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AFOSR TN 60-1209

ELECTROCHEMICAL BEHAVIOUR OF OXYGEN AND HYDROGEN PEROXIDE

ON MAGNETITE ELECTRODES

by

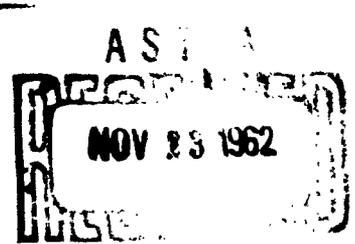
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Technical (Scientific) Note No. 3

Contract No. AF 61(052) - 260

October 1960



CREDIT LINE

The researches reported in this document has been sponsored by the Air Force Office of Scientific Research of the AIR RESEARCH AND DEVELOPMENT COMMAND, UNITED STATES AIR FORCE, through its European Office.

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## S u m m a r y

The electrochemical behaviour of oxygen and hydrogen peroxide on magnetite electrodes was studied by means of polarization curves and by means of tension build - up and tension decay curves.

In alkaline solutions the oxygen is reduced at a tension near to that corresponding to the process  $O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$ . Also the hydrogen peroxide in concentrated solutions ( $10^{-2}$  M) is reduced at the same tension : the electrochemical process probably concerns the oxygen arising from the  $H_2O_2$  decomposition. Anodic and cathodic processes for  $H_2O_2$  are symmetric.

In neutral solutions the processes concerning oxygen and hydrogen peroxide occur with the intervention of the redox systems of the iron compounds. The surface of the electrode is modified during a cathodic or anodic polarization. The surface modifications were evidenced by means of electron diffraction.

## 1. - INTRODUCTION

The corrosion of iron is accelerated by the presence of magnetite on the surface of metal. This is usually attributed to the cathodic behaviour of magnetite in respect to iron during the processes of "oxygen" corrosion. This type of galvanic corrosion is dangerous especially when the anodic area is smaller than the cathodic area, as was showed by Eisenstecken (1) and confirmed by the daily experience.

Herzog (2) showed that the cathodically active magnetite is not only the one formed on iron at high temperature, but also the hydrate one formed on iron during the processes of wet corrosion at low temperature. Herzog showed that also other corrosion products of iron can have a "depolarizing" action that accelerates the corrosion of the metal. This fact was mentioned also by Evans (3) in the case of atmospheric corrosion. The formation of ferric hydroxide by oxidation and hydrolysis of ferrous sulphate is followed by the reduction of ferric hydroxide with formation of magnetite and dissolution of a corresponding quantity of metallic iron.

Several authors considered the process of cathodic reduction of oxygen on the magnetite electrode. Tomashov (4) found that oxygen is cathodically reduced on the oxidized iron ( $\text{Fe}_3\text{O}_4$ ) and on the natural magnetite with a remarkable overvoltage. In  $\text{NaCl}$  0,5 M + 0.005  $\text{Na}_2\text{CO}_3$  + 0.005  $\text{NaHCO}_3$  stirred solution at pH 9.2, the limiting current for the cathodic reduction of oxygen is about 1.5  $\text{mA}/\text{cm}^2$ . At 0.5  $\text{mA}/\text{cm}^2$  the tension is -0.4 V (NHS); at 1  $\text{mA}/\text{cm}^2$  the tension is -0.48 V (NHS). At tensions more negative than -0.5 V, the cathodic reduction of oxygen occurs with the simultaneous reduction of magnetite; iron is formed and the hydrogen is easily developed on it. By lowering the current density above the value of the limiting current (1.5  $\text{mA}/\text{cm}^2$ )

the iron is oxidized once more and the electrode behaves as at the beginning.

Afanas'ev and Chankova (5) working with the same Tomashov's solution found tension  $(-0.25 + 0.8 \text{ V})$  and limiting current  $(1 \text{ mA/cm}^2)$  values analogous to the Tomashov's ones with slopes of the straight section of the polarization curves of  $0.14 + 0.44$ . Bianchi (6) working with solutions at pH 8.8 and 12.2, finds that the tension for oxygen reduction on artificial magnetite electrode at very low current density  $(0.01 \text{ mA/cm}^2)$  is 40 mV at pH 8.8 and -20 mV at pH 12.2 (NHS). He also observed that the polarization curves plotted at increasing and at decreasing current densities show a remarkable hysteresis and that in neutral solution (pH 6) the redox processes of the iron compounds arising from the electrode may interfere.

In the study of the electrochemical processes on the magnetite electrode, the processes involving the electrode material may be considered. Some modifications of the electrode surface have been observed by Tomashov in the case of the cathodic reduction at high current densities with formation of metallic iron. Other modifications have been observed with formation of  $\alpha\text{-FeOOH}$  or  $\text{Fe(OH)}_3$  (see experimental results).

The thermodynamic aspect of these processes has been considered by Deltombe and Pourbaix (7) who plotted the diagram potential-pH in the case that the solid phases are  $\text{Fe(OH)}_2$  and  $\text{Fe(OH)}_3$  or in the case that the solid phases are  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . Table 1 indicates some processes that have been considered for the interpretation of the experimental results; the reversible tension values for these processes have been calculated at pH 7 and 13 corresponding to our experimental conditions.



redox systems through which the cathodic reduction of oxygen occurs indirectly.

In the study of the cathodic reduction of oxygen and hydrogen peroxide on magnetite electrode is necessary to distinguish amongst the cases of acid, neutral and alkaline solutions on account of the ionic concentration of the redox systems arising from iron compounds (solid or in solution).

In the case of acid solutions the ions  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  may be present in high concentration. The cathodic process is the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . The ferrous ions are reoxidized to the ferric ions by the oxygen dissolved in the solution. So the ferric ions play the role of "oxygen carriers" and the limiting currents are higher than that corresponding to the diffusion transfer of the oxygen.

In the case of neutral solutions (pH 7) the trivalent iron is almost insoluble and the bivalent iron soluble ( $\text{Fe}(\text{OH})_2$ ). In absence of complexing ions, the redox system is formed by the  $\text{Fe}^{2+}$  ions present in the solution (depending from the solubility product of  $\text{Fe}(\text{OH})_2$ ) and by the solid compounds of trivalent iron (for ex.  $\text{Fe}(\text{OH})_3$ ) present on the electrode surface. In this case the limiting current may correspond to the diffusion transfer of the oxygen.

In the case of alkaline solution (but not reaching the field of the stability of  $\text{HFeO}_2^-$  or  $\text{FeO}_4^{--}$ ) the ferrous and ferric compounds are almost insoluble. The stability of magnetite between pH 9 and 14 makes the electrodic behaviour of the magnetite more important than that of the redox systems of the iron compounds.

## 2. - EXPERIMENTAL

The experimental work was performed by means of a

polarization cell already described (14), the cell being filled with the required solution, O<sub>2</sub> or N<sub>2</sub> bubbled through. When N<sub>2</sub> was bubbled, the solution was previously de-aerated with the same nitrogen. As electrode a disc (diameter 25 mm) of artificial magnetite was used. The analysis is as follows :

Fe (total)	63.61 %
SiO <sub>2</sub>	6.76 %
MgO	0.50 %

The microstructure (fig. 1) show the crystals of magnetite (light) and the gray vitreous phase (that may be etched by HF).

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

neutral	0.5 M H <sub>3</sub> BO <sub>3</sub>	+	0.5 M Na <sub>2</sub> SO <sub>4</sub>
alkaline	0.1 M NaOH	+	0.5 M Na <sub>2</sub> SO <sub>4</sub>

The pH of the neutral solution was adjusted to 7, by the addition of small quantities of NaOH. The requisite quantity of H<sub>2</sub>O<sub>2</sub> (Perhydrol Merck) was then added to obtain the desired concentration.

The gases were pure commercial O<sub>2</sub> (with traces of N<sub>2</sub> and rare gases) or high purity N<sub>2</sub> (99.999 %); they were bubbled at a flow rate of 150 cm<sup>3</sup>/min.

All measurements were carried out in an air thermostat at 25 ± 0.1 °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 polarization curves of the figures were obtained in two methods :

a) potentiostatic

The cell was connected to an electronic potentiostat.

Starting from the static value, the tensions were increased successively and the corresponding current values were measured. When the maximum value of the tension was reached, the same procedure was followed for decreasing tension and the polarization curves plotted at increasing and decreasing tensions.

b) intensiostatic

Polarizing currents were obtained from a 150 V battery with resistances in series in order to obtain the desired constant current. Tension measurements were made with a precision potentiometer (Leeds and Northrup, Model K 3) and, as a zero instrument, a high impedance electronic voltmeter (Philips, Model 6010). The current density values were increased successively and the corresponding values of the tension measured, the polarizing current circuit being opened between two successive measurements. The polarization curve was plotted at increasing current densities. When the maximum value was reached the procedure was reversed and the polarization curve replotted at decreasing current densities.

### 3. - EXPERIMENTAL RESULTS

Table II show the static tensions at 25°C of the magnetite electrode in neutral and alkaline solutions at various H<sub>2</sub>O<sub>2</sub> concentrations, O<sub>2</sub> or N<sub>2</sub> bubbling through. In 10<sup>-4</sup> M H<sub>2</sub>O<sub>2</sub> neutral solution, stirred with oxygen, the static tension (0.385 V) is almost coincident with the theoretic one (0.375 V) calculated for the process  $\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}^+ + 2\text{e}$  ( $p_{\text{O}_2} = 1 \text{ atm}$ ). In the other cases, similarly to what has been observed with other electrodes like platinum and gold, the experimental static tensions are more noble than the theoretic tensions for the above mentioned process. It may be remembered that the solutions of hydrogen peroxide are thermodynamically unstable and the measured static tension

corresponds to the mixed tension arising from anodic and cathodic partial processes of decomposition (15).

TABLE II

$\text{H}_2\text{O}_2$ M	STATIC TENSIONS (Volts NHS)					
	Neutral solution pH 7			Alkaline solution pH 13		
	Theoric	Experimental with $\text{O}_2$	with $\text{N}_2$	Theoric	Experimental with $\text{O}_2$	with $\text{N}_2$
0	-	+0.310	+0.320	-	+0.205	+0.245
$10^{-4}$	+0.385	+0.375	+0.310	+0.031	+0.140	+0.140
$10^{-3}$	+0.356	+0.390	+0.355	+0.001	+0.155	+0.160
$10^{-2}$	+0.326	+0.425	+0.400	-0.029	+0.175	+0.145
$10^{-1}$	+0.296	+0.455	+0.525	-0.059	+0.190	+0.175

The theoric values are calculated for the process :

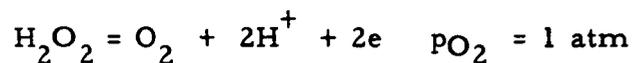


Figure 2 shows the polarization curve (potentiostatic) for the process of cathodic reduction of oxygen in neutral solution. The value of the limiting current ( $1 \text{ mA/cm}^2$ ) and the values of the tensions are reproducible very well. Also the phenomenon observed at  $-460 \text{ mV}$  when the polarization curve is plotted at decreasing tension is reproducible : the current decreases to a little value and after some minutes restablishes itself to a normal value. The explication is that the metallic iron, formed on the electrode during the hydrogen discharge, is oxidized at  $-0.46 \text{ V}$  (see Table I) with direct consumption of oxygen that is momentarily not disposable for the circulation of the external current. This interpretation agrees with the other experimental results afterwards mentioned.

When the polarization curve is obtained by the intensiostatic

method (fig. 3) the modifications of the surface state due to a previous anodic or cathodic treatment differentiate the polarization curves. The cathodic after cathodic curve plotted at decreasing current densities clearly shows the step at about  $-0.4$  V due to the reoxidation of the iron deposited on the electrode during the precedent cathodic treatment. In the case of the curve after anodic polarization (with formation on the electrode of a layer of ferric hydroxide) the cathodic process at low current densities occurs at a more noble tension almost corresponding to the value of the static tension.

Such a differentiation is present also for the cathodic polarization curves of diluted hydrogen peroxide solution ( $10^{-4}$  M) with circulation of nitrogen (fig. 4). In the case of the more concentrated hydrogen peroxide solution ( $10^{-2}$  M; fig. 5) the differentiation of the anodic and cathodic polarization curves after the various surface treatments of the electrode is not present.

Figure 6 shows the variation of the anodic and the cathodic tension with time starting from the moment at which the polarizing current circuit is opened. In the case of the cathodic current the electrode tension quickly raises when an oxidizer is present ( $\text{H}_2\text{O}_2$   $10^{-2}$  M and  $\text{O}_2$ ), with a step at about  $-0.4$  V due to the reoxidation of the iron that was reduced during the cathodic polarization. In the case of the anodic current the more concentrated hydrogen peroxide solution quickly depolarizes the electrode and the hysteresis of the polarization curves disappears. The mechanism of this depolarization was already discussed in the case of the platinum electrode (16) by considering the probable reaction between the hydrogen peroxide and the radicals present on the electrode surface.

Figure 7 shows the variation of the electrode tension

with time starting from the moment of the inversion of the polarizing current ( $0.5 \text{ mA/cm}^2$ ): from anodic to cathodic (point A) and from cathodic to anodic (point B). At the anodic to cathodic inversion, we can observe the presence of a cathodic process that occurs between  $-100$  and  $-400$  mV (this process may be observed also in the potentiostatic polarization curve showed in fig. 2).

The process as far as  $-100$  mV is attributed to the reduction of the ferric hydroxide present on the electrode with formation of ferrous ions until the solubility product of  $\text{Fe(OH)}_2$  is reached. The process at  $-400$  mV is attributed to the cathodic deposition of metallic iron from ferrous hydroxide. Between the two tension values the two processes occur together.

At the cathodic to anodic inversion, we can observe a step at about  $-400$  mV, attributed to the reoxidation of iron. The step is larger in the case of  $10^{-4}$  M  $\text{H}_2\text{O}_2$  solution stirred with  $\text{N}_2$ : this solution is less oxidizing than the more concentrated  $\text{H}_2\text{O}_2$  solution or than the solution saturated with oxygen.

Figure 8 shows the potentiostatic polarization curve for the cathodic reduction of oxygen in alkaline solution. Also in this case the intensiostatic polarization curve (fig. 9) emphasizes the modifications of the electrodic surface caused by the polarizing current. Similar hysteresis phenomena may be observed in the polarization curves of the magnetite in the diluted  $\text{H}_2\text{O}_2$  solutions ( $10^{-4}$  M; fig. 10). The hysteresis is almost absent for the more concentrated  $\text{H}_2\text{O}_2$  solutions ( $10^{-2}$  M; fig. 11) the variation of the electrode tension with time starting from the moment at which the polarizing current ( $3.3 \text{ mA/cm}^2$ ) is shut off, is showed in the figure 12.

After a cathodic polarization the electrode tension raises with two steps at about  $-800$  and  $-500$  mV. The first is attributed

to the reoxidation to ferrous hydroxide of the iron cathodically formed; the second to the oxidation of the ferrous hydroxide to ferric hydroxide.

After an anodic polarization, the figure shows the rapid depolarizing action of the more concentrated hydrogen peroxide solutions ( $10^{-2}$  M) that may be due to the reaction between  $H_2O_2$  and the radicals (presumably OH) present on the electrode surface.

Figure 13 shows the results obtained at the inversion of the polarizing current : from anodic to cathodic (point A) and from cathodic to anodic (point B). In the first case three steps are present : the first is attributed to the reduction of  $Fe(OH)_3$  to  $Fe(OH)_2$  (-0.496 V); the second to the reduction of  $Fe(OH)_2$  to Fe (-0.815 V) and the latter to the reduction of  $Fe_3O_4$  to Fe (-0.853 V). In the second case the processes of iron dissolution with formation of  $Fe(OH)_2$  and of oxidation of  $Fe(OH)_2$  to  $Fe(OH)_3$  may be observed .

By means of the electron diffraction it was possible to emphasize the surface modifications of the magnetite acting as electrode for the cathodic process of oxygen reduction. The specimens of magnetite were cathodically polarized (current density  $3.3 \text{ mA/cm}^2$ ) for 12 hours at  $25^\circ\text{C}$  in solutions at pH 7 or 13. After the cathodic treatment the specimens were leaved for some hours in the same solution in which oxygen was bubbling. The specimens were then observed with the electron diffractometer <sup>(o)</sup> under a tension of 50 KV.

On the surface of the magnetite specimen treated in alkaline

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<sup>(o)</sup> Our thanks are due to Professor R. Piontelli for permission to use the diffractometer Trub Tauber placed in the Institute of Physical Chemistry, Electrochemistry and Metallurgy of the Polytechnic of Milano.

solution very little crystals are formed. These crystals, of gray colour, are showed to be  $\alpha$ -FeOOH from the electron diffraction (17). Figure 14 shows the reflection electron diffraction pattern of the cathodically treated magnetite electrode compared with the trans-  
 parence pattern of a specimen of powdered  $\alpha$ -FeOOH prepared according to Bandisch and Albrecht (18). The results agree with what was found by Feitknecht (19) that  $\alpha$ -FeOOH is formed by oxidation of the ferrous salts in a pH 13 solution.

On the specimen of magnetite cathodically polarized in neutral solution, a yellow compact layer is formed. This layer results to be  $\text{Fe}(\text{OH})_3$ , cubic with  $a = 5.70 \text{ \AA}$ . The reflection pattern is compared (fig. 15) with the pattern that Fordham and Tyson (20) published for such a compound.

#### 4. - CONCLUSIONS

In alkaline solution the oxygen is cathodically reduced on magnetite at tension very near to that corresponding to the process  $\text{O}_2 + 2\text{H}_2\text{O} + 2e = \text{H}_2\text{O}_2 + 2\text{OH}^-$ . The slope of the polarization curve (see figure 8) is about  $0.06 \left(\frac{RT}{F}\right)$ . In the case of the sufficiently concentrated  $\text{H}_2\text{O}_2$  solutions, the anodic and cathodic processes are symmetric (see fig. 11). The extrapolation of the straight part of the anodic and cathodic polarization curves gives an exchange current of  $0.005 \text{ mA/cm}^2$  at a tension of 0 mV near to the theoretic value of -30 mV corresponding to the process  $\text{O}_2 + 2\text{H}_2\text{O} + 2e = \text{H}_2\text{O}_2 + 2\text{OH}^-$  at pH 13 and  $(\text{H}_2\text{O}_2) = 10^{-2}$  moles/liter. Also in this case one may think that the cathodic process corresponds to the reduction of the oxygen arising from the decomposition of the hydrogen peroxide with reformation of an half of the hydrogen peroxide that was decomposed.

The difference between the theoretic value of -30mV and that of 0 mV obtained for extrapolation can be explained by the fact

that the  $\text{H}_2\text{O}_2$  concentration near the electrode can be lower on account of the decomposition of the hydrogen peroxide.

Only at very negative tensions, lower than  $-500$  mV, the electrochemical processes concerning the electrode material can be observed. These processes may be the reduction of the ferric to the ferrous compounds and the reduction of these latter to iron. The second process is accompanied by the cathodic discharge of hydrogen that activates the iron. The activated iron can be easily reoxidized (action of  $\text{O}_2$  or  $\text{H}_2\text{O}_2$ ) nevertheless the pH of the solution corresponds to the passivation of iron.

In neutral solution the situation is different on account of the intervention, also at the little current densities, of the redox processes of the iron compounds. The static tension values of the magnetite in the very diluted  $\text{H}_2\text{O}_2$  solutions are near to those corresponding to the reaction  $\text{H}_2\text{O}_2 + 2 \text{OH}^- = \text{O}_2 + 2 \text{H}_2\text{O} + 2 e$ , but probably this reaction is not able to efficaciously contribute to the flow of the current. In fact the potentiostatic (fig. 2) and the intensiostatic (fig. 3) curves show that the flow of the current begins only at the more cathodic tensions (about  $+100$  mV). If the reaction  $\text{Fe}(\text{OH})_3 + 3 \text{H}^+ + e = \text{Fe}^{++} + 3 \text{H}_2\text{O}$  is considered, the reversible tension at pH 7 is  $+139$  mV for  $(\text{Fe}^{++}) = 10^{-5}$  moles/liter and  $-142$  mV when  $\text{Fe}(\text{OH})_2$  begins to precipitate. This interval corresponds with sufficient approximation to that of the first step (between  $+140$  mV and  $-180$  mV) of the potentiostatic polarization curve.

Therefore one can think that the cathodic process is the reduction of the ferric hydroxide present on the magnetite electrode with formation of ferrous ions that are reoxidized by the oxygen to ferric hydroxide on the electrode surface. By increasing the current density the concentration of the ferrous ions on the electrode

surface can reach the value corresponding to the solubility product of the ferrous hydroxide that can precipitate on the electrode.

The second very inclined step of the potentiostatic polarization curve (fig. 2) between -180 and -400 mV should correspond to the reduction of the ferric hydroxide to ferrous hydroxide (solid phase). This latter is successively reoxidized by the oxygen (the limiting current of  $1 \text{ mA/cm}^2$  is due to the oxygen diffusion and corresponds to the one obtained in the same conditions with other electrodes like platinum). The electrode should result to be covered by a film of ferrous hydroxide and ferric hydroxide (or hydrated magnetite) and the strong ohmic drop in the film can explicate the high slope of the polarization curve.

At tension lower than -400 mV occurs the reduction of the electrode compounds to iron, on which the hydrogen is easily discharged. Also in this case the iron should result activated and may be immediately reoxidized at the opening of the current circuit and momentarily consumes all the disposable oxygen or hydrogen peroxide.

In the alkaline solutions the magnetite is inert as electrode for the cathodic reduction of oxygen till a value of the current density very near to the limiting current of oxygen diffusion.

In the neutral solutions the cathodic reduction of oxygen on a magnetite electrode occurs, also at the low current densities, with the intervention of the redox systems concerning the iron compounds. The accelerating action of the hydrated magnetite and of the other corrosion products of the iron on the iron corrosion in neutral media is explicated on the basis of the redox systems concerning the corrosion products themselves.

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Fig. 1

Microstructure of the artificial magnetite used as electrode. Magnetite (light) and vitreous phase (gray) (X 230).

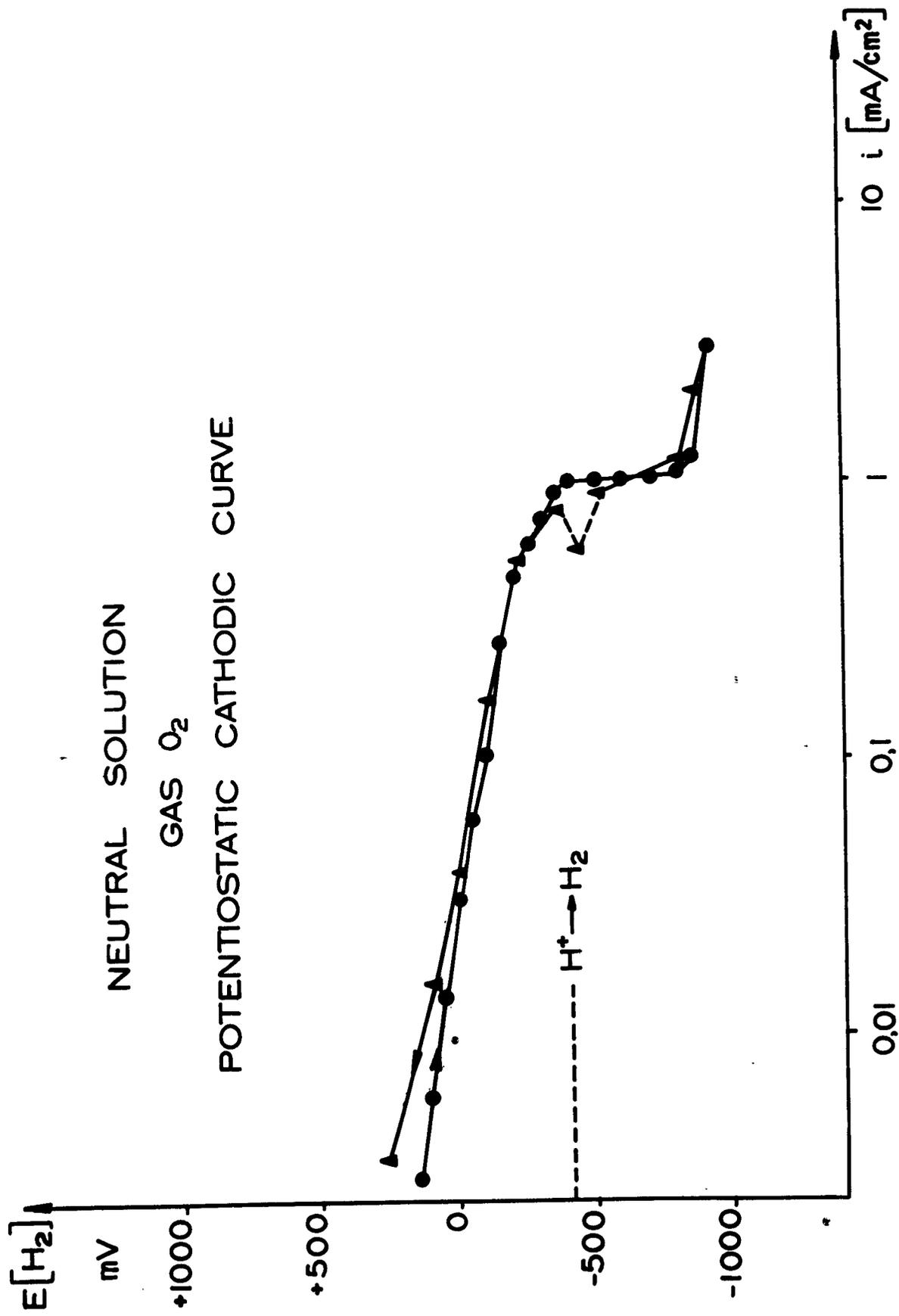


FIG.2

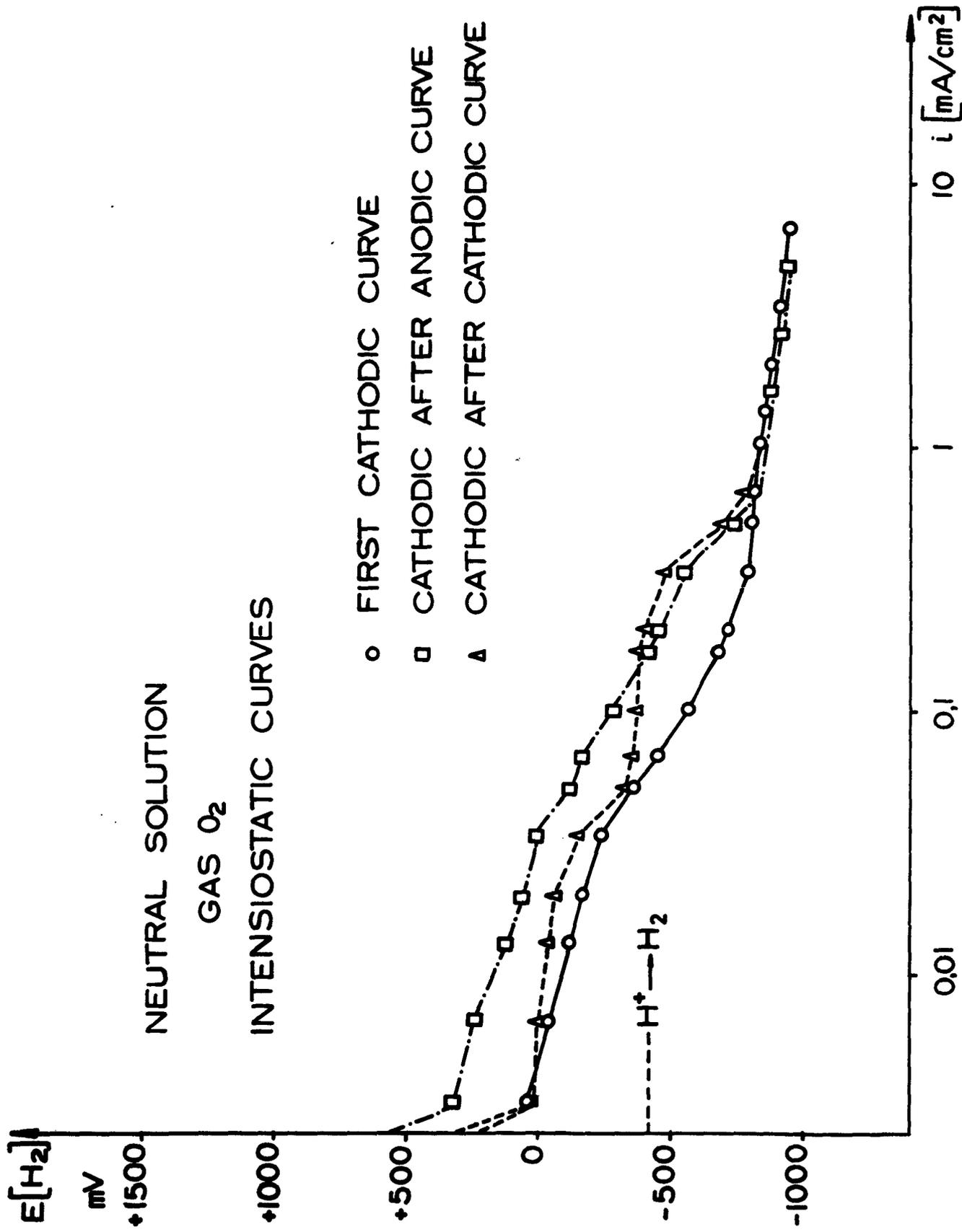


FIG.3

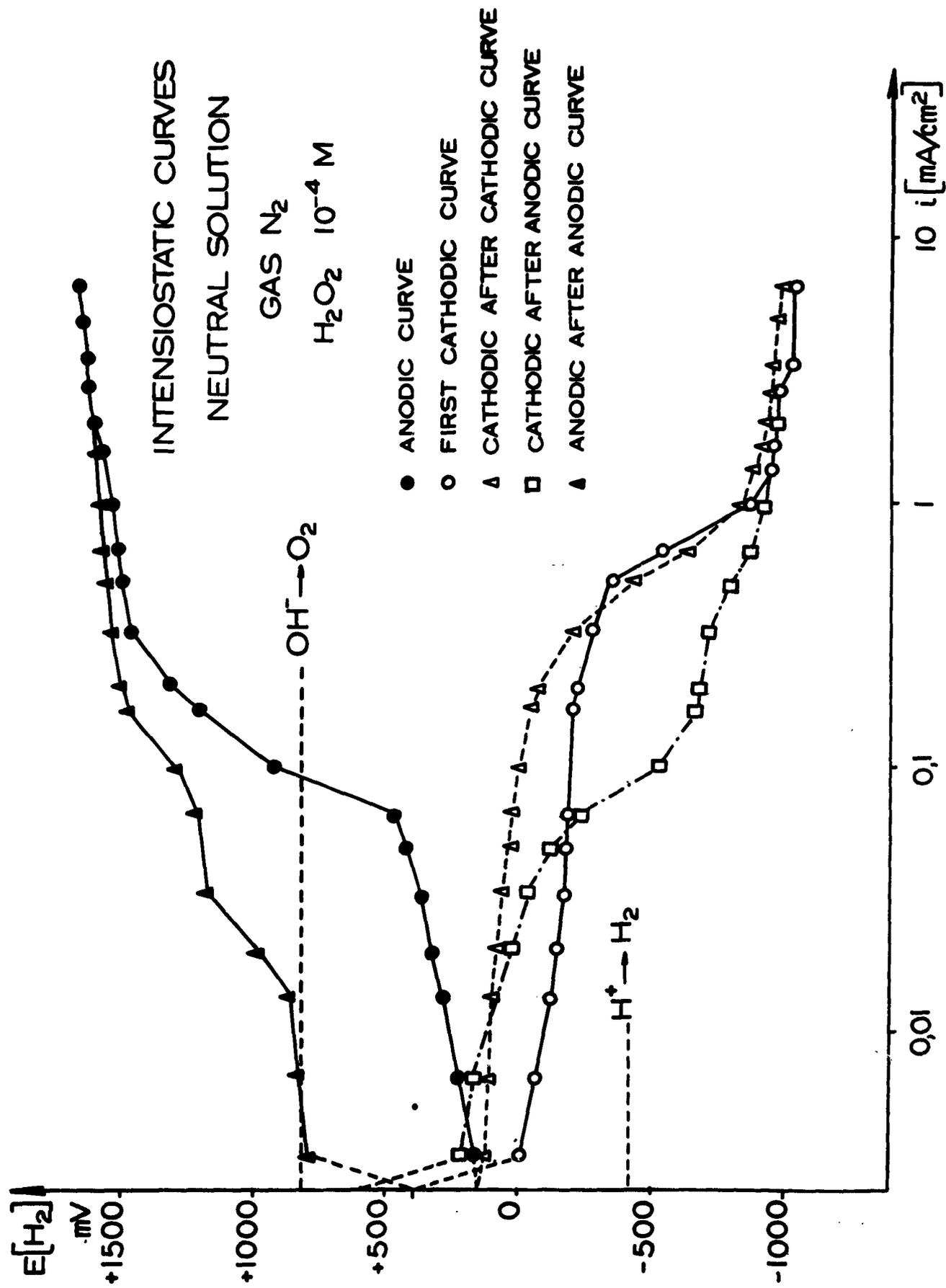


FIG.4

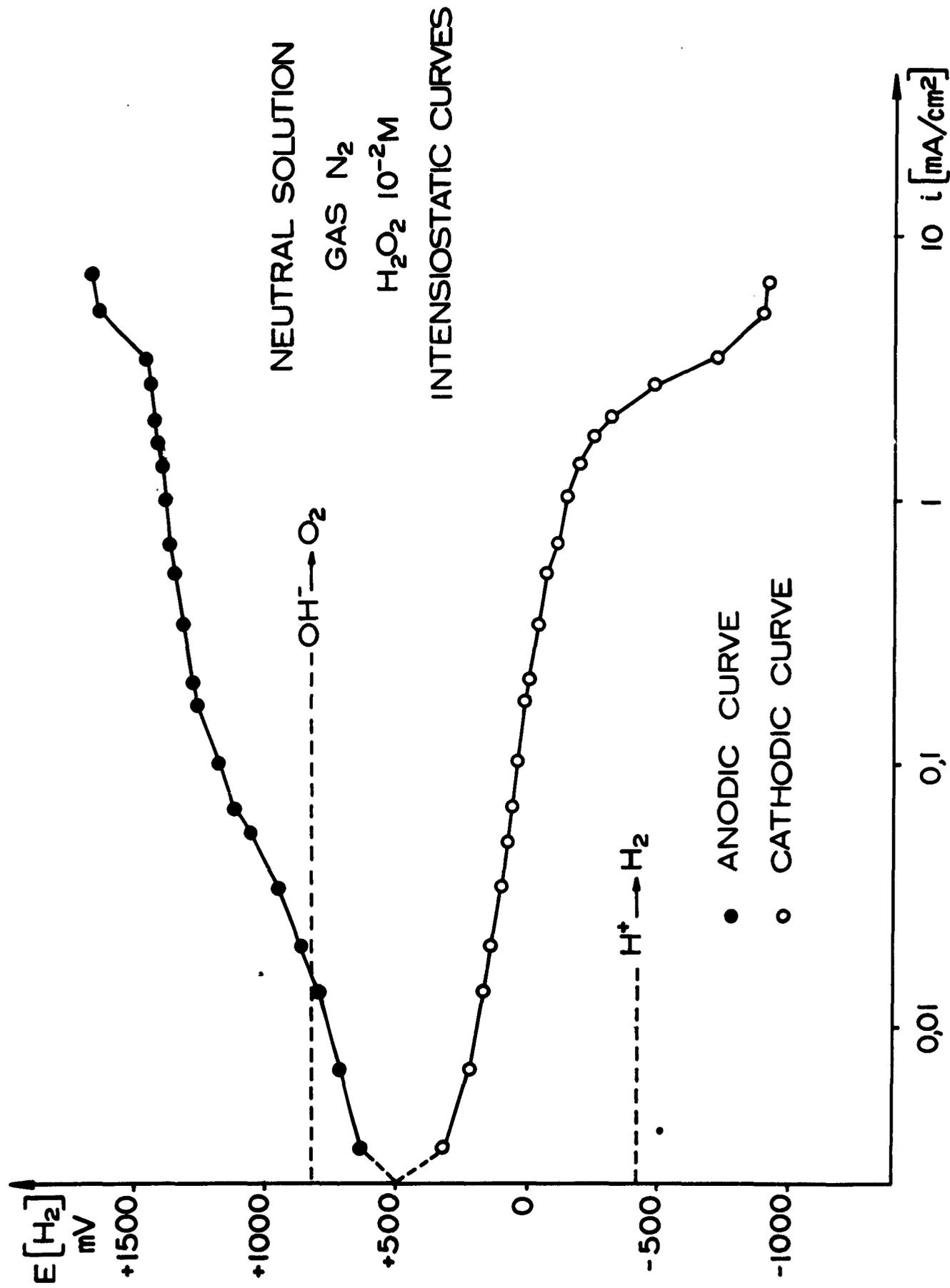


FIG.5



0.5 mA/cm<sup>2</sup> CURRENT INVERSIONS

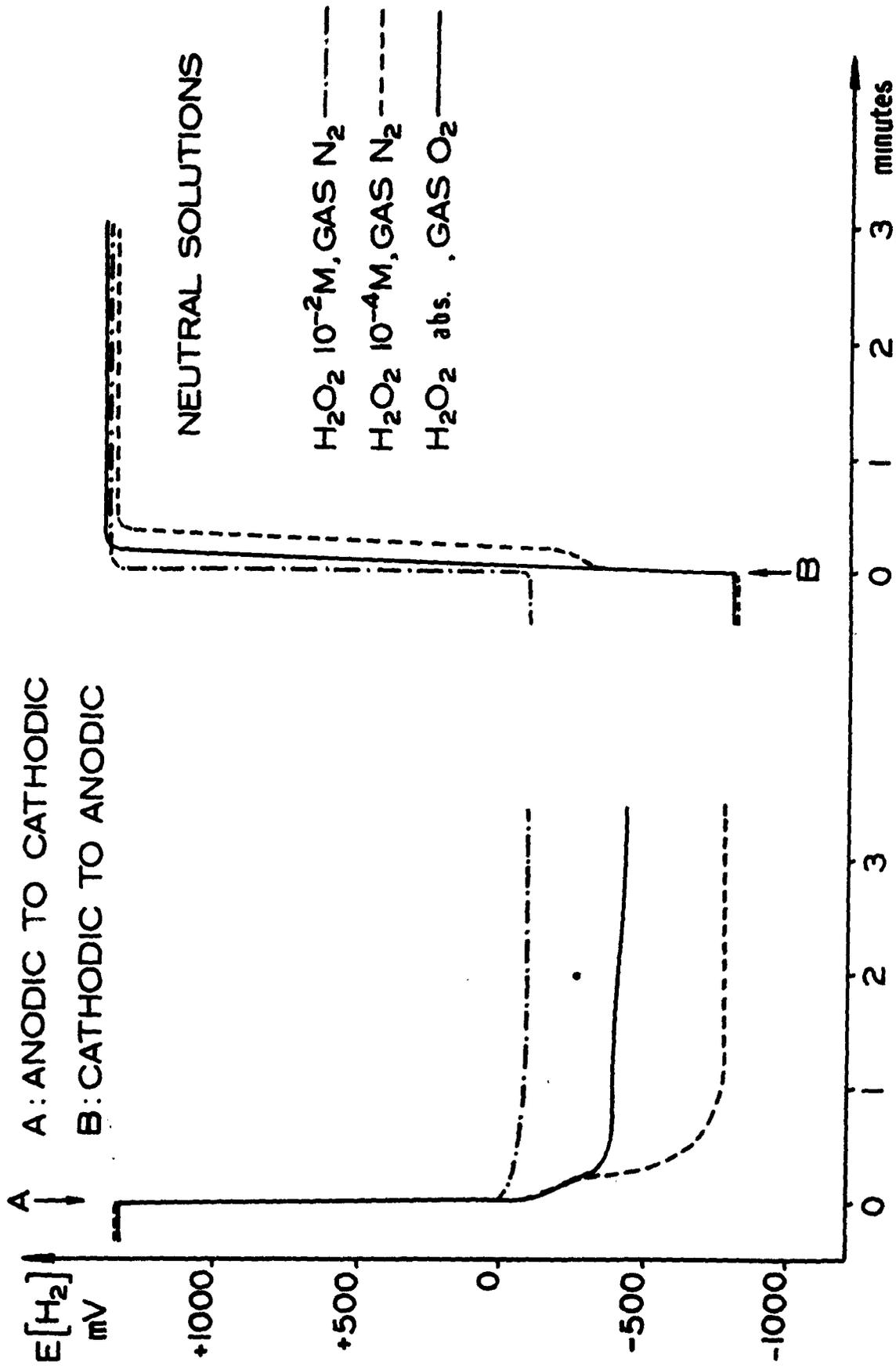


FIG.7

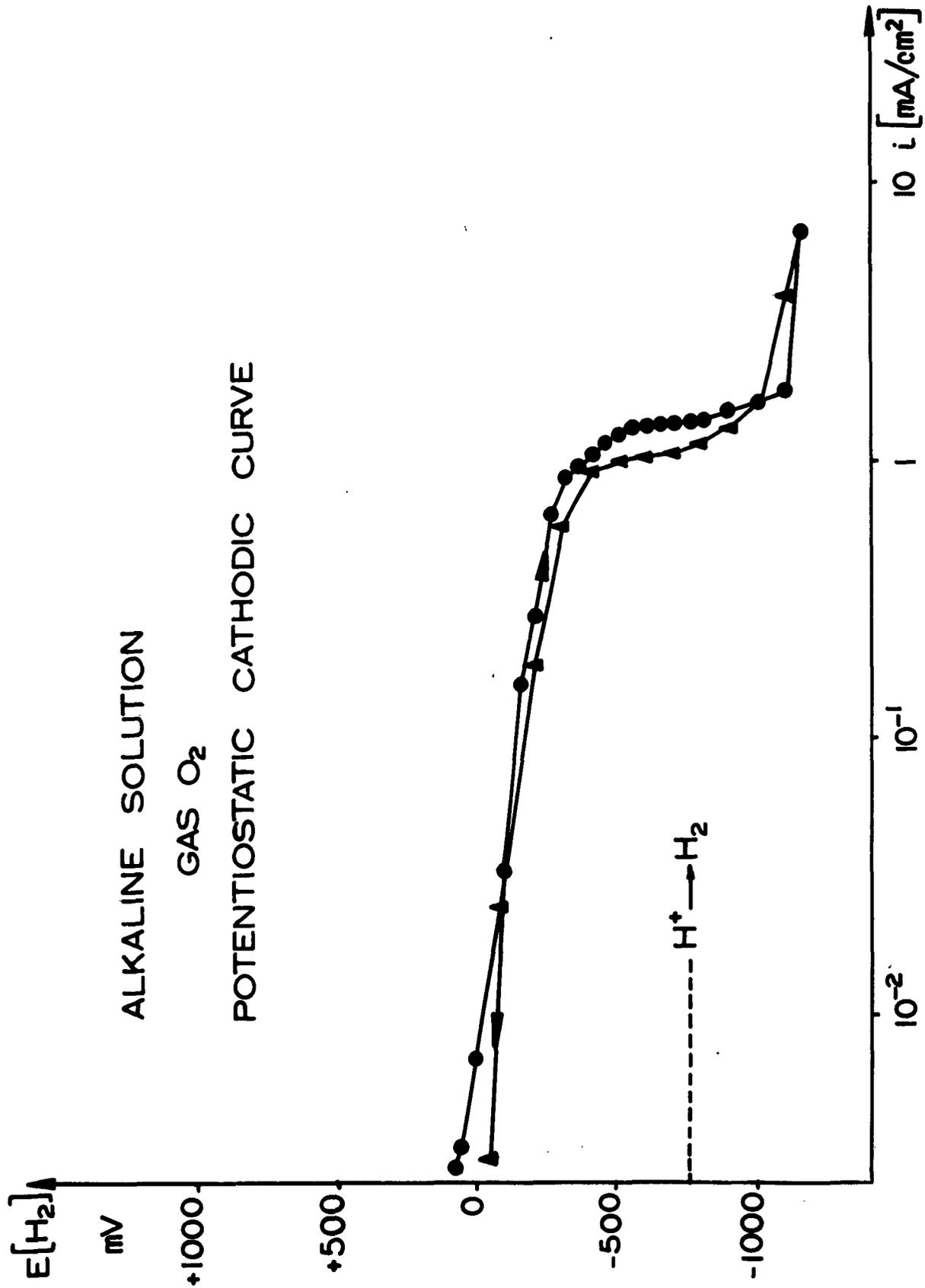


FIG. 8

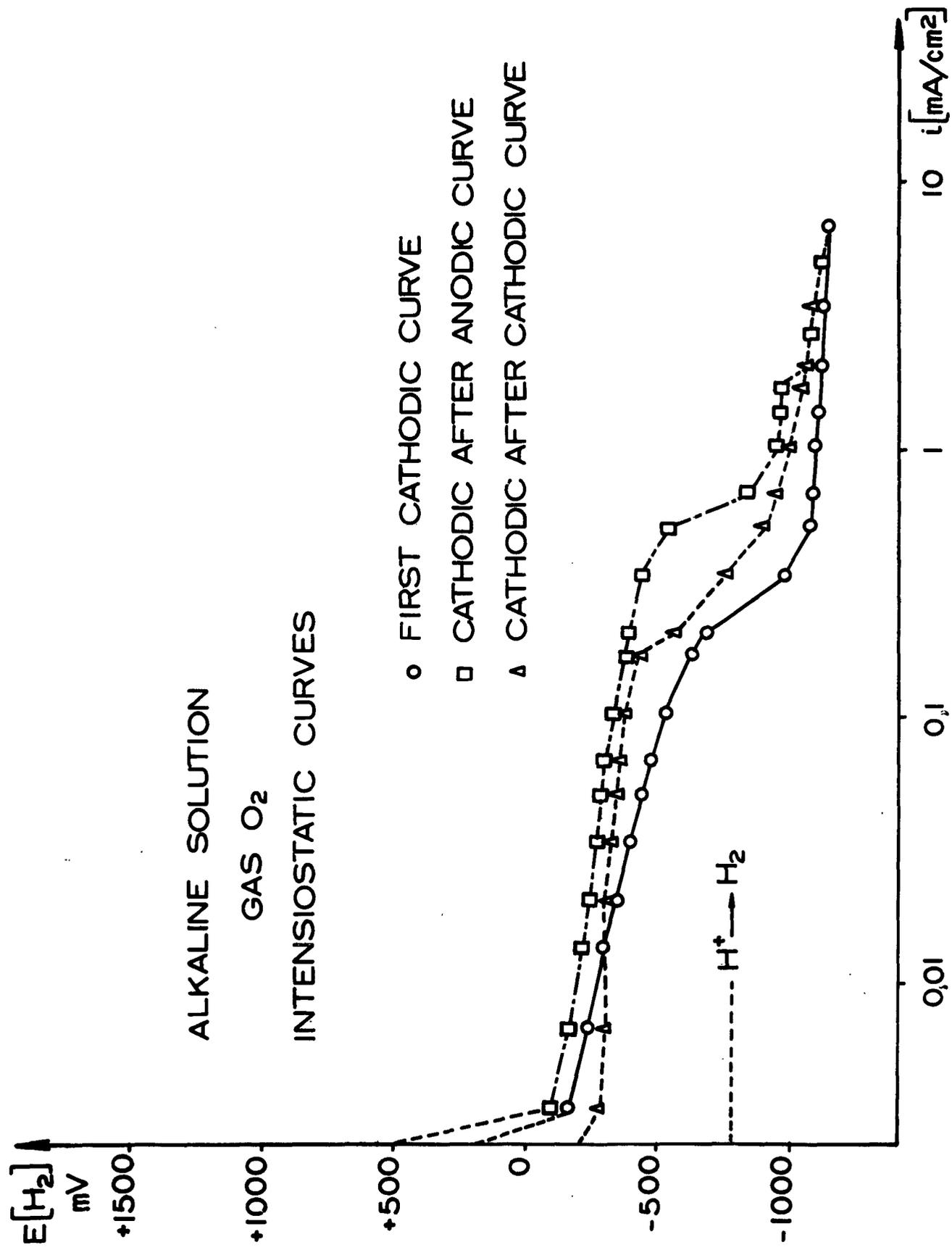


FIG.9

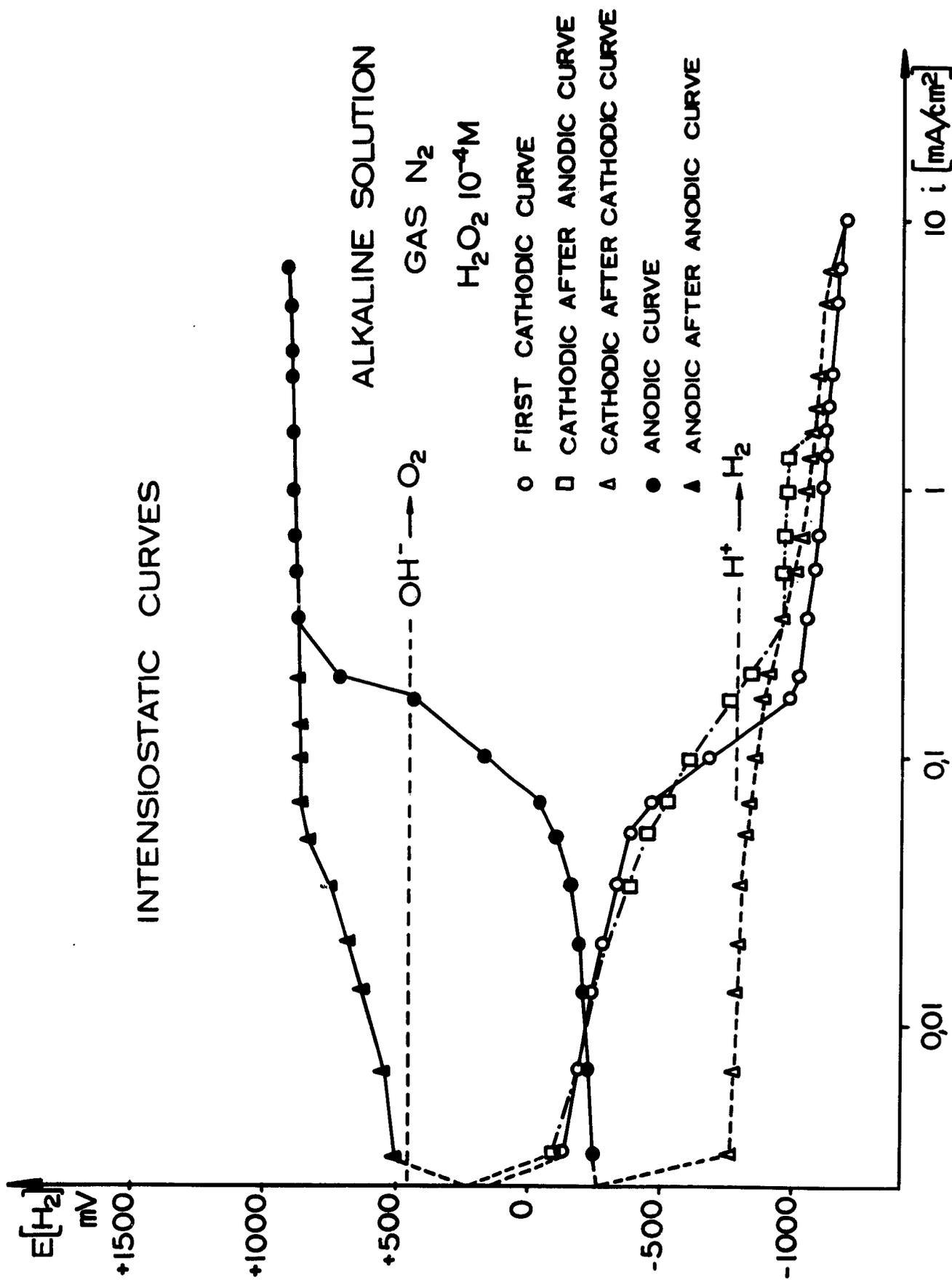


FIG.10

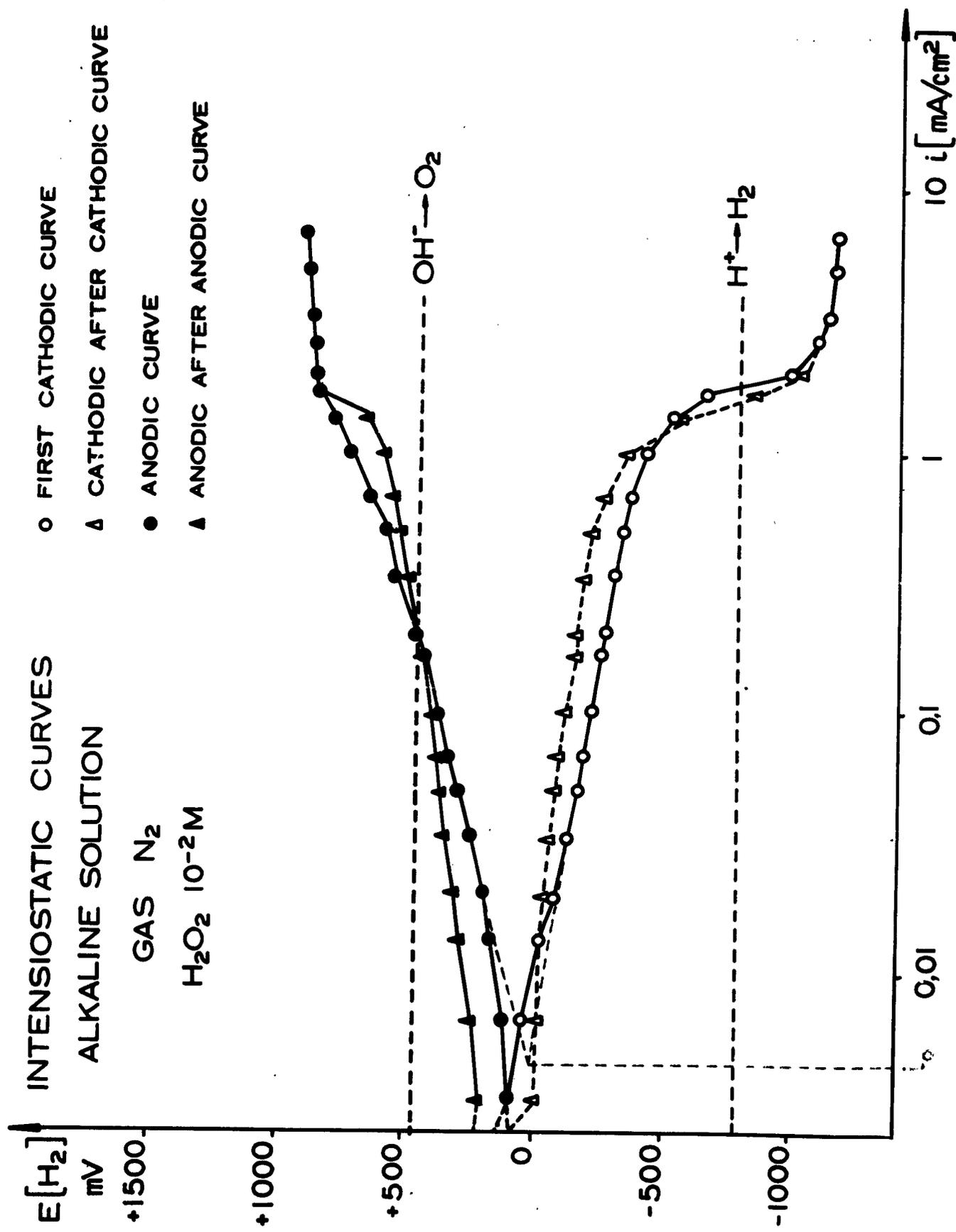
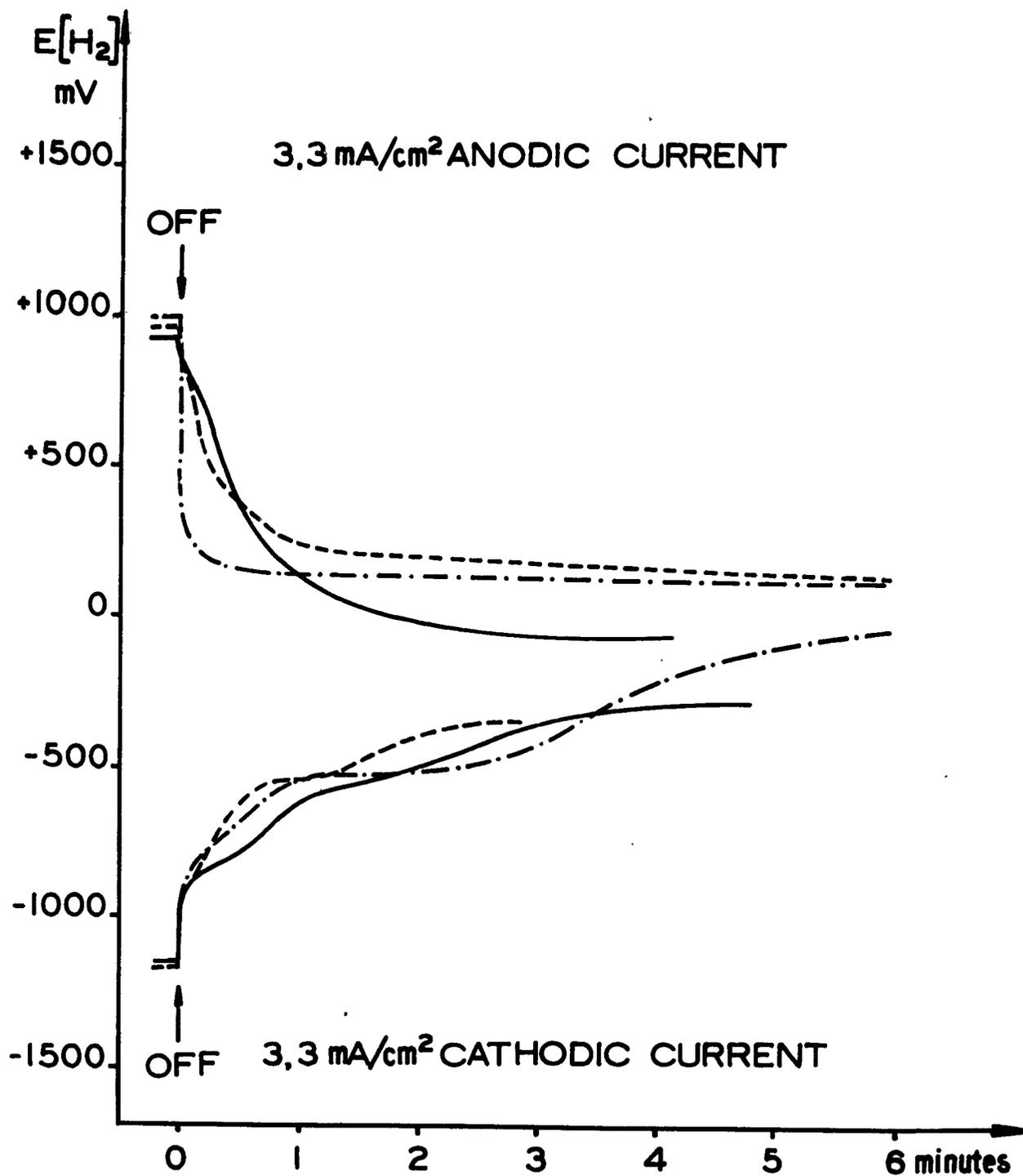


FIG.11



ALKALINE SOLUTIONS

$H_2O_2$   $10^{-2}M$ , GAS  $N_2$  -----

$H_2O_2$   $10^{-4}M$ , GAS  $N_2$  - - - - -

$H_2O_2$  abs., GAS  $O_2$  \_\_\_\_\_

FIG.12

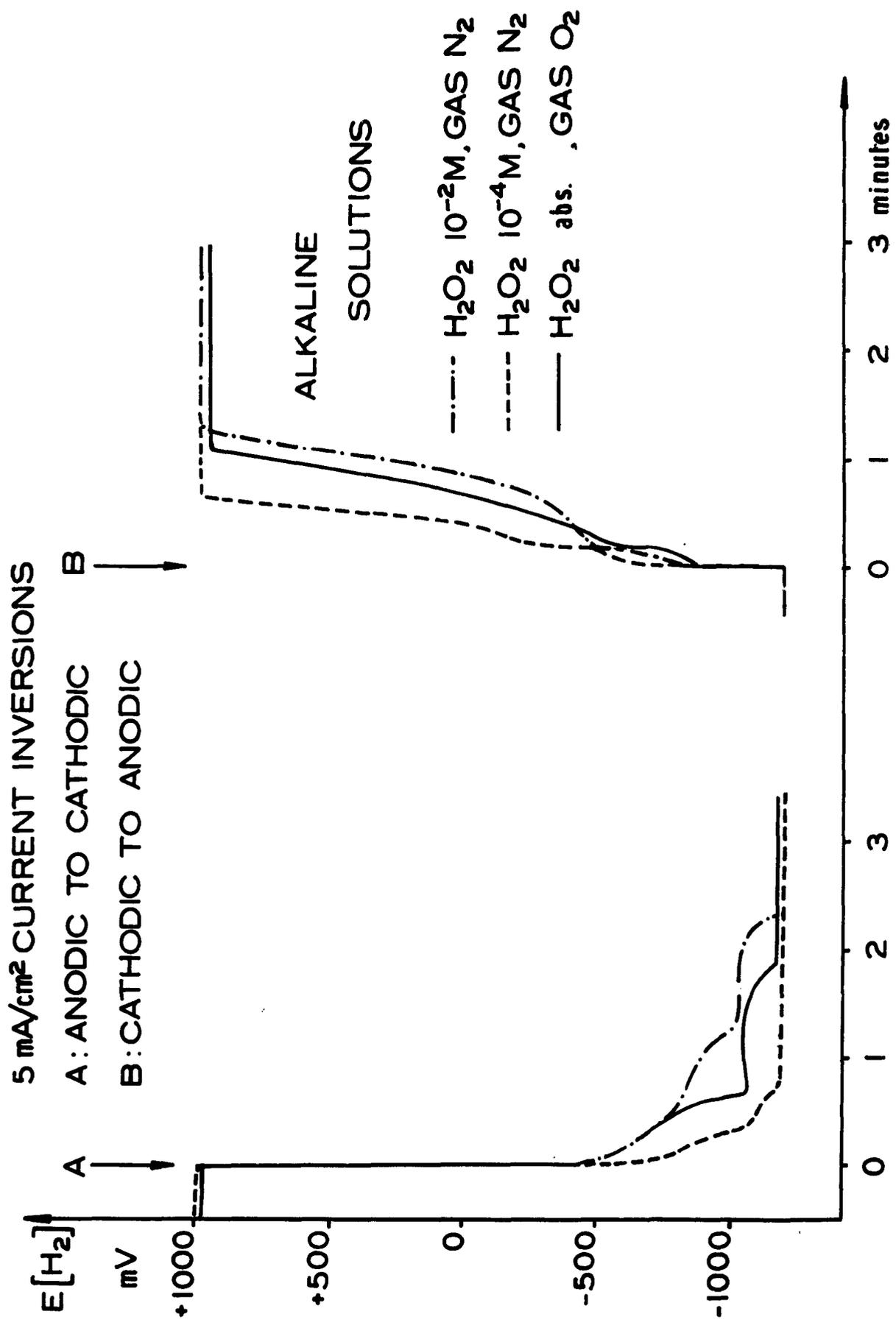
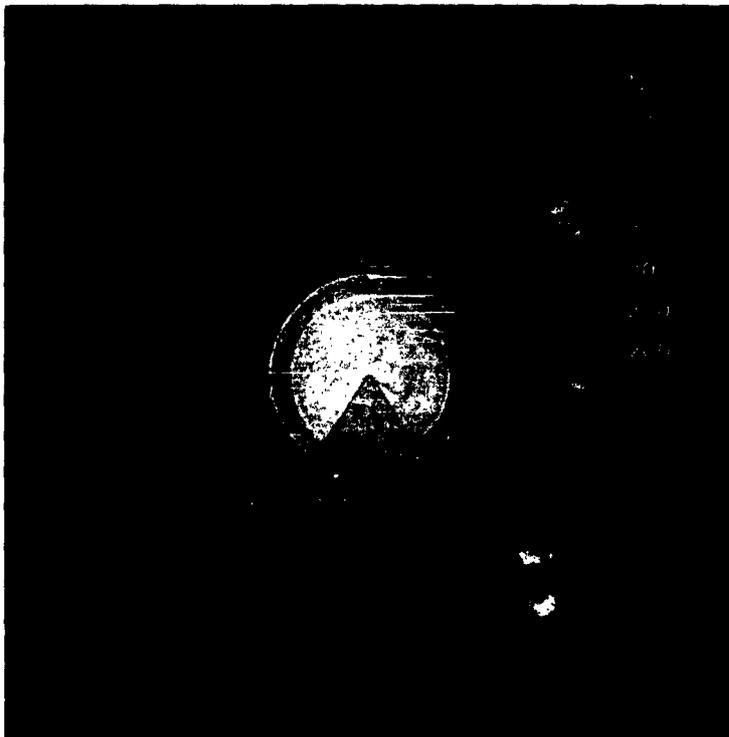
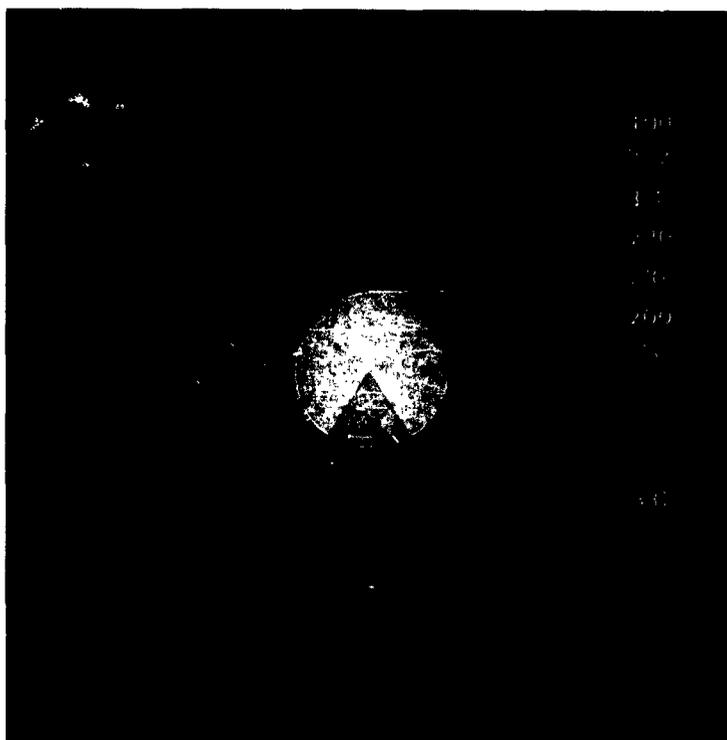


FIG.13



**Fig. 14**

**Surface status of the magnetite electrode after the cathodic treatment in alkaline solution. The electron diffraction pattern (central part at the bottom of the figure) is compared with that of a  $\alpha$ -FeOOH specimen (18).**



**Fig. 15**

**Surface status of the magnetite electrode after the cathodic treatment in neutral solution. The electron diffraction pattern (central part at the bottom of the figure) is compared with that published by Fordham and Tyson for  $\text{Fe}(\text{OH})_3$  (20).**

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October 1960 - No. pages and ills. 31

University of Milano (Italy)

A B S T R A C T : The electrochemical behaviour of oxygen and hydrogen peroxide on magnetite electrodes was studied by means of polarization curves and by means of tension build-up and tension decay curves.

In alkaline solutions the oxygen is reduced at a tension near to that corresponding to the process  $O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$ . Also the hydrogen peroxide in concentrated solutions ( $10^{-2}M$ ) is reduced at the same tension : the electrochemical process probably concerns the oxygen arising from the  $H_2O_2$  decomposition.

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Anodic and cathodic processes for  $H_2O_2$  are symmetric.

In neutral solutions the processes concerning oxygen and hydrogen peroxide occur with the intervention of the redox systems of the iron compounds. The surface of the electrode is modified during a cathodic or anodic polarization. The surface modifications were evidenced by means of electron diffraction.

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