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EVALUATION OF FUEL CELL ELECTROLYTES FOR DIRECT AND INDIRECT OXIDATION OF CARBONACEOUS FUELS

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Table of Contents

ABSTRACT

1. OBJECTIVE AND SCOPE 1

2. INTRODUCTION AND STATEMENT OF THE PROBLEM 1

3. PROGRESS TO DATE 3
Experimental Techniques and Results on Various Electrolytes 3

3.1 Introduction 3

3.2 Electrical Resistivity Measurements 5

3.3 Vapor Pressure Measurements 5

3.4 Electrochemical Measurements:

3.4.1 Gas Diffusion Electrodes 8

3.4.2 Current Potential Curves for Gas Diffusion Electrodes 10

Pentafluoropropanoic acid $C_2F_5CO_2H$; 90 wt%

Trichloroacetic acid $CCl_3 \cdot CO_2H$

Chloro-difluoroacetic acid $ClF_2 \cdot C \cdot CO_2H$

Benzene sulfonic acid hydrate $C_6H_5SO_3H \cdot 1: 5H_2O$

Methane disulfonic acid (50% aqueous) $CH_2(SO_2H)$

Benzoic acid C_6H_5COOH

Methane sulfonic acid CH_3SO_3H

3.4.3 Rotating disk electrodes 12

Phosphoric Acid 13

Methane Sulfonic Acid 13

4. FUTURE WORK 14

4.1 General 14

4.2 Methane Sulfonic Acid 14

4.3 Higher Alkane Sulfonic Acids 15

4.4 Screening of Electrolytes 15

Sulfoacetic acid monohydrate, $HO_3S \cdot CH_2 \cdot CO_2 \cdot H \cdot H_2O$

Methane disulfonic acid

Silico-benzoic acid, $C_6H_5 \cdot SiOOH$

Other Aromatic Acids

4.5 Additional Tests 16

References 17

Figure Captions 19

ABSTRACT

In the initial period of this contract we have established comprehensive testing systems for the following tasks:

(i) Measurements of electrical resistivity of the electrolytes at various temperatures.

(ii) Measurement of vapor pressure at various temperatures.

(iii) Measurements of fuel oxidation and oxygen reduction rates at rotating disk electrodes in the selected electrolytes at various temperatures.

(iv) The same as (iii) on gas diffusion electrodes.

We have evaluated the following electrolytes and compared their performance to that of 85% H_3PO_4 at 135°C; pentafluoropropanoic acid, trichloroacetic acid, chlorodifluoroacetic acid, methane disulfonic acid (50 wt% aqueous solution), methane sulfonic acid, benzoic acid and benzene sulfonic acid. Many of these acids performed very poorly; the only one that proved to be superior to 85% H_3PO_4 is the methane sulfonic acid.

1. OBJECTIVE AND SCOPE OF WORK

The objective of this research program is to find an electrolyte for direct or indirect oxidation of carbonaceous fuels in a fuel cell in which the electro-oxidation rates of hydrogen or the carbonaceous fuel are greater than when 85% H_3PO_4 is used as the electrolyte. The standard temperature for comparison is 135°C.

There are three main tasks involved as follows:

Task 1. This includes a literature search to identify possible organic acid electrolytes on the basis of their acidity, melting and boiling points as well as the type of functional groups. This is followed by measurement of the electrical resistivity.

Task 2. This includes measurement of the vapor pressure of the electrolyte. A desirable electrolyte must have a low vapor pressure, e.g., less than about 1 torr. This minimizes the loss of electrolyte by evaporation and facilitates the removal of water which is a by-product of the reaction.

Task 3. This includes electrochemical anodic oxidation measurements on (a) - planar rotating disk electrodes to estimate the solubility-diffusivity product of the fuel gas in the particular electrolyte (for mass transfer limited reactions) and (b) - gas diffusion electrodes since any electrolyte would ultimately be used with this type of electrode in an operating fuel cell.

2. INTRODUCTION AND STATEMENT OF THE PROBLEM

The electro-oxidation of carbonaceous fuels such as propane at a fuel cell anode has received much investigation, and it has been established that the process is one of slow electrochemical kinetics leading to low current densities. The reaction process can be speeded up by (a) high reactive electrode surface area, (b) surface catalysis, and (c) high temperature.

The molten alkali-H_2O electrolyte used in the medium temperature Pratt and Whitney fuel cells (Apollo mission) is not suitable for carbonaceous or reformed fuels containing significant amounts of CO_2. However, the success of moderate temperature fuel cells in terms of electrical activity, lifetime of components, and ease of engineering shows great promise for commercial application IF a liquid electrolyte suitable for carbonaceous fuels can be discovered, operating at about the same temperatures as the Pratt & Whitney cell, e.g., 200°C at ordinary pressures. There are several obvious requirements for the "ideal" electrolyte (1) as follows:

(i) availability of suitable ions for fuel oxidation at the anode and oxygen reduction at the cathode

(ii) high ionic conductivity

(iii) good solvent (high values of solubility-diffusivity product) for fuels and oxidants

(iv) chemically inert towards fuels, oxidant and reaction products e.g., CO_2 and water

(v) stability over the voltage ranges involved; that is the electrolyte must have low residual currents over the potential ranges of the oxidation of the fuel and the cathodic reduction of the oxidant

(vi) since water must be removed from the cell, the electrolyte must have a low vapor pressure (high boiling point) to avoid a complicated condensing-separation system

(vii) equally important but less obvious requirements are negligible adsorbability on, and poisoning of, the electrode surface.

(viii) noncorrosive towards cell and electrode materials.

The obvious candidates are high boiling point strong acids and much work has been done on the conventional inorganic acids. Of these, hydrofluoric acid has been found to support higher currents of propane oxidation than $HClO_4$, H_2SO_4, and H_3PO_4 at 100-105°C (2). However, HF is not a practical electrolyte because of its volatility and the intractable materials problems it poses. On the other hand, phospheric acid has some advantages, e.g., it is less corrosive and less volatile than HF. Its main virtue is that, unlike H_2SO_4, HCl, HNO_3, . . . etc, it is formed from a non-volatile compound (P_2O_5) and water. Hence its long term thermal stability only requires keeping water in balance. The activity of aqueous solutions of phospheric acid for propane oxidation has been investigated over a broad range of concentration. The optimum concentration was found to be 85% (3).

Although it has some desirable features, it also shows undesirable characteristics which could reduce the cell efficiency and the selection of construction materials. These are:

(i) Phosphorous, which forms the nucleus of the phosphate anion, has many valence states. Phosphoric acid undergoes reduction at a platinum electrode to give lower phosphorous compounds which adsorb onto, and poison, the catalyst. The extent of this reduction process is undetermined and could, in principle, generate various quantities of all valence states. In fact, phosphine gas has been suspected (4) as a reduction product when platinized platinum is brought in contact with 85% phospheric acid at 135°C under open circuit conditions. It has been shown repeatedly (2,5) that additions of phosphorous acid decreases the catalytic activity of platinum.

(ii) The 85% acid has a fairly high vapor pressure (108mm Hg at 100°C. (6)).

(iii) Phospheric acid enhances the sintering of the pt black particles used in fabricating the Teflon-bonded gas-diffusion electrodes used in fuel cells (7). This causes a loss of catalytic surface area and possible cleavage of the electrode structure with a consequent loss in the efficiency of the electrode.

(iv) The acid etches glass especially at higher temperatures.

Due to these problems with the 85% H_3PO_4 there has been a concerted effort in the last few years to find alternate electrolytes. Adams et al. have shown that tri-fluoromethane sulfonic acid (TFMSA) is superior to 85% H_3PO_4 for the oxidation of H_2 and propane (8) and the reduction of air (9). However, TFMSA was found to wet Teflon (10) and hence cannot be used with a Teflon-bonded gas-diffusion electrode. In addition, it is extremely corrosive as is the case with many fluorine-containing compounds. It has also been shown that it decomposes above 60°C giving rise to products which poison the electrode (11). The halogenated derivatives of methane sulfonic, and disulfonic, acids are currently under study by Baker (12) and Brummer (13).

3. EXPERIMENTAL TECHNIQUES AND RESULTS ON VARIOUS ELECTROLYTES

3.1 Introduction.

With the above requirements of an ideal electrolyte in mind, we have performed a literature search which suggested several organic acid electrolytes. Table 1 lists some electrolytes, their melting and boiling points, and includes 85% phosphoric acid and trifluoro methane sulfonic acid for comparison. Many of these compounds are only examples of a certain class of compounds, e.g., the pentafluoropropanoic acid is the second member of the homologous series $C_nF_{2n+1}CO_2H$. The boiling point of the various members of this series of compounds increases with n, e.g., the b.p. increases from 72°C for n = 1 to 270°C for n = 13 (14).

We have followed three different and complementary techniques to evaluate the usefulness of a certain electrolyte. These include measuring the electrical resistivity of the chosen electrolyte at various temperatures. The electrolytes were further tested for vapor pressure and for electrochemical behavior at both a rotating disk electrode, and a Teflon-bonded, pt-black gas-diffusion electrode. The following is an outline of the experimental systems and the results obtained on the various electrolytes.

TABLE 1

MELTING AND BOILING POINTS OF SOME SELECTED ELECTROLYTES

electrolyte	formula	m.p.°C	b.p.°C	supplier
Benzene sulfonic acid-hydrate	$C_6H_5SO_3H\cdot 1.5H_2O$	45-46	---	Eastman Kodak
Methane di-sulfonic acid	$CH_2(S)_3H)_2$	---	220	Eastman Kodak
Tri-chloroacetic acid	CCl_3CO_2H	54-58	196	Aldrich
Pentafluoropropanoic acid	$C_2F_5CO_2H$	---	96	ICN Pharmaceutical Inc.
Chloro-difloroacetic acid	$ClCF_2CO_2H$	24-26	122	Aldrich
Benzoic acid	$C_6H_5CO_2H$	118	249	Baker
85% Phosphoric acid	H_3PO_4	---	158	Baker
Trifluoro methane sulfonic acid monohydrate	$CF_3SO_3H\cdot H_2O$	34	218	Aldrich
Methane sulfonic acid	$CH_3\cdot SO_3H$	20	---	Eastman Kodak

3.2 Electrical Resistivity Measurements

The resistivity of the various electrolytes was measured at various temperatures using a micro-conductivity cell (3403 Yellow Springs Co., cell constant 1 cm^{-1}) and a digital conductivity bridge (Barnsted PM-70CB). The temperature was adjusted using an oil both. Measurements were performed in both the ascending and descending directions with respect to temperature. No significant hysteresis was observed except when significant amounts of water existed in the electrolyte and only when measurements were taken at higher temperatures as, for example, with the 90% aqueous solution of CCl_3CO_2H. Figure 1a shows the variation of electrical resistivity with temperature for several electrolytes. The resistivity results obtained here on 85% phosphoric acid agree with literature values (15). With the exception of the 50% aqueous solution of methane disulfonic acid, all the electrolytes tested here have higher resistivity than 85% phosphoric acid. In some of the tests, the temperature was kept below 100°C to minimize the loss of water. In Figure 1b, log conductivity is plotted versus 1/T.

The straight lines shown in Figure 1b are the least squares correlations of the data. Table 2 lists, for each electrolyte, the straight line equation, the correlation coefficient and the temperature range over which the measurements were taken.

3.3 Vapor Pressure Measurements

The objective of the vapor pressure measurements is to find out whether appreciable quantities of an electrolyte will be lost by evaporation when it is used at 135°C. To achieve this objective, it will be sufficient to show that the vapor pressure of various electrolytes at 135°C is below an acceptable minimum, by comparison with water: we expect desirable vapor pressures to be 1 torr or less.

There are a number of methods (16) for measuring the saturated vapor pressure of a liquid. These include (i) the inclined piston method, (ii) gas saturation method, (iii) isoteniscope method, . . . etc. The essential requirements of a satisfactory technique for vapor pressure measurement are as follows:

(i) The measurable parameter should be directly related to the vapor pressure.
(ii) The measurable parameter should be independent of the type of vapor.
(iii) There should be no sourse of build-in errors.
(iv) The system should attain equilibrium rapidly.

TABLE 2

Least Squares Correlations of the Data of Log (Conductivity) Versus Reciprocal of Absolute Temperature for Some Electrolytes

Compound[†]	Equation[*]	Correlation Coefficient	Temperature Range, °C
$C_6H_5SO_3H$	$\log \kappa = 1.82 - 1.28 \times 10^3/T$	0.98	48-136
$CH_2(SO_3H)_2$(50%)	$\log \kappa = 0.68 - 0.351 \times 10^3/T$	0.95	23-97
CCl_3CO_2H(70%)	$\log \kappa = 0.48 - 0.253 \times 10^3/T$	0.84	23-81
CCl_3CO_2H(90%)	$\log \kappa = 1.57 - 0.453 \times 10^3/T$	0.98	24-126[+]
$C_2F_5CO_2H$(90%)	$\log \kappa = -1.97 - 0.165 \times 10^3/T$	0.81	24-71
$CF_3SO_3H \cdot H_2O$	$\log \kappa = 1.00 - 0.835 \times 10^3/T$	1.00	29-138
H_3PO_4(85%)	$\log \kappa = 1.28 - 0.702 \times 10^3/T$	0.95	23-138
CH_3SO_3H	$\log \kappa = -0.39 - 0.388 \times 10^3/T$	0.95	30-135

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[*] κ is the conductivity of electrolyte.

[+] Hysteresis occurred due to loss of water. The correlation is based on the low temperature results.

[†] The concentrations are in wt.% in an aqueous solution.

It is desirable that several measurements can be made without dismantling the apparatus. Of course, the residual vapor pressures from the vacuum pump, stopcock grease, other fluids of the system, etc. must be negligible.

With these requirements in mind, we have selected the isoteniscope technique for measuring the vapor pressure. The apparatus consists simply of a U-tube manometer containing a "non-volatile" liquid. One arm of the U-tube is connected to a trapped quantity of the electrolyte and the other arm to a system capable of measuring the pressure with the required precision. When the level of the non-volatile isoteniscope fluid is the same in the two arms of the U-tube, then the measured pressure equals the vapor pressure of the entrapped liquid. The test substance is cooled to give a low vapor pressure, trapped air pumped out to a sufficiently high vacuum, and the test material closed off from the rest of the system by pouring the oil into the U-tube. The test substance is heated, and air leaked into the other arm of the U-tube to keep the pressures equal on both sides. At equilibrium at a given temperature, the air pressure is measured with a McCleod gauge.

The only vapors with which it cannot be used are those soluble in the U-tube fluid. This problem along with the pressure contributed by the vapor of the U-tube fluid, can be controlled by proper choice of the fluid. The equilibrium is reached fairly rapidly, and repeated measurements are easily made. The isoteniscope system is shown in Figure 2 which also includes a cathetometer to enable a precise determination of the level of the isoteniscope fluid in the U-tube.

The McLeod gauge is graduated to read pressures from 25 mm down to 0.001 mm Hg. Vacuum is obtained with a duo-seal vacuum pump. The isoteniscope is connected to the vacuum system by an o-ring joint. The fluid in the null manometer N is a silicon oil (Dow Corning 704 diffusion pump). It isolates the electrolyte in the sample container, and also acts as the fluid for the pressure equalizing manometer. The vapor pressure of this fluid is reported to be 10^{-3} torr at 135°C (17). Before the final design of the isoteniscope was achieved, it was found necessary to replace this fluid with Hg. The results so obtained were corrected for the vapor pressure and agreed with those obtained using the silicon oil.

The dependence of saturated vapor pressure on temperature is given by the integrated form of the Claussius-Clapeyron equation

$$\log(P/P_o) = \frac{\Delta H_{vap}}{2.3R}\left[\frac{1}{T} - \frac{1}{T_b}\right] \qquad (1)$$

where ΔH_{vap} is the heat of vaporization in cal/mole, which is assumed to be constant over a certain range of temperature, P is the electrolyte vapor pressure at T°K, P_o is the standard state pressure and T_b is the boiling point of the electrolyte at the standard state pressure. Consequently a linear relationship is expected between log P and the reciprocal of absolute temperature.

The test procedure is as follows: the isoteniscope and the sample holder are thoroughly washed and flame-dried with a heat gun. The silicon oil is then placed in the null manometer through valve V_6. The electrolyte is then placed in the sample holder and the latter secured to the isoteniscope.

The next phase involves degassing both the test sample and the silicon oil. This was done by alternately immersing the sample holder and null manometer in a cold bath while pumping down the system, and letting these two compartments warm up to room temperature with valve V_4 closed. Liquid nitrogen was used for cooling the sample; dry ice/acetone was used for the null manometer oil. Valves V_5 and V_6 were manipulated to ensure that both sample and manometer oil are adequately out-gassed. This is indicated by a constant pressure reading for two consecutive de-gassing cycles, which also served as the background pressure. A pressure reading is taken after the levels of the U-tube oil have been equalized. With the cathetometer, the levels can be adjusted precisely. Equalizing of the levels is done by admitting an appropriate amount of air through the Drierite-needle-valve inlet into the system, or by pumping out more air from the system depending on the relative positions of the oil levels in the U-tube.

Figure 3 shows the variation of vapor pressure of benzoic acid with temperature as measured with the apparatus in Figure 2. The straight lines show the literature values (18). The heat of vaporization is found to be 16.3K cal/mole, which is in agreement with the literature value.

Figure 4 shows the corresponding plots for benzene sulfonic acid, both 10% aqueous solution and anhydrous pentafluoropropanoic acid and trichloracetic acid. The results satisfactorily fit straight lines over the studied range of temperatures. Table 2 lists the values of ΔH_{vap}. for various electrolytes calculated according to equation 1 and the temperature range over which the measurements were taken.

The table also includes the calculated (via equation 1) and the literature values of boiling points at 1 atmosphere, the literature values of ΔH_{vap} whenever available and the vapor pressure at 135°C.

3.4 Electrochemical Measurements:

3.4.1 Gas diffusion electrodes:

The porous gas diffusion electrodes were made from a mix of platinum black (Fisher) with Teflon dispersion (Dupont 30, containing 59-61% solids, sp gr 0.6-0.9g Teflon/mℓ) diluted 10 times with distilled water, in approximate proportions of 10/1.5 of platinum-black to Teflon by weight, spread uniformly on a 45 mesh platinum screen. The mix was made to give a homogeneous paste, and the amount of Teflon stated above is not exact. This was pressed at 18,000 psi for 2 min., dried at 50°C for 1 hr., taken to 350°C over 5 min. and sintered for 2 min. at 350°C. After cooling, the electrode was rinsed with pure water and redried. The cell used in gas diffusion electrode tests is shown in Figure (5).

The counter electrode is separated by a glass frit from the working electrode compartment to prevent contamination of the electrolyte by the products of the reactions occuring at the counter electrode. The reference electrode is the dynamic hydrogen electode, DHE (19). In addition to measuring the potential near the electrode usrface, the extended Luggin capillary effectively prevents the mixing of the electrolytes of the working and reference electrode compartments.

SUMMARY OF VAPOR PRESSURE RESULTS

ELECTROLYTE	FORMULA	b.p. (°C), Tb		ΔH_{vap} (KCal/mole)		P, mm-Hg at 135°C
		CALC.	LIT (18)	CALC	LIT(18)	
Benzoic Acid	$C_6H_5CO_2H$	246	249	16·3	16·29	10.3
Benzene sulfonic acid-hydrate	$C_6H_5SO_3H \cdot 1.5H_2O$	174	d at 100	12.4	-	209.0
Pentafluoropropanoic Acid; an 90 wt.% aqueous solution	$C_2F_5CO_2H$	253	-	4.9	-	194.7
Pentafluoropropanoic Acid; anhydrous		132	96	7.2	-	815.6
Tri-chloroacetic Acid	$CCl_3 \cdot CO_2H$	185.2	196	10.9	13·8	173.6

The design of the porous gas-diffusion electrode holder is essentially the same as used before for hydrogen oxidation in sulfuric acid (20), shown in Figure 6. The main components of the holder are: (i) top part: This is a cylinderical piece of Teflon (1" x 1/2") with a bore drilled along its axis. A narrow hole is drilled off center through its length to accommodate a platinum wire which is used as contact to the gas diffusion electrode. The end of this top part is threaded to give a tight screw fit to the similarly threaded bottom part, (ii) two concentric glass tubes; the inner is gas inlet and the outer is outlet for unconsumed gas. The outer tube is tight-fitted in the top part of the holder, and (iii) bottom part which is also a cylinderical piece of Teflon (5/8" x 5/8"). This is threaded at one end to fit tightly on the threaded end of the top part. The other end of this bottom part is machined to accommodate the porous gas diffusion electrode and to expose only a certain area of it (1/4" diameter) to the electrolyte.

The organic electrolytes were used as supplied. The commercial reagent grade H_3PO_4 has been shown to contain significant amounts of phosphorous acid (5). It was purified by refluxing with H_2O_2 (20) and the final acid concentration evaluated by determining the density (21).

All the electrochemical measurements were obtained using the potentiostatic technique. The ohmic potential drop between the tip of the Luggin capillary and the electrode surface was evaluated using an interrupter circuit and the blanked-out portion of the voltage-time trace on an oscelloscope.

3.4.2 Current-Potential Curves for Gas Diffusion Electrode

Due to the experimental difficulties encountered with obtaining reproducible results from phosphoric acid, and the differences in the properties of various electrodes, a comparison technique has been followed. Before each electrolyte was run at the desired temperature on a certain electrode, the electrode was tested with H_2 fuel in 1N H_2SO_4 at 25°C. The ratio of the limiting current obtained in the particular electrolyte to that obtained in sulfuric acid is taken as a measure of the efficiency of the electrolyte. This ratio was found to be about 1.5 for 85% H_3PO_4 at 135°C, compared to sulfuric acid at 25°C. Figure 7 shows the current-potential relations obtained on the same electrode (catalyst loading 133 mg/cm^2 and porosity of 0.47) in 1 NH_2SO_4 at 25°C, and in 85% H_3PO_4 at 135°C using H_2 as fuel. The limiting current was taken to be the current at 500mv versus the DHE. The experimental results obtained on the various electrolytes are presented below along with the relevant experimental observations. All the electrolytes were tested with H_2 and some were also tested with H_2 - 3%CO. Figure 8 summarizes the results obtained on various electrolytes.

Pentafluoropropanoic acid $C_2F_5CO_2H$; 90 wt%

The ratio of $i_L/i_L(1NH_2SO_4)$ at 25°C is $\simeq 10^{-3}$. The resistivity of this solution at 25°C is 335Ωcm. The electrolyte underwent excessive polymerization upon heating to 50°C. This electrolyte also had an undesirably high vapor pressure (see Figure 4).

Trichloroacetic acid $CCl_3 \cdot CO_2H$:

This electrolyte had to be diluted with water to give reasonable resistivity. The measured resistivities were 1240 and 23 Ω cm at 25°C for the 90% and 70 wt% acid solutions, respectively. Figure 8 shows the current-potential relations obtained on the 70% acid solution at 25°C. The ratio of limiting currents is 0.22. It was noticed that chlorine gas evolved upon heating this electrolyte. The acid itself (without dilution) also has an excessively high vapor pressure (see Figure 4) and it is known to be hygroscopic.

Chloro-difluoroacetic acid $ClF_2 \cdot C \cdot CO_2H$

Measurements were done on this acid at 23 and 50°C, see Figure 8 The ratio of limiting currents was less than 10^{-3}. The decomposition of the acid leading to production of chlorine was also evident. The resistivities were 168 and 140 Ω cm at 23 and 50°C, respectively.

Benzene sulfonic acid hydrate $C_6H_5SO_3H \cdot 1.5H_2O$:

At 60°C the limiting current ratio is 0.06, see Figure 8. The acid resistivity is 108 Ω cm at 60°C and the vapor pressure is fairly high. The acid decomposes turning the light brown color into a black color upon heating to higher temperatures in presence of the Pt-black electrode.

Methane disulfonic acid (50% aqueous) $CH_2(SO_3H)_2$:

Figure 9 shows the results obtained in this acid at two different temperatures for H_2 fuel. The limiting current ratios are: 0.33 and 0.47 at 27 and 54°C, respectively. The electrical resistivities were quite low; 3 and 2.5 Ω cm at 27 and 54°C, respectively. Measurement at 80°C gave irreproducible results due to the excessive loss of water.

The nonaqueous acid is a very hygroscopic material which boils at 220°C. The only commercially available form is the 50% aqueous solution. This obviously is not a good electrolyte at high temperature. When tested for propane oxidation at 50°C, it performed very poorly.

Benzoic acid C_6H_5COOH

Although this acid has a reasonable vapor pressure, it was ruled out because of its extremely high resistivity; the values obtained were 2.1×10^7, 2.0×10^7 and 1.9×10^7 Ω cm at 135, 141 and 153°C. respectively. The acid is also insoluble in water.

Methane sulfonic acid CH_3SO_3H:

This electrolyte was chosen on the basis of its low vapor pressure, 10mm Hg at 167°C(22), and relatively low resistivity of 66 Ω cm at 135°C. This electrolyte is also available in reagent (>98%) and practical (>95%) grades; the latter is much cheaper than the former. Figure 10 shows the results obtained on the practical grade acid for both H_2 and H_2-CO fuels at 50, 90 and 135°C. The limiting current ratios for H_2 are 0.14, 0.09 and 0.55, respectively. Similar results have been obtained with H_2-CO.

The presence of CO poisons the electrode surface and causes continuous decrease in the current. The above results (on H_2-CO) were obtained by returning to open circuit after each current and potential reading; the former was recorded before the start of the excessive drift.

The value of 0.55 at 135°C seems low in view of the fact that the limiting current at a planar rde in MSA at 135°C is about ten times greater than that obtainable in 1 N H_2SO_4 at 25°C (c.f. under rotating disk electrode).

The above results also suggest that the oxidation of H_2 and H_2-CO in MSA is strongly temperature dependent. This means that a slight temperature increase should have a significant effect on the performance.

3.4.3 Rotating disc electrodes

There are several reasons for using the rotating disk electrode technique in this work:

(i) It clearly distinguished between chemical and mass transfer limited reactions.

(ii) It can be used to indicate whether the poor performance of an electrolyte at the Teflon-bonded porous gas-diffusion electrodes is due to wetting of Teflon or due to the chemical limitations of the reaction rate.

(iii) It provides for well-defined and reproducible hydrodynamic conditions at the electrode surface regardless of the electrolyte or the fuel gas used.

For those reactions which are mass-transport limited, it is possible to obtain an estimate of the solubility-diffusivity product of the fuel gas in the particular electrolyte. This is obtainable from the Levich equation(23)

$$i_L = 0.62\ nF\ D^{2/3}\omega^{1/2}\nu^{-1/6}c \qquad (2)$$

where i_L is the mass-transfer limiting current density, n is the number of electrons, F is the Faraday constant, D is the diffusion coefficient, $\omega = 2\pi N$ where N is the number of rotations per second, ν is the kinematic viscosity and c is the equilibrium concentration of the fuel gas in the electrolyte at a certain temperature. There are several modifications to this equation (24-26). At the relatively high rotation speeds used here, such corrections become insignificant. In order to obtain the product $cD^{2/3}$ from the above equation, the kinematic viscosity ν must be known. This is available in the literature for phosphoric acid (15) and can be measured for the other electrolytes. If the solubility of the fuel gas is measured, equation (2) can be used to calculate the diffusivity D. The product of the diffusivity-solubility can then be calculated. It is this product which is the basis of comparison among the various electrolytes. For reactions where the limiting current proves to be independent of rotation speed, the results will unequivocally confirm the chemical nature of the limiting current.

Figure 11 shows the final design of the rde. It is made of a stainless steel shaft, a Teflon head to prevent its corrosion in the acid medium and various other parts to ensure good electrical contact and insulation from the motor. Figure 12 shows the electrochemical cell used with the rde.

Phosphoric Acid

Experiments were performed to study the dependence on electrode rotation speed of the hydrogen oxidation rate in 85% H_3PO_4 at 135°C.

The results of hydrogen oxidation in 85% H_3PO_4 at 135°C on a platinized Pt electrode gave poorly defined limiting currents which varied with rotation speed as shown in Figure 13. The limiting currents were taken at a potential of +600 mv DHE. These poorly defined limiting currents may be due to:

(i) The possible failure of the rotating disk to maintain an "infinite lamina" at the electrode surface, in the small cell as required by the Levich theory, or

(ii) chemical rather than mass transfer limitation of the hydrogen oxidation process. This possibility may also explain the low currents obtained at high polarization.

To distinguish between these two possibilities, we performed current-polarization measurements on the following systems:

(a) Hydrogen oxidation in 1N H_2SO_4 at room temperature in the small cell and in a much larger cell, with a diameter about 15 times greater than that of the electrode. This reaction is known to be mass transfer limited.

(b) The ferrocyanide-ferricyanide redox couple in the small cell and in the large cell at room temperature. This reaction is also known to be a mss-transfer limited.

(c) Hydrogen oxidation in 85% H_3PO_4 at 135°C in the large cell.

It was concluded from these tests that the small cell gave good results which fitted the Levich theory. Therefore the above results suggest that the process of hydrogen oxidation on platinized Pt on 85% H_3PO_4 at 135°C is <u>chemically limited</u>, and that the phosphoric acid poisons the electrode surface.

Methane Sulfonic Acid

Current-potential relations have been measured at various electrode rotation speeds in methane sulfonic acid for the anodic oxidation of H_2 at platinized pt over temperatures from 35 to 135°C. The limiting currents were well defined.

Figure 14 shows the results. A satisfactory straight line fit is obtained between the limiting current and $\omega^{1/2}$ even at relatively low temperatures. This indicates that all the hydrogen that reaches the electrode surface is oxidized, and hence the electorde surface is not poisoned by the electrolyte.

Figure 15 shows the Arrhenius plot of normalized limiling current ($i_L/\omega^{1/2}$) versus 1/T. The points show the mean values obtained at 5 different rotation speeds. The differences between the various points for the same temperature were insignificant. A satisfactory straight line relationship is obtained between 35 and 95°C giving an activation energy ΔH_a=3·5 K cal/mole. This is a value characteristic of diffusion-limited processes. Above 95°C. there is a definite trend of a steeper increase in reaction rate with temperature.

4. FUTURE WORK

4.1 General

As a result of this work, several avenues have been opened for future work in this area. The following is a more specific outline of future work.

4.2 Methane Sulfonic Acid

It is clear that methane sulfonic acid (MSA) is superior to many organic and some inorganic acids as an electrolyte for fuel cell. It is superios to 85% H_3PO_4 in so far as the vapor pressure, thermal stability and inertness towards the electrode material are concerned. It also seems to be superior to other organic acids currently under investigation, namely TFMSA and the 50 wt% methane disulfonic acid. It is less corrosive than the former, does not wet Teflon, and is far less volatile than the latter. Further work on this electrolyte is suggested as follows.

(i) Evaluate its performance for H_2 oxidation at gas diffusion and rotating disk electrodes at temperatures above 135°C on platinized platinum electrodes. There is reason to believe that the performance of this electrolyte increases rapidly with temperature, see above.

(ii) The same as above for both H_2-CO and propane.

(iii) Evaluation of the solubility - diffusivity product for H_2, which is an important engineering parameter. In order to achieve that, the solubility of the gas in the electrolyte and the electrolyte viscosity are to be measured.

(iv) Evaluate the performance of commercial Teflon-bonded gas diffusion electrodes in MSA for the oxidation of H_2, H_2-CO and propane. These electrodes have a Pt loading of 2 mg/cm^2.

(v) Test the effect of MSA on the reduction of oxygen and air. This is necessary since a successful electrolyte must be used for both the anode and cathode Compartments of a fuel cell. Oxygen and air reduction are to be performed for both the rotating disk and gas diffusion electrodes.

4.3 Higher Alkane Sulfonic Acids:

Ethane and n-propane sulfonic acid are known to have lower vapor pressure than the methane analogue of the series. These acids are to be evaluated similarly, especially at high temperatures.

4.4 Screening of Electrolytes:

On the basis of the results to date, we are ruling out the class of halogenated (especially flourinated) alkane carboxylic acids, benzoic, tolueic and salicylic acids. Certain types of aromatic sulfonic acids, e.g., benzene sulfonic acid are also ruled out, see below.

The tests performed on the sulfonic acid electrolytes reported here can be repeated on other possible electrolytes, which may result from the literature search. Some electrolytes are already at hand. They are given below along with the justification for each:

(i) Sulfoacetic acid monohydrate, $HO_3S \cdot CH_2 \cdot CO_2 \cdot H \cdot H_2O$:

This is a strong acid, m.p. 84-86 and b.p. 245. Therefore, we expect it to have satisfactory resistivity and vapor pressure at 135°C.

(ii) Methane disulfonic acid:

Since the 50wt% aqueous solution of this electrolyte performed well for H_2 oxidation at 50°C., it seems worthwhile to continue working on it with the objective of finding the optimaium acid concentration where its electrochemical behavior is best and loss of water by evaporation is least.

(iii) Silico-benzoic acid, $C_6H_5 \cdot SiOOH$:

This acid melts at 40-50°C, and boils at 215°C. This makes it considerably different from benzoic acid, and hence its properties may be different e.g. electrical conductivity.

(iv) Other Aromatic Acids:

It is known (27) that the sulfonation of aromatic compounds is generally a reversible process, i.e. certain sulfonic acids are easily hydrolyzed. However, by proper substitution of certain functional groups, the sulfonic acid group can be substantially strengthened. Thus whereas benzene sulfonic acid readily hydrolyzes by heating in water, various di-tri-and tetrabromobenzene sulfonic acids hydrolyze only upon refluxing with concentrated HCl up to 250°C(27). Similarly 3,5-dinitro-4-bromobenzene sulfonic acid is not affected by refluxing with 60% H_2SO_4 whereas the completely brominated compound is hydrolyzed by refluxing with water. There is a great deal of information on this subject in the organic chemistry literature. We have developed the needed guidelines and plan to review the literature in this area for the possible electrolytes. As a beginning, the above two brominated benzene sulfonic acids are to be evaluated.

4.5 Additional Tests:

(i) The above tests do not include a crucial part of electrochemical testing, namely, the completeness of reaction. Accurate testing of faradaic efficiency is an expensive and time consuming process, since it involves long-term mass balance of fuel into the system. However, with a ring-disc electrode one may be able to detect incomplete reaction, quite simply. The ring on the outside of a rotating ring-disc electrode (RRDE) receives a flow of liquid containing products of reaction and if it is swept in potential independently of the disc, it may indicate further electrochemical oxidation of the dissolved partially oxidized reactant.

In long-term tests of 100 hours, carried out on the diffusion electrode system, the fuel leaving the anode is to be passed through a CO_2 collector, to give an estimate of faradaic efficiency. Gas-liquid and high-pressure-liquid chromatography will be used to analyze the electrolyte for unreacted dissolved intermediates such as oxalic acid, formic acid, etc.

(ii) Promising electrolytes should be tested similarly with platinum cathodes using oxygen

(iii) Promising electrolytes should be tested for their effects on common cell materials, such as stainless steel, nickel-plated steel, butyl rubber, neoprene, silicone, epoxy fiberglass, etc., by weight change, optical and electron metallography, etc., if necessary.

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Figure Captions

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(4) Benzene sulfonic acid hydrate, $C_6H_5SO_3H \cdot 1.5H_2O$ at 60°C, $i_L(1NH_2SO_4)$ is 200 mA cm^{-2};

(5) Trichloroacetic acid (70wt% aqueous solution) at 27°C, $i_L(1NH_2SO_4)$ is 284 mA cm^{-2}.

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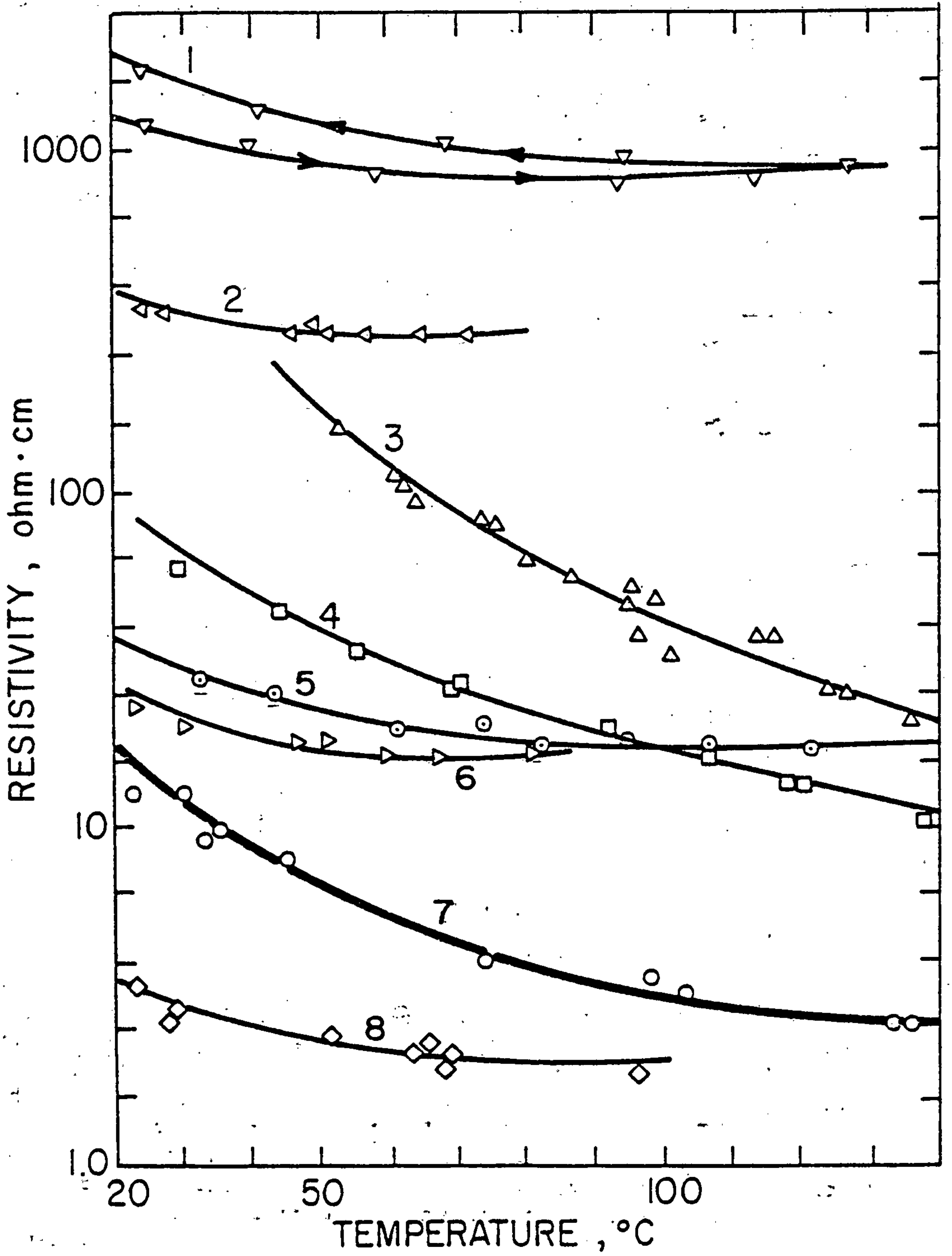

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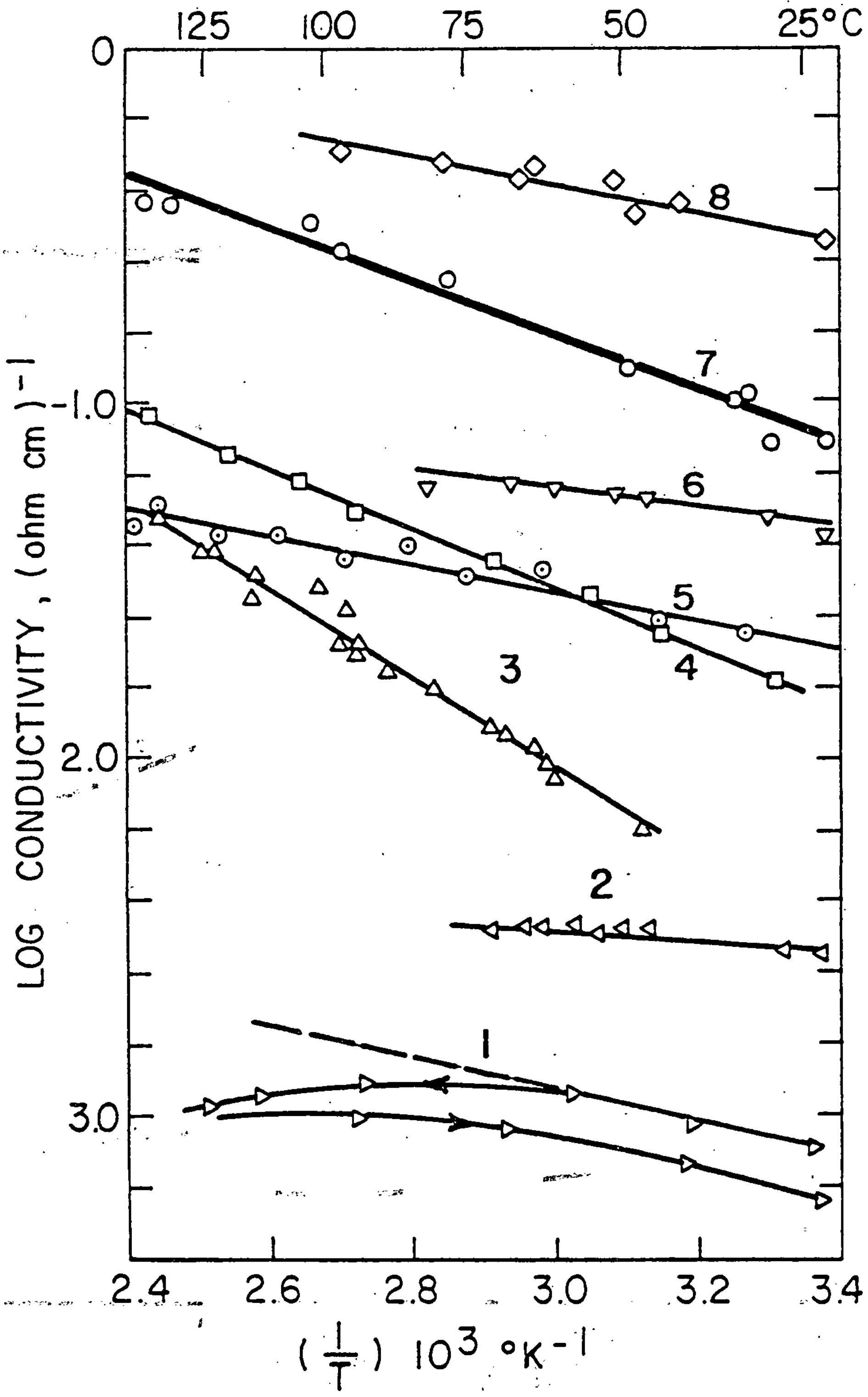

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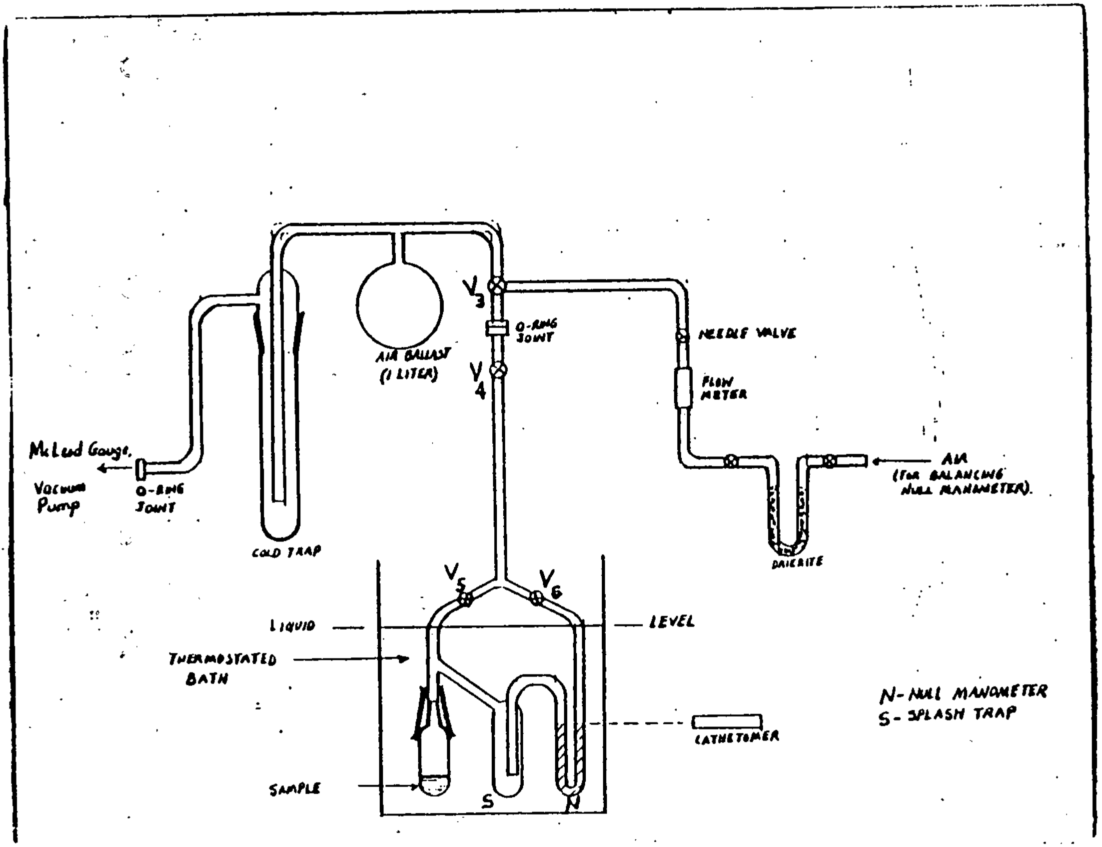

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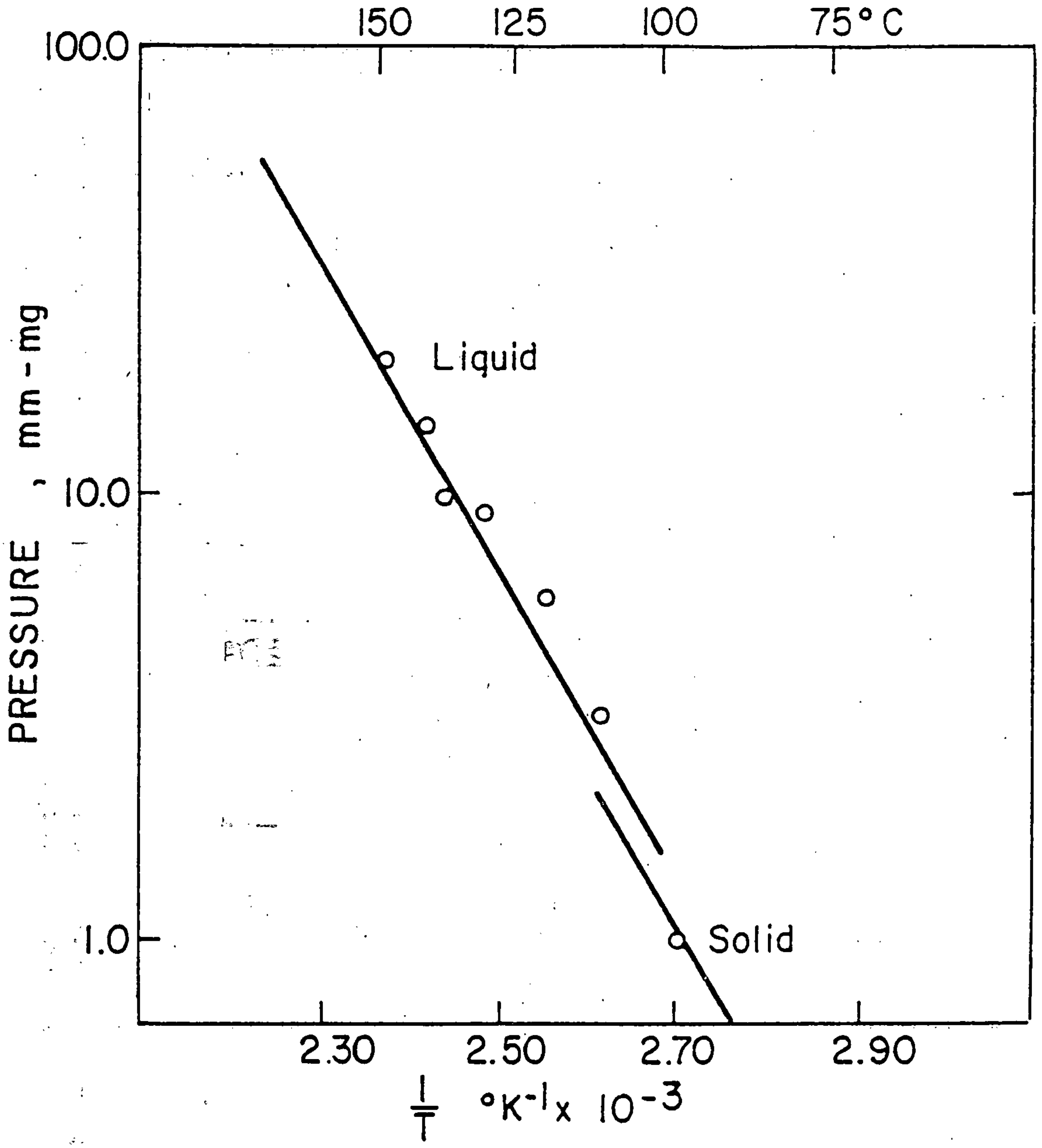

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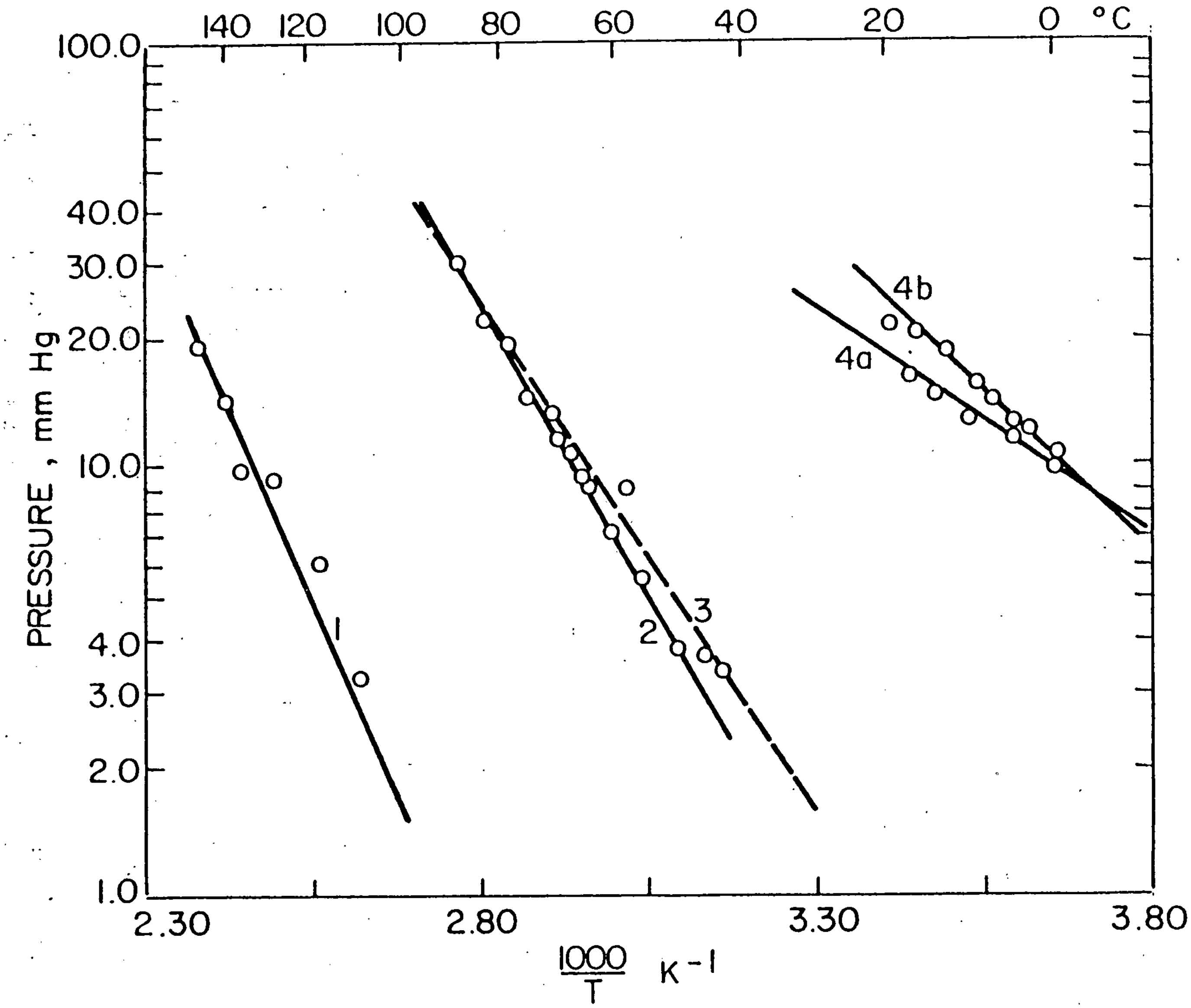

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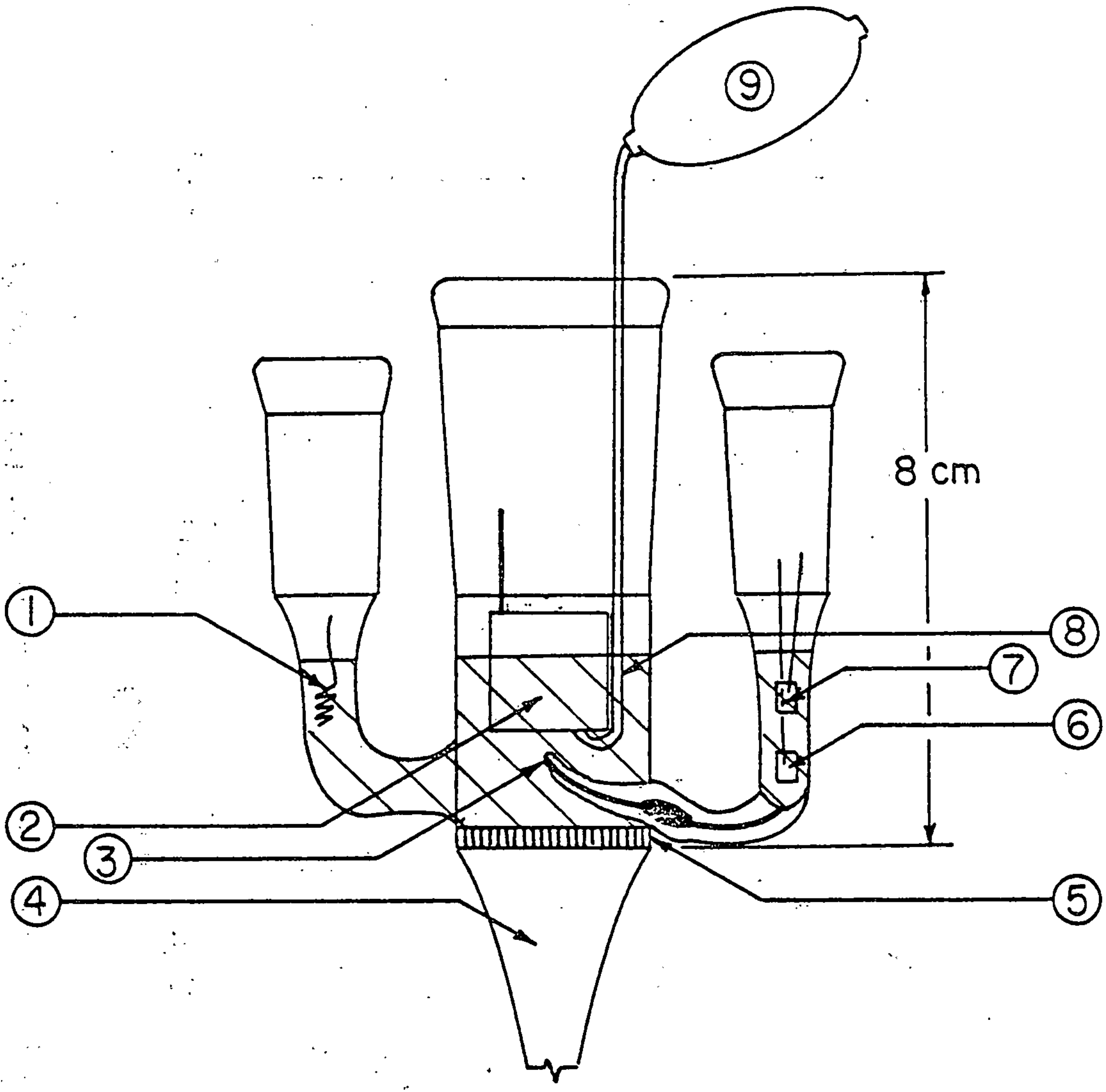

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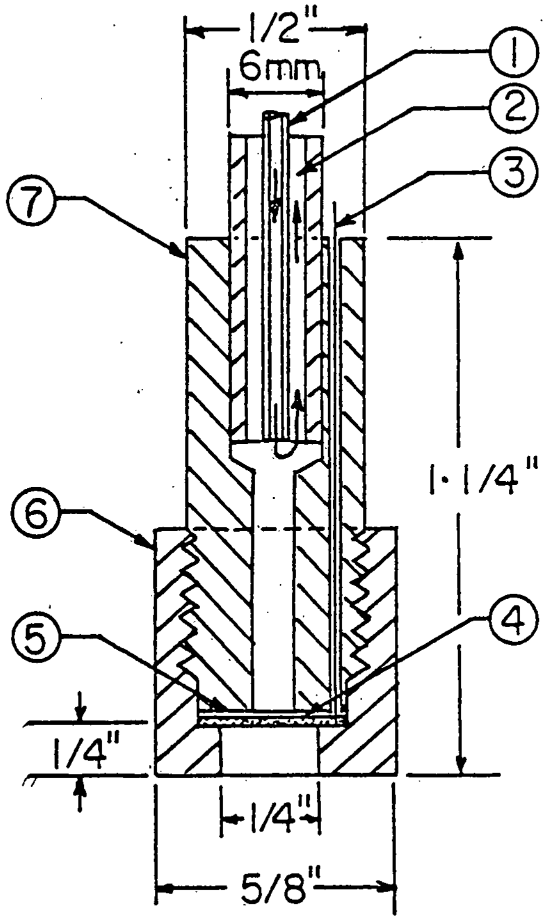

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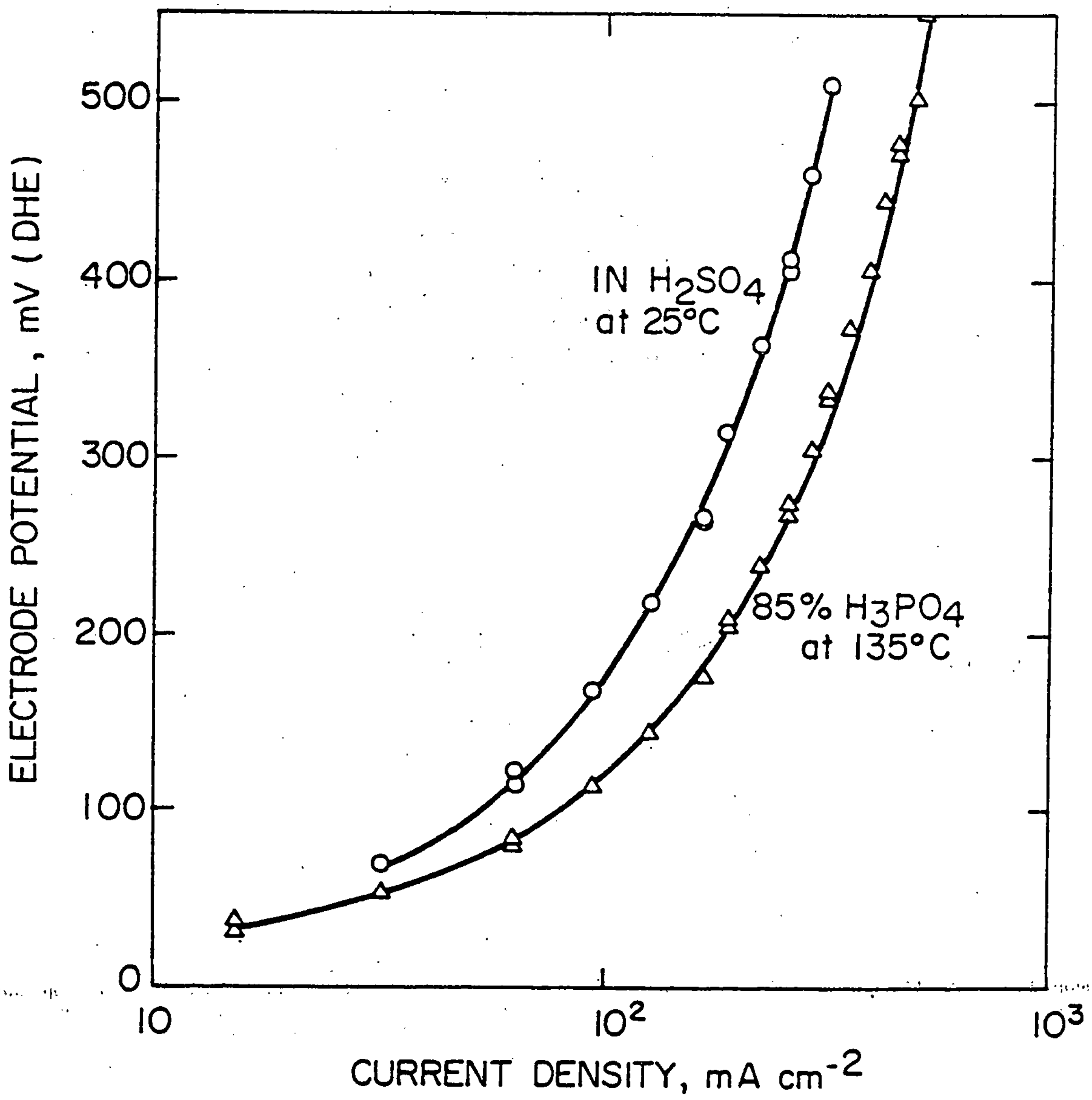

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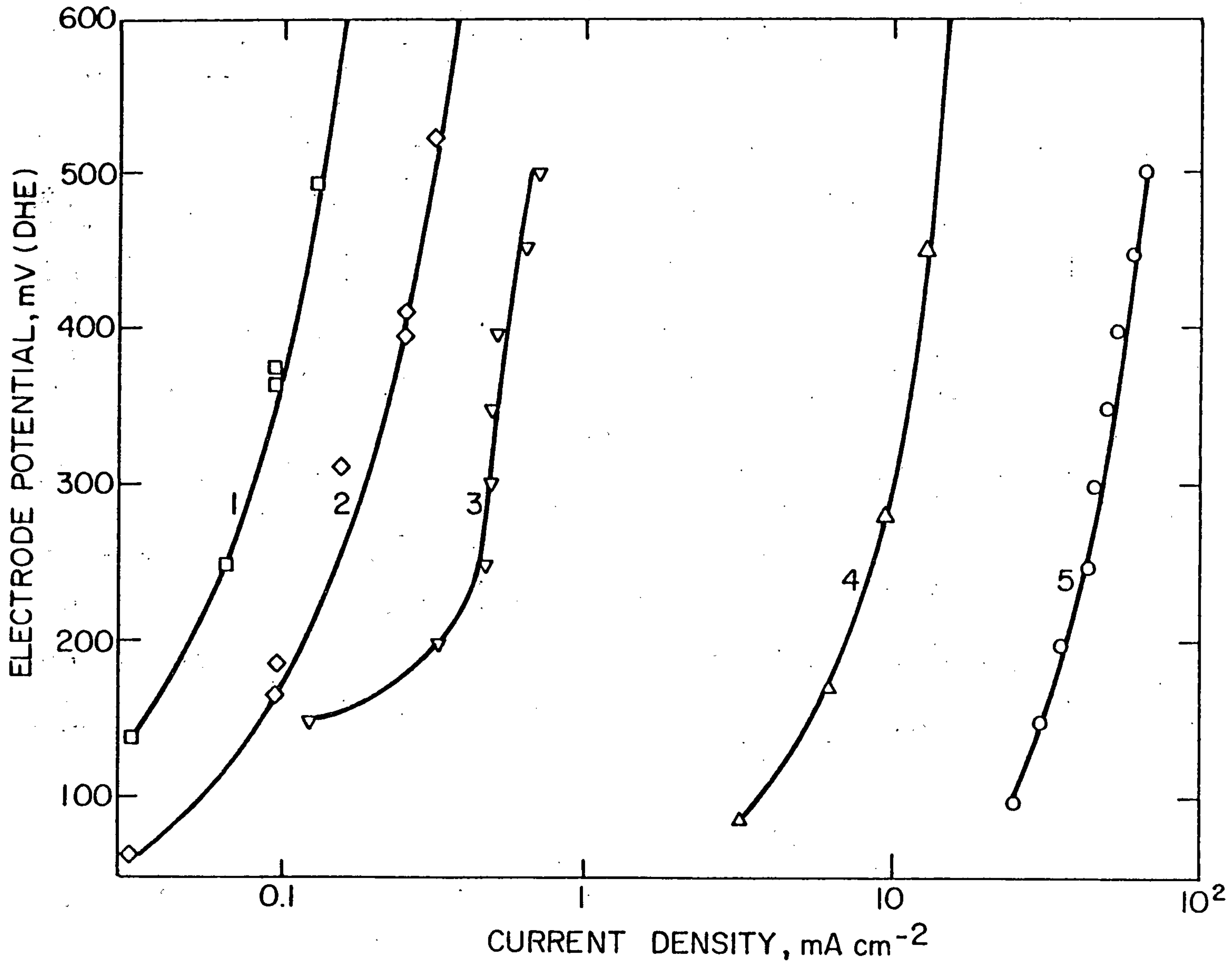

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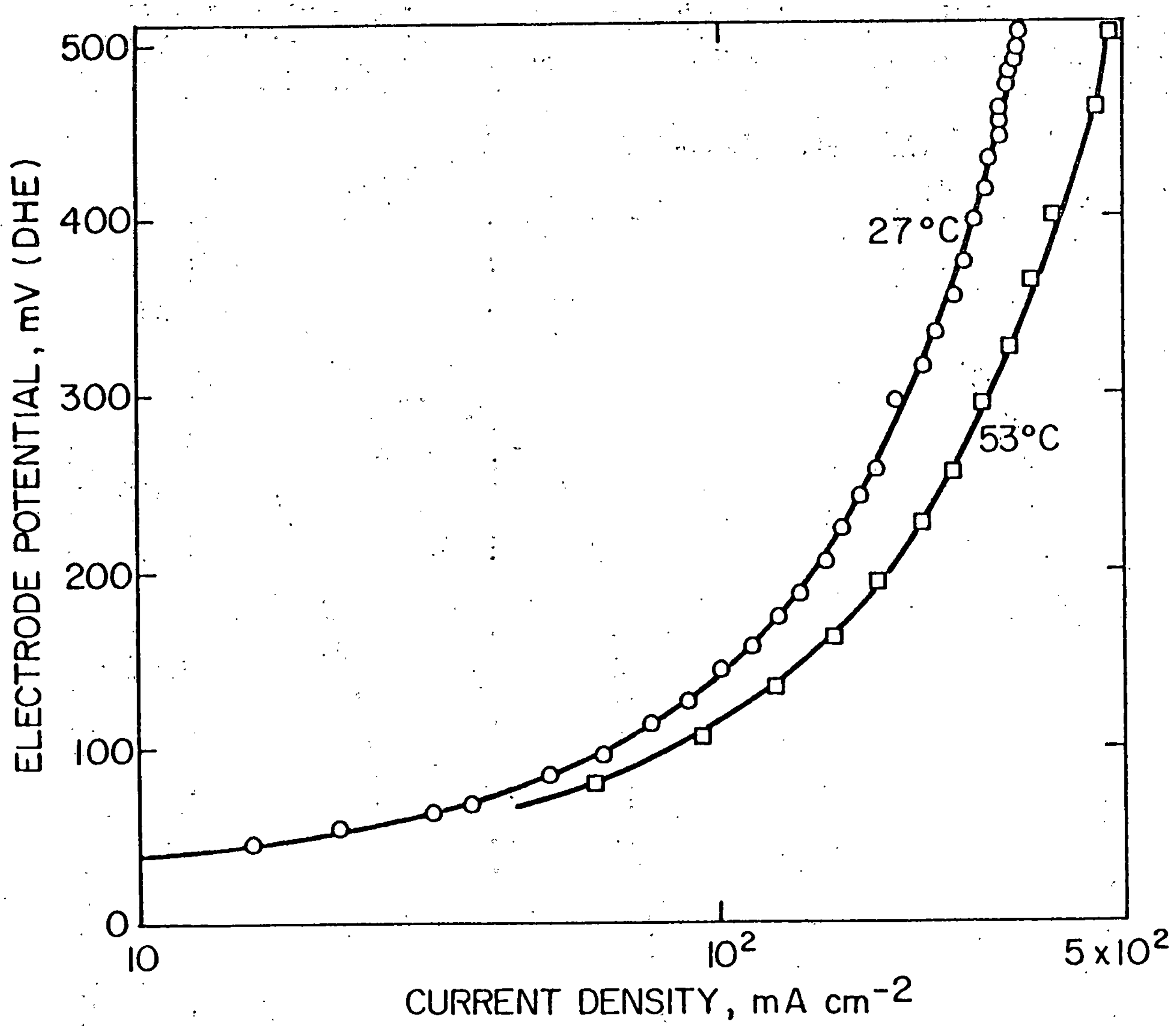

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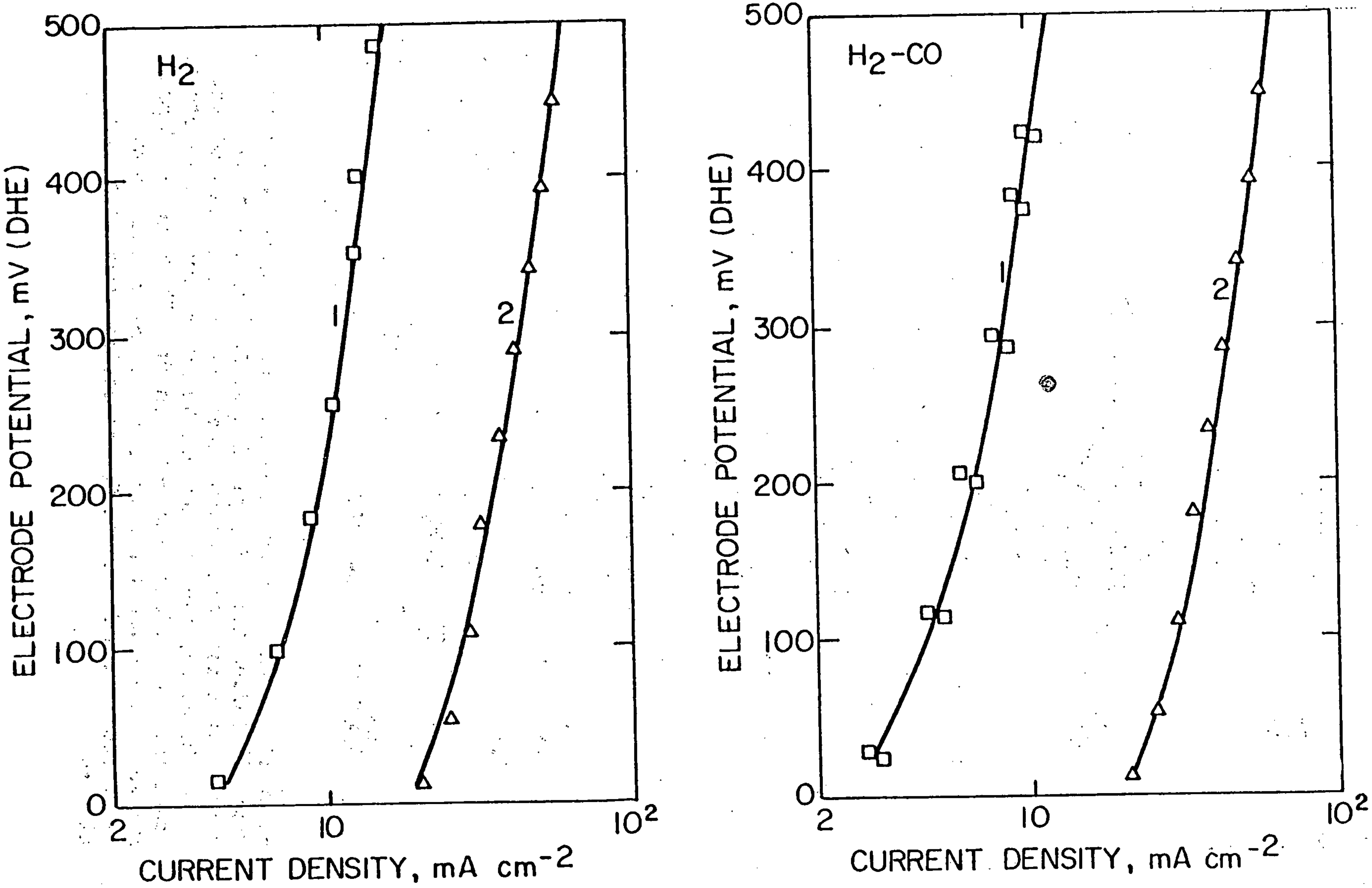

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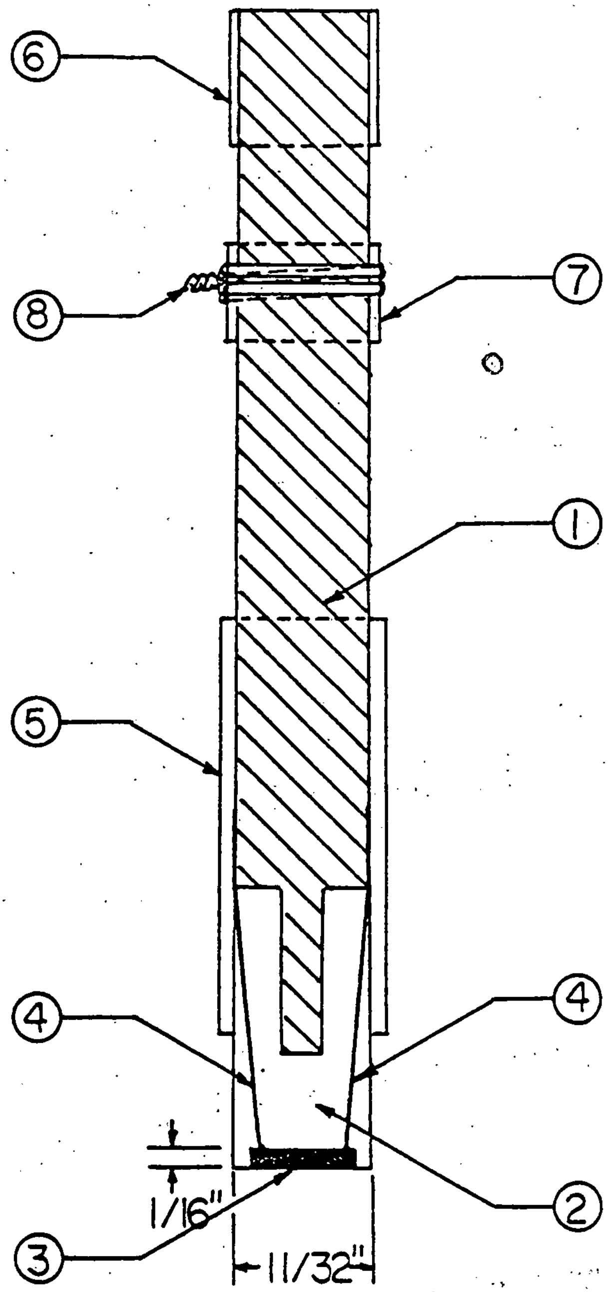

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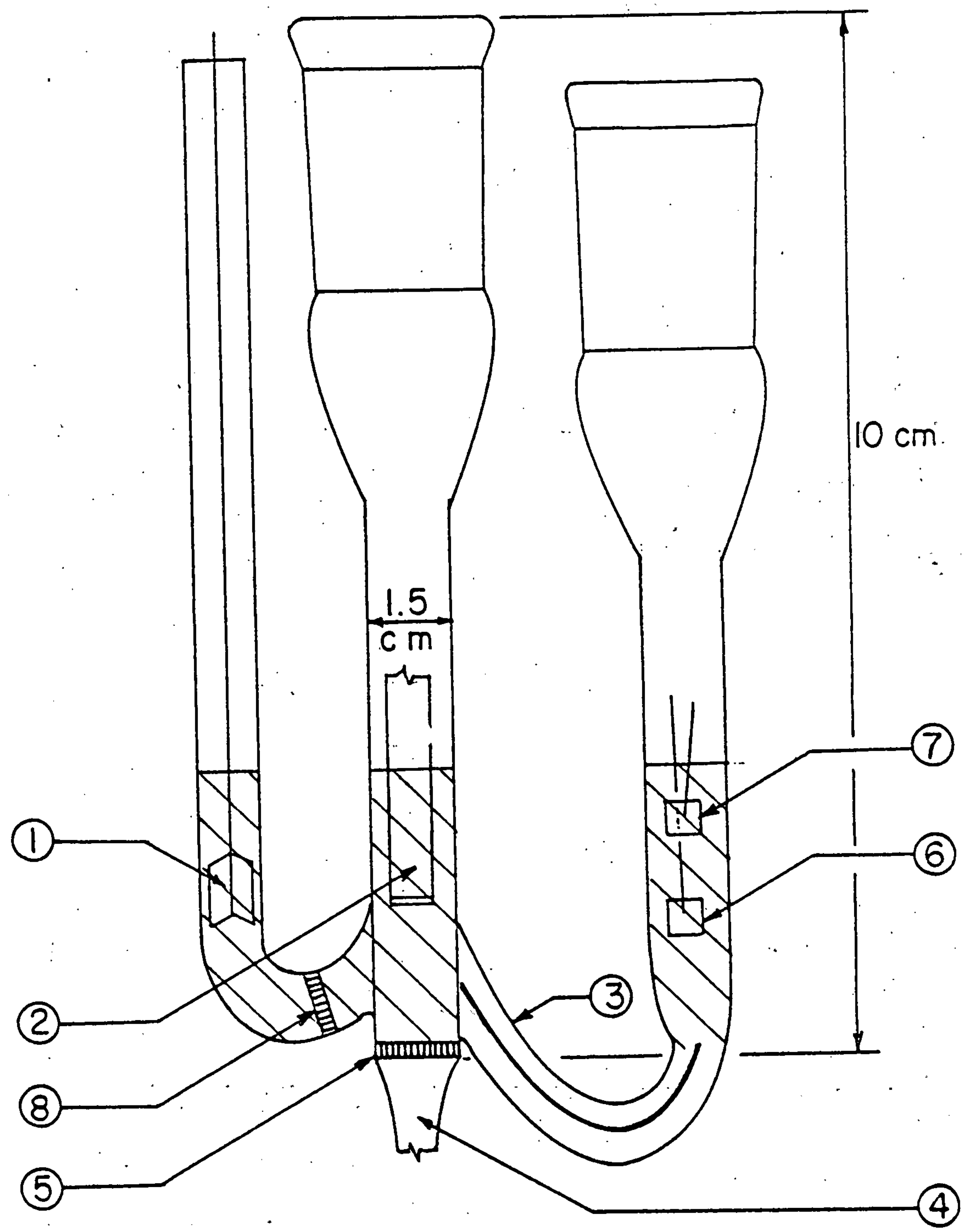

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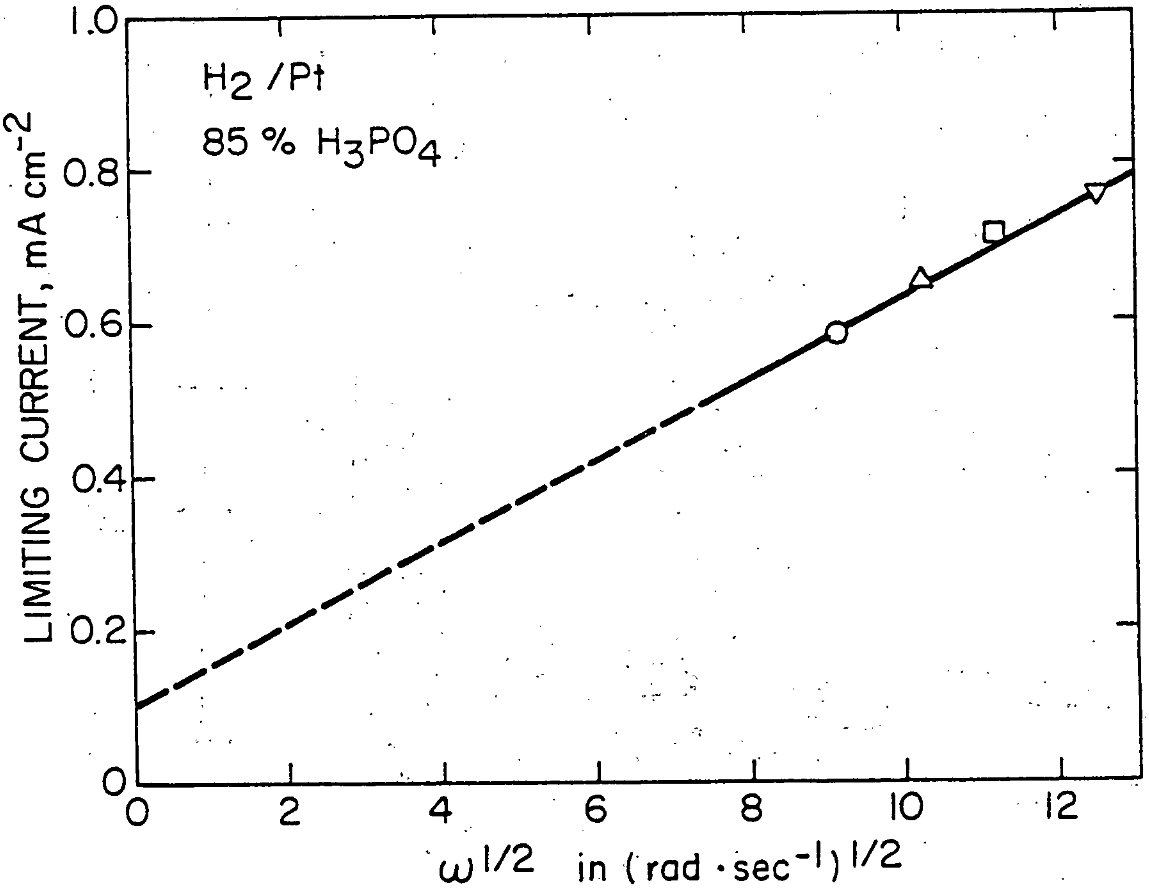

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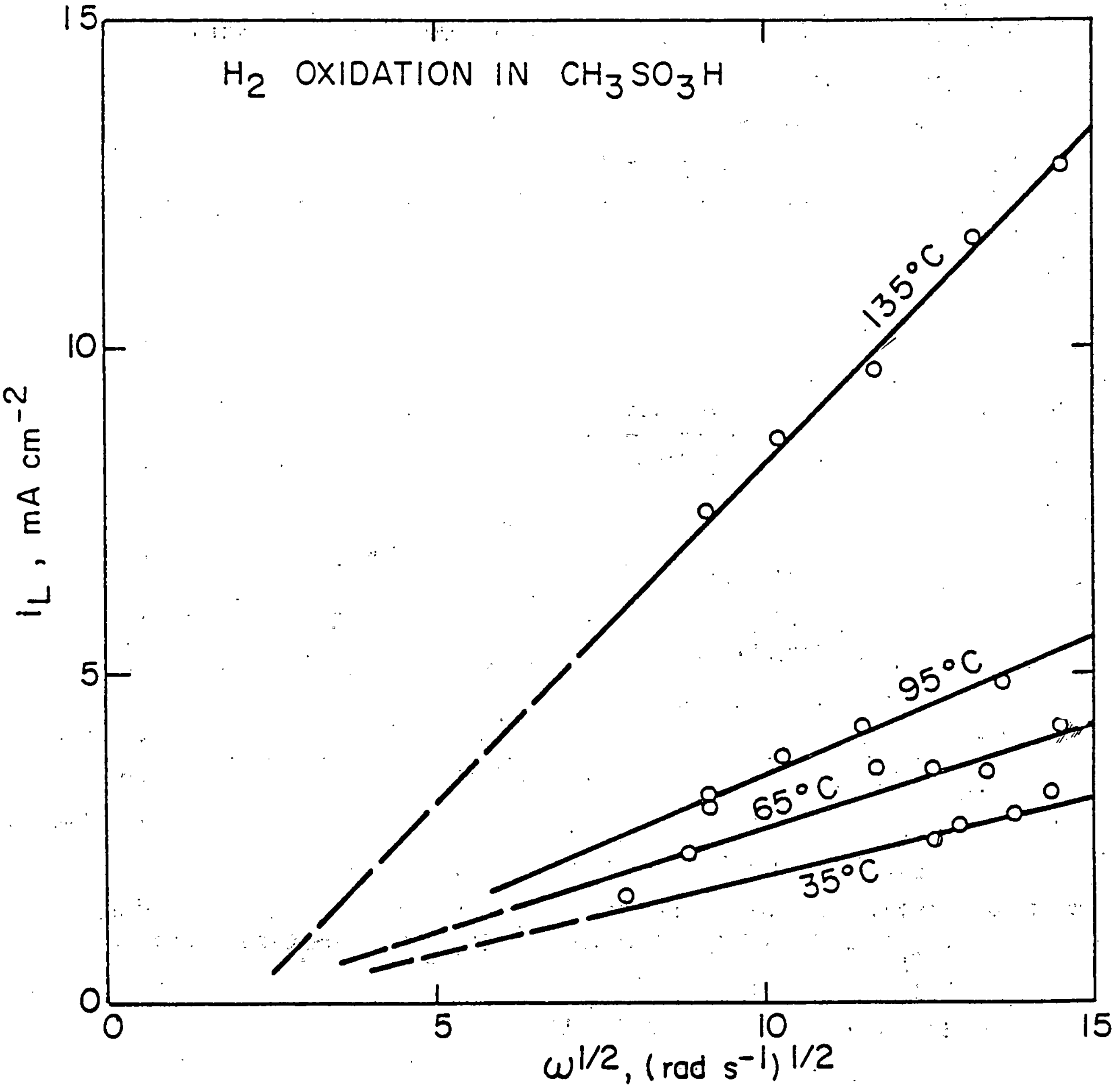

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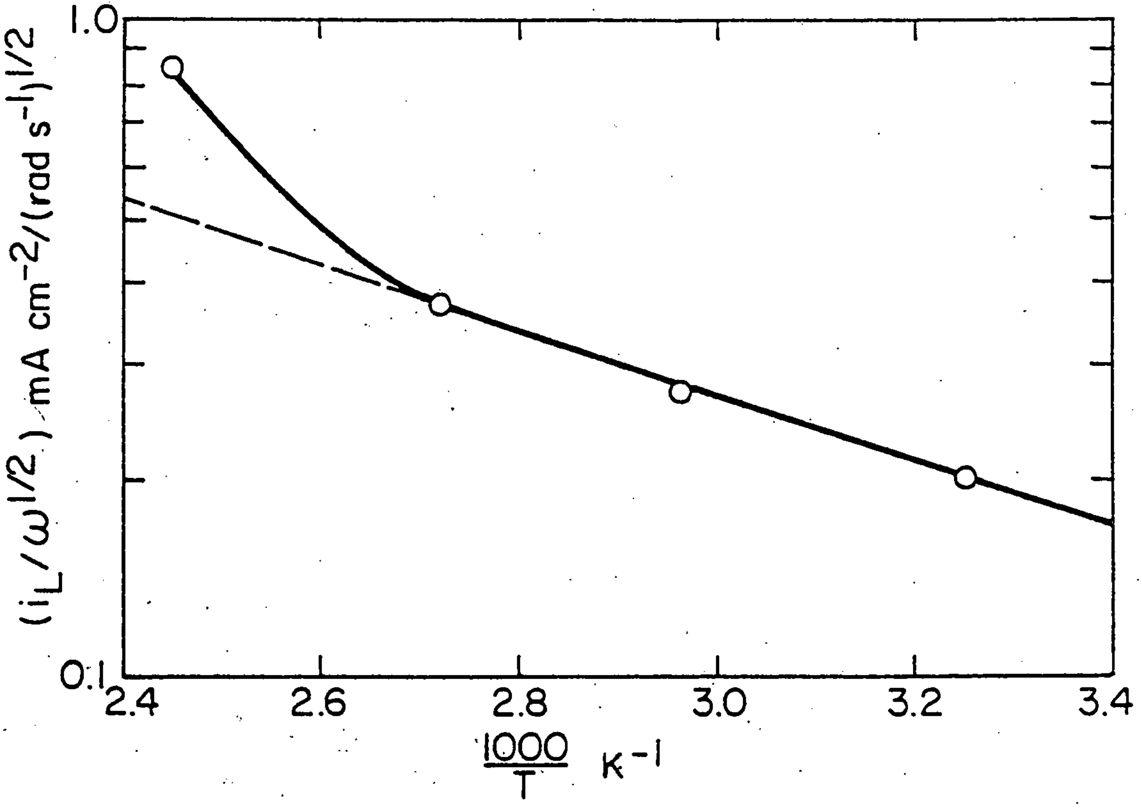

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