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ELECTROCHEMICAL BEHAVIOUR OF OXYGEN AND HYDROGEN PEROXIDE
ON ALUMINUM, TANTALUM AND ZIRCONIUM ELECTRODES

by

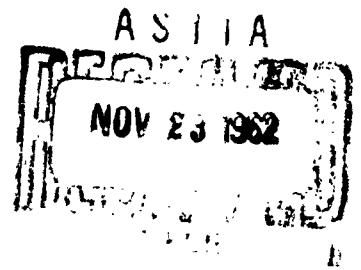
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S u m m a r y

Aluminum, tantalum and zirconium, although covered by an oxide layer, are able to act as cathode for the processes of oxygen and hydrogen peroxide reduction.

The value of overvoltage and the polarization curves are reported.

The results obtained on these three metals are compared with those previously obtained on titanium.

Overvoltages for cathodic reduction of oxygen decrease in the following order :

Zr, Ta, Ti for acid solutions; Al, Ta, Zr, Ti for neutral solutions; Zr, Ti, Ta for alkaline solutions.

1. - INTRODUCTION

The cathodic reduction of oxygen and hydrogen peroxide on various metals, and particularly on Al, Zr and Ta, was considered by Delahay (1) who obtained, by means of a polarographic method in buffer solution at pH 6.9, the following results.

Aluminum - Oxygen is cathodically reduced to H_2O_2 or to H_2O depending by the electrode tension. As far as -1.0 V (NHS) the reduction to H_2O_2 occurs ; at tensions more negative than -1.5 V (NHS) only the reduction to H_2O occurs. The H_2O_2 concentration in the solution does not raise beyond a limiting value on account of the spontaneous decomposition.

Zirconium - The cathodic reduction of oxygen always leads to the formation of water. This behaviour is explicated by Delahay by considering the formation of percompounds, as in the case of molybdenum.

Tantalum - The electrode process is abruptly changed at a tension of -0.5 V (NHS). At more noble tensions the cathodic reduction of oxygen leads to the formation of hydrogen peroxide only; at more negative tensions to the formation of water only.

Tomashov (2) examined the cathodic reduction of oxygen on metals covered by an oxide layer (as Al and Ta). He discussed the hysteresis observed when the polarization curves are plotted at increasing and at decreasing current densities. He distinguishes the case in which the oxide layer has an electronic conductance from the case in which the oxide layer is porous.

In solution NaCl 0.5 M + NaHCO_3 0.005 M + Na_2CO_3 0.005 M at pH 9.2, Tomashov found the limiting current for aluminum in stirred solution is about 1 mA/cm^2 at a tension of

-1.2 V (NHS); for tantalum the limiting current is 1.1 mA/cm^2 at a tension of -0.9 V (NHS). The static tensions for aluminum and tantalum are, respectively, of -0.83 V and -0.05 V.

Recently Meyer (3) studied in the case of zirconium the problem of the cathodic reduction of O_2 and H_2O_2 (and of the H^+ and Cu^{++} ions) on the electrodes covered by an oxide film. According to this author (that relates also the opinion of Vetter) it is very improbable that the current flows through the pores and the singularities of the oxide layer, while, being the film vary thin, it may be considered the electrical conductance through the same film.

At high temperature the conductance of the zirconium oxide layer is due to anion vacancies and depends from the heat treatment, like the heating in vacuum at 450°C (4). Some experiences at a more high temperature (1432°C) (5) showed that the oxygen present as solid solution migrates into the zirconium as negative ion. At room temperature the cathodic current flow should be due to the electronic conductance of the non-stoichiometric oxide film that in some particular conditions may result black coloured.

Similar considerations may be deduced in the case of the tantalum oxide films that also show a remarkable dissymmetry between the anodic and the cathodic conductance. In the first case it is a general opinion that the conductance is due only to the migration of the metal ions (6). In the second case the conductance may be due to the flow of electrons arising from the presence of the anion vacancies. Moreover the tantalum oxide films can result black and their electric conductivity is higher when the film was subjected to a treatment that leaved an excess of metal into the oxide film (for ex. annealing at 350°C in vacuum) (7).

Also for aluminum it was recently demonstrated (8) that the oxide layer spontaneously formed on air contains an excess of metal with several anion vacancies (9) where electrons become trapped. Also for aluminum the formation of black oxides is verified in particular conditions (10).

It was above mentioned that Delahay considered the formation of the percompounds to explicate the particular behaviour of zirconium. Hydrogen peroxyde can form some peroxydes (Zr_2O_5 , ZrO_3 , Zr_2O_7) little soluble in diluted acid media and soluble in alkaline media with formation of peroxyzirconates, such as $\text{K}_4\text{ZrO}_8 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$ (11). Also tantalum can form some complexes with hydrogen peroxide (12). Unfortunately there are not data on the electrochemical behaviour of these percompounds. A concise summary of a paper of Krauze and Hermann (13) informs that tantalum does not act as oxygen carrier in the $\text{HCOOH} - \text{H}_2\text{O}_2$ or indigo - carmine - H_2O_2 systems. Moreover tantalum does not react with H_2O_2 to form Ta_2O_5 . It may be remembered that the percompounds formed by titanium with hydrogen peroxide in acid solution act, from the electrochemical point of view, as the hydrogen peroxide solutions (14).

For zirconium and tantalum it may be considered the possibility that the cathodic discharge of hydrogen form an hydride on the surface with modification of the surface state (15). Some modifications of the surface state can be caused also by anodic polarizations. Tomashov already underlined the dispersion of experimental results in the case of tantalum, attributed to the variations of the surface state. This fact may be considered also for zirconium and aluminum, as it is emphasized by the rectifying phenomena that are observed with these metals on account of the dissymmetry in the conductance of the oxide layer (16).

2. - EXPERIMENTAL

The experimental work was performed by means of the polarization cell already described (17), the cell being filled with the required solution, O_2 or N_2 bubbled through. When N_2 was bubbled, the solution was previously de-aerated with the same nitrogen. As electrodes, discs (diameter 25mm) of tantalum, aluminum or zirconium were used. The analysis are as follows :

<u>Tantalum 99,9 %</u>	<u>Aluminum 99.99 %</u>	<u>Zirconium 99.99 %</u>
Nb 0.02 + 0.08 %	Fe+Si+Cu+Ti $\leq$ 0.01 %	Al 0.0173 % C 0.0082 %
Fe 0.01 + 0.03 %		Cr 0.0080 % Fe 0.0830 %
Ti $\leq$ 0.05 %		Hf 2.3 % N_2 0.0038 %
C $\leq$ 0.01 %		O_2 0.0785 % Si 0.0070 %

Before each experiment the electrodes were ground with emery paper N. 0000 and kept for 12 hours in a dessicator.

The solutions were prepared from analytically pure Merck products and had the following compositions :

acid	0.5 M H_2SO_4
neutral	0.5 M H_3BO_3 + 0.5 M Na_2SO_4
alkaline	0.1 M NaOH + 0.5 M Na_2SO_4

The pH of the neutral solution was adjusted to 7, by the addition of small quantities of NaOH. The requisite quantity of H_2O_2 (Perhydrol Merck) was then added to obtain the desired concentration.

The gases were pure commercial O_2 (with traces of N_2 and rare gases) or high purity N_2 (99.999 %); they were bubbled at a flow rate of $150 \text{ cm}^3/\text{min}$.

All measurements were carried out in an air thermostat at $25 \pm 0.1^\circ\text{C}$.

A saturated silver chloride electrode was used as a reference electrode; all the tensions were reported on hydrogen scale (NHS) by adding 0.196 V to the experimental values without making any correction for the liquid junction.

The figures show the cathodic polarization curves. The logarithm of the current density (mA/cm^2) is the abscissa, and the tension (mV, NHS) is the ordinate.

As experimental procedure the cell was connected to an electronic potentiostat and, starting from the static value, the tensions were decreased successively and the corresponding current values were measured. The tension of hydrogen discharge was reached; on account of this the return curve at increasing tensions was not plotted in consideration of the fact that the electrode surface could be modified by the formation of hydride. On account of similar considerations on the possible surface state modifications, anodic polarization curves have not been carried out.

3. - EXPERIMENTAL RESULTS

In the case of aluminum the experiences were limited to the neutral solutions, to avoid the corrosion phenomena of the electrode that can hide the processes of oxygen and hydrogen peroxide reduction.

The cathodic reduction of oxygen (fig. 1) takes place with formation of little quantities of hydrogen peroxide and occurs at tensions more negative than that observed on other metals (like Pt, Au). The limiting current ($1 \text{ mA}/\text{cm}^2$) corresponds to the diffusion of the oxygen; the slope of the curve is 0.11.

In the case of the neutral solutions containing hydrogen peroxide (fig. 2), the slope of the cathodic polarization curve is high and it is not possible to read certainly the value of the limiting current (concerning hydrogen peroxide) that could result of 3 mA/cm^2 . The high slope of the polarization curve is attributed to the presence of a thicker protective oxide layer formed on aluminum by the hydrogen peroxide solution of sufficient concentration. Although in different conditions as regards the pH of the solution, it was possible to emphasize that hydrogen peroxide beyond a fixed concentration acts as inhibitor of the aluminum corrosion (10).

The figure 3 shows the polarization curves for the cathodic reduction of oxygen on zirconium in acid, neutral and alkaline solution. It may be observed that for neutral and alkaline solutions the tension of the process depends on the pH in the same way observed with other metals (about 0.059 V/pH). The limiting current is 1 mA/cm^2 and the slope of the polarization curve is about 0.24 . The behaviour in acid solutions is different : the cathodic reduction of oxygen occurs at a very negative tension near to that corresponding to the hydrogen discharge; on the contrary the slope of the curve (0.24) and the limiting current (1 mA/cm^2) are the same for acid, ^{and} neutral ~~and alkaline~~ solutions. In all cases it was verified that the cathodic reduction of oxygen on zirconium occurs with formation of hydrogen peroxide, analogously to what was observed with other metals (Pt, Au, Ti, etc.)

The same considerations can be done for the polarization curves for the cathodic reduction of hydrogen peroxide solutions, except the greater slope of the polarization curve in alkaline solution.

In the case of tantalum the cathodic reduction of oxygen occurs with formation of hydrogen peroxide. Also in this case (fig. 5) the process occurs in acid solution at unusually negative tensions, although the slope of the polarization curve (0.24) and the limiting current (1 mA/cm^2) are normal. With hydrogen peroxide solutions the situation is the same as with zirconium. The polarization curve in alkaline solution has a slope more high than that of the acid and neutral solutions. ~~The polarization curve in acid solution has a slope higher than that of the acid and neutral solutions.~~ The polarization curve in acid solution does not let us see the limiting current, in consideration of the fact that the part of the polarization curve at which corresponds the cathodic reduction of hydrogen peroxide is connected with the part at which hydrogen is discharged. The same behaviour can be observed in the case of titanium and gold (18).

4. - CONCLUSIONS

Tables I and II show the most significant data obtained with Ti, Al, Zr and Ta. Also titanium was included (the results on this metals were recently published) on account of the analogy presented with the other considered metals. All these metals are covered by an oxide film and the above mentioned Tomashov's considerations on the kind of the electric conductance can be remembered.

It was confirmed that Ti, Ta, Zr and Al, although covered by an oxide layer, are able to act as cathode for the processes of oxygen and hydrogen peroxide reduction. In the case of the cathodic reduction of oxygen the formation of small quantities

T A B L E I

Solutions saturated with O_2 at $25^\circ C$

		Static tensions (NHS)	Electrode tensions (NHS) for $i = 10^{-1}$ mA/cm ²	Slope of polarization curves
		mV	mV	V/log i
Acid Solutions	Ti	+ 360	+ 120	0.18
	Zr	+ 40	- 360	0.26
	Ta	+ 220	- 120	0.26
Neutral Solutions	Al	- 220	- 300	0.22
	Ti	+ 380	- 40	0.13
	Zr	+ 200	- 240	0.24
	Ta	+ 25	- 300	0.26
Alkaline Solutions	Ti	- 170	- 590	0.18
	Zr	- 220	- 810	0.84
	Ta	- 90	- 350	0.37

T A B L E II

Solutions (H_2O_2) = 10^{-2} M a 25°C ; Gas N_2

		Static tensions (NHS)	Electrode tensions (NHS) for $i = 10^{-1}$ mA/cm ²	Slope of polarization curves
		mV	mV	V/log i
Acid Solutions	Ti	+ 340	- 70	0.21
	Zr	+ 200	- 200	0.26
	Ta	+ 110	- 300	0.23
Neutral Solutions	Al	- 240	- 600	0.74
	Ti	+ 180	- 80	0.24
	Zr	0	- 480	0.50
	Ta	- 20	- 380	0.28
Alkaline Solutions	Ti	+ 120	- 300	0.22
	Zr	- 350	- 1230	0.46
	Ta	0	- 680	0.44

of hydrogen peroxide is always observed and the limiting current results about 1 mA/cm^2 , equal to that observed on platinum and on other "bare" metals. In the case of the cathodic reduction of hydrogen peroxide (10^{-2} M), the hydrogen peroxide contributes to the growth of the oxide film covering the electrode and the polarization curves are very inclined with limiting currents not defined or smaller than those corresponding to the solutions of the same concentration on platinum electrode (about 3 mA/cm^2). This effect is very strong in the case of zirconium; with tantalum it is observed only in alkaline solution, according with the above mentioned information that tantalum does not react with H_2O_2 to form Ta_2O_5 .

Table III shows the overvoltage values at various current densities for the cathodic reduction of oxygen on titanium, zirconium, tantalum and aluminum. It results clearly that the overvoltage on titanium is always less than on zirconium, on tantalum and on aluminum. Amongst those, aluminum presents the maximum overvoltage in neutral solution.

The comparison between zirconium and tantalum emphasizes that, except the neutral solutions, the overvoltage for the cathodic reduction of oxygen is higher on zirconium than on tantalum.

These results make us able to conclude that with zirconium and tantalum the dangers of galvanic corrosion are less than in the case of titanium. With zirconium and tantalum in acid solution it is more clearly emphasized the phenomenon already observed with titanium : the cathodic reduction of oxygen and hydrogen peroxide occurs at tensions very near to that corresponding to the reversible hydrogen discharge and the polarization curve

T A B L E III

Overvoltage for the cathodic reduction of oxygen on titanium, zirconium and tantalum, related to the reaction $O_2 + 2H^+ + 2e = H_2O_2$ ($H_2O_2 = 10^{-3} M$ and $P_{O_2} = 1$)			
		0.01 mA/cm ²	0.1 mA/cm ²
Acid solutions $E_{rev} = 0.72 V$	Titanium	0.5	0.6
	Zirconium	0.83	1.08
	Tantalum	0.68	0.84
Neutral solutions $E_{rev} = 0.36 V$	Titanium	0.3	0.4
	Zirconium	0.36	0.60
	Tantalum	0.46	0.66
	Aluminium	0.62	0.66
Alkaline solutions $E_{rev} = 0.01$	Titanium	0.3	0.6
	Zirconium	0.37	0.82
	Tantalum	0.18	0.36
			1 mA/cm ²
			0.8
			-
			1.24
			0.7
			1.56
			1.40
			1.58
			0.8
			-
			1.31

presents only a little inflection at the limiting current point being directly jointed with the part corresponding to the hydrogen discharge at the high current densities. Apparently the cathodic reduction of oxygen occurs at almost the same tension in acid and in neutral solution.

To explicate this behaviour one can think that in acid solutions the cathodic reduction of oxygen and hydrogen peroxide cannot occur with the same mechanism verified in alkaline solutions on account of the difficulties in adsorbing oxygen and in disadsorbing hydrogen peroxide on the electrode surface. If the cathodic discharge of hydrogen ions occurs, the adsorbed atomic hydrogen so formed should be consumed in a secondary "depolarization" reaction by the oxygen and the hydrogen peroxide.

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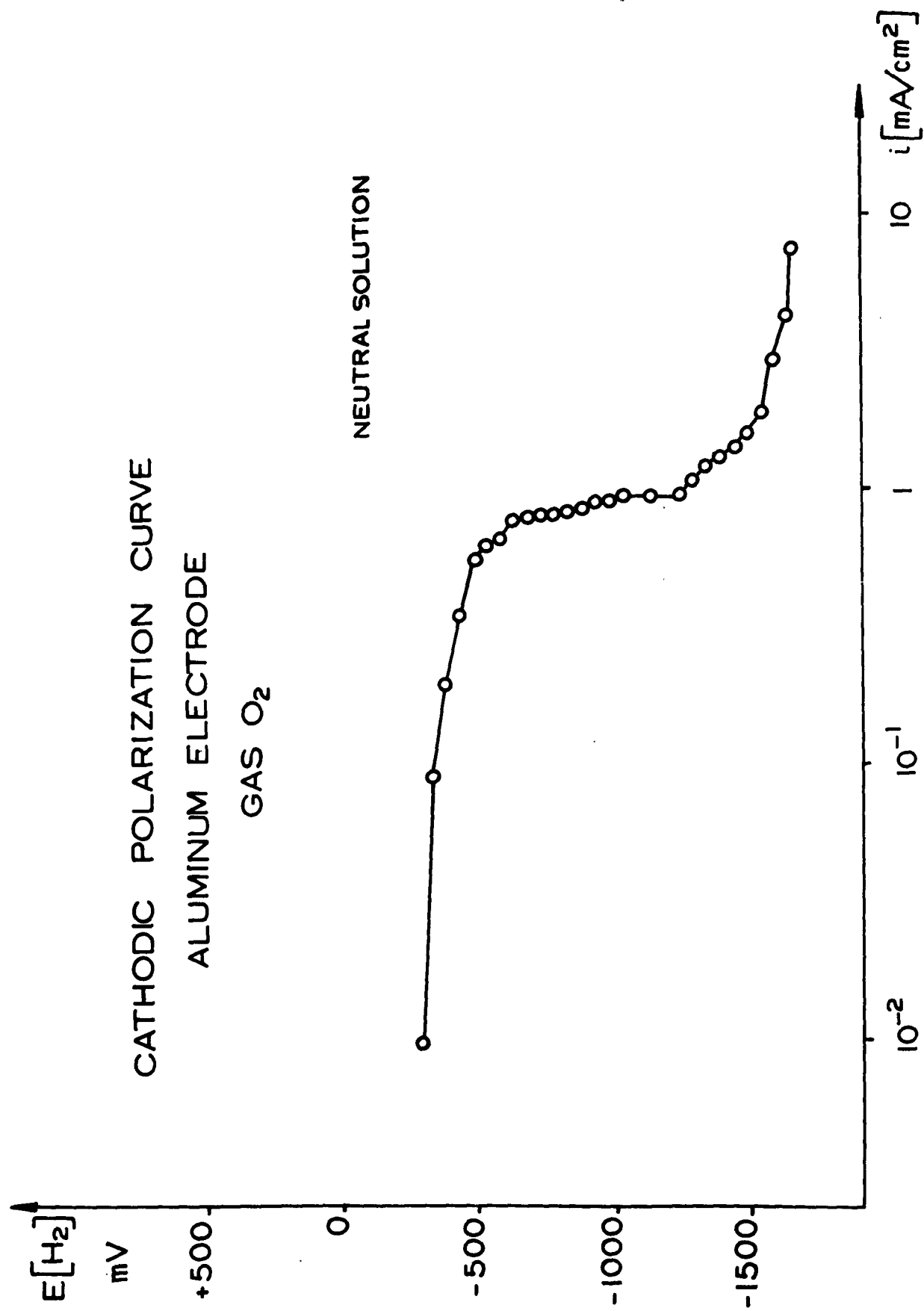


FIG.1

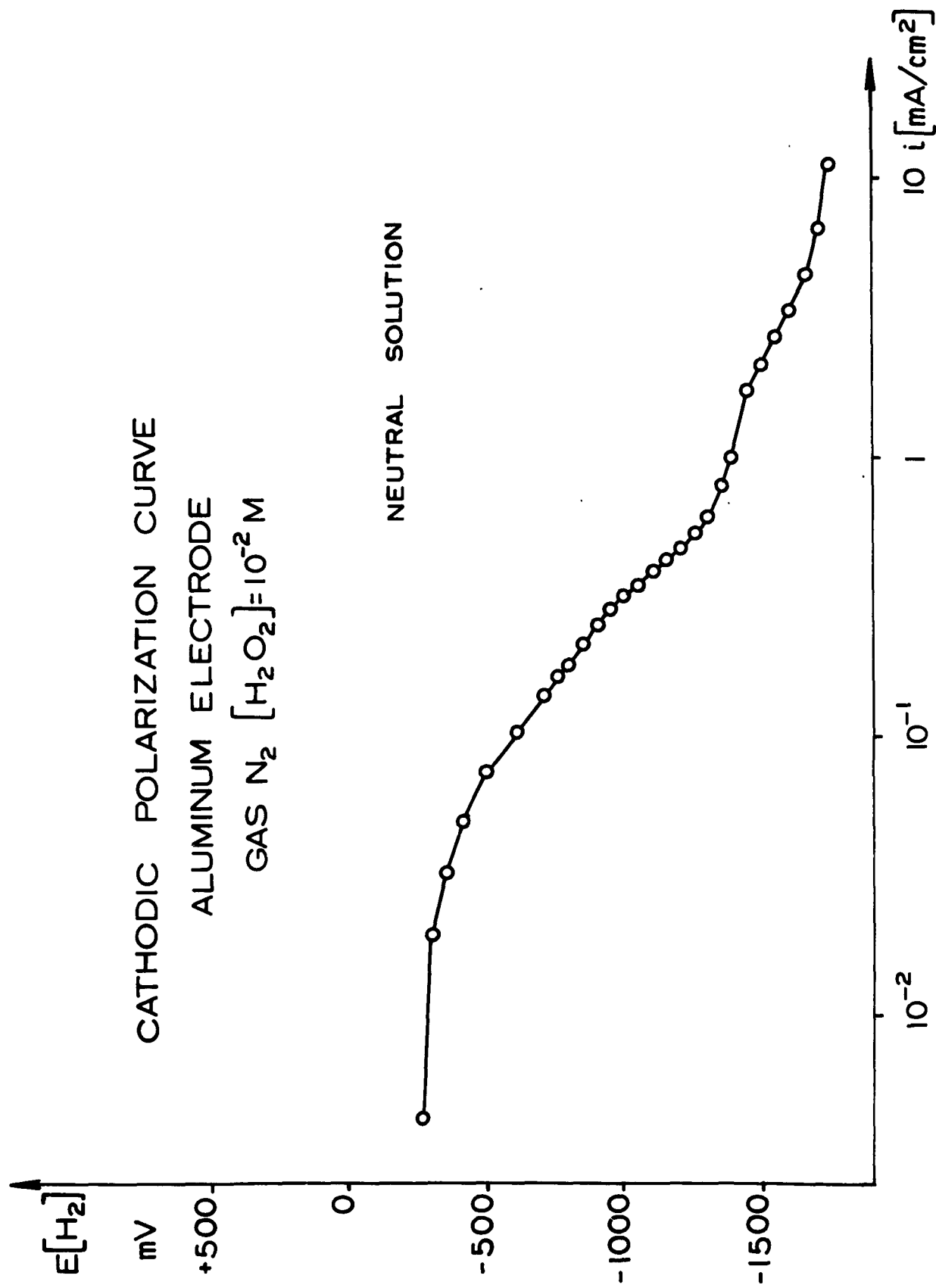


FIG.2

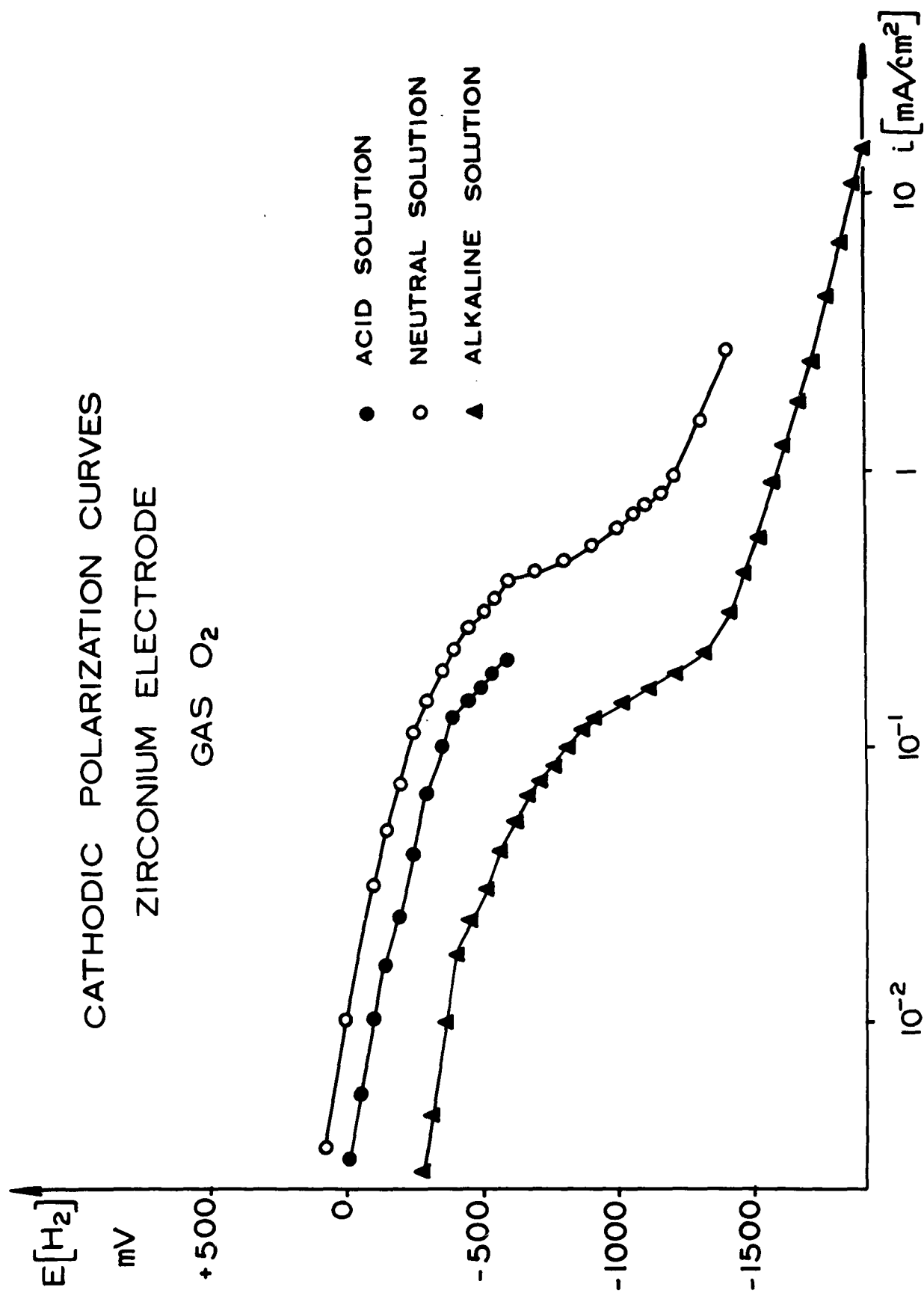


FIG.3

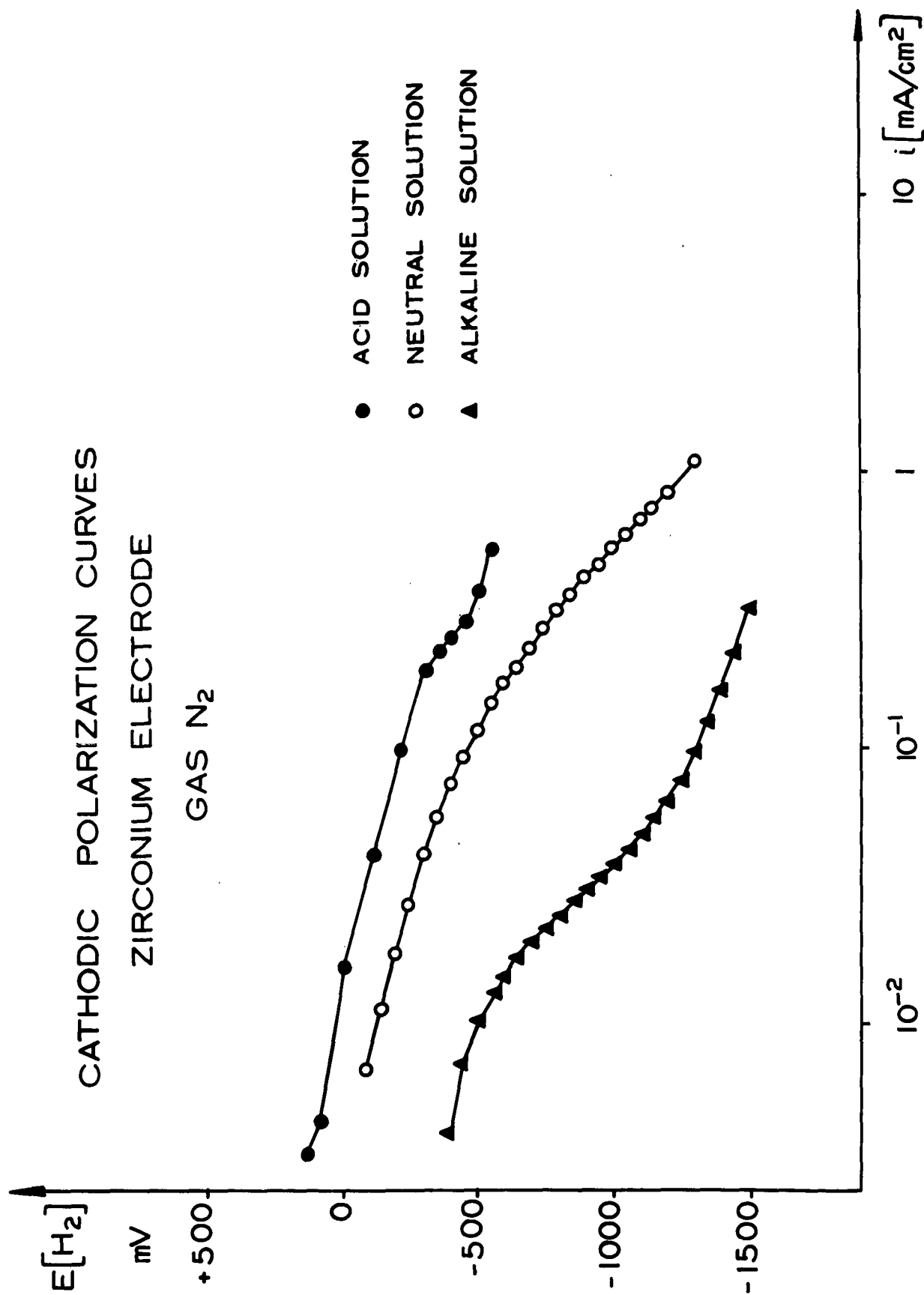


FIG. 4

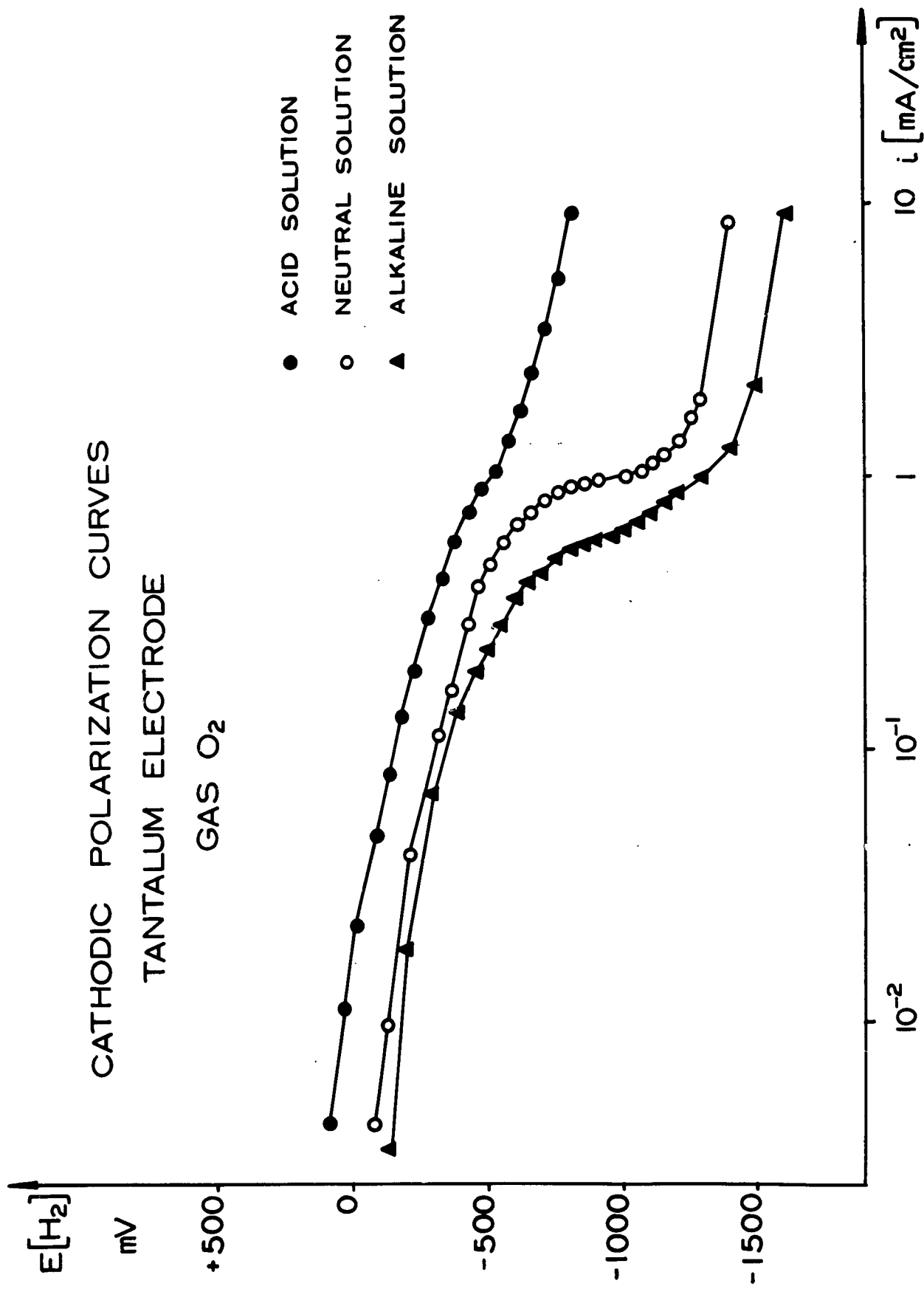


FIG. 5

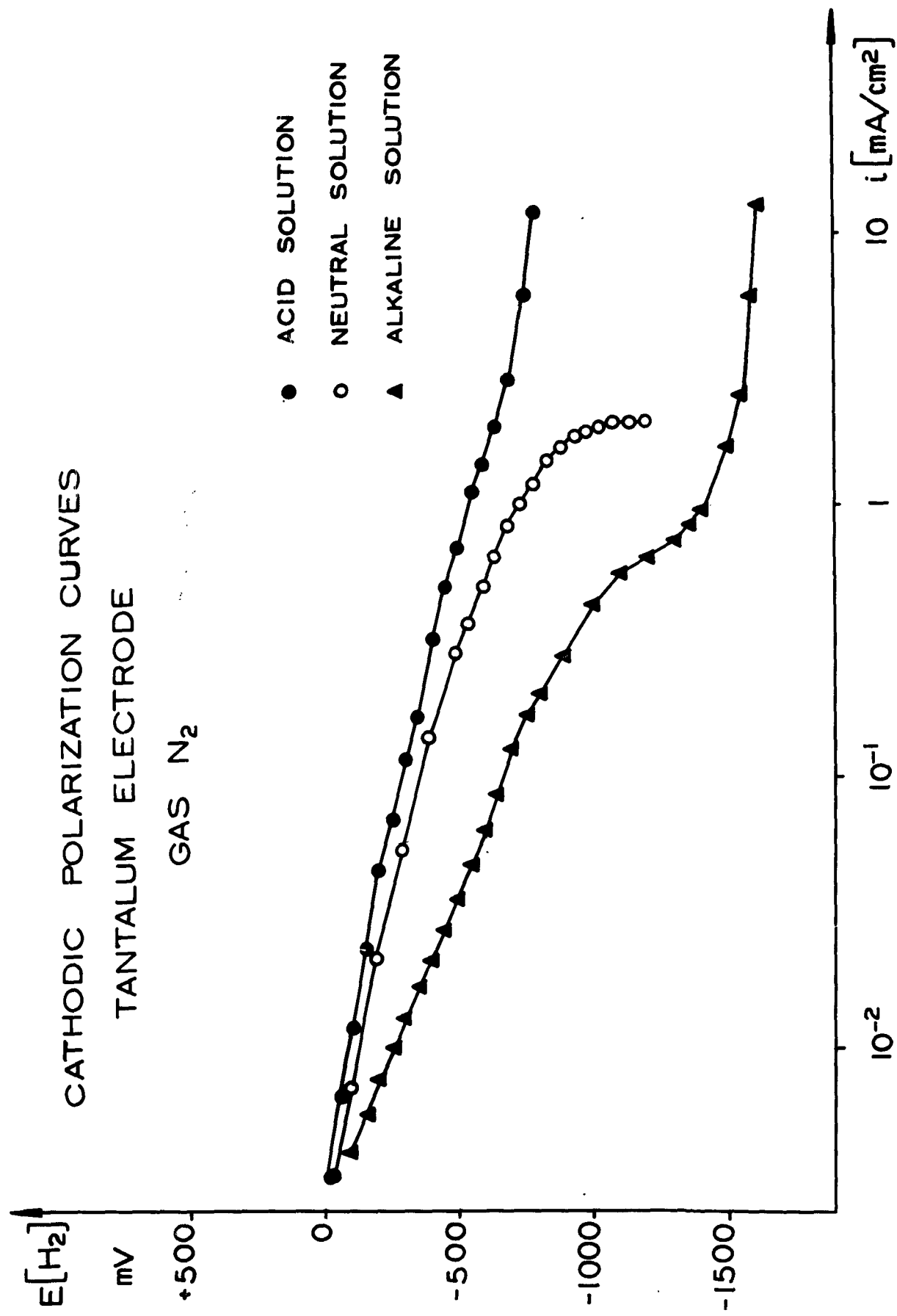


FIG. 6

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