PENNSYLVANIA RESEARCH ASSOCIATES, INC.
Wilford Building, 101 North 33 Street
Philadelphia, Pennsylvania 19104

STATUS REPORT

EC-SR - 3

ADVANCED FUEL CELL CATALYSTS

Carlo Bocciarelli, Director

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NAS 7 - 574

November 10 to February 10
1968

PENNSYLVANIA RESEARCH ASSOCIATES, INC.
Recorded in Document Register
No. U68-1096 Cy. 11

TABLE OF CONTENTS

1. INTRODUCTION

The work performed during the first nine months of Contract NAS 7-574 is partially reflected in an article submitted to Advanced Energy Conversion as the second article of a series of three under the general title of "New Approaches to the Theory of Electrocatalysis". The article, scheduled for publication in the June 1968 issue of Advanced Energy Conversion, constitutes Section 2 of this report.

1.1 ELEMENTARY FUEL CELLS

We are at present preparing to assemble several small fuel cells roughly four centimaters in diameter. Following the example of Allis-Chalmers, we propose to utilize a thin (10 mil) layer of asbestos to hold the electrolyte. Pressed against it will be two nickel mesh electrodes suitably treated with catalyst.

Initial results are expected in time for the next report. If the results prove acceptable, these small cells will be used for all future testing purposes.

2. NEW APPROACHES TO THE THEORY OF ELECTROCATALYSIS

PART II: THE CATALYTIC PROCESS IN FUEL CELLS*

C. V. Bocciarelli
Pennsylvania Research Associates, Inc., Philadelphia, Pennsylvania

ABSTRACT

The surface properties of metals and their dependence on bulk characteristics were discussed in the first article of this series.

Implied, but not explicitly stated, was the fact that the surface properties of a metal can be changed by changing its bulk properties.

In the present article, it is shown how electrocatalysis depends on the catalyst's surface properties, particular attention being paid to the oxygen electrode. On the basis of this theory together with the knowledge of how surface properties may be modified, a class of improved catalytic materials are chosen.

Details on the preparation of these catalysts are given; experimental evidence is produced showing that these catalysts are significant improvements on platinum bright.

The logical sequence outlined above is believed to be unique. Theories of catalysis have been traditionally derived

---

* The work reported in this article has been supported under NASA Contract No. NAS 7-574.

from and tailored to fit experimental observations, a procedure that has not proven satisfactory, as the theories so developed proved unable to predict new results or to lead to new and better catalysts.

The last article of this series will discuss the theory in greater detail.

NEW APPROACHES TO THE THEORY OF ELECTROCATALYSIS

PART II: THE CATALYTIC PROCESS IN FUEL CELLS

C. V. Bocciarelli

2.1 THE SEARCH FOR A PLATINUM SUBSTITUTE

The practical application of fuel cells is very much restricted by the high cost and scarcity of platinum. Unfortunately, no successful substitute has been found for Pt on the oxygen side of an oxygen-hydrogen cell.

This article presents theoretical and experimental research results which may fill this need.

An improved catalyst should possess the following characteristics:

a) It should outperform Pt black; that is, it should permit greater current densities than Pt at smaller activation polarization overpotentials--at useful current levels.

b) The new catalyst should have an equal or superior life to Pt under similar circumstances.

c) The new catalyst should cost less than Pt, as a raw material, and as a finished catalyst ready to use.

Such a material has proven difficult to find, and not for lack of effort or motivation. A very brief review of existing information, exclusive of the merely exploratory, follows. By exploratory, is meant the random measurements of catalyst materials in the hope of improved performance but with little or no attempt to find a theoretical basis for catalyst selection and improvement.

Occasionally, results are tentatively graphed against some known physical property of metal catalysts. Even when the performance of a catalyst is graphed against some physical property and some correlation between the two appears to exist, cogent explanations are rarely offered. Unfortunately, without an explanation, or without a great deal of "circumstantial" evidence, these relationships must be considered suspect.

Materials used as catalysts, are, in nearly all cases, polycrystalline. In fact, it is generally difficult to obtain material in single crystal form. But, it is also true that measurements performed on polycrystalline materials can be, and often are, very misleading.

Most metals are very poor catalysts. This is illustrated in Fig. 1, which shows the dependence of the exchange current density for the hydrogen electrode reaction on the metal's work function (Ref. 1).

INSERT
FIG. 1

However, the exchange current density can also be shown to be dependent on the presence of d shell vacancies in the

the catalyst metal; see, for instance, Ref. 2. Fig. 2 shows the dependence of this current on the percentage of Au in Pd; the current drops over two orders of magnitude between extremes and correlates rather well with the known fact that at 60 atomic percent of Au, the d vacancies of the Pd are all filled. Not all materials with d vacancies are good catalysts, just those that also show high work functions; this would appear to suggest that for a good catalyst at the hydrogen electrode, both d character and a high work function are needed.

INSERT
FIG. 2

The situation at the oxygen electrode is different. A high work function still appears to be a requirement but not d character.

Pt, for instance, is still a very good catalyst; but Au and Ag are among the best available, and these show no d character.

This difference of behavior will be shown to be an inherent difference between a "donor" catalyst (i.e., a catalyst that releases electrons, a cathode) and an "acceptor" catalyst (one that receives electrons, an anode). It will be shown that this is the result of relatively simple physical causes.

A consequence of this theory is that at the oxygen electrode, only a high work function matters or equivalently a high electron density.

Work funtions are ill defined except for specific faces of single crystals when they are highest for the densest faces (this clarifies the results of Ref. 3 that found that the best catalytic properties of single crystal Ni corresponded to the 111 face, the densest and highest work function face, a fact which is otherwise difficult to explain).

The dependence of catalytic activity on the work function of the metal is far from generally accepted proposition. However, J. O'M. Bockris et al. (4) in what is probably the most thoughtful experimental paper to date, find that a dependence on work function exists. In arriving at this conclusion, the authors have allowed for the existing wide spread of experimental work function data. However, they failed to take into account the fact that for a given catalyst the spread of current into the electrolyte at the oxygen electrode of a fuel cell vs. the activation polarization overvoltage is even larger. The current varies with the degrees of crystalline order of the metal catalyst, increasing with increasing order (see Section 2.5, in particular, Fig. 12).

As no elementary metal shows a higher work function than Pt, it would appear difficult, in fact, impossible, to improve on it by using any kind of alloy of lower work function material. That this is not quite true is perhaps a rather fortuitous property of noble metals. Finally, and for this reason, the catalysts derived in this study are likely to be unique.

2.2 A GENERAL OUTLINE OF THE THEORY

We will use a hydrogenic model for an ion (or atom) in a high dielectric constant medium. This model has been used with conspicuous success to explain the role of impurities in Ga and Si, both rather high dielectric constant materials. Hence, it will be natural to start with considerations of water as a dielectric, and particularly, its behavior near a metal's surface with its very high local fields.

The dielectric constant of polarizable material (i.e., water) may be written as

$$\varepsilon = 1 + 4\pi K \qquad /1/$$

where K is the polarizability; for water at very low frequency or D.C., ε=80 in bulk. But within some 10 Å of a metal surface, ε changes rapidly under the influence of the surface fields which tend to immobilize the water molecules to a much lower value; a value of 6 is sometimes mentioned* (5). However,

---

* The value of 6 was derived from very detailed work on mercury electrodes. To extend this value to all electrodes seems quite unwarranted; on the other hand, McDonald (6) gives a value of from 3 to 6 as a probable value of dielectric constant for water in contact with an electrode.

these fields (of the order of x 10^8 volts/cm. but as high as 1.5 x 10^9 volts/cm. for Pt.) must vary by a substantial factor (see Ref. 7), at least by 3 and possibly more, depending on the electrode metal. If the surface fields were infinite, the dielectric constant would be one; these fields are very high so that a low dielectric constant would not be surprising for a water molecule in contact with higher work function electrodes. Schematically, this is shown in Fig. 3 where the minimum values may be and probably are considerably lower than 6, possibly less than 2 for materials with the highest work functions. Hereafter, we shall consider water as such a medium of changing dielectric constant through which atoms and ions may move.

INSERT
FIG. 3

Electronic Exchanges

A metal cannot absorb electrons with energies that fall in the filled band; only those electrons can be absorbed whose energies fall above the Fermi level. Conversely, a metal cannot donate electrons except to levels at or below the Fermi level. This is a consequence of the rule that an electron may change position between states of equal energy, one of which is not occupied.

INSERT
FIG. 4

Since the ground level of both hydrogen and oxygen is about 13.5 e.v. below vacuum and the Fermi levels of metal catalysts around 5 e.v., it is not immediately apparent how exchanges may happen between the two. It is at this point that recourse must be made to the hydrogenic model for impurities in media whose dielectric constant $\epsilon \neq 1$.

The Schroedinger wave equation for a central field in a medium of dielectric constant ϵ is

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \left(E + \frac{e^2}{\epsilon r} \right) = 0 \qquad /2/$$

which differs from the usual expression (Ref. 8) only in the potential term.

The solution follows completely analogous lines, and one obtains

$$E = \frac{me^4}{2\hbar^2 \epsilon^2} \qquad /3/$$

$$(r_o) = \frac{1}{a} = \frac{\hbar^2 \epsilon}{me^2} \qquad /4/$$

$$a = \frac{me^2}{\hbar^2 \epsilon} \qquad /5/$$

where E describes the ground state of hydrogen, r_o is the most probable distance of the electron from the nucleus, a is given by $\psi(r) = e^{-ar}$, a solution of the wave equation.

As a consequence, at a great distance from the electrode in water, where $\epsilon = 80$, for hydrogen (and similarly for oxygen), the wells are very broad, 80 Bohr's radia wide and extremely shallow, a quantum mechanical way of describing the fact that the atoms are completely ionized. As they near the electrode surface, they begin to feel the influence of the surface field, their image forces, and especially the rapidly changing dielectric constant of water. Two things happen: First, the wells narrow and the ground levels deepen; as a consequence, the atoms recapture their electrons. Second, the wells are distorted by the interaction of their potential walls with the metal's surface field. These facts are diagrammatically illustrated in Fig. 4 and Fig. 5, Fig. 5 being an enlargement of Fig. 4 for the first 10 Å away from the metal surface at a point where the dielectric constant of water equals 1.7; the Fermi level of the metal being assumed to be 5 e.v. The ground level now is below the metal's Fermi level; thus, at some point as the hydrogen atom nears the metal, the ground and Fermi levels were identical.

From the above, it appears that the voltage current relationship is an exaggerated inverse function of the actual ε at contact, which is a function of the field at the metal surface. This, in turn, is a function of the metal's electron density; one concludes that catalysis in fuel cells is directly related to the electrode's electron density, other things being equal, as obviously the requirement that the metal surface behaves as described. If coated by oxides, for instance, the whole surface field will be completely changed. Fortunately, noble metals resist oxidation or produce labile surface oxides.

The case of Pt is interesting because it is a good catalyst at the oxygen and the hydrogen electrodes.

At the oxygen electrode, the high work function, hence high surface field, of platinum has lowered the acceptor level of oxygen below the Fermi level of the platinum; and electronic tunnelling is possible.

As a hydrogen catalyst, this would completely fail if in Pt, as in most metals, the Fermi sea were fully occupied. But, in Pt, there exists below the Fermi level a d band capable of electrical conduction; hence H can donate to Pt, but H cannot donate to Au nor to any of our newly developed alloys because they have no d band, though their work function be higher than that of Pt.

In what follows, the problem of the H electrode is no longer considered; everything refers to the oxygen electrode.

2.3 A BRIEF OUTLINE OF THE PERTINENT THEORY OF THE METAL STATE

At room temperature, in the absence of extremely high fields, electron emission, i.e., cold emission, is impossible (exclusive of photoelectric effects, etc.). In vacuum, emission is easier the lower the work function; and a great deal of effort in early vacuum tube work was aimed to secure cathode coverings of sufficiently low work function to permit emission at relatively low temperatures. Quite differently for electron emission to occur at the oxygen electrode of an oxygen hydrogen fuel cell, the catalyst, i.e., the cathode coating to parallel the preceding example, has to be a high work function material, Pt, for instance. We have just discussed this rather surprising fact and how the properties of polar liquids permit emission in the presence of high rather than low work function materials.

The relationships between the properties of the metal surface and its bulk characteristics are discussed in Ref. 7. The relationship

$$W_A = W_F + E_F = \hbar \left(\frac{4\pi ne^2}{m}\right)^{1/2} = 2.4\ E_F^{3/4} \qquad /6/$$

is obtained where W_A is the electron affinity, W_F the work function, E_F the Fermi level, e the electronic charge, n the density of conduction electrons per unit volume, and $\hbar$ Plank's constant divided by 2π (see also Ref. 9).

In Ref. 7, this is derived on the assumption of spherical Fermi surfaces, showing that the value of W_A is solely dependent on the mean value of Fermi energy. It follows that the values of electron affinities, hence also of work functions, are essentially insensitive to the detailed structure of the Fermi surface.

This is not the case when we inquire about electron emission; here only the most energetic electrons of the Fermi distribution participate; and hence, emission depends completely on the detailed structure of the Fermi surface.

One way to increase the number of electrons available to the emission process is to raise the energy of the metal's electrons with respect to the electrolyte by appling a positive voltage to the cathode. →

This is an activation polarization overvoltage, and it is not a desirable way of achieving higher currents compared to the alternate possibility to increase the number and the level of the high energy electrons in the metal.

INSERT FIG. 6

Fig. 6 shows schematically the function N(E) vs. E where N(E) is the population of states available for electron occupation in a face-centered cubic crystal vs. the electron energy, E. Such a crystal (Ag, Au, Au-Cu, etc.) is normally monovalent, the Fermi surface* may be considered roughly spherical; and the relation between N(E) and E is

$$N(E) \simeq E^{\frac{1}{2}} .$$

The Fermi level is shown arbitrarily at 10 volts. This is about the right level for a metal like Ag.

If a face-centered cubic lattice has a free electron density per atom higher than one, the Fermi surface necessarily moves to higher energies; but now a considerably greater number of states become available than the one that would be obtained from the simple relationship $N(E) \sim E^{\frac{1}{2}}$. This is shown by the high peak. This highest value of N(E) is actually reached for an electron

---

* More sophisticated descriptions of the Fermi surface in noble metals are available, without materially changing these simpler considerations, see, for instance, (10).

density of 1.36 per atom. At this density, the Fermi surface has moved up in energy and is actually touching the center of the octahedral faces of the Brillouin Zone. Beyond this value of electron density, the noble metal structure changes from face to body-centered cubic (11).

Such an increase in density can be achieved by substitutional trivalent impurities such as In, Ga, and Al; that is by replacing atoms of Au with, say, atoms of Al. The effects due to interstitial doping are presently unknown.

For the purpose of electron emission, we have achieved two advantages with respect to the "undoped" crystals. It will be seen from the following experimental data that we have achieved a higher W_A and W_F thus further lowering the acceptor levels in the oxygen atoms in the electrolyte near the metal's surface with respect to the electron donor levels in the metal. Further, as the electron levels line up or exceed the acceptor levels in the oxygen atoms, considerably more electrons are available to contribute to the current. This advantage continues to be very marked for the first few hundreds of millivolts below the Fermi level; and hence, any low current advantage may be expected to continue at very high currents.

The mathematics of emission are complex. These will be discussed in the last article of this series, when this and other theoretical aspects of this problem will be taken up.

2.4 THE GOLD-COPPER AND SILVER-COPPER ALLOYS

It has been shown that the density of electrons in gold and silver can be raised by adding substitutionally higher valency "dopants." When this is done, either gold or silver become competitive with platinum as a catalyst. These catalysts become still better if single crystals are used. Particularly, if the most suitable (001) face is selected.

The large improvement in performance that can be obtained by going from polycrystalline to single crystal films has been shown in the course of this study (Section 2.5, Fig. 12).

Gold and silver have fairly high ($\sim$ 4.8 e.v.) work functions. This permits them, by alloying with substitutionally polyvalent dopants, to obtain materials with unusually high values of work functions.

Finally, Au-Cu alloys in certain proportions are known to present the property called ordering; e.g., Au-Cu and Au-Cu_3 are ordered alloys resembling a crystal like NaCl in the completely orderly arrangement of atoms. Other alloys of similar composition are disordered, even though single crystal, because their composition is constant only on the average.

The ordered alloys of gold and copper show extraordinary resistance to chemical attack (12), much better than pure gold (see also closing paragraph of Section 2.5).

Because of this property that promises long life, their relative low cost, and because they are completely analogous to other noble metals and should similarly improve by doping with polyvalent addition, it was believed that these alloys would produce excellent catalysts.

It was therefore decided to explore the catalytic properties of single crystals of noble metals and to start with single crystals of Au and Ag because they are relatively easy to grow as single crystal films. These were to be followed by their ordered alloys such as Au-Cu and Au-Cu_3 and finally by ordered alloys to which up to 20 atomic percent of trivalent substitutional impurities were added.

The vacuum depositions were performed in a Kinney vacuum evaporator (13) which was capable of maintaining a vacuum of better than 10^{-5} mm. The metals were evaporated on cleaved single crystals of NaCl oriented in the 100 direction, measuring 2 inches on the side, clamped against a heated copper block 3/4-inch thick in which three "Hotwatts" (14) were imbedded. The temperature across the crystall face at 300°C varied very little, about 0.1°C maximum. The temperatures were measured with an iron constantan thermocouple, and the thickness determined with a Sloan-Deposit thickness meter (15).

Evaporations, at first, were performed from as many as three adjacent boats; this arrangement was later modified so that each boat was successively shifted to the same position, and the evaporation geometry kept invariant.

The films were deposited on the carefully outgassed crystals at predetermined temperatures. As already noticed by Sato (16), for thin (1,000 Å) films diffusion and equilibration processes take place very rapidly at relatively low temperature. The films were, when desired, brought to ordering temperature and allowed to cool in vacuum to room temperature.

Measurements

1 cm.^{2} section of film was bonded to nickel mesh using Araldite® * under pressure at temperatures of about 200°C.

The mounted films were spot welded to 1 mm. diameter Ni wire which was sealed by melting the glass around it into a Pyrex® tube, the outer diameter of which was ground to a close fit in ¼-inch I.D. precision bore Pyrex® tubing. The exposed Ni was then covered with a cold setting epoxy resin. All of the electrodes were placed in an 80°C oven overnight to ensure that the curing process was completed. Before being

INSERT
FIG. 7
FIG. 8

---

* Trade name for a commercial thermo-setting compound produced in England by Ciba, Ltd.

placed in the cell shown schematically in Figs. 7 and 8, the electrodes were treated by placing them in dilute HNO_3 for 15 minutes, then thoroughly rinsed in distilled water and finally in a KOH solution of the same concentration as the electrolyte in the cell.

The cell was thoroughly cleaned in chromic acid, washed in copious amounts of distilled water and finally 2N KOH, the liquids being forced through the glass frits by means of a water aspirator. After each series of measurements, the cell was washed well in copious amounts of distilled water, dried in a 60°C oven, and stored there until needed again. It is then again rinsed out with fresh KOH solution before being used. The electrodes are introduced into the cell, tank fuel gases connected to the gas inlets, and the cell allowed to equilibrate. Equilibration is taken as being achieved when the open circuit voltage does not change over 10 minutes. The electrodes are connected through a decade resistance box and a 1 ohm precision resistance. Varying the load varies the reaction rate at the electrodes and so yields a plot of overvoltage vs. current which is used for comparative purposes. The current is measured by a Keithley ——————————→

Model 150 B Electrometer placed across the 1 ohm resistance. The potential of the cathode with reference to the standard hydrogen electrode (S.H.E.) is measured by a Keithley Model 610 B Electrometer. The outputs of both Keithley meters are connected to a Varian Model G 22A recorder.

The method for mounting the films leaves ohmic contacts across the film. At the very small currents measured however, ohmic overvoltage may be ignored.

There is a considerable diffusion overvoltage present. Here once again, if only the initial part of the curve where very small currents are drawn is used, the diffusion overpotential may be disregarded. Undoubtedly, a better method will entail using short current pulses.

Further effects will be found from the impurities in the system. The distilled water used is normal tap water which has been distilled once in a commercial stainless steel still. The fuel gases undoubtedly contain many contaminants which will have an adverse effect upon the electrode performance. It has been assumed that, as all of the electrodes are measured under the same conditions, the results are satisfactory for the purpose of relative comparisons.

The current densities are given per $cm.^2$ of apparent area. The true area of single crystal films grown on cleaved salt may be some 20 percent higher than the apparent, but the true surface of polycrystalline Pt will be still greater. So that, if anything, the graphs are slanted in favor of platinum.

2.5 RESULTS

Smith and Smith (17), see Fig. 9, report results on indium-doped polycrystalline silver which are quite similar to ours. Furthermore, their thinking is also analogous.

INSERT
FIG. 9

It is interesting to note how different the characteristics of polycrystalline, single crystal, and ordered alloys are. Figs. 10 and 11 show the current-voltage characteristics of a number of materials grown during a four-week period. In Fig. 10, the measurements extend to 200 μ amps/cm.^{2}. Fig. 11 is a detail of Fig. 10 and covers only the first 20 μ amps/cm.^{2}.

Three different classes of curves can be distinguished. The first class consists of curves that are very nearly straight, curves 2, 4, 21, and 10 fall in this class. Furthermore, their slopes are very nearly parallel to each other, they are more horizontal; their slopes are flatter than those of the other curves.

INSERT
FIG. 10
FIG. 11

The curve marked single crystal Au, as well as the curves for Ag and Ag-Cu in Fig. 15, show much greater initial curvatures; their catalytic properties are excellent. These curves belong to single crystal but disordered material.

The third group shows very high curvature at low currents and a slope that varies markedly and unpredictably with current, see Fig. 10. To this group belong Pt bright and a number of our failures, like 15, 26, and 7 (Fig. 10). All these materials are polycrystalline.

The first, possibly the second, group may be described by some physically significant mathematical expression connecting current and voltage as a function of some crystal parameter, though not materials belonging to the third group.

Gold

Gold is one of the easiest materials to grow in single crystal form by evaporation on heated salts, and thus it was the first material tried. Results are shown in Fig. 12. The upper line is for single crystal gold and is, in effect, a narrow stripe, as the result of measuring four distinct crystals produced many weeks apart under somewhat different conditions. It also includes the same material measured a month apart and another measured before and after running at 200 μ amps/cm.^{2} for an hour period. Such consistency and repeatability is the result of ————————→

operating with single crystals. This is necessary if a match between a theory and experiment is to be achieved.

The lowest curve refers to polycrystalline gold and the next lowest of polycrystalline Pt. The next curve above polycrystalline platinum is very interesting. It shows the change with time of the original polycrystalline Au film; this film was stressed and grew progressively larger crystallites by stress-relief, becoming, in effect, more nearly a single crystal in the process.

<u>Au-Cu</u>

Au-Cu is the best known of the ordered alloys. It is relatively easy to obtain as a single crystal ordered film. It proved easy to "dope" with Al, In proved difficult, and Ga has not been tried yet but should prove relatively straightforward, like Al. Fig. 13 shows the characteristics of Au-Cu undoped and doped with various atomic percent of Al. The highest curve was doped with 16 percent of Al very close to the theoretical optimum 18 percent. It is the best catalyst of the group and probably the best obtained to date.

$\underline{\text{Au-Cu}_3}$

This material proved considerably more difficult to handle than Au-Cu, in part, because it requires higher deposition and ordering temperatures, viz., about 400°C.

Fig. 14 shows the current *vs.* voltage characteristics of a group of Au-Cu_3 catalysts. All these catalysts are superior to Pt.

The curves are very closely bunched, as one expects, because they are all doped with the same percent of trivalent dopants. Note, however, that two are Al; and one is In doped. Because aluminum is trivalent as is indium, the near identity of their characteristics is reasonable. The high degree of repeatability is, of course, a result of being single crystals and ordered metals.

INSERT
FIG. 12
FIG. 13
FIG. 14

Ag and Ag-Cu

To grow single crystals of Ag with the present method requires the highest substrate temperatures, over 500°C. Two samples that were obtained are shown in Fig. 15. Ag-Cu properly doped should make one of the best and certainly the least expensive of known catalysts.

Chemical Properties

We have mentioned that the ordered alloys show remarkable resistance to chemical attack. In very crude etching tests in 50 percent aqua regia using ½ cm.^{2}, 3,000 Å thick films, the Au film lasted about 5 minutes and the Au-Cu about 2¼ hours, a factor of 25 or so better. With doping, this advantage diminishes. Optimally, Al doped Au-Cu and Au-Cu$_3$ shows about the same etching properties as Au in aqua regia.

INSERT
FIG. 15

2.6 CONCLUSIONS

A number of noble metal catalysts with fully repeatable characteristics superior to Pt bright in the low current region were obtained. A feature of their characteristic curves is that they lie flatter and show smaller exponential decays than those of polycrystalline materials--indeed of any material that has come to our attention heretofore. It is fully expected that these improved characteristics will extend to high currents.

The fact that the alloys selected on the basis of the present theory, did indeed prove themselves superior to Pt, is encouraging. The search for Pt substitutes has been extensive and has, in effect, revealed little useful new material. Indeed it has often been claimed that Pt would prove impossible to improve upon. So that coincidence can be effectively excluded.

The desired characteristics mentioned at the start of this paper are briefly:

a) better performance than Pt,

b) at least equal life to Pt, and

c) lower cost.

Of these, a) can be considered accomplished, b) longer life is expected but remains to be shown, and c) is presently under preliminary investigation. It is hoped that nearly trivial costs will be achieved. It will be the subject of a future communication.

In conclusion, it has been shown that the catalytic properties of metals and of metal alloys can be inferred from an understanding of the catalytic process and of the metal surface.

It has also been shown that the current density depends strongly on the metal's work function and increases with the same. Hence, no measurement can claim any significance unless the degree of crystal order of the metal catalyst is specified. It follows, and it has been shown experimentally, that repeatable and interpretable measurements can only be made on single crystal faces.

** * **

The writer wishes to acknowledge the many friendly discussions with Professor Manfred Altman, Director, of the Energy Conversion Institute of the University of Pennsylvania, as well as his gratitude to Mr. Allan Saunders, of the same Institute, who performed the measurements, and to Professor Felix Guttman, of the University of South Wales, New Zealand, for reading the manuscript. Thanks are finally due to Mr. Ernst Cohn, of the National Aeronautics and Space Administration, for encouragement and stimulation. The work reported in this article was largely supported by NASA Contract No. NAS 7-574.

REFERENCES

1 Matthews, D. B., Ph.D. thesis, University of Pennsylvania, 1965.

Srinivasan, S., Wroblowa, H., and Bockris, J. O'M., Advances in Catalysis, 17, (1967).

2 Bockris, J. O'M., Damjanoric, A., and Jahan, R., to be published in 1967.

3 Piontelli, R., Peraldo Bicelli, L., and La Vecchia, A., Atti. Accad. Nazl. Lincei, 27, 312 (1959).

4 Bockris, J. O'M., Mannan, R. J., and Damjanoric, A., report to NASA, 1966.

5 Bockris, J. O'M., Devanathan, M., and Müller, K., Proceedings of the Royal Society, A, 274, (1963).

6 McDonald, J. R., Proceedings of the 138th Meeting of American Chemical Society, (1960).

7 Bocciarelli, C. V., Advanced Energy Conversion, (1968), in press.

8 Heitler, W., Elementary Wave Mechanics, Oxford (1948).

9 Bocciarelli, C. V., Solid State Communications, 5, 821-823, Pergamon Press, Great Britain, (1967).

10 "The Fermi Surface," Proceedings of an International Conference at Cooperstown, New York, Wiley, New York, (1960).

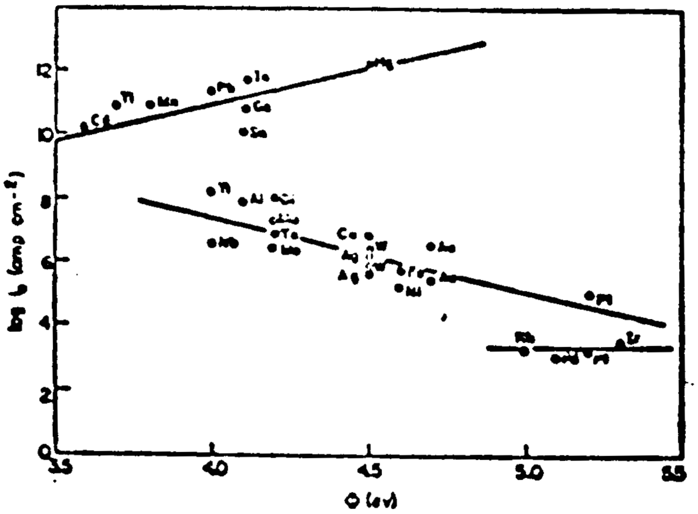
11 Hume-Rothery, Atomic Theory for Students of Metallurgy, The Institute of Metals publication, London, (1952).

12 Bakish, R. and Robertson, W. D., Journal of Metals, (February 1952).

13 Kinney Vacuum Division, New York Air Brake Company, Boston, Massachusetts.

14 Hotwatt, Inc., Danvers, Massachusetts.

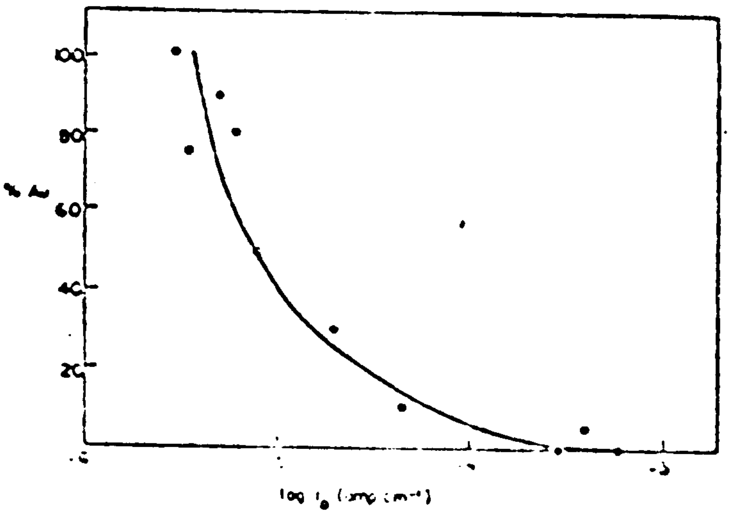
15 Sloan Instruments Corporation, Santa Barbara, California.



Dependence of exchange current density for the hydrogen electrode reaction on the work function of the metal (7)

FIGURE 1

Only the lowest group Rh, Pd, Pt, and Ir are good catalysts; they are, incidentally, the materials with the highest work functions.



Dependence of exchange current density for the hydrogen electrode reaction on percentage gold composition for Au, Pd, and their alloys (2)

FIGURE 2

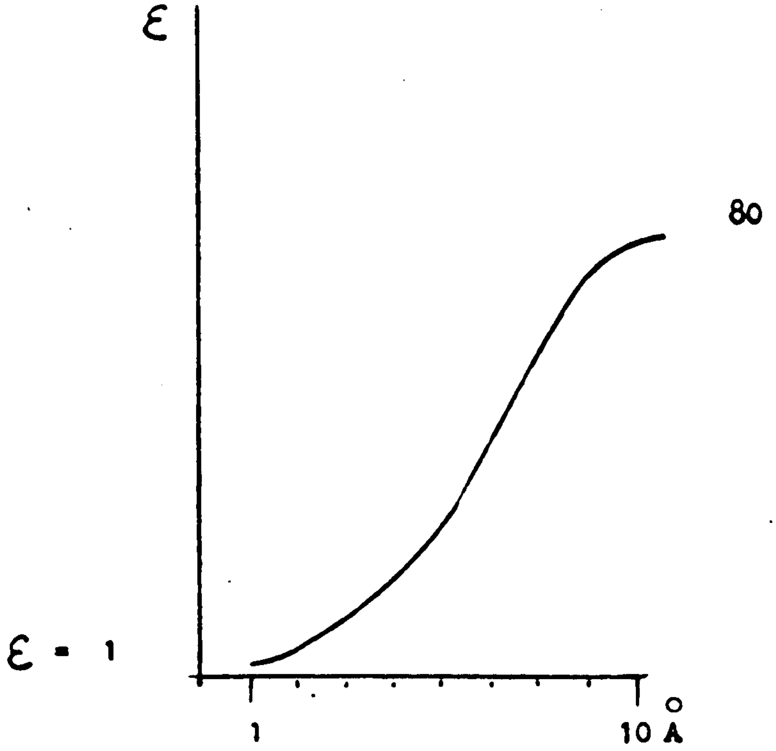


FIGURE 3

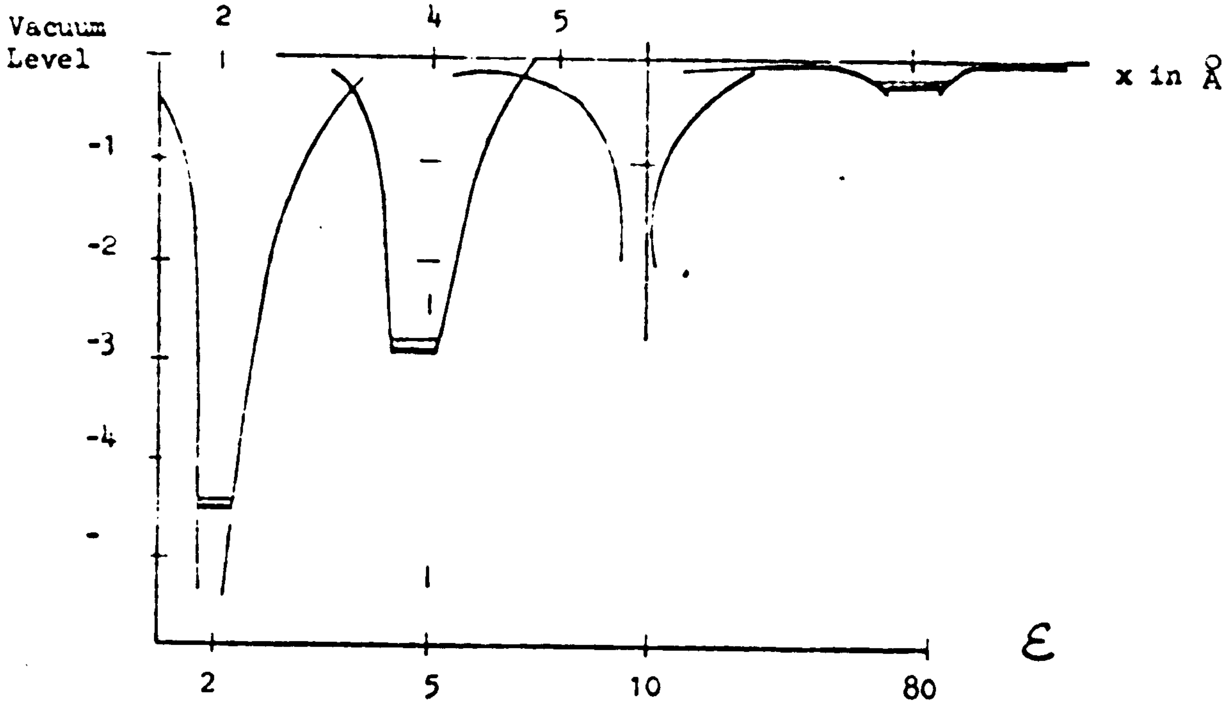


FIGURE 4

Fig. 4 shows schematically the first ionization level of either oxygen or hydrogen in a medium of varying dielectric constant.

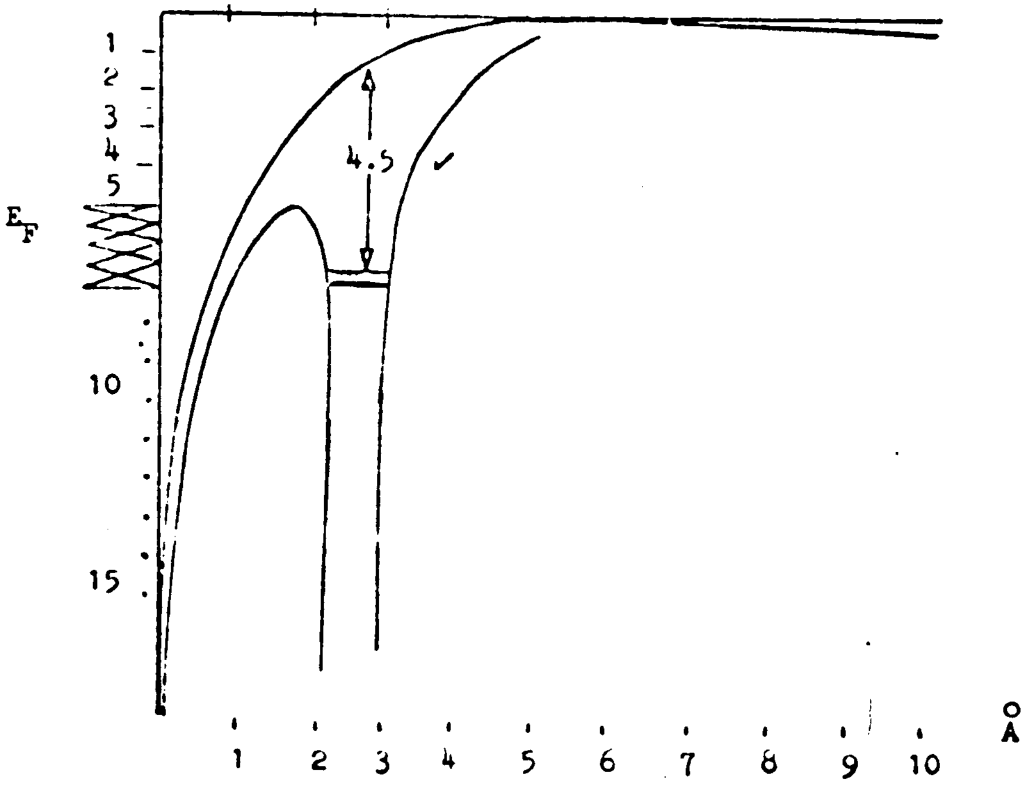


FIGURE 5

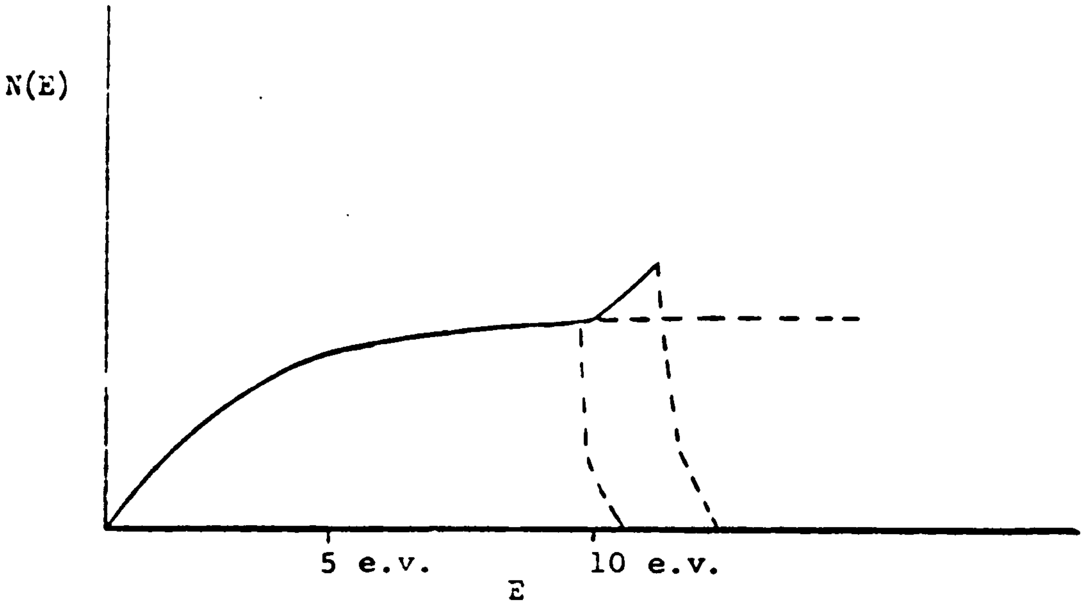


FIGURE 6

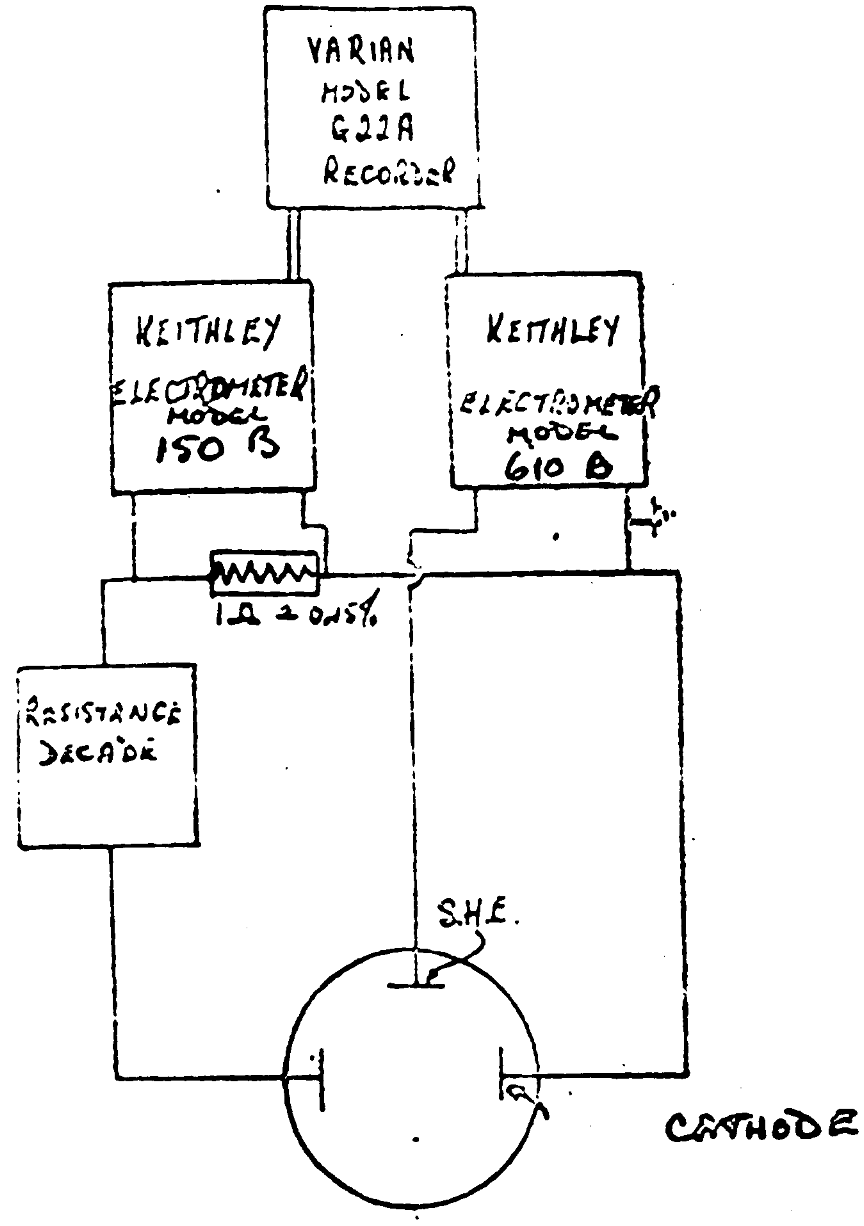
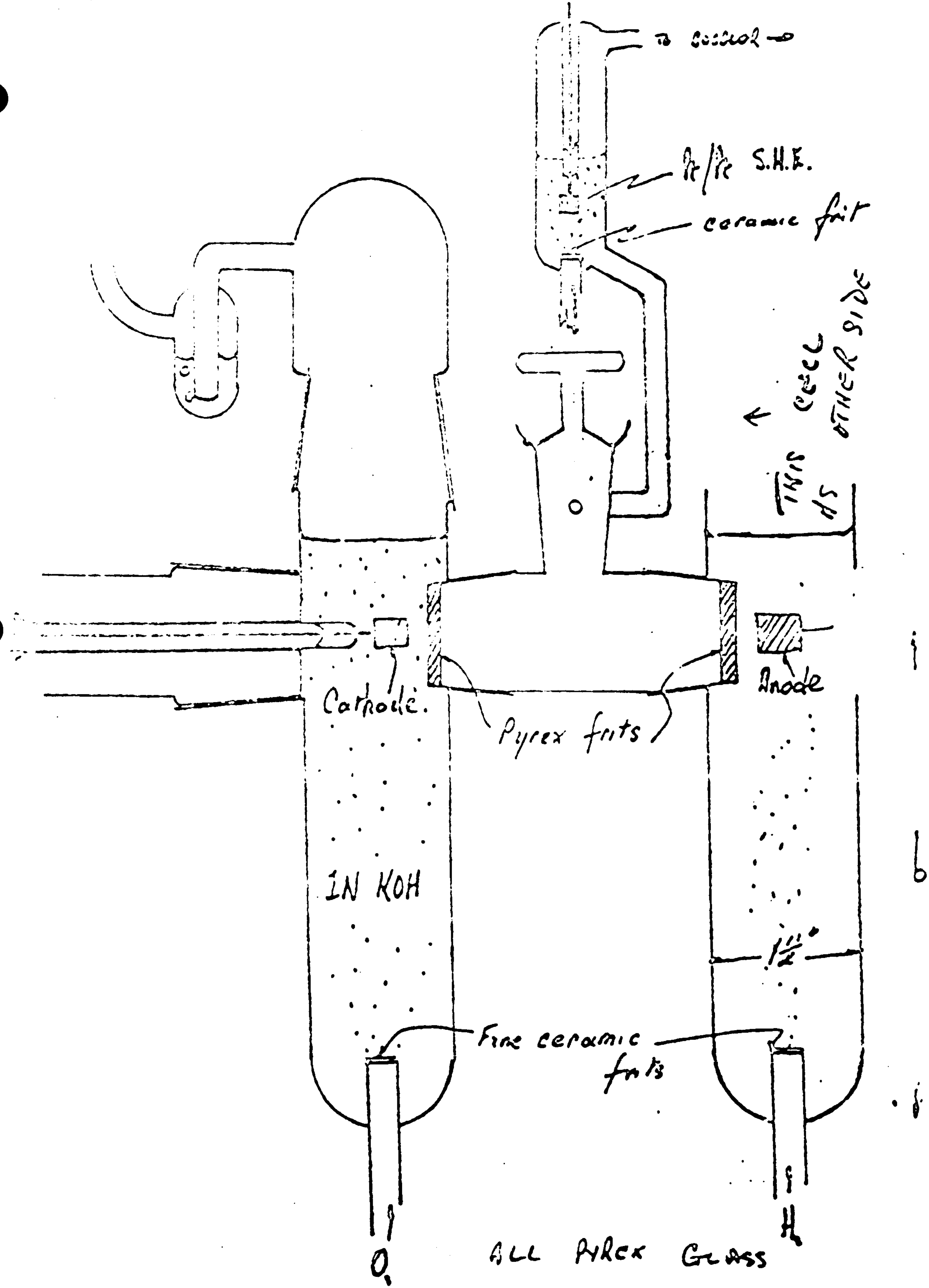
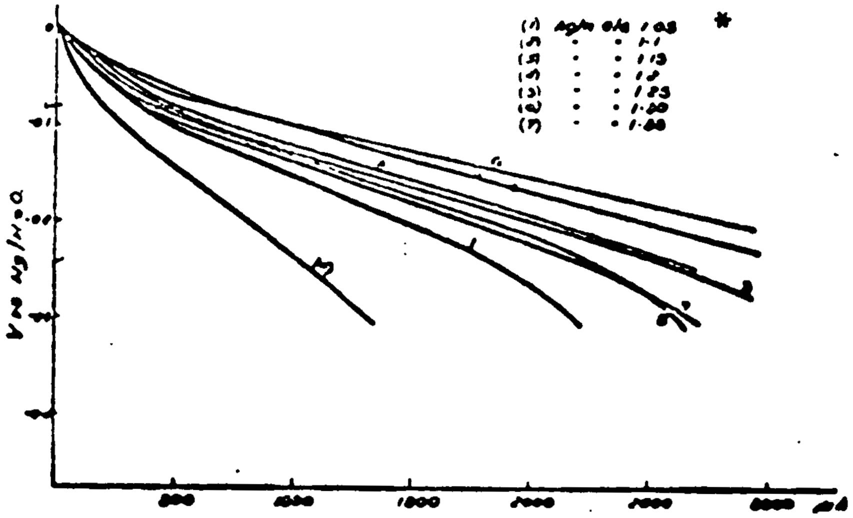

VARIAN
MODEL
G22A
RECORDER
KEITHLEY
ELECTROMETER
MODEL
150 B
KEITHLEY
ELECTROMETER
MODEL
610 B
1Ω ± 0.05%
RESISTANCE
DECADE
S.H.E.
CATHODE

FIGURE 7



ALL PYREX GLASS EXCEPT WHERE DESIGNATED.

FIGURE 8



a-Silver-indium alloy oxygen electrodes.

FIGURE 9

* e/a = number of electrons per atom

FIGURE 10

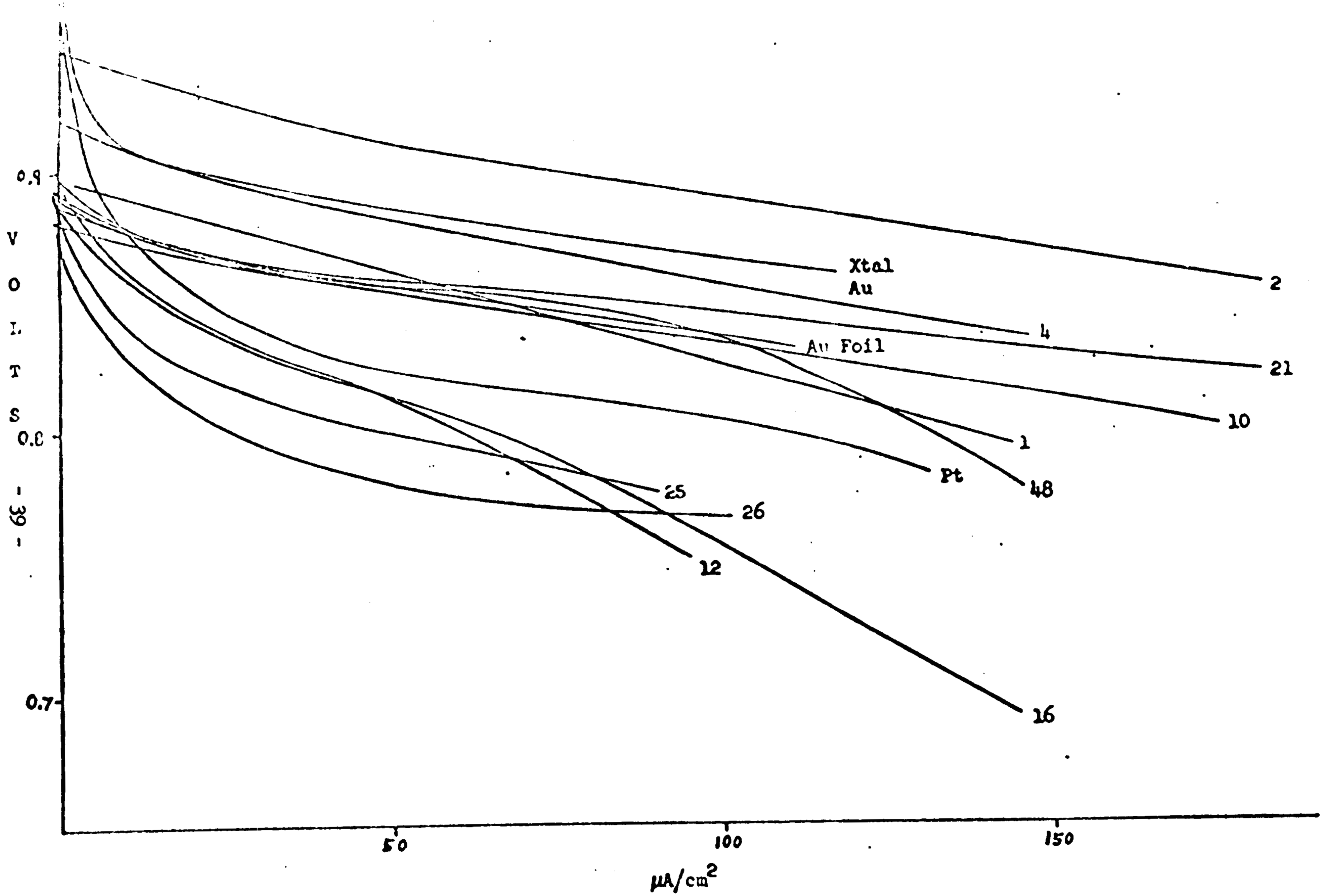

VOLTS
0.9
0.8
0.7
50
100
150
μA/cm^2
Xtal Au
Au Foil
2
4
21
10
1
Pt
48
25
26
12
16

FIGURE 11

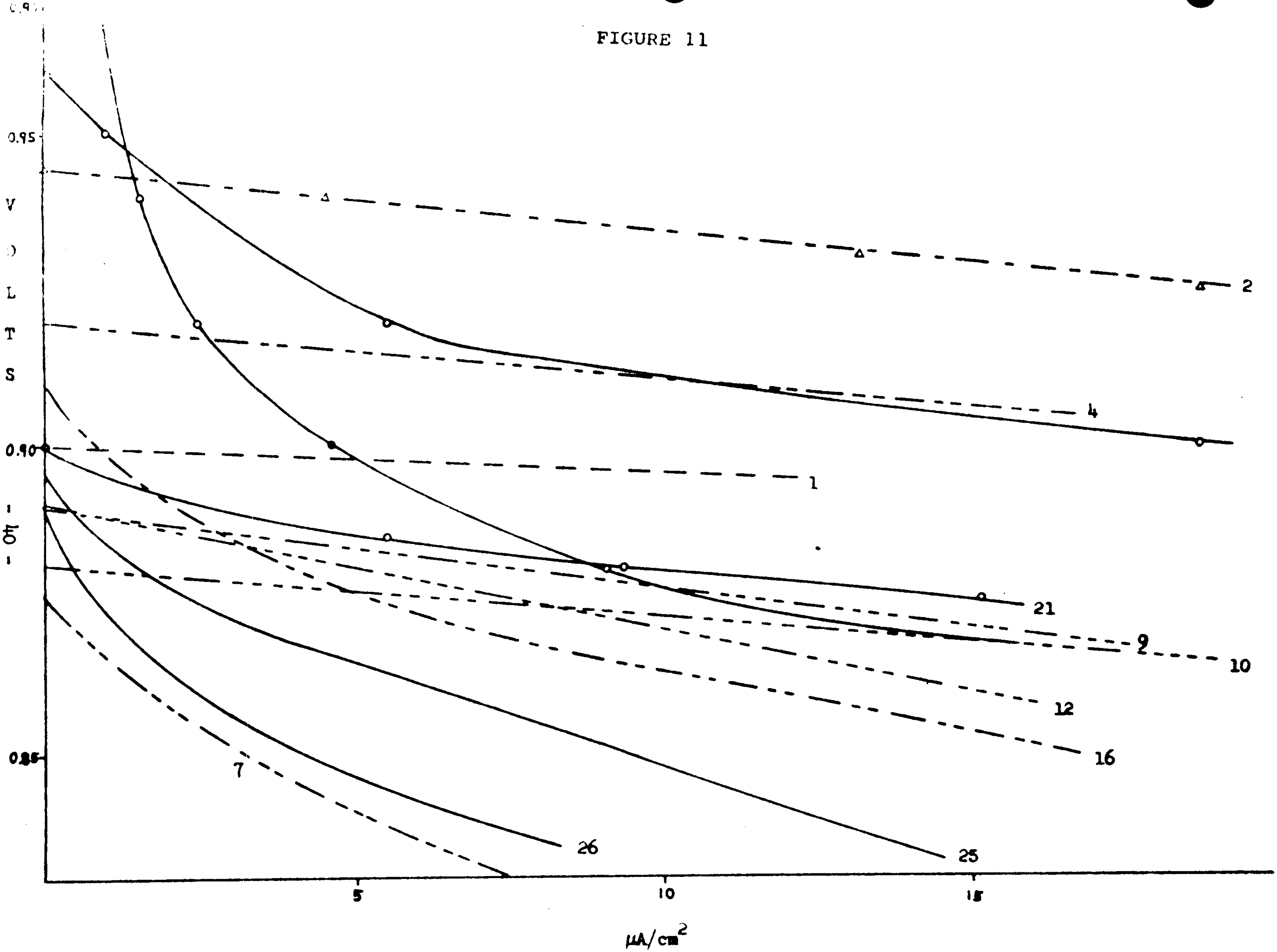


FIGURE 12

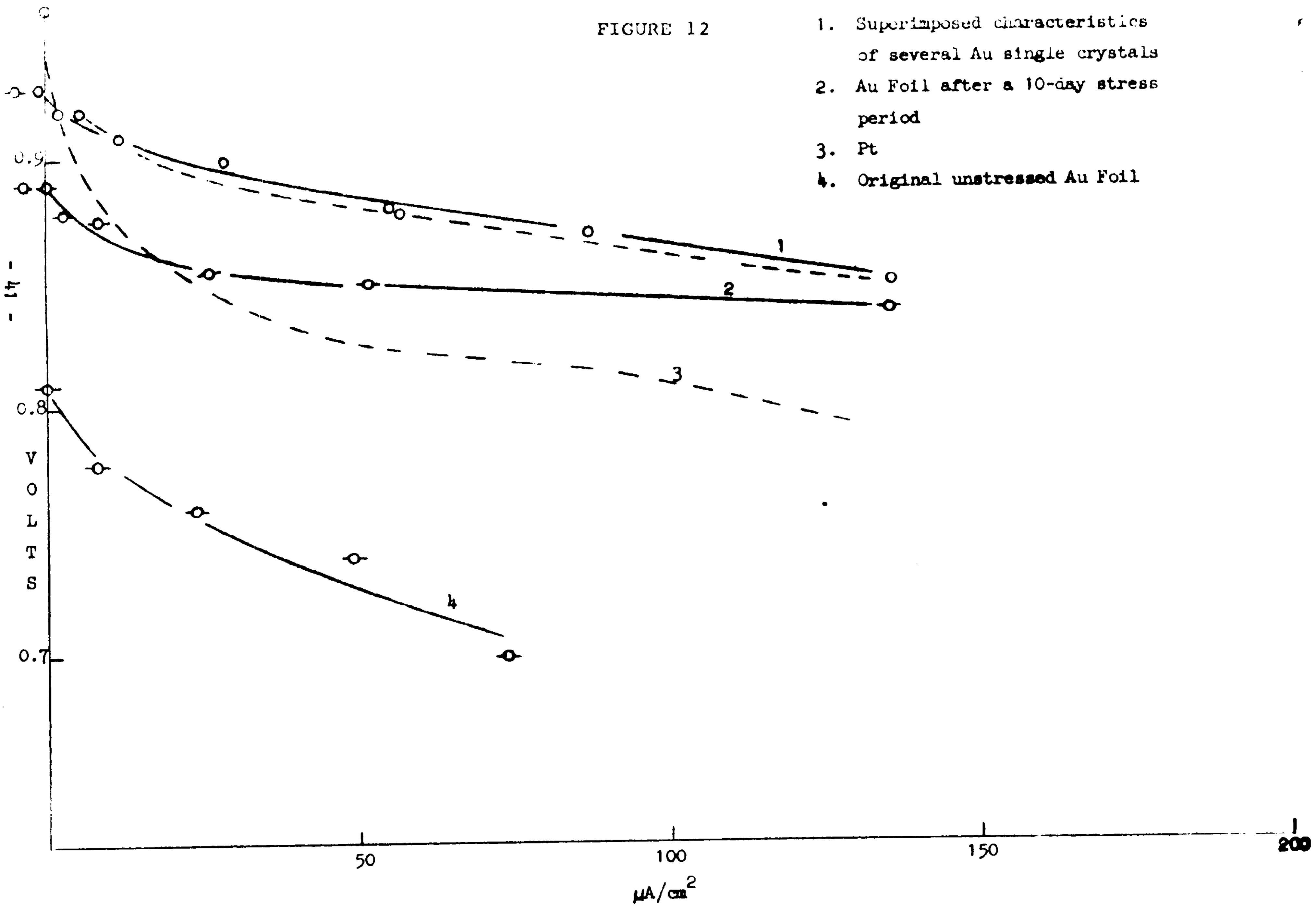
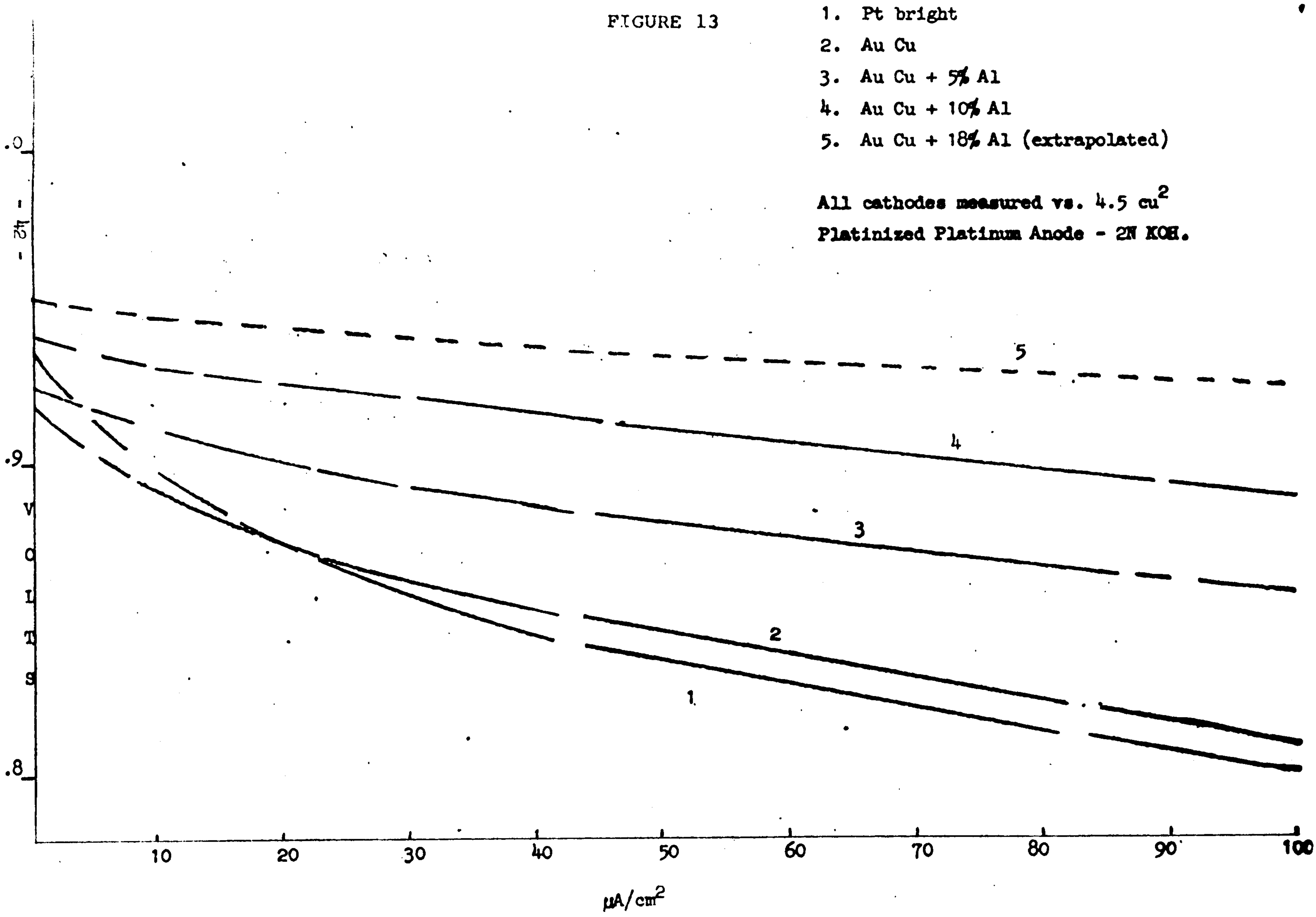

1. Superimposed characteristics of several Au single crystals
2. Au Foil after a 10-day stress period
3. Pt
4. Original unstressed Au Foil
1
2
3
4
0.9
0.8
0.7
VOLTS
50
100
150
200
μA/cm²

FIGURE 13



1. Pt bright
2. Au Cu
3. Au Cu + 5% Al
4. Au Cu + 10% Al
5. Au Cu + 18% Al (extrapolated)

All cathodes measured vs. 4.5 cu^2
Platinized Platinum Anode - 2N KOH.

FIGURE 14

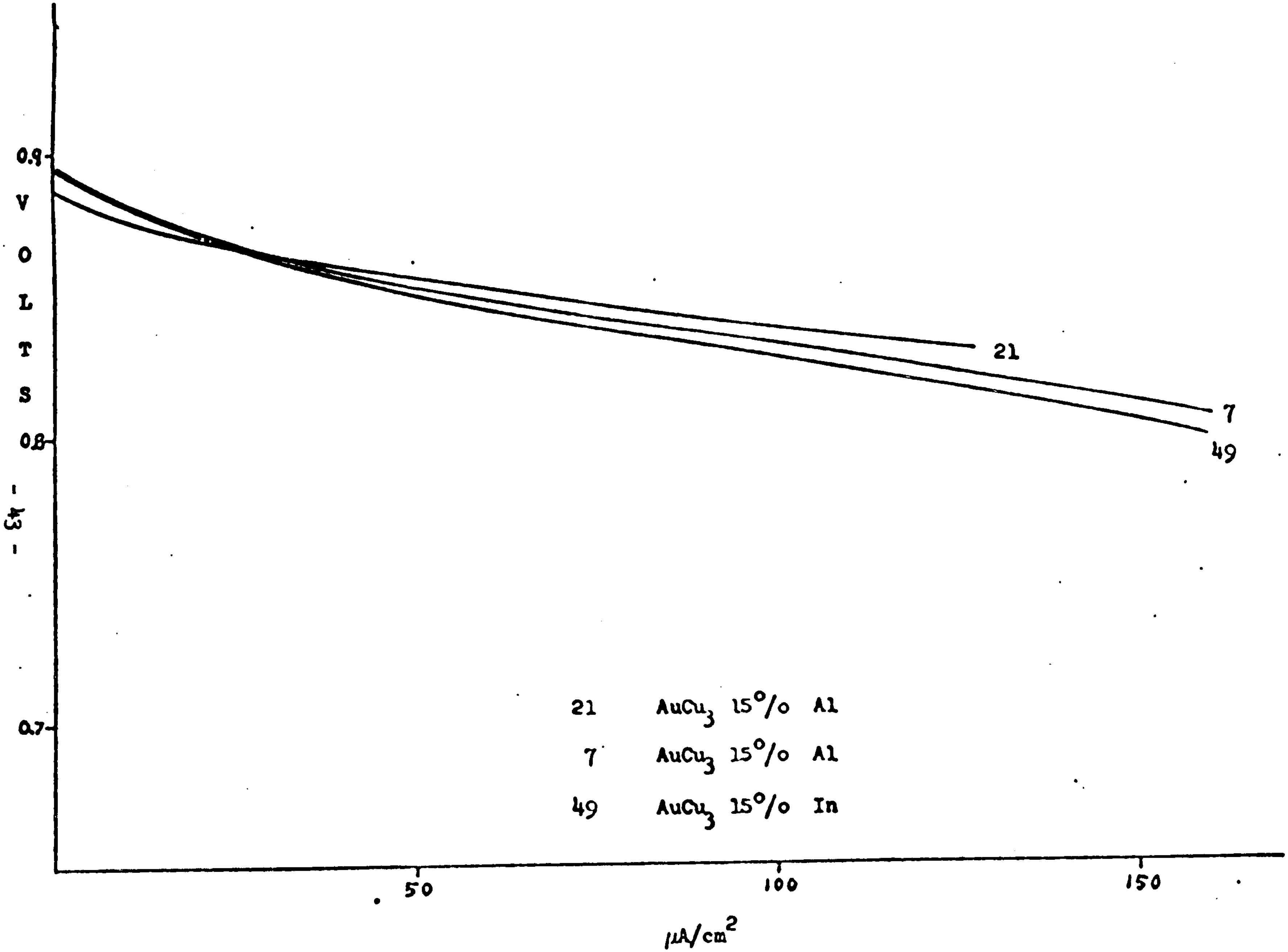

0.9
V
O
L
T
S
0.8
0.7
21
7
49
21 AuCu$_3$ 15°/o Al
7 AuCu$_3$ 15°/o Al
49 AuCu$_3$ 15°/o In
50
100
150
μA/cm^2

FIGURE 15