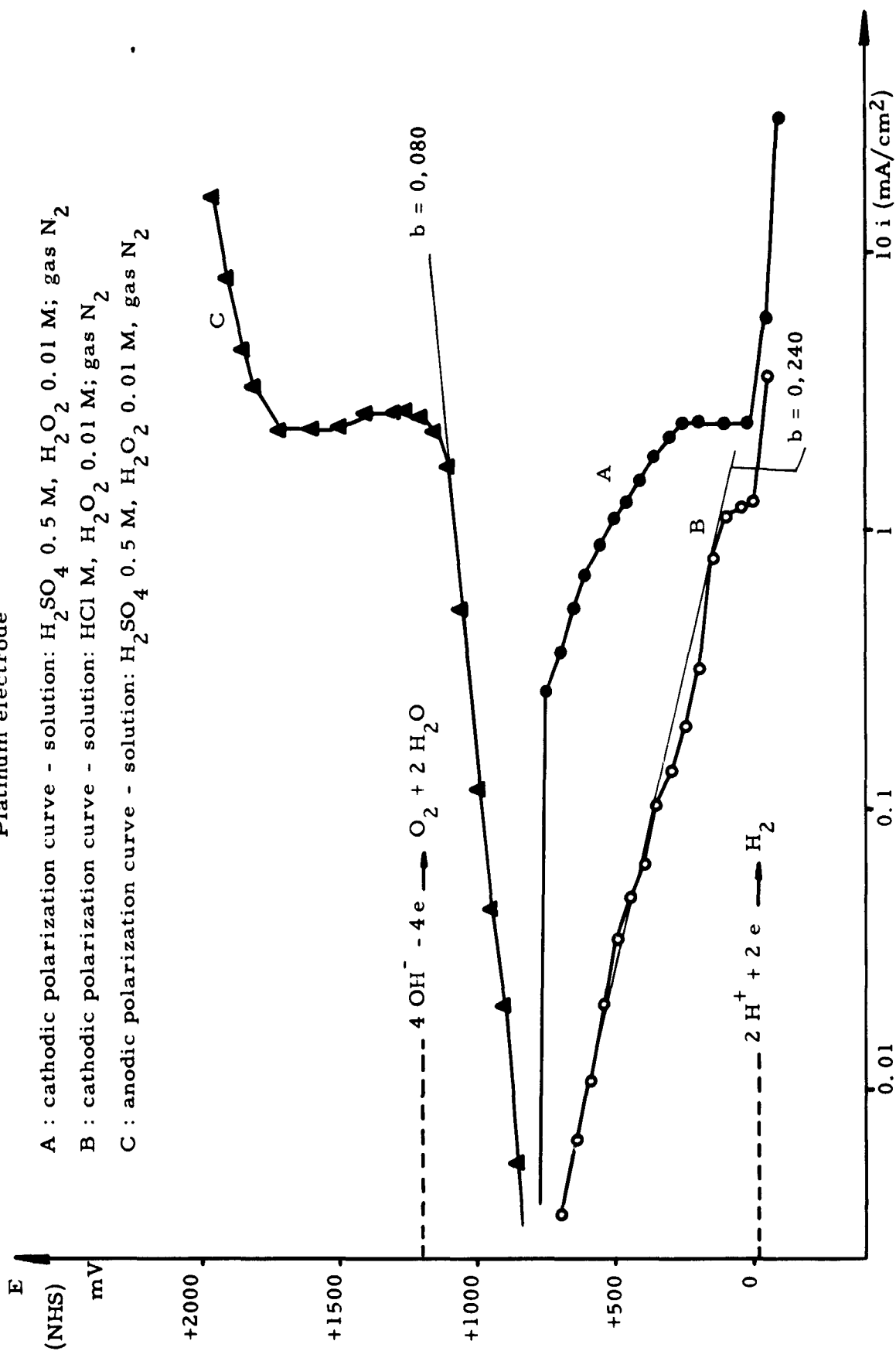


Fig. 14

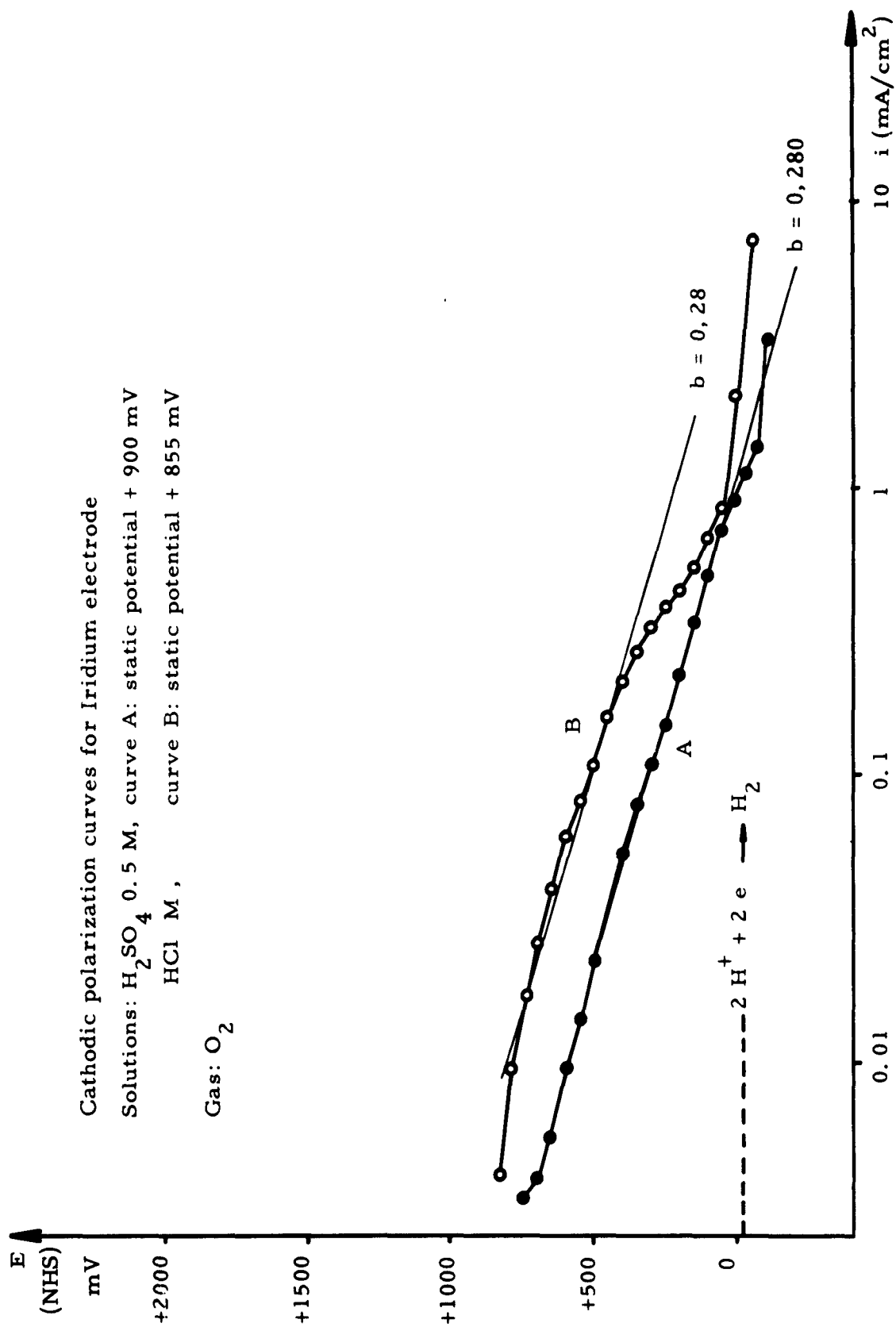


Fig. 15

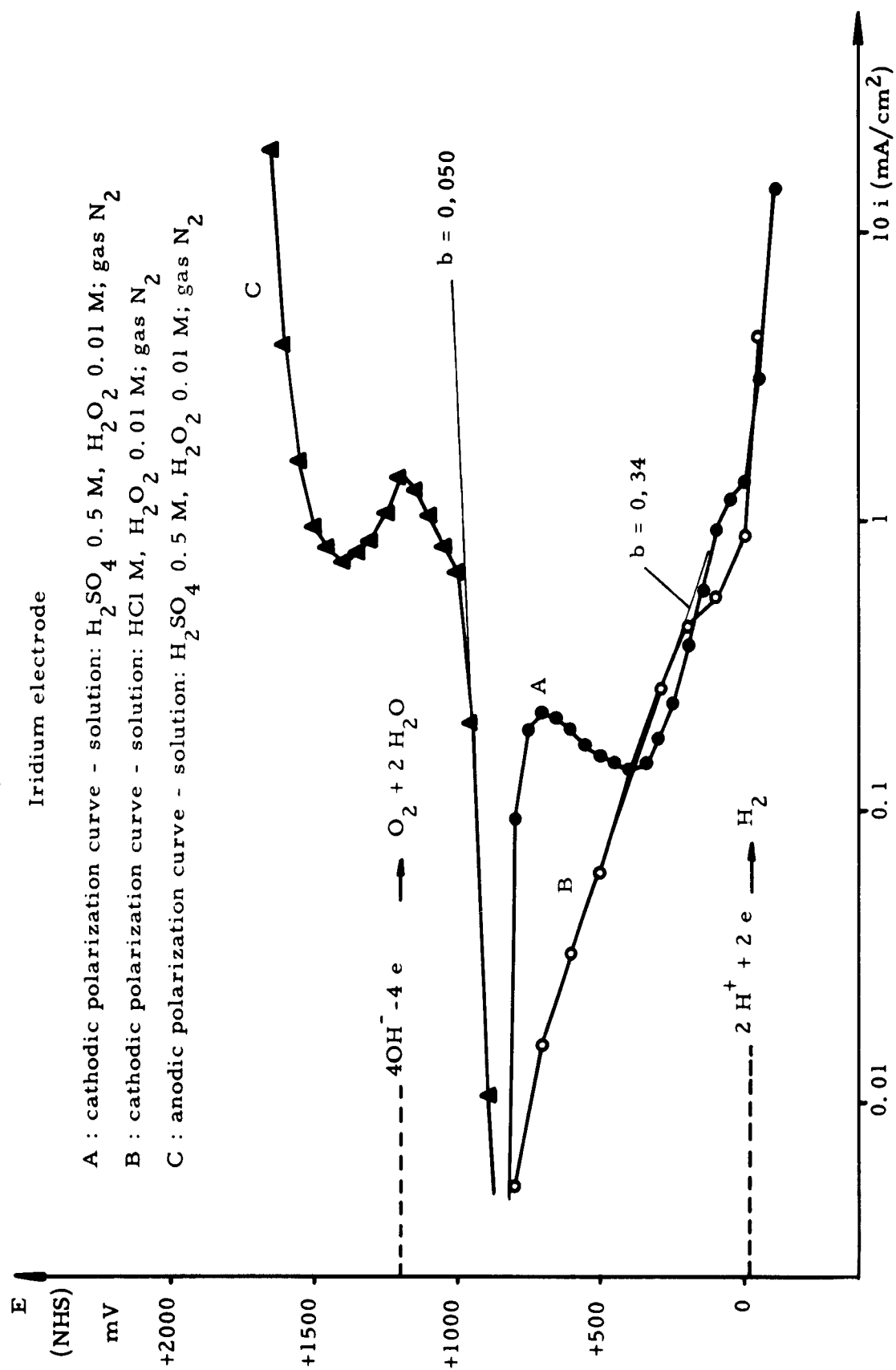


Fig. 16

E
(NHS)

mV

Cathodic polarization curves for Platinum - 10% Iridium electrode

Solutions: H_2SO_4 0.5 M, curve A : static potential + 900 mV

HCl M, curve B : static potential + 850 mV

Gas: O_2

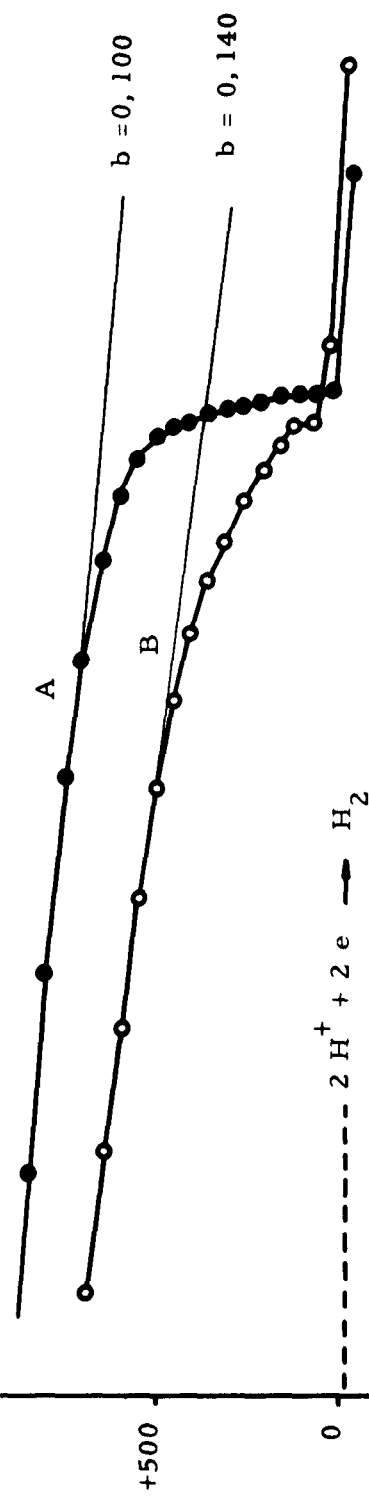


Fig. 17

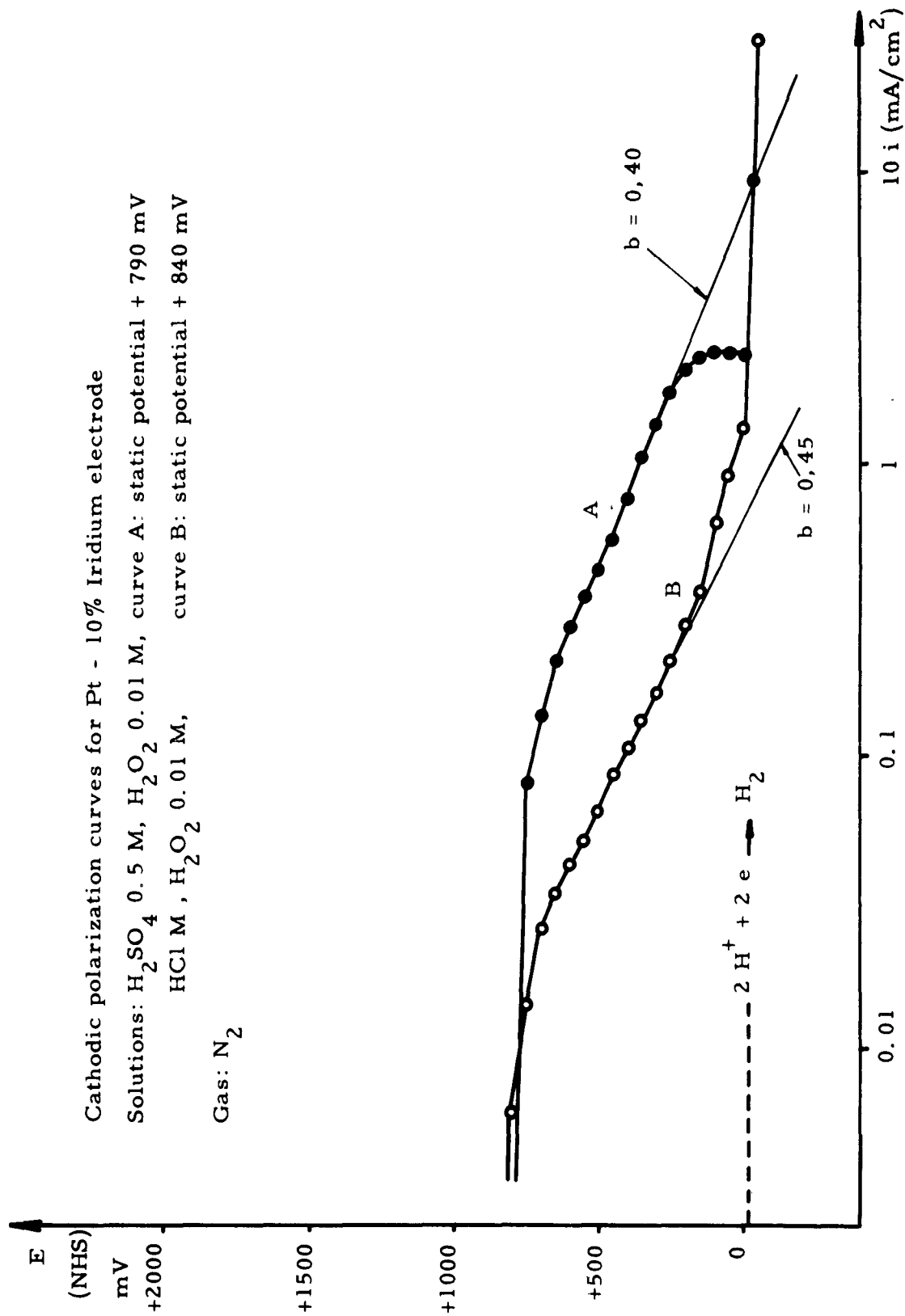


Fig. 18

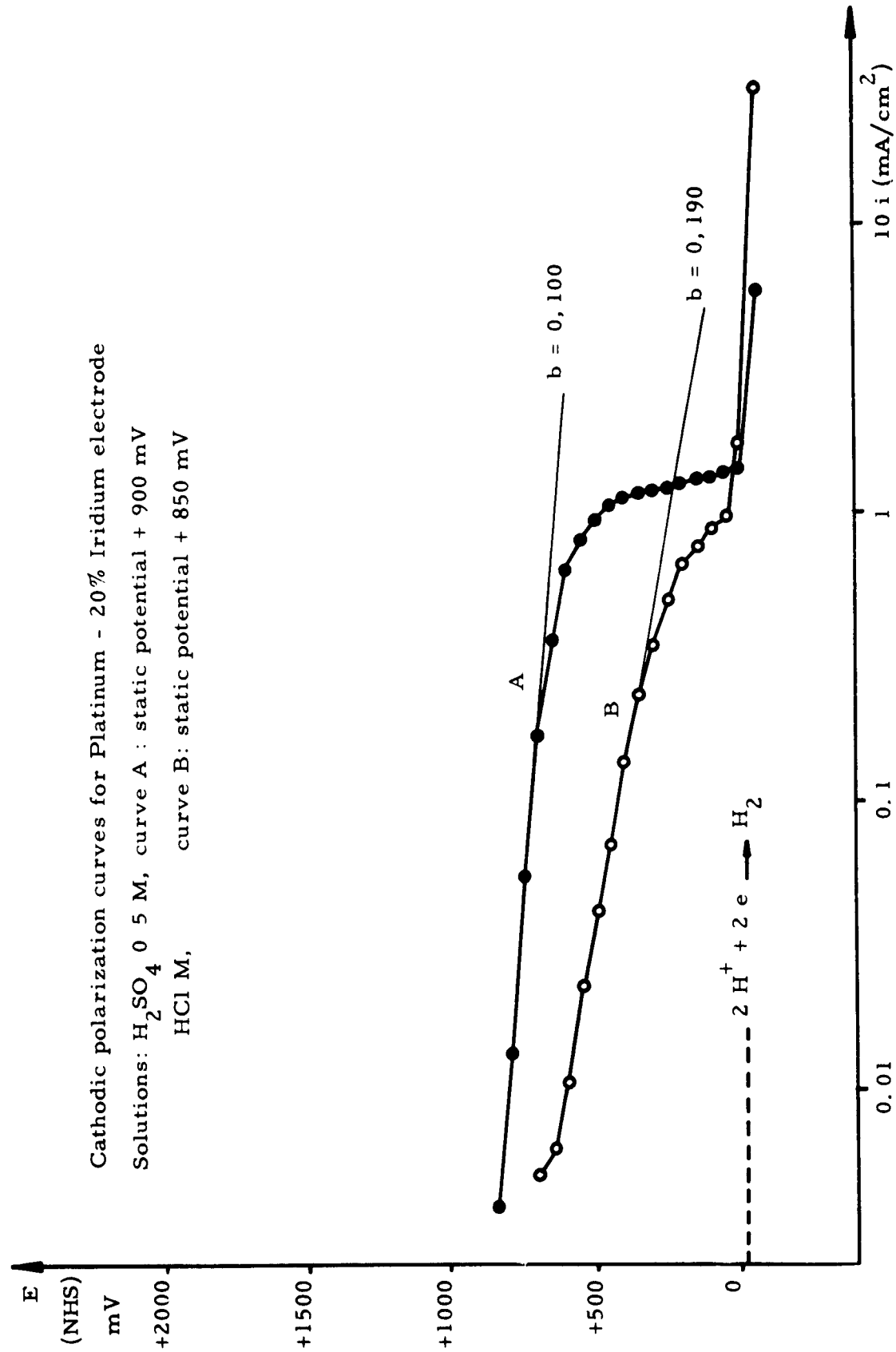


Fig. 19

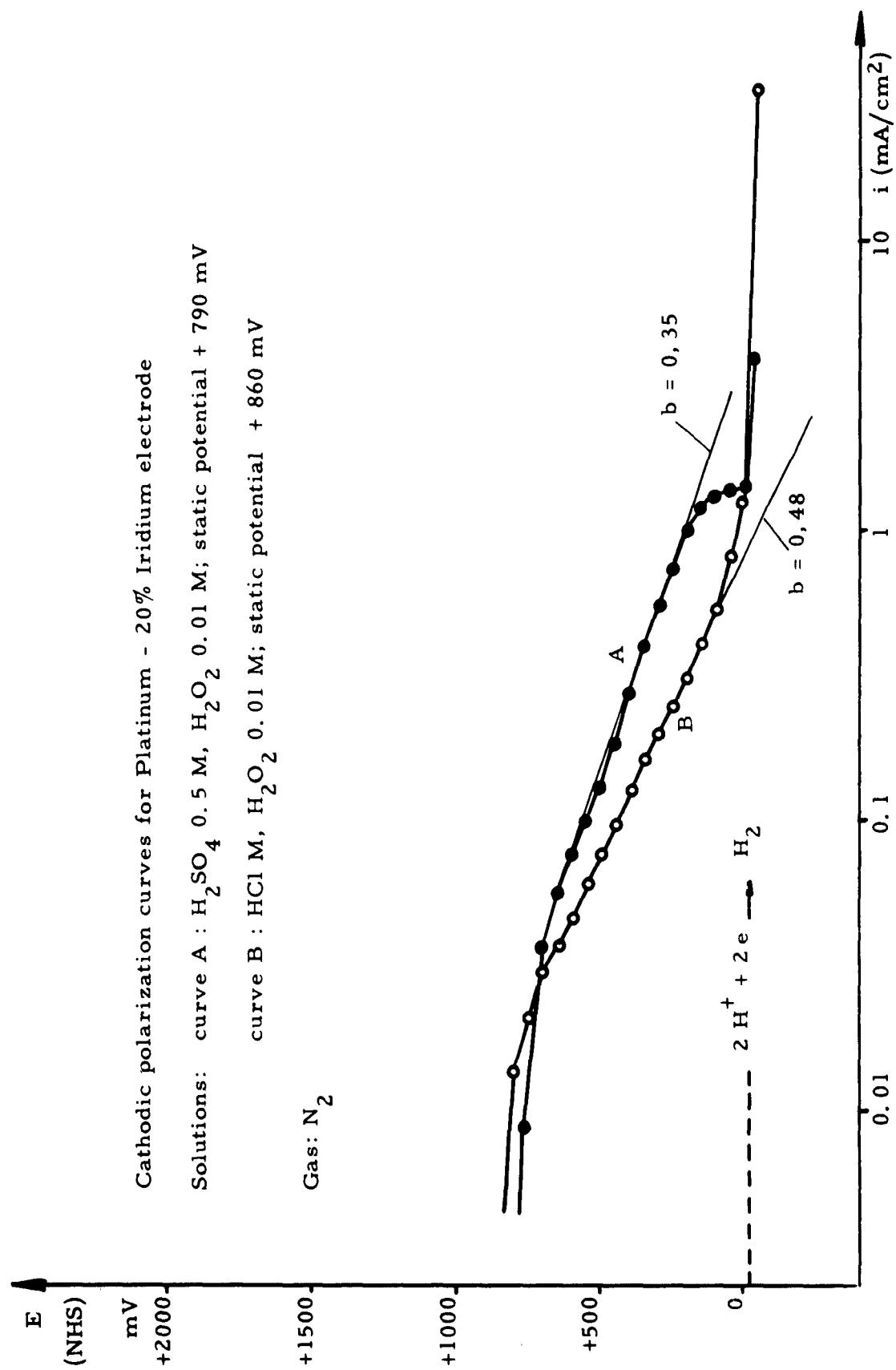


Fig. 20

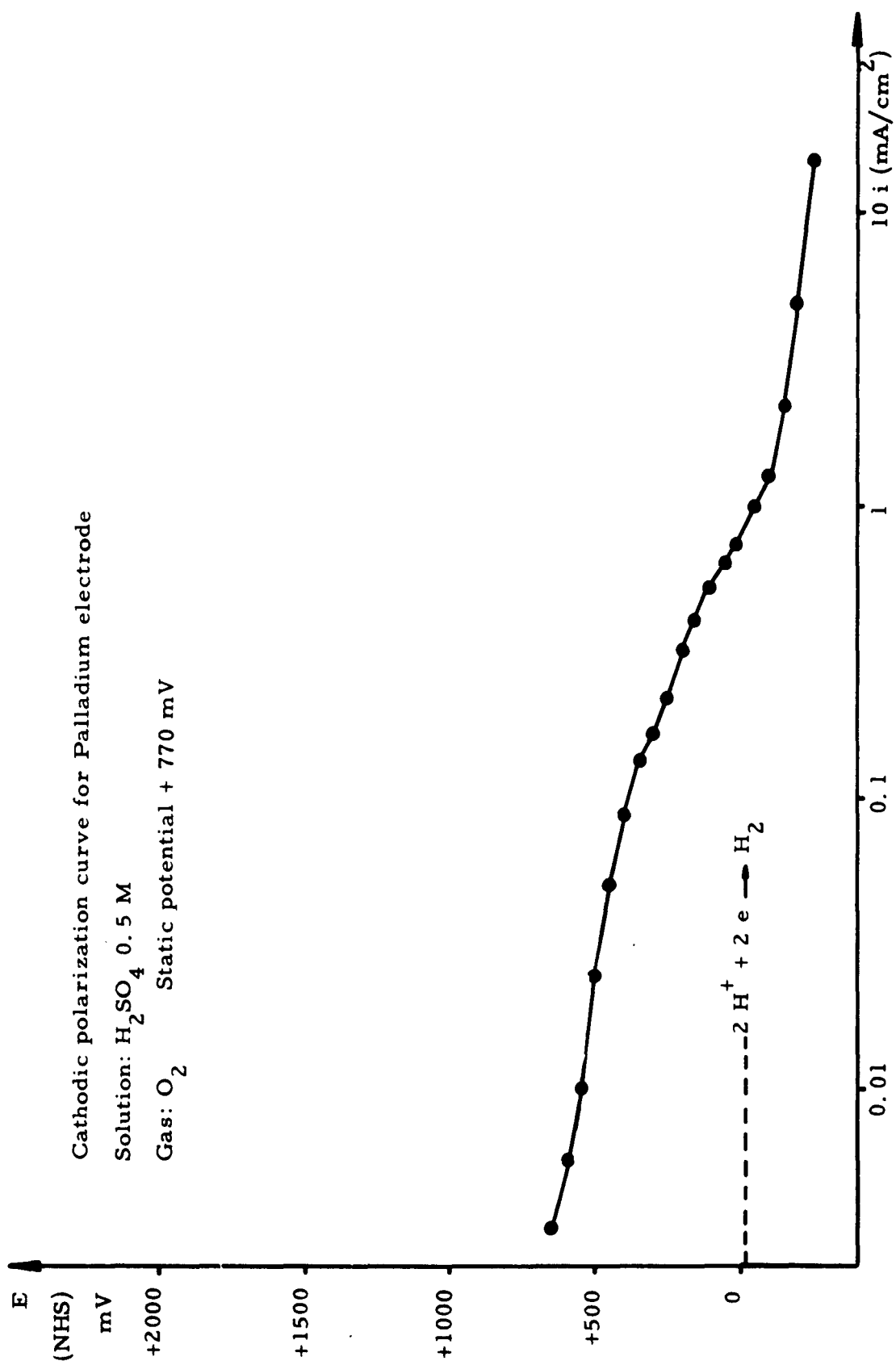


Fig. 21

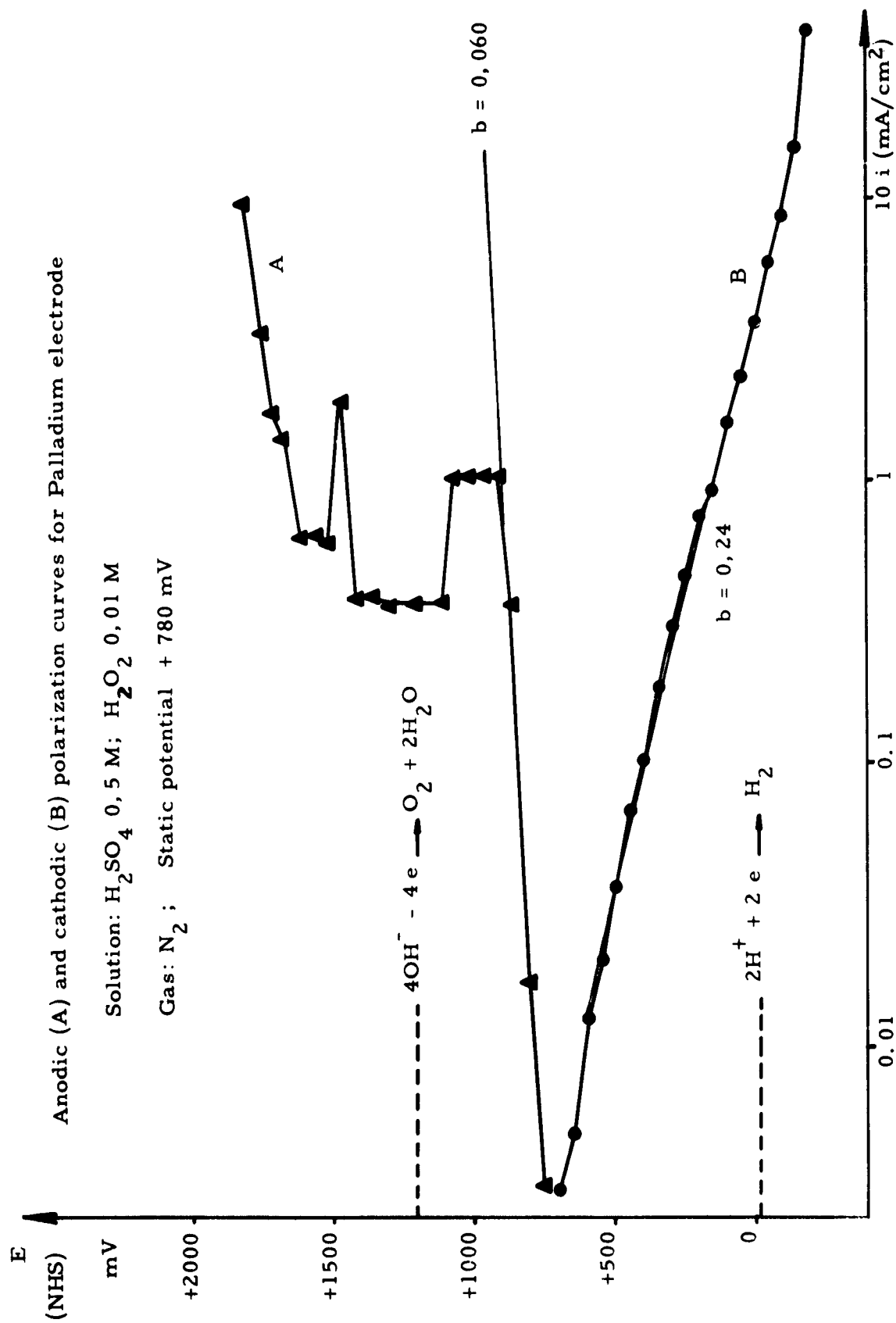


Fig. 22

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"CATHODIC REDUCTION OF O_2 AND H_2O_2 ON Pt, Pd AND Ir SMOOTH ELECTRODES"
by G. Bianchi, F. Mazza and I. Mussini; December 1961
ABSTRACT / Polarization curves in acid, neutral and alkaline solutions have been drawn by potentiostatic method, for O_2 and H_2O_2 reduction processes and for H_2O_2 oxidation process on Pt, Ir and Pd electrodes. These curves could be classified as follows: those whose slopes are 0.03 to 0.12, and those with slopes higher than 0.12. The former can be explained through already proposed mechanisms (addition of one electron or one atom of hydrogen to an adsorbed oxygen molecule; or addition of one electron to an HO_2 adsorbed radical) which

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mechanisms imply that the adsorption process is so quick as not to result kinetically determining. The latter involve a slow oxygen or HO_2 -radical adsorption which becomes kinetically determining, first of all for Iridium in both acid and neutral solutions. For Palladium in H_2SO_4 solutions and for Platinum in HCl solutions the oxygen adsorption process is very slow essentially due to the complexing action of the solution with resulting formation of surface complexes which engage the metal atoms, thus preventing or reducing the formation of adsorbed oxide.

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