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First Partial Report

on

Study of Methods for Converting Latent Heat Energy Directly into Electrical Energy.

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON DC

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Prepared by:

Ross Gunn, Principal Physicist,
Technical Adviser.

Approved by:

H.M. Cooley, Captain, U.S.N.,
Director.

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ABSTRACT

An investigation of the possible methods of converting latent heat energy directly into electrical energy has been made. A "fuel cell" deriving its energy from the heat of combustion of hydrogen and oxygen was studied in some detail. Employing a newly developed electrode and operating the cell at moderate pressures and temperatures, a maintained output of about 50 milliamperes per square centimeter of electrode area has been obtained. The terminal potential of the cell under such a load approximates 0.75 volts

AUTHORIZATION

1. This problem is authorized by Bureau of Engineering letter NP14(5-6-W8) of 12 July 1935.

STATEMENT OF PROBLEM

2. The object of this investigation is to examine the important possibility of developing an efficient and practical means for converting the energy of combustion of a fuel directly into electrical energy, without the use of the usual prime movers and electrical generators. Thus, by avoiding the use of heat engines, thermodynamic efficiencies as high as 70 to 90 percent may be attained even at practical combustion rates. The simplification of the necessary equipment is of considerable additional importance.

KNOWN FACTS BEARING ON THE PROBLEM

3. Because of the low thermodynamic efficiencies of all types of heat engines, several investigators have attempted to obtain electricity directly by the electrochemical combustion of the fuel gases and by the employment of various other thermo-electrical effects. Several more or less obvious methods of approach are possible which employ thermocouples or heated conductors having a high Thompson coefficient and certain forms of photo cells. With the possible exception of the latter, further work on these devices does not appear warranted because of their known very low thermodynamic efficiencies which in no case would probably exceed 1 percent. The most promising method of attack is to make use of the heat of combustion of common fuel gases by "burning" them electrically in a suitable fuel cell. The process is somewhat involved and requires that the two elements or compounds that are to be burned must be ionized either in a conducting solution or in a melted electrolyte. These two ionized gases diffusing from their appropriate electrodes form other ions and finally combine chemically and electrically. This results in the migration of electrical charge from one electrode to the other in such a manner as to maintain a potential difference at the cell terminals. The simplest example of this type of combustion cell commonly called "a fuel cell" is due to Grove who, in 1839, immersed platinum electrodes in an acid solution and exposed one of these electrodes to gaseous oxygen while the other was exposed to gaseous hydrogen. It was found as a result of his experiments that the oxygen and hydrogen would dissolve in the electrolyte and "burn" electrically and would produce electric power, but at an <u>exceedingly low rate</u>. This cell has therefore been a scientific curiosity for nearly a century. It has since been established that the rate of combustion depends on the area of contact between (a) the platinum electrode, (b) the electrolyte, and (c) the area exposed to the gas. Some improvements have been made in the cell, such as the so-called Mond-Langer cell, but its rate of electrical production is still insufficient to be of any practical interest. It has been the universal practice to employ platinum or palladium black on the electrodes to promote the ionization of the gases supplied and dissolved in the electrolyte of the cell. Finally, it is known that the mass per mole of the common gases is quite small and therefore it is evident that a gaseous type cell would be relatively light compared, for example to the ordinary lead storage cell. The storage of the combustible gases in tanks does not offer any known difficulty.

THEORETICAL CONSIDERATIONS

4. It has been determined that the free energy of formation of liquid water at 25°C from the constituent gases under standard pressure at this temperature is 56,600 calories per gram mole. Since two faradays of electricity are required for the electrolysis of one gram mole of water, the e.m.f. of a hydrogen-oxygen fuel cell at 25°C is

$$E \times 2 \times 96,500 = 4.19 \times 56,600$$
$$E = 1.227 \text{ volts.}$$

Thus, for every pound of hydrogen consumed in such a cell, eight pounds of oxygen will be required and 12,100 ampere-hours of electricity will be delivered. Assuming that a cell could be made to convert chemical energy to electrical energy with an efficiency of 70 percent, this weight of fuel gases will furnish 10.4 kw-hours of electricity. Similar calculations show that the e.m.f. of a reversible carbon-oxygen fuel cell at 25°C would be 1.05 volts.

5. The nature of the electrochemical combustion of hydrogen and oxygen is somewhat as follows: Hydrogen at the anode forms the hydrogen ion; oxygen combines with a water molecule at the cathode and ionizes to form the hydroxyl ion. The combination of these two ions results in the formation of water. As each ion passes into the electrolyte, an appropriate charge is removed from the electrode which thus becomes electrically charged.

6. Several facts concerning the electrode processes may be enumerated. The ionization of the gases takes place only at catalytic surfaces with any degree of ease. Such surfaces are the extended or "black" forms of platinum, palladium, rhodium and iridium. Even the electrolyte is a minor catalyst to the reaction. If the electrode process is to be rapid, one must have fuel gas, electrolyte, electrode, and catalyst in very intimate contact. The effect of pressure at the electrode cannot be predicted with any certainty. It is known that in general a rise in temperature of 10°C will double the rate of a chemical reaction, though when a catalyst is present, as in the present experiments, this is far from being true under all circumstances. Unfortunately, the present theory of gas electrodes is not at all complete and therefore one is forced to use experimental methods in the study of such electrodes.

NARRATIVE OF ORIGINAL WORK DONE AT THIS LABORATORY ON THE HYDROGEN-OXYGEN FUEL CELL.

(a) Preliminary

7. A model of the Grove cell was set up first because it was simple and offered a chance to investigate the effect of various electrolytes with platinum and palladium electrodes. Following this, experiments were made with electrodes of porous carbon through which were forced the fuel gas, hydrogen, and the oxygen. These so-called diffusion electrodes of carbon treated in different ways were employed in several electrolytes at room temperatures and atmospheric pressure.

(b) High Pressure Experiment

8. A high pressure chamber capable of withstanding several atmospheres was designed and constructed so that experiments could be carried on under

conditions of high pressure. Sheet electrodes of platinum and palladium were used. The investigation on the modified Grove cell was continued at high pressures and room temperatures and the improvement in performance noted.

(c) New "Diffusion-mesh" Electrode

9. A strong need existed for an electrode which would be light in weight, strong, durable and which would present a large surface of low resistance to the fuel gas and to the electrolyte. This need was met in many respects through the development of a new type of electrode made of porous material or wire screen which depended on electrode surface tension forces to keep the fuel gas from breaking through the electrolyte and bubbling away from the electrode. Many different metallic screens were tried of different weaving and material and with several different types of catalysts as electrodes. The advantages of the new electrode over previous types were found to be of considerable importance and a cell properly employing the new electrodes could produce electric current at comparatively high rates.

(d) Electrolytes

10. A series of experiments with the new electrodes was made in both aqueous electrolytes at atmospheric pressure and room temperatures, and in molten electrolytes of different compositions at temperatures up to 600°C at atmospheric pressure. The experiments of Greger (U.S. Patent No. 1,963,550) were reproduced and the advantages claimed by him for melted electrolytes could not be verified. Aqueous solutions at slightly elevated temperatures gave equally good or better performance.

(e) Moderate Pressures and Moderate Temperatures

11. Following the experiments with molten electrolytes, a large number of cells using the new mesh electrode were tried at moderate pressures and moderate temperatures in a specially constructed chamber. The maximum temperature employed was slightly above 100°C and the maximum pressure was 50 lbs./sq.in. gauge.

METHODS

(a) Cell Construction

(1) Grove Cell

12. The construction of the experimental form of the Grove cell is best shown by the diagram, Plate 3a.

(2) High Pressure Cell with Liquid Electrolyte

13. The high pressure cell was constructed as shown in Plate 3b with a pressure chamber of nickel steel. The electrodes were partially enclosed in glass cylinders that were sealed at the upper end.

(3) High Temperature Cell with Molten Electrolyte

14. A nickel or iron crucible of about 250 c.c. capacity served as con-

tainer for the molten electrolyte which was exposed to the air. An electric heater was used to keep the electrolyte molten. Temperatures were measured by means of a chromel-copel thermocouple whose protecting tube of nickel extended down into the electrolyte. The fuel gas was conducted down into the electrolyte to the "diffusion-mesh" electrode, which was the only type used, through a small iron tube.

(4) Moderate Pressure - Moderate Temperature Cell with Liquid Electrolyte.

15. The experimental model of this cell was set up as shown in Plate 4a which shows the pressure chamber of wrought iron with the removable cap and the beaker of one liter capacity which contained the electrolyte. The two diffusion-mesh electrodes and one reference electrode are shown in place. The gas inlet tubes were of glass. The cap of the chamber contained five insulated terminals which were connected to the electrodes within somewhat as shown. The reference electrode was a strip of platinized platinum whose upper end was in an atmosphere of hydrogen gas and whose lower end extended into the electrolyte.

16. As will be explained later, the diffusion-mesh electrodes were open at the bottom. When the gas content inside the electrode was enough to free the platinum tip of the gas content indicator (see Plate 4b) from the electrolyte, this was indicated on the electric meter in the circuit of Plate 4c. Thus a guide to regulating the gas supply was provided.

17. A thermometer extending into the cell chamber from outside in a closed iron tube served to measure the cell temperature which in turn was controlled by an electrical heating coil that was wound on the outside of the chamber. The maximum cell temperature employed was 135°C.

18. The pressure within the chamber was regulated by the amount of excess gas supplied through the gas inlet tubes and was seldom allowed to go above 50 lbs./sq.in. gauge pressure.

(5) Electrodes.

19. A standardized form of the porous carbon diffusion electrode is shown in Plate 5a. The porous carbon was of various grades manufactured by the National Carbon Company. This electrode was tested in an open beaker of 600 c.c. capacity at room temperatures and atmospheric pressure.

20. The new type electrode which was developed as a result of this investigation and may be called a "diffusion-mesh" electrode, is shown in Plate 5b. As may be seen, it consisted of an electrically welded box of metallic screen which was normally open at the bottom. The inside of the electrode was usually filled with gas from the bottom opening. No gas could escape from the box because of the acting forces of surface tension as long as the electrolyte wet the surface of the screen. If L denotes the width of the square openings of the screen, and if T be the surface tension of the electrolyte in dynes per centimeter, then the maximum permissible height of the electrolyte in centimeters is

$$h = \frac{4T}{Ldg}$$

where d is the density of the electrolyte in grams per c.c. and g is the acceleration due to gravity, in cm./sec.^{2}.

21. Since the catalyst can be placed on the surface of the electrode, the very intimate contact between gas, electrolyte, catalyst and electrode that is necessary for rapid "combustion" can be practically realized.

(b) Measurements

22. In general, the cell voltage and the electrode voltages with respect to the reference electrode were measured at various cell loads for each cell type studied. Sufficient time was always allowed to secure steady state values.

FACTS ESTABLISHED

23. Both oxygen and hydrogen can be made electromotively active and can be made to deliver a reasonably high output in a fuel cell.

24. There is little to choose between acid and alkaline electrolytes for fuel cells of the type studied except that the metal "diffusion-mesh" electrodes in many cases cannot be used in an acid electrolyte.

25. It has been found that unless the gas pressure is carefully controlled, the carbon diffusion electrodes waste several times as much gas as they use through the escape of gas bubbles from the electrode surface, though they do provide an extended electrode surface that is supplied with gas. In addition, they have an undesirably high electrical resistance.

26. The necessary and useful catalysts for the electrode reactions must have an extended active surface and must be in good electrical contact with the electrode metal. Palladium black and platinum black have been used satisfactorily, though rhodium and iridium blacks may well be used instead.

27. The newly developed "diffusion-mesh" electrode provides the close contact between fuel gas, electrolyte, catalyst and electrode material that is needed. In addition, it provides an electrode of large area, of low electrical resistance, and one which does not waste the fuel gases.

28. High temperatures and high pressures greatly increase the performance of the hydrogen-oxygen fuel cell.

29. Molten electrolytes at 500°C-600°C seem impractical because:

(a) Chemical reactions occur between the electrolyte and the iron cell body and electrodes and insulation pieces.

(b) The solubility and rate of diffusion of dissolved gases in the molten electrolytes causes loss of fuel gases and lowered cell voltages.

(c) Explosions are liable at the high temperature of operation in the presence of the iron and nickel catalytic surfaces provided by the cell body and electrode materials.

30. The high temperature limit for the fuel cell with aqueous electrolytes at 50 lbs./sq.in. is about 120°C. This limit is set by the properties of the palladium catalyst and the vapor pressure increase of the electrolyte with temperature. See Plates 1 and 2.

31. All electrodes exhibit the phenomena of "fatigue" and loss of catalyst material. Fatigue is reduced by periodic exposure of the electrodes to oxygen. The loss of catalyst has been reduced by heating the electrode after palladiumizing in an alcohol flame to "carbonize" the palladium. Such treatment does not injure the catalyst.

32. A cell output of about 50 m.a./cm.^{2} at 0.75 volts, an efficiency of 60%, has been attained at 120°C and 50 lbs./in.^{2} gauge pressure. The maximum efficiency attained was about 75 percent under these conditions with a cell voltage of 0.9 volts at a load of 5-10 m.a./cm.^{2}. For comparison, the current density in a lead submarine battery discharging at the 10-hour rate is about 5 m.a./cm.^{2}.

SUMMARY OF DATA

33. The summary of data is contained in Table 1.

CONCLUSIONS AND RECOMMENDATIONS

34. The hydrogen-oxygen fuel cell offers promise because it uses an easily available fuel and has water as its product of combustion. Using the newly developed "diffusion-mesh" gas electrode, the output of the cell is high and the thermodynamic and overall efficiencies are quite good, being better than 60 percent even when well loaded. The cell is not damaged by an overload of any amount. It operates best at a moderate temperature, 120°C, and needs only moderate pressures, say 50 lbs./sq.in., for good operation.

35. There are various undesirable factors in the use of such a fuel cell. For example, the cell voltage is low, i.e. about 0.75 volts per cell under load. The cell is complex in its present state of development, even though it does not need particular care. The present electrodes exhibit the phenomena of fatigue which lowers the output after a time. Corrosion difficulties exist and impurities must be guarded against. The danger of an explosion in the cell exists even though proper design could reduce the probability so low as to make it non-existent practically.

36. Preliminary calculations indicate that a battery of cells capable of delivering 2000 H.P. would occupy 2770 cu.ft. and would weigh 237,000 pounds. Working at an efficiency of 60 percent, these cells would require about 1400 pounds of oxygen and 175 pounds of hydrogen per hour. The storage cylinders would weigh something like 25,000 pounds. A lead battery of comparable maximum capacity would weigh about 400,000 pounds and would occupy 2500 cu.ft.

37. In conclusion, the present state of development of the hydrogen-oxygen fuel cell does not seem to be far enough advanced to be of immediate military importance.

DISCUSSION

38. The developments on improved fuel cells are thought to offer at least some possibility for use as an improved storage battery on submarines. The weight is considerably less than the weight of the present lead cells but the volume for a given capacity is comparable to the present cells. It is evident that the oxygen and hydrogen necessary to operate these cells can be produced on the submarine by the well known electrolytic processes using water and electricity produced by a diesel driven generator. There appears to be no advantage over the ordinary lead cell in regard to the time taken to charge the gas storage tanks and the main advantage, if the cell worked perfectly, would be something like a reduction in weight to perhaps one-half.

39. One possible military advantage of such a cell should be kept in mind, for a submarine equipped with this type of cell could come alongside a mother ship or tie up to it direct and be completely recharged and ready for duty in a matter of 20 to 30 minutes by the simple process of transferring gas from a tender to the storage tanks of the submarine. It is conceivable that the small coast defense submarine charged in this manner might be of considerable military value. The scientist responsible for this development recognizes that the fuel cell considered in this report is in no sense a finished product and many difficulties must be overcome. However, a very real advance has been made in the development of such specialized cells and because of their very high known thermodynamic efficiency, it is considered that further work could be profitably carried on.

TABLE 1.

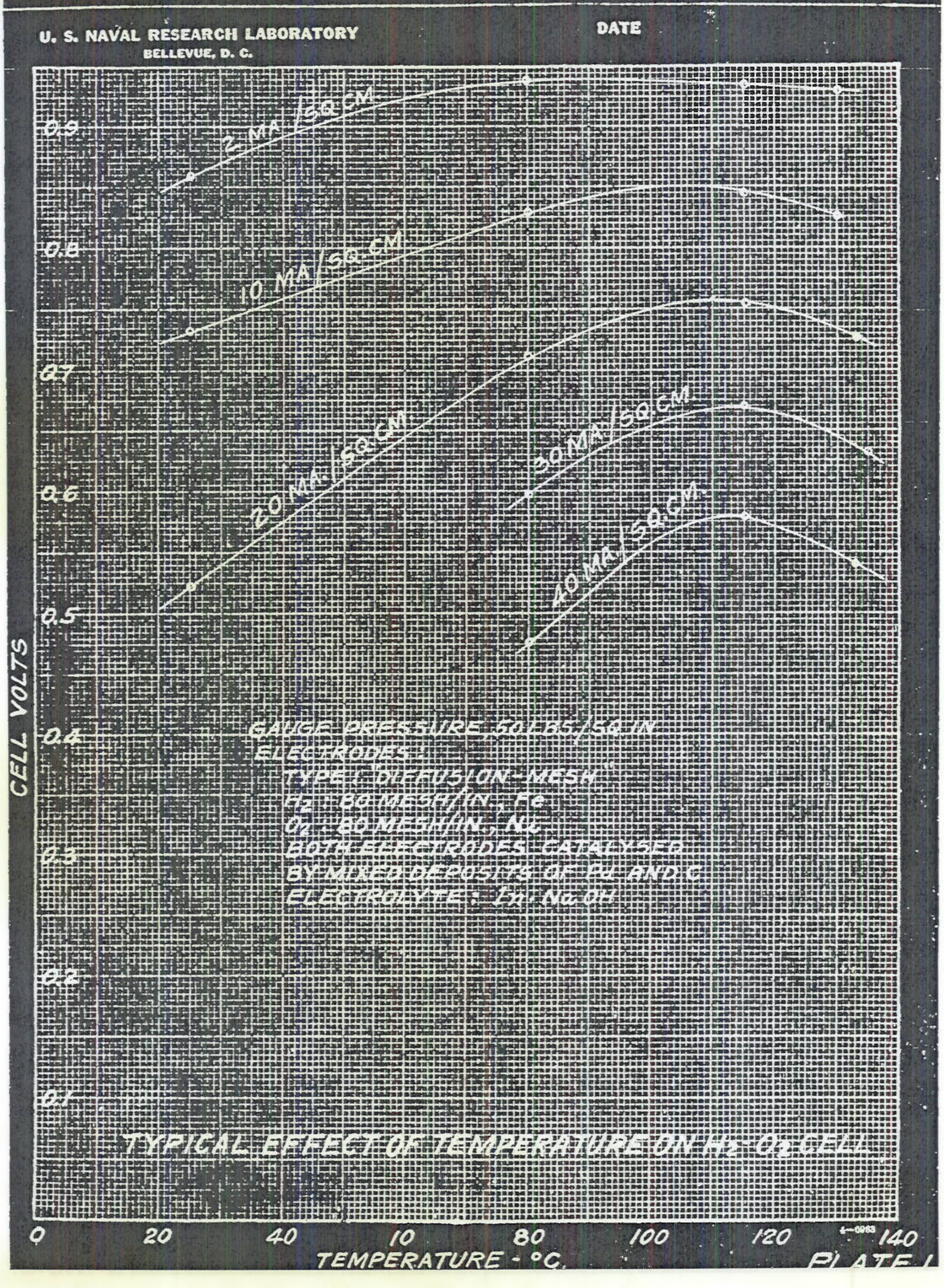
SUMMARY OF RESULTS

Cell Type	Aqueous Electrolyte	Temperature	put	Remarks
Grove cell with platinized Pt or Pd sheet electrodes.	29% KOH or 60% H_2SO_4		0.93 v. at 1 m.a.	Room temperature Atmospheric pressure Output very low.
Carbon "diffusion" electrodes. A. Treated or H_2 treated and O_2 untreated.	2.5 n. NaOH		0.34 v. at 4 m.a./sq.cm. 0.70 v. at 1 m.a./sq.cm.	Treatment consists in electroplating electrodes with Pt-black or Pd-black.
B. Untreated.	2 n. H_2SO 2.5 n. NaOH		.05-.08 v. at .005 m.a.	
High pressure measurements.			0.6 v. at 2 m.a./sq.cm.	1600 lbs./sq.in.
A. Electrodes of platinized Pt or Pd sheet.	2.2 n. KOH		0.6 v. at 2 m.a./sq.cm.	1000 lbs./sq.in.
			0.5 v. at 0.5 m.a./sq.cm.	14.7 lbs./sq.in.
B. Electrodes of 80 mesh nickel screen palladiumized.	4 n. KOH		0.6 v. at 5 m.a./sq.cm. 0.6 v. at 1.5 m.a./sq.cm.	1300 lbs./sq.in. 14.7 lbs./sq.in.
C. "Diffusion-mesh" electrodes of nickel screen, 80 mesh,	4 n. KOH		0.6 v. at 9 m.a./sq.cm. 0.6 v. at 3 m.a./sq.cm.	850 lbs./sq.in. 14.7 lbs./sq.in.
High temperature cell. "Diffusion-mesh" electrodes of Ni or Fe, not catalysed.	NaOH 60%) KOH 40%)	340°C	0.75 v. at 6 m.a./sq.in.	Electrolyte is very corrosive.
	$BaCO_3$ 32%) K_2CO_3 43%) KCl 7%) NaF 18%)	515°C	0.5 v. at 2 m.a./sq.cm.	Neutral electrolyte.

Table 1 (continued)

Cell Type	Aqueous Electrolyte	Temperature	Output	Remarks
	$BaCO_3$ 9%) Na_2CO_3 28%) K_2CO_3 37%) KCl 15%) NaCl 11%)	600°C – 635°C	0.5 v. at 6 m.a./sq.cm.	Neutral electrolyte. U.S. Patent No. 1,963,550
Moderate temperature, moderate pressure cell. Diffusion-mesh electrodes.				
80 mesh Ni - untreated	4 n. KOH	20°C	0.5 v. at .001 m.a./sq.cm.	14.7 lbs./sq.in.
80 mesh Ni - Pd black catalyst	4 n. KOH	24°C	0.6 v. at 3 m.a./sq.cm.	14.7 " "
200 mesh Ni - " " "	2 n. KOH	17°C	0.6 v. at 6.2 m.a./sq.cm.	14.7 " "
200 mesh Ni - " " "	2 n. KOH	80°C	0.6 v. at 12 m.a./sq.cm.	14.7 " "

See also curves 1 and 2 on this cell.

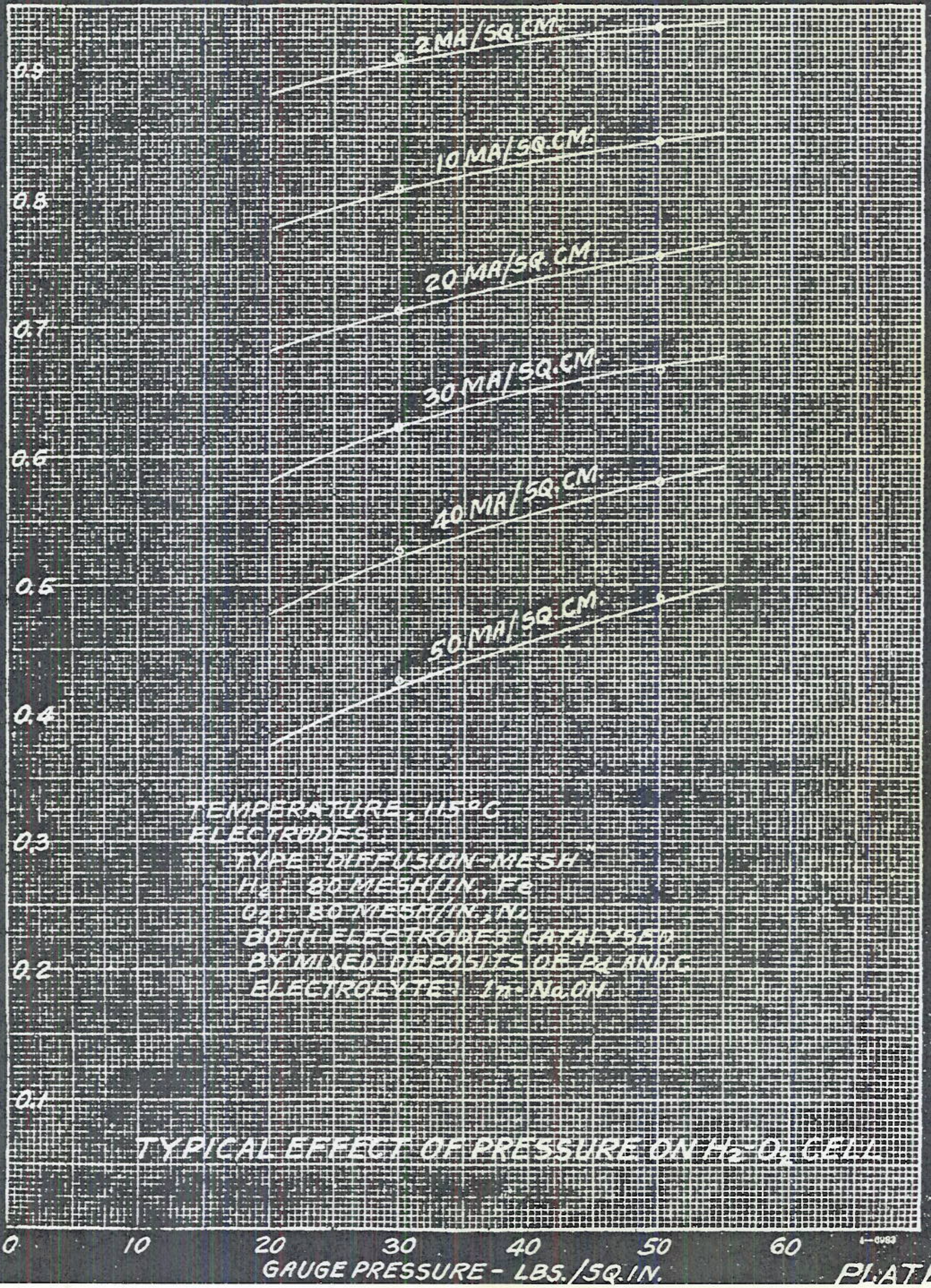


TYPICAL EFFECT OF TEMPERATURE ON H_2-O_2 CELL

PLATE I

U. S. NAVAL RESEARCH LABORATORY
BELLEVUE, D. C.

DATE



TEMPERATURE, 115°C
ELECTRODES:
TYPE "DIFFUSION-MESH"
H_2: 80 MESH/IN, Fe
O_2: 80 MESH/IN, Ni
BOTH ELECTRODES CATALYSED
BY MIXED DEPOSITS OF Pd AND C
ELECTROLYTE: 1n NaOH

TYPICAL EFFECT OF PRESSURE ON H_2-O_2 CELL

PLATE

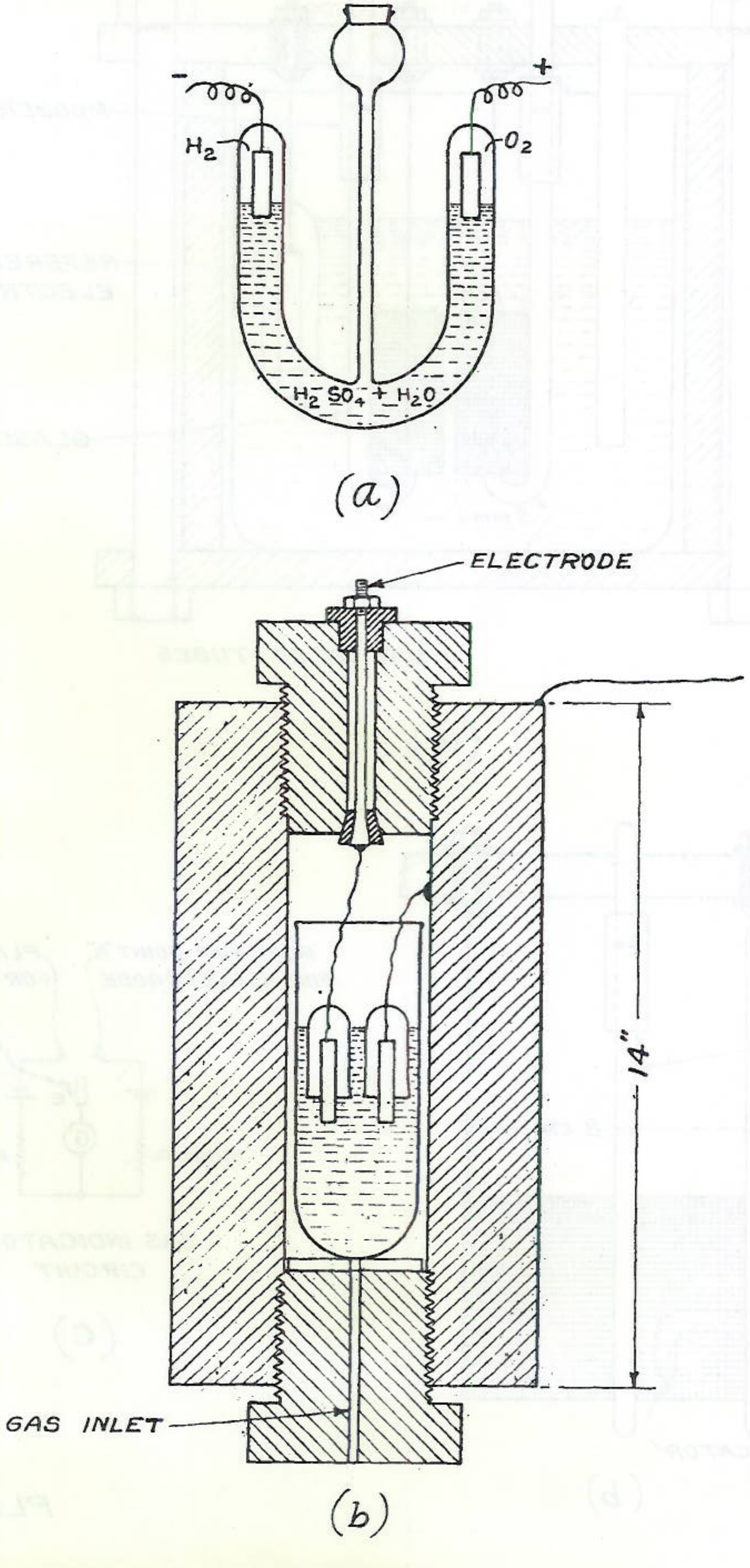
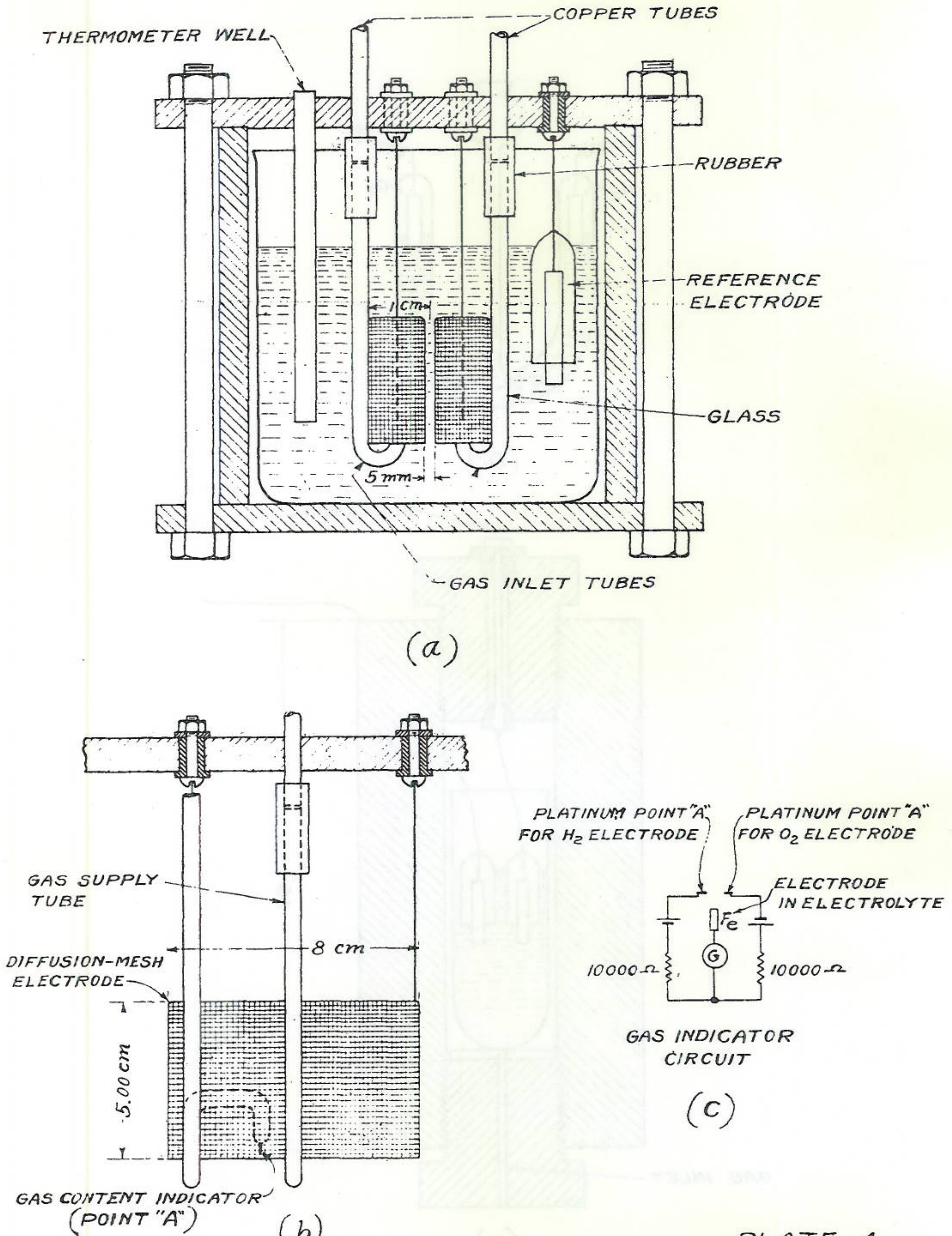


PLATE 3



(a)

(b)

GAS INDICATOR CIRCUIT

(c)

PLATE 4

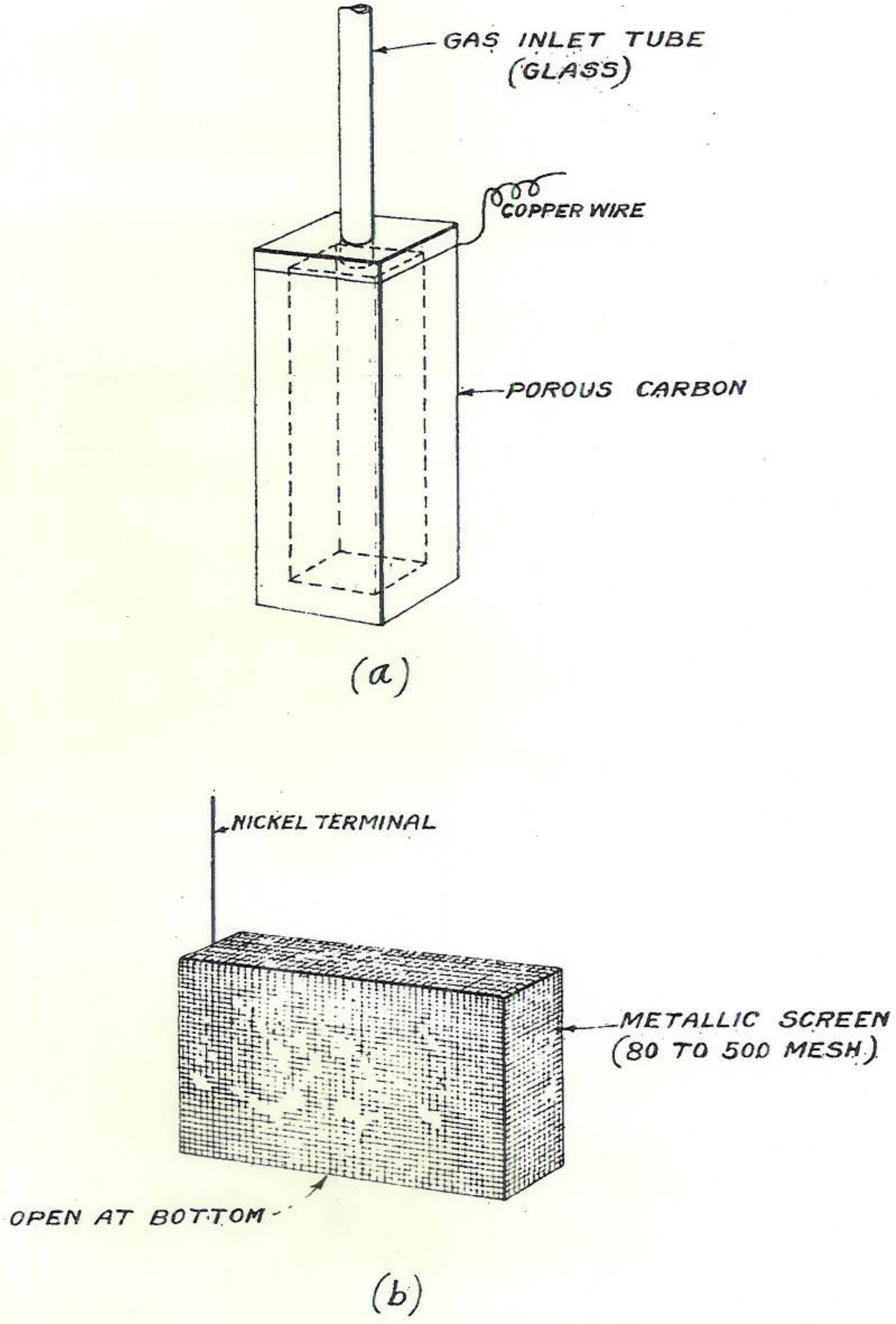

GAS INLET TUBE (GLASS)
COPPER WIRE
POROUS CARBON
(a)
NICKEL TERMINAL
METALLIC SCREEN (80 TO 500 MESH)
OPEN AT BOTTOM
(b)

PLATE 5