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THE HIGH PRESSURE HYDROGEN/OXYGEN FUEL CELL

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1. Introduction.

The hydrogen/oxygen cell is particularly attractive, when compared with other types of fuel cell, for a number of reasons; it has always appeared likely that a practical unit could be developed working at low or medium temperatures, and it raises the interesting possibility that it could be used as a kind of electrical storage battery, the two gases having been previously generated by the electrolysis of water, using power produced on a large scale.

Moreover, when the author first became interested in fuel cells in 1932, a search through the available literature soon showed that the most promising results had in fact been obtained with this type of cell. The cell was first described by Sir William Grove in 1839<sup>(1)</sup>, and in 1889, particularly good results were recorded by the great chemist Ludwig Mond and his associate Charles Langer (11), they achieved a current density of 6A/ft.<sup>2</sup> (6.5m A/cm<sup>2</sup>) at 0.75 V., using either oxygen or air, and they also showed that the best results were obtained when the platinized platinum electrodes were kept substantially dry on the gas side. Further progress was prevented largely because of the high cost of the platinum electrodes.

Since the end of the second World War, a great deal of interesting work has been done in many countries on the hydrogen/oxygen cell, and this need not be referred to in detail here. Particular reference, however, should be made to the work of Davtyan(111) and Kordesch(iv) and his associates.

2. Types of Cell Investigated.

In 1938 a small cell similar to Grove's original gas battery was constructed, and fair results obtained; but when activated nickel gauze electrodes were used, in conjunction with an alkaline electrolyte of potassium hydroxide, the results were poor, even when the temperature was raised to the boiling point of the liquid.

It was next decided that the problem would have to be attacked essentially from an engineering point of view, and that with this type of cell operation under pressure could not be avoided if high current densities were to be obtained, in conjunction with comparatively cheap materials of construction such as nickel. So in 1939 a cell was designed which would stand a pressure of 3000 p.s.i. and any reasonable temperature (Fig.1).

The electrolyte was a 27% solution of potassium hydroxide and the cylindrical electrodes were of nickel gauze, activated by alternate oxidation in air and reduction in hydrogen; they were separated by a diaphragm of asbestos cloth. Other metals, such as platinum, palladium, silver and copper were tried, but were discarded in favour of nickel, partly because of cost and corrosion difficulties, but mainly because of the superior performance shown by nickel under these circumstances. The cell was tested by alternately charging it from an external source of direct current and discharging it through an ammeter and variable resistance at a constant current. It was found finally that a current density of 12.2 A/ft.<sup>2</sup> (13.1m A/cm<sup>2</sup>) of the external surface of the inner electrode could be maintained for 48 minutes at about 0.89 V., with a temperature of 100°C; many thicknesses of gauze and fairly high pressures were used to get these results. Curiously enough, no advantage was obtained by using higher temperatures than 100°C., and this was tentatively ascribed to the irreversible anodic oxidation of the oxygen electrode during the charging period.

The next stage was to construct two cells, one acting as an electrolyser for generating the two gases and the other being the current-producing cell (Fig.2). The gases produced in the electrolyser were carried separately up into the cell in solution in the electrolyte, the liquid returning to the electrolyser through separate pipes. Activated nickel gauze electrodes and asbestos diaphragms were again used, but this time in the form of flat discs.

It was found that the performances of this cell improved continuously with increasing temperatures and pressures up to 240°C. and 1075 p.s.i., the highest tried. The highest current density obtained at 240°C. was 75A/ft.<sup>2</sup> (81m A/cm<sup>2</sup>) at 0.65 V. with six gauze electrodes on each side of the cell. The current density appeared to be limited by the rate at which fresh gas could be brought up to each electrode in solution in the electrolyte. The materials and methods of construction used proved to be reasonably satisfactory.

### 3. The Present Cell with Diffusion Electrodes.

At this stage it was still considered that the performance was not good enough for any practical application, bearing in mind that high pressures inevitably lead to higher container weights than would be necessary with a fuel cell working at atmospheric pressure. So it was decided that a new apparatus should be built with the gases confined to the backs of porous nickel electrodes; this design has been used with very little change ever since.

The details of the construction of the cell have often been described before (v), but it is probably best to recapitulate them briefly here.

A single cell is illustrated diagrammatically in Fig.3. The electrodes are made of porous sintered nickel, and the main cell parts are of nickel-plated steel or pure nickel; the electrolyte is strong potassium hydroxide solution, between 37 and 50% concentration. The normal operating conditions are 200°C. and 300-600 p.s.i.. At the present time a pressure of 400 p.s.i. is normally being used. The porous nickel electrodes, which are about one sixteenth of an inch thick, have a pore size of about 30 microns or more, on the gas side, with a thin layer of much smaller pores on the liquid side; a small pressure difference is

set up in the apparatus across each electrode, so that the liquid is expelled from the large pores on the gas side, but the gas cannot bubble through the smaller pores on the liquid side owing to the surface tension of the liquid. The interior of the 50 micron pores, which are wetted throughout with electrolyte, presents a large surface for absorption of gas. The oxygen electrodes are subjected to a pre-oxidation treatment at a high temperature in air, and this protects them from corrosion by the high pressure oxygen and electrolyte. Lithium atoms are incorporated into the crystal lattice of the nickel oxide, thus converting the ordinary green nickel oxide, which is an insulator, into a black double oxide of nickel and lithium, which is a good semi-conductor.

With this arrangement, the gases are of course supplied from cylinders in the normal way; other advantages over previous designs are that the gas sides of the electrodes are coated with only a very thin layer of electrolyte, giving a very short diffusion path for the gases in solution before reaching the active surface of the electrodes, the useful surface area of the electrodes is greatly increased, and the asbestos diaphragm is eliminated.

#### 4. Electrode Design.

A good electrode design is of course of the utmost importance, and several different designs have been tried. The largest electrodes made so far are 10 in. effective diameter, though this does not by any means represent the limit in size; they are sintered directly onto a flat circular perforated sheet of nickel or nickel-plated steel, about one sixteenth of an inch thick; this provides adequate strength, and serves also to conduct away the current generated. Electrodes up to 5 in. diameter were previously made without a backing plate of solid metal, but it was considered unlikely that larger ones would be satisfactory, without adequate support. Separators, in the form of narrow vertical strips of p.t.f.e., have to be used with 10 in. diameter electrodes, to prevent internal short-circuits when the pressure difference is applied.

An alternative form of electrode which has been employed comprises a bipolar structure with recesses machined on either side of a solid metal plate, each recess then being filled with porous sintered nickel for a hydrogen and oxygen electrode respectively. A thin dimpled perforated plate is first sintered into each recess, and this leaves a narrow space for leading the gas from ports in the rim to all parts of the porous metal. When bipolar electrodes of this type are assembled in series, with gaskets of insulating material between each, they form a series of cells which do not require any external current connection except at each end of the battery. This electrode construction is attractive in many ways, and leads to a very compact battery, but it has temporarily been abandoned in favour of the simple unipolar design, mainly owing to difficulties in manufacture.

The coarse pore layers of hydrogen electrodes are made from Grade B carbonyl nickel powder (average particle size 2-5 microns) mixed with about 20% by weight of 100-240 mesh ammonium bicarbonate which acts as a spacing agent during sintering; it is pressed lightly in a rubber press, and then sintered for about  $\frac{1}{2}$  hour at 850 C. in a reducing atmosphere. The fine pore layer is then applied as a suspension of Grade A carbonyl nickel powder (average particle size 4-5 microns) in alcohol; this is sintered for  $\frac{1}{2}$  hour at 800 C., any leaks being repaired by further thin applications of A nickel as before.

The coarse pore layers of oxygen electrodes are now usually made from Grade D carbonyl nickel powder (average particle size 7-9 microns) mixed with 15-20% of 100-240 mesh ammonium bicarbonate; it is pressed lightly and sintered for  $\frac{1}{2}$  to 1 hour at 1000-1150°C. in a reducing atmosphere. The fine pore layer is again of Grade A nickel, sintered for  $\frac{1}{2}$  to 1 hour at 950-1000°C. Alternatively, the coarse pore layers of the oxygen electrodes may be made from a coarse nickel powder, about 200-250 mesh, without a spacing agent; but in this case a higher compressing pressure and a higher sintering temperature (1150°C. as a minimum) are required to get a really strong compact.

Finally the oxygen electrodes are pre-oxidised after impregnation with a dilute solution of lithium hydroxide and drying; air is used for oxidation, and a satisfactory thickness of oxide is formed in  $\frac{1}{4}$  to 1 hour at 700-800°C.

Hydrogen electrodes are activated by impregnation with a strong solution of nickel nitrate, followed by a roasting treatment in air at 400°C. and finally reduction in hydrogen at about the same temperature. Work is proceeding on the activation of oxygen electrodes, but a standard treatment has not yet been arrived at.

Typical microsections of hydrogen and oxygen electrodes are shown in Figs. 4 and 5.

#### 5. Prevention of Corrosion of Oxygen Electrodes.

When porous nickel electrodes were first put into use, serious trouble arose with the gradual corrosion of oxygen electrodes, leading first to a drop in output and finally to complete breakdown. This trouble has now been largely overcome by the pre-oxidation treatment already described. It was first found that samples of nickel pre-oxidised in air at about 800°C. were extremely resistant to corrosion when subsequently exposed to strong KOH solution and oxygen under similar conditions to those in the cell. But the green oxide layer produced during pre-oxidation is an electrical insulator, so an electrode protected in this way would be useless in the cell. However, it was ascertained that if lithium atoms are incorporated into the crystal lattice of the nickel oxide, a black double oxide of nickel and lithium is produced, which is a good semiconductor(6); and the corrosion resistance is unimpaired, or even enhanced. Using this technique, oxygen electrodes have been in operation in the cell for periods up to 1500 hours at 200°C. without failure, and with only a very small drop in performance. Specimens of pre-oxidised nickel have been exposed to oxygen under pressure and potassium hydroxide solution at 200°C. for more than 10,000 hours without visible deterioration; and accelerated corrosion tests at a higher temperature have shown that considerable improvement on this figure should be possible. It should be mentioned here that before the pre-oxidation treatment had been introduced, experiments were made with various corrosion inhibitors which were dissolved in the electrolyte; potassium silicate and potassium aluminate were particularly successful in arresting corrosion of oxygen electrodes, but they also reduced the performance of the cell to a serious extent. It is believed that this provides the explanation for the curious fact that no corrosion of oxygen electrodes was observed when using the previous cells with nickel gauze electrodes; these earlier cells all had diaphragms of asbestos cloth, and it is to be expected that the electrolyte would therefore become somewhat contaminated with potassium silicate or aluminate. It is interesting also that a small amount of copper, added to the KOH in the form of copper oxide, was also effective as a corrosion inhibitor and in all cases led to the formation of a black oxide on the nickel.

The results of some accelerated corrosion tests on samples of nickel pre-oxidised in the presence of lithium hydroxide, and exposed to 65% KOH and oxygen at 300°C. and 800 p.s.i. total pressure, are shown graphically in Fig.6. The samples were placed in oxidized nickel crucibles, which were set up in autoclaves; the samples were half in and half out of the KOH solution. The gas space was filled with oxygen under pressure, and readings of temperature and pressure were recorded periodically. The autoclaves were opened at intervals and the samples washed in distilled water, dried and weighed; the extent of corrosion was indicated by the weight change. Fresh KOH solution was used in each run. These curves emphasize the importance of a sufficiently thick oxide layer, in order to obtain really good durability. It is estimated that an oxide layer about 3 microns thick can be obtained by coating the nickel with 2 g. of lithium hydroxide per square metre of surface and oxidising in air at 800°C. for 16 minutes.

In Fig. 7 some results of tests at 200°C, 260°C. and 300°C. have been plotted together. These samples are not exactly comparable due to differences in the initial thickness of the oxide coating and in the conditions under which the corrosion tests were carried out. It is possible to say, however, that similar samples corrode at 200°C. much more slowly than at 260°C.. Also a further considerable increase in corrosion rate is produced if the temperature is raised to 300°C.. By pre-oxidising the samples to produce an increase in weight of 5g/metre<sup>2</sup> instead of 2-3g/metre<sup>2</sup>, the rate of corrosion at 300°C was reduced considerably as shown in Fig.6. It seems reasonable to suppose that if the samples oxidized, with lithium present, to give an increase in weight of 5g/metre<sup>2</sup> were tested at 200°C., they would give a life many times longer than those already tested at this temperature (Fig.7). Even if it were to prove impossible to produce such a thick oxide layer on the oxygen electrode, a thinner layer of 2g/metre<sup>2</sup> will protect an electrode for more than 10,000 hours at 200°C.

#### 6. Jointing Material.

There must be at least one electrically insulating gasket per cell, and at the present time, using unipolar electrodes, four gaskets must be used per cell.

Many different materials have been tried, but at the present time nothing has been found which is superior in all respects to ordinary compressed asbestos fibre jointing, which is mainly composed of asbestos fibre and rubber (generally neoprene). This has a number of disadvantages, the principal one being that the rubber content is gradually oxidised where exposed to the high pressure oxygen; this finally leads to loss of strength and leakage to atmosphere. However, runs as long as 800 hours have been achieved without failure, and runs greatly exceeding this should be possible with a superior design. One other fault is that substances given off when the rubber decomposes on heating, poison the hydrogen electrode and tend to reduce the output of the cell.

The most attractive alternative to CAF jointing would appear to be p.t.f.e. loaded with asbestos fibre, or possibly loaded with powdered glass, but these materials are only now in process of development in England; and the metal surfaces would certainly have to be specially roughened to prevent slip. End pressure on the gaskets could no doubt be reduced by the use of a pressure cylinder or tank, in which the whole cell pack is contained under pressure, but this line of development is not being pursued at present in England, owing to the extra complication involved.

7. Cell Performance.

The performance of the cell improves with both temperature and pressure, but in order to attain a long life it will probably prove desirable to limit the working temperature to 200°C or slightly higher. The best performance obtained so far with a 10" dia. cell at 200°C and 400 p.s.i. is shown in the table, and plotted as a voltage-current density characteristic in Fig. 8; the diameter of the sinter is somewhat less than 10", and is approximately 9 3/8", but it is felt that it is more precise to base the figures for current density on the internal diameter of the body of the cell.

TABLE.

Current { $A/ft.^2$	0	10	50	100	200	300	440
Density { $mA/cm^2$	0	11	54	107.6	215	323	473
Voltage, V	1.04	1.005	0.93	0.885	0.82	0.755	0.68

These figures were taken from one cell in a 10-cell battery, and using 37% KOH as electrolyte; both these factors contribute to the rather low open-circuit voltage obtained. Under the above conditions of 0.68 V. and 440  $A/ft.^2$  (or 240A), the power output per unit of internal volume corresponds to 8.2 kW/ft<sup>3</sup>.

The current efficiency has been measured over a period of some hundreds of hours in a 5 in diameter unit with two cells in series, and works out at 98%. This means that the energy efficiency, based on the free energy of the reaction, will approximate at any useful current density to the voltage efficiency; e.g. at 0.9V and 200°C and 600 p.s.i. the energy efficiency will be  $\frac{0.9}{1.20} \times 100 = 75\%$ ; at 0.8V. it will be 66%, and at 0.6V. it will be 50%.

When the cell is on load, the losses which appear in the form of heat, are mainly due to the irreversibility of the electrode reactions, or what may be called activation polarization; a smaller proportion of the losses are due to resistance and concentration polarization. On open circuit, and at low current densities, there will in addition be a 'lost current' due to diffusion of the two gases in solution through the electrolyte, followed by combination on the opposite electrode.

A graph showing the relative proportions of polarization due to each electrode and to the electrolyte is shown in Fig. 9. Ordinary G.F. jointing was used, so the hydrogen electrode was somewhat "poisoned". Assuming that activation of the hydrogen electrode can easily reduce polarization from this source to a negligible amount, while electrolyte resistance and oxygen electrode polarization are less easily improved, then a curve showing the best easily obtained performance to be expected from a cell can be drawn (see Fig. 9). This shows that 223  $A/ft.^2$  (240  $mA/cm^2$ ) at 0.8 V. and 650  $A/ft.^2$  (700  $mA/cm^2$ ) at 0.6V can reasonably be expected at 200°C. and 620 p.s.i..

The experimental method has been improved by the measurement of purely resistive polarization in the cell circuit using a commutator technique in conjunction with a cathode ray oscilloscope, so that individual electrode performance can be studied precisely. This is particularly important in the case of the hydrogen electrode, where both resistance and activation polarization have the same linear dependence on the current passing. The use of a reference electrode, in the form of a small resting (i.e. unloaded) hydrogen electrode of porous nickel, situated in the electrolyte space, about halfway between the main hydrogen and oxygen electrodes, has made it possible to study the polarization in each electrode separately; a reference electrode of this kind is used fairly regularly in cell operation, even when the commutator technique is not being employed. This has shown that the polarization of the hydrogen electrode at 200°C., when plotted against current density, gives approximately a straight line; at lower temperatures, the behaviour becomes logarithmic (see Fig.10). In the case of the oxygen electrode, however, the behaviour is logarithmic even up to the highest temperature yet tried the shape of the curve which it gives at 200°C, can be seen in Fig.9. The difference in the shape of the polarization curves shown by hydrogen and oxygen electrodes at 200°C. can be explained by the fact that the exchange current is much less in the latter case, or in other words the oxygen electrode is much less reversible than the hydrogen one; in addition to this, the surface area of the oxygen electrode is much less than that of the hydrogen one. But even an oxygen electrode of large surface, made from Grade B nickel, will polarize more than a hydrogen one made from the same powder and having the same surface area. To improve the performance of oxygen electrodes, a very large increase in surface area will be required; this can probably best be obtained by some form of activation.

Since electrodes have been made with a backing plate, it has been possible to test hydrogen and oxygen electrodes as thin as 1/32 in. The performance of these thin electrodes is within 20% of that of the previous electrodes which were  $\frac{1}{8}$ " - 5/32" thick. If the electrodes are made 1/16 inch thick, there does not appear to be any sacrifice in performance. A number of other hydrogen and oxygen electrodes of varying structures have been tested, but so far none has shown a striking improvement in performance when compared with the standard types.

## 8. The Effect of Cell Conditions on Performance.

### (8.1). Pressure.

The effect of temperature and pressure on the reversible voltage of the hydrogen/oxygen cell can be seen in Fig.11. Measurements of electrode and cell performance at varying pressures of gas (the electrolyte vapour pressure having been measured, see Fig. 12) show that small variations in pressure have only a small effect. A tenfold change in gas pressure from 30 atmospheres to 3 atmospheres (441 to 44 p.s.i.) approximately halves the cell performance at normal operating voltages (see Fig. 13). A theoretical analysis done fairly recently shows that for a given power output, and assuming that the gases are both stored in high tensile steel cylinders at 3,000 p.s.i., the overall weight of the battery and storage cylinders would not be increased if the operating pressure were reduced from 600 to 300 p.s.i.; the efficiency would be slightly reduced, however; this calculation allows for the "dead" fuel left in the cylinders when the battery is discharged, and also for the reduction in weight of the battery itself.

(8.2). Temperature.

The maximum cell temperature is limited by the materials used in its construction. Thus, p.t.f.e. is found to corrode relatively quickly at 250°C. undercell conditions, where in contact with porous nickel; and the nickel-lithium oxide of the oxygen electrode breaks down fairly quickly at 300°C.. Between 100° and 250°C. the cell output at normal operating voltage increases rapidly with rise in temperature, as the hydrogen electrode changes from logarithmic behaviour at 100°C. to linear behaviour. After 200°C. the output does not increase as rapidly as it does between 100° and 200°C.. Taking 100°C. as unit performance, that at 150°C. is roughly 4, at 200°C. it is 10, and at 250°C. it is 15. The actual maximum power available (at a low efficiency) rises increasingly steeply with increasing temperature, and is roughly doubled with each 50 C. rise in temperature.

(8.3). Electrolyte Concentration.

The effect of the vapour pressure of the electrolyte on the reversible voltage of the hydrogen/oxygen cell at a temperature of 200°C. is shown in Fig.14. This assumes that the total pressure is kept constant at 600 p.s.i.. It has been necessary to plot the vapour pressure of the electrolyte, rather than the concentration, as the relationship between concentration and vapour pressure of very strong KOH solutions has not been measured, as far as is known.

It has been assumed that the disposable energy in the formation of water vapour at a constant pressure of one atmosphere is 219.4 kilo-joules per gramme formula weight, at 200°C. At other values of pressure the disposable energy is increased by an amount

$$\frac{0.5 R T \log_n (P_{H_2}^2 \cdot P_{O_2})}{P_{H_2O}^2}$$

the pressures being measured in atmospheres.

The theoretical voltage is obtained by dividing the disposable energy by  $2F$ , where  $F$  is the Faraday, 96,500 coulombs.

Increasing the concentration of the potassium hydroxide electrolyte to 35% by weight, increases the cell output progressively, but further increase from 35% to 45% has a smaller effect. Operation at higher concentrations than 45% leads to practical difficulties with the KOH electrolyte going solid on cooling down. Long continuous operation of cells on load for periods of 50-100 hours has shown that the very high concentrations of KOH lead to build-up of concentration polarization (absence of water in the oxygen electrode is the most probable cause), so that a concentration of about 35% KOH seems likely to be the optimum at present. If later it proves feasible to condense out twice the water formed from the hydrogen electrodes, and then return one half of this, in the form of steam mixed with the oxygen, to the oxygen electrodes, this difficulty should disappear and stronger concentrations could be contemplated.

The values obtained for specific conductivities of a range of electrolytes at various temperatures are shown in Fig.15; these have been obtained by measuring cell resistance with two different inter-electrode distances using the commutator technique mentioned previously; they are only approximate. Results for 36% KOH are particularly erratic, and the measurement of conductivity using an a.c. bridge and high temperature conductivity cell should provide accurate results.

The values predicted by T.M. Fry<sup>(7)</sup> are also plotted; these were obtained by using the relationship between conductivity and viscosity, and using an estimated value of viscosity; also values quoted for KOH by C.E. Bowen (deduced from work by Kohlrausch in 1898); a general agreement is observed.

The contribution of electrolyte resistances to cell operation will be approximately  $0.25 \text{ ohm/cm}^2$  of apparent electrode surface, for  $\frac{1}{8}$  in. electrode spacing using electrodes of the types described. For a current density of  $250 \text{ mA/cm}^2$ , this would give a polarization of  $0.0625 \text{ V.}$ , i.e. a voltage drop corresponding to about 5% of the total free energy available.

#### (8.4). Shunt currents in Multi-cell Packs.

A six cell pack of 5 in. diameter electrodes was constructed in 1954 and fair results were obtained.

Measurements of the shunt currents along the common electrolyte ports, and a theoretical treatment, suggest that the magnitude of the shunt currents will depend largely on the dimensions of the axial electrolyte ports through the pack.

If  $V$  = the open circuit voltage of one cell  
 $n$  = the number of cells in the pack  
 $R$  = the resistance of one pair of axial ports in one cell, and  
 $r$  = the resistance of one pair of radial ports in one cell,  
then the shunt current = 
$$\frac{(n-1) V}{2r + (n-1) R}$$

For large packs, where distribution of liquid may be important, it might be better to have a number of axial ports serving groups of cells, rather than one large port serving all the cells.

#### 9. Use of Other Gases.

It has often been suggested that a cell of this type could be used as a genuine fuel cell for generating power on a large scale, using hydrogen produced from coal by ordinary chemical methods, and oxygen from the air. This is, of course, a very ambitious project and cannot honestly be envisaged at present, owing to the high cost of pure hydrogen produced in this way; pure oxygen is also expensive.

Nevertheless, it is obvious that the scope of the whole project could be greatly widened if it were found to be possible to make use of a liquid fuel which could be converted into some gas which is electrochemically active in the cell; in this way it would become possible to compete on rather more level terms with the internal combustion engine.

A number of experiments have been carried out using other gases, and with mixtures of gases, and the conclusions can be summarized as follows :-

1. No other fuel gas, apart from hydrogen, has been found to be electrochemically active on a nickel electrode at temperatures which it would be practical to use in a cell of this type. Carbon monoxide, methane and methanol were tried and were all unsuccessful.

2. Both carbon monoxide and carbon dioxide are soluble in caustic potash and would lead to the eventual carbonation of the electrolyte.

3. Complete carbonation of the electrolyte would lead to a serious loss in performance, amounting to a reduction to one quarter of the normal performance; this is partly due to loss in oxygen electrode performance and partly to increased cell resistance.

4. Hydrogen containing inert diluents, such as nitrogen or methane, can be used with a high volume percentage of inert gas, as long as provision is made for exhausting the residue; some hydrogen would no doubt be wasted in the exhaust, but the amount lost is not likely to be serious.

5. Possibly because of its solubility in hot caustic potash solution, carbon monoxide does not poison the fuel electrode, but it may attack the nickel pipe-work leading gas into the cell. No poisoning was observed with other gases used.

6. Experiments using nitrogen-oxygen mixtures showed that air could be used in place of oxygen, as long as the nitrogen left over was continuously removed, and the carbon dioxide extracted before entry into the cell.

The above conclusions show that the presence of any gases, apart from hydrogen and oxygen, may lead to rather awkward problems which it would probably be wise to avoid at present. On the other hand, small percentages of inert gases would do no harm to the cell, provided adequate means were worked out for exhausting them to atmosphere from time to time, before they had built up to large proportions inside the electrodes. A small purification plant could no doubt be designed for continuously purifying a slightly carbonated electrolyte.

The additional polarization at the oxygen electrode, caused by using air instead of pure oxygen, can be seen in Fig.16; this also shows the effect of oxygen pressure on polarization. Fig.17 shows the effect of various fuel gases on the polarization at the fuel electrode; the curve for technical hydrogen, and also for the mixture of 90% hydrogen plus 10% carbon monoxide is identical with that for pure hydrogen, over short periods of time. The "technical hydrogen" is the gas which is produced as a by-product in oil refineries, from the "platforming process".

#### 10. Present Design.

In 1957, the National Research Development Corporation of Great Britain agreed to finance the development and construction of a unit developing 5-10 kW., complete with all automatic controls, and a contract for this work was placed with Marshall of Cambridge, England.

It was decided that a 10 in. diameter cell should be constructed, and this has been in operation since March 1958. The present electrode design has already been described; axial ports for the admission of the two gases and the electrolyte are drilled in the rim, as shown in Fig.18; when these electrodes are bolted up together in the correct order, with rings to provide space for the electrolyte and with flat discs of metal to separate the hydrogen from the oxygen in the adjacent cell, they form a battery, the voltage of which depends upon the number of cells connected in series. Radial ports for admitting gas or electrolyte from the axial ports to each cell are provided simply by slotting the gaskets. A distributor plate for leading the gases and electrolyte into and out of the battery is provided either at one end, or else in the centre of the cell-pack. The whole assembly is bolted up between two ribbed end plates, with powerful bolts, with electrical insulation between the ends of the pack and the end plates. Electrical connections are silver-soldered onto each electrode, and the inter cell connections are made externally; the main connections are of course made to the electrodes at each end of the pack.

Up to 30 cells in series have been operated so far (see Fig.19), and no special difficulties have been encountered with, for example, sealing of the joints, excessive shunt currents between cells, excessive electrolysis in the electrolyte ports, etc. But more experience will have to be obtained with large multi-cell packs before reliable results can be quoted.

#### 11. Development of Control Gear.

Control of gas admission has always been a problem, as a very delicate pressure balance has to be maintained between the two gases in the battery. A system has now been worked out whereby as a basis the pressure of the oxygen remains constant under all conditions of load; this is achieved with a standard two-stage reducing valve. The hydrogen then has to be admitted at precisely the correct rate, so that the two gas pressures are balanced to within a few inches water gauge; this is done by fitting an accurate differential pressure meter, which actuates a power-operated valve admitting the hydrogen, the valve-opening being controlled by a servo mechanism operating with compressed air. A fair amount of experience has been obtained with this gear which works extremely well. Figure 20 shows various items which made up this control gear, mounted on the front of the protective framework enclosing the cell pack.

Much thought has also been given to the problem of the removal of water, at the same rate at which it is formed. Previously this has been achieved by circulating the hydrogen steam mixture by thermosyphonic action, the steam being condensed out in a small vessel outside the lagging. In order to do this in a large battery, very large hydrogen circulating pipes and ports would be needed, so it was decided that a small hydrogen blower would be used; it was considered that a glandless form of drive would be necessary, in view of the difficulty of preventing hydrogen leakage with a standard type of gland. A magnetically driven pump using a sealing shroud of thin non-magnetic metal has been successfully employed for some time; it can be seen mounted underneath the battery in Fig.19. The rate at which the condensate is removed from the system is controlled by switching the blower on and off at intervals, the switch being controlled by a second differential pressure meter which operates on the pressure difference between the hydrogen in the system and the electrolyte. In this way, the removal of water is controlled by the total volume of electrolyte which should of course be kept approximately constant. The condensate collects in a small vessel, from which it is released periodically by a level-sensing device such as a capacitor probe. The main parts of this gear, which can be also seen in Fig.20, have been in operation and appear to work perfectly well.

Until more experience with this gear is obtained, the main level gauges will be retained in use, but eventually it should be possible to remove them.

The initial heating of the battery is accomplished by electrical heaters mounted on the end plates and round the main body of the battery inside the lagging. Various plans have been suggested for maintaining the battery at a constant temperature when on load, but the simplest is undoubtedly to allow cold air to circulate round the battery, inside the lagging, the amount of cold air introduced depending on the temperature of the cell pack.

Lastly, there is the problem of removing gas from the electrolyte system; it is difficult to prevent entirely some generation of hydrogen and oxygen by electrolysis in the common electrolyte ports, although insulation with p.t.f.c. helps considerably in this respect. Moreover, there is always the possibility that an electrode may start leaking, thus allowing gas to get into the electrolyte system. This is taken care of by a level-sensing device, which will release any gas which may collect at the top of the electrolyte system, by means of a solenoid operated valve.

All these controls may seem somewhat complicated and expensive, but there is no doubt that they can be made to work, and with a larger battery they should not be any more complex and would then represent only a small proportion of the cost of the whole plant.

## 12. Advantages and Applications.

From what has been said, it will be seen that it is unlikely that this kind of battery could be competitive with existing types of accumulator in small sizes, owing to the high cost of the control gear in comparison with the overall cost of the plant. And in very small sizes it would be difficult to keep the cells up to the working temperature unless they were on load continuously and unless very efficient heat insulation were employed. It is difficult to quote exact figures for minimum sizes until more experience is obtained, but a power output as small as 100 watts is believed to be feasible with really good lagging.

One other factor that must be appreciated is that it could not compete with say lead accumulators on a weight basis unless the length of time of discharge is greater than about 1 hour; however, for longer times than this, the saving in weight should become increasingly important, as shown in Fig.21. The figures for conventional accumulators are a few years out-of-date, but the general picture to-day is undoubtedly roughly the same. It is on a weight basis that the hydrogen-oxygen battery should be able to show its principal advantage over conventional accumulators. A curve for a Diesel engine with fuel is also included, and this serves to show that it will always be difficult to compete on a weight basis with a power generator which can draw its oxygen from the atmosphere. However, it is as well to bear in mind that both accumulators and internal combustion engines have a great many years of careful development behind them, whereas the fuel cell is still in its infancy.

The fuel cell weight of 50 lb./kW shown in Fig.21 was worked out for a large battery developing about 44 kW.; this weight to power ratio will not be achieved in the small experimental unit now being built, and it would be unwise to hazard a guess about this until it is completed. The first requirement has been that it should work, rather than that it should have minimum weight or volume.

As regards power per unit volume, the figure of  $8.2 \text{ kW/ft.}^3$  of internal cell volume has already been quoted for a cell voltage of 0.68; a figure of  $3 \text{ kW/ft.}^3$  for the whole battery without control gear, was quoted by an independent body some years ago, for a cell voltage of 0.8.

It has always been hoped that some specialised application will arise first, an application for which a fuel cell is particularly suited. In this connection, the possible use of fuel cells in satellites and space vehicles is of great interest. Then, when further experience has been obtained, it should be possible to enter the commercial field in competition with storage batteries which have already been developed to a high pitch.

It would seem that fuel cells of this type are most suitable for traction purposes, both road and rail; the combination of battery and direct current series wound motor provides an ideal propulsion unit for many types of vehicle, the limiting factor so far being the weight of the battery. The gases would probably be generated by electrolysis of water, and in this connection the development of an efficient high pressure electrolyser in Germany is of great interest. It is well known that the cost of electrical power from the National grid is considerably less than that of power produced in a petrol engine, and this is of special importance where the vehicle is subject to repeated starts and stops.

Further, if finally most of the power is generated on a large scale from nuclear energy, the cost of the electricity will be mainly due to the capital cost of the plant rather than to the cost of the nuclear fuel; and the need for some kind of large scale storage will become increasingly important, as little will be saved by shutting down the plants during times of light load.

Other advantages of this kind of fuel cell are that it is able to take large overloads at reduced efficiency without damage, it is silent and free from vibration in operation, it has very few moving parts and the "exhaust" is only water; moreover, the "charging" process would merely consist of refilling with the two gases, a very rapid process.

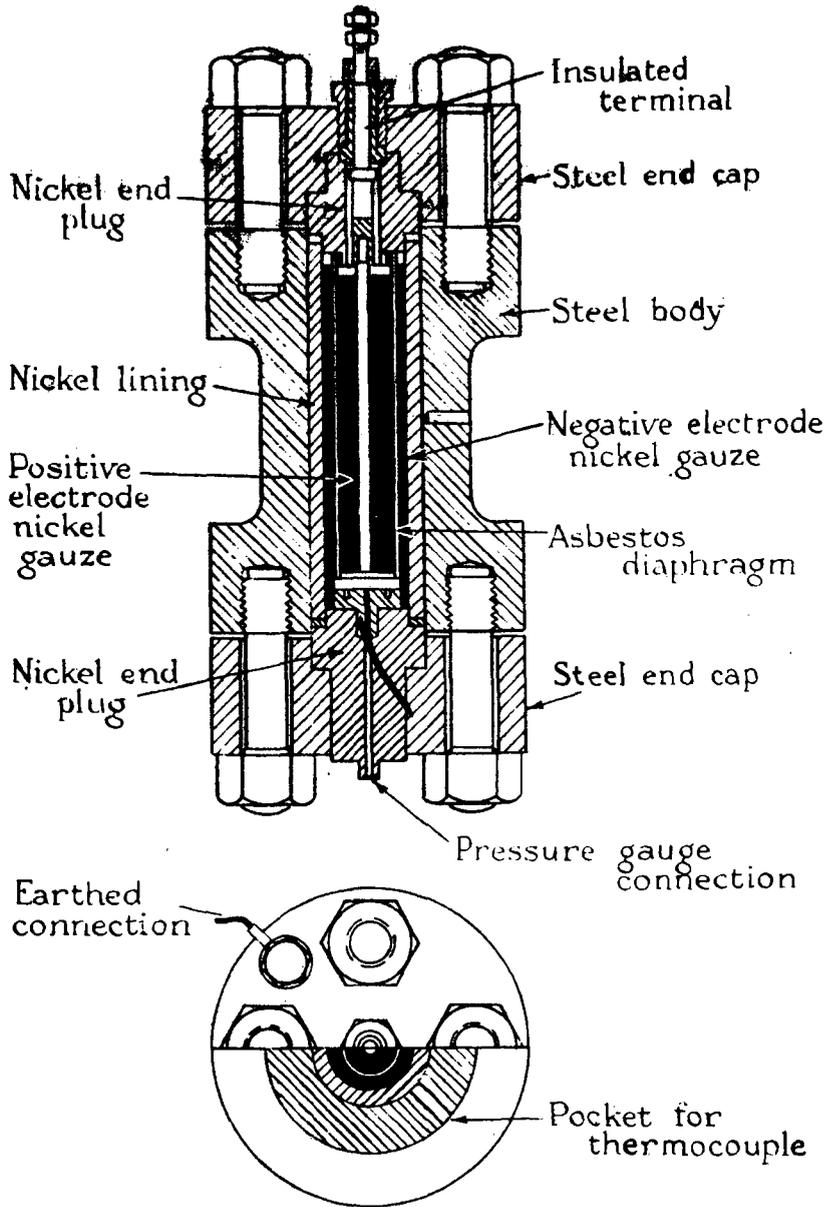
With the advent of new methods of storing hydrogen and oxygen, either in liquid form, or else in the former case as a compressed gas at a very low temperature, it would seem conceivable that vehicles could be propelled over really long distances with fuel cells; and in view of the rapid depletion of the world's oil supplies, the development of a practical fuel cell should, in the author's opinion, be given a high priority.

The author would like to thank his colleagues who have given invaluable help in the preparation of this paper; and in particular Dr. R.G.H. Watson, now at the Admiralty Materials Laboratory, Holton Heath, England.

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**FIG. 1. APPARATUS FOR USING COILS OF GAUZE AS ELECTRODES. GAS SUPPLY BY INITIAL ELECTROLYSIS**



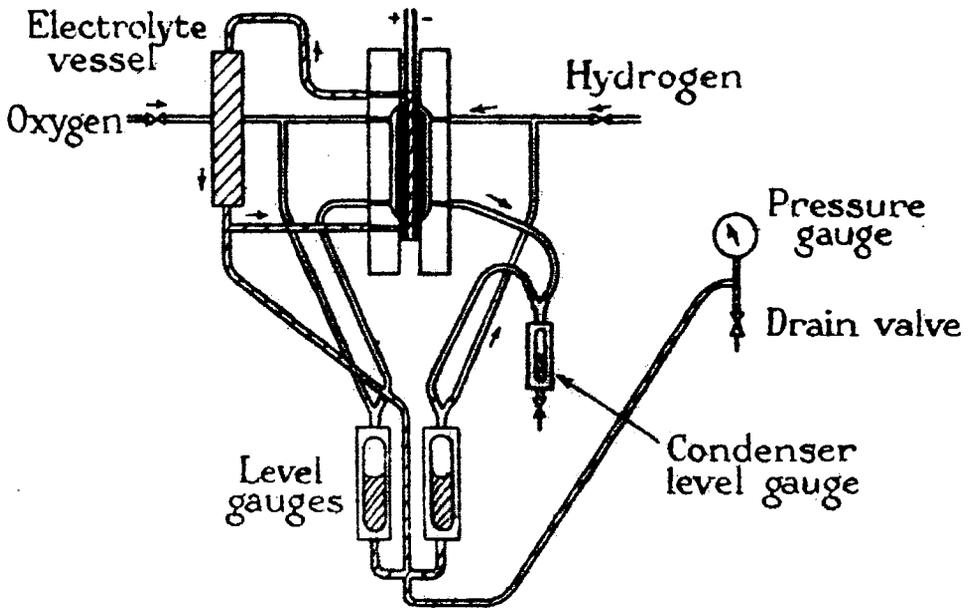


FIG. 3 APPARATUS EMBODYING CELL WITH POROUS DIFFUSION ELECTRODES.

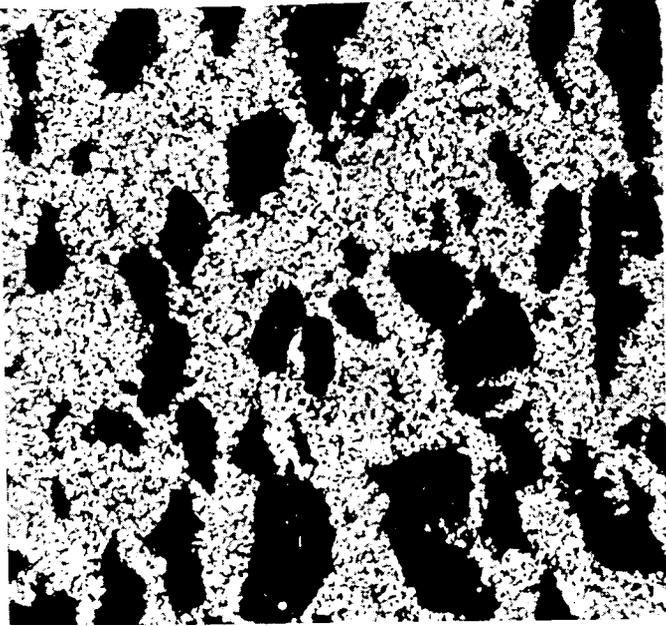


FIG. 4. MICROSECTION SHOWING COARSE PORE SIDE  
OF HYDROGEN ELECTRODE (x 150)

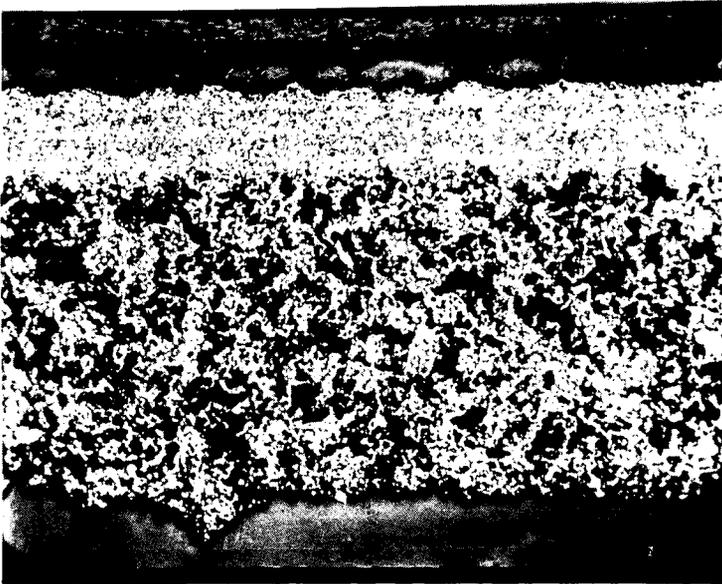


FIG. 5. MICROSECTION SHOWING COARSE AND FINE  
PORE LAYERS OF OXYGEN ELECTRODE  
(x 38)

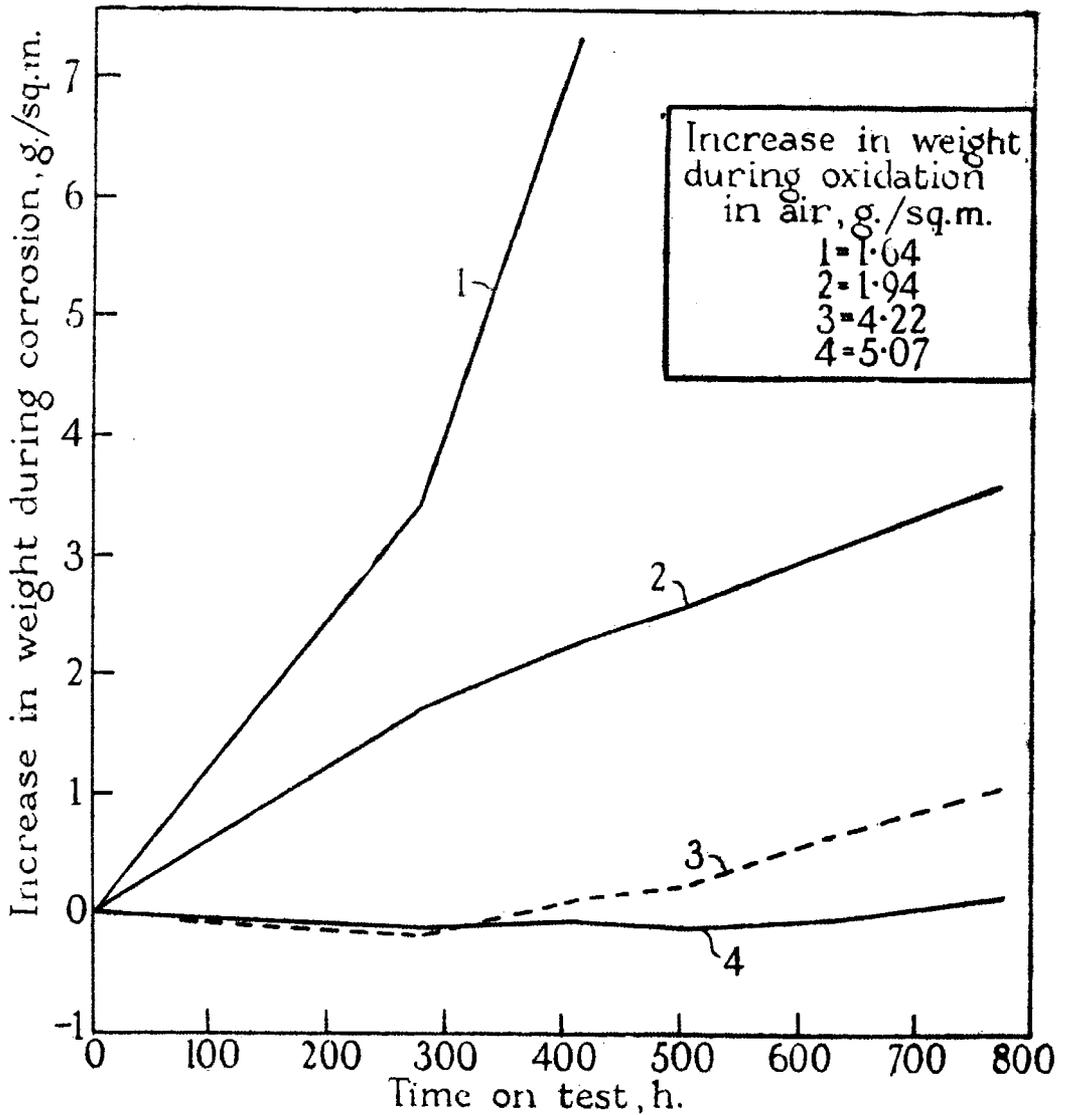
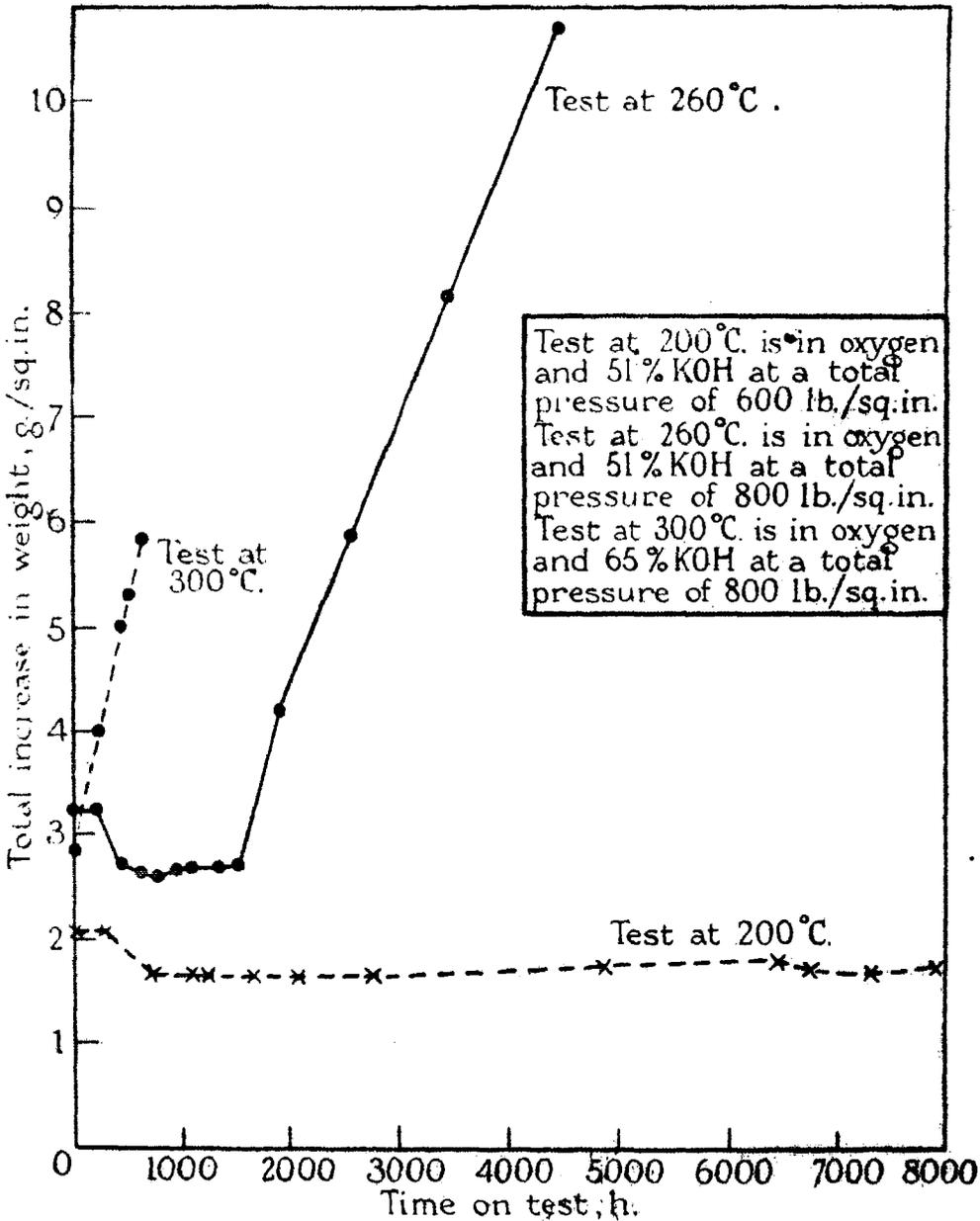


FIG. 6 CORROSION OF SAMPLES OF NICKEL PREOXIDIZED IN THE PRESENCE OF LITHIUM HYDROXIDE AND EXPOSED TO 65 % KOH AND OXYGEN AT 300°C. AND 800 lb./sq. in. TOTAL PRESSURE.

Each curve represents a pair of samples.



Test at 200°C. is in oxygen and 51% KOH at a total pressure of 600 lb./sq.in.  
Test at 260°C. is in oxygen and 51% KOH at a total pressure of 800 lb./sq.in.  
Test at 300°C. is in oxygen and 65% KOH at a total pressure of 800 lb./sq.in.

FIG. 7 CURVES SHOWING THE EFFECT OF TEMPERATURE ON CORROSION RATE

Values plotted are averaged from a series of samples coated with a protective oxide containing lithium, the oxide layers being of similar thickness.

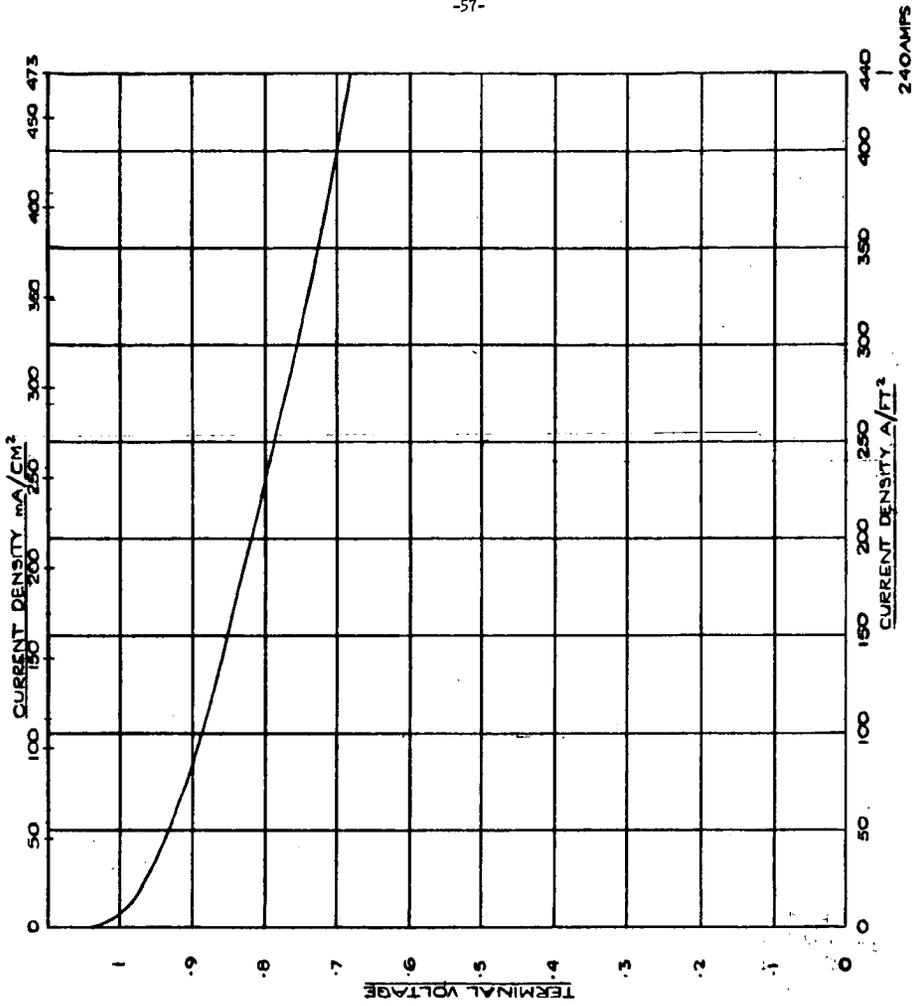


FIG. 8. BEST PERFORMANCE OBTAINED SO FAR WITH 10" DIA CELL (MULTI-CELL PACK)  
(200°C; 400 PSI; 37% KOH)

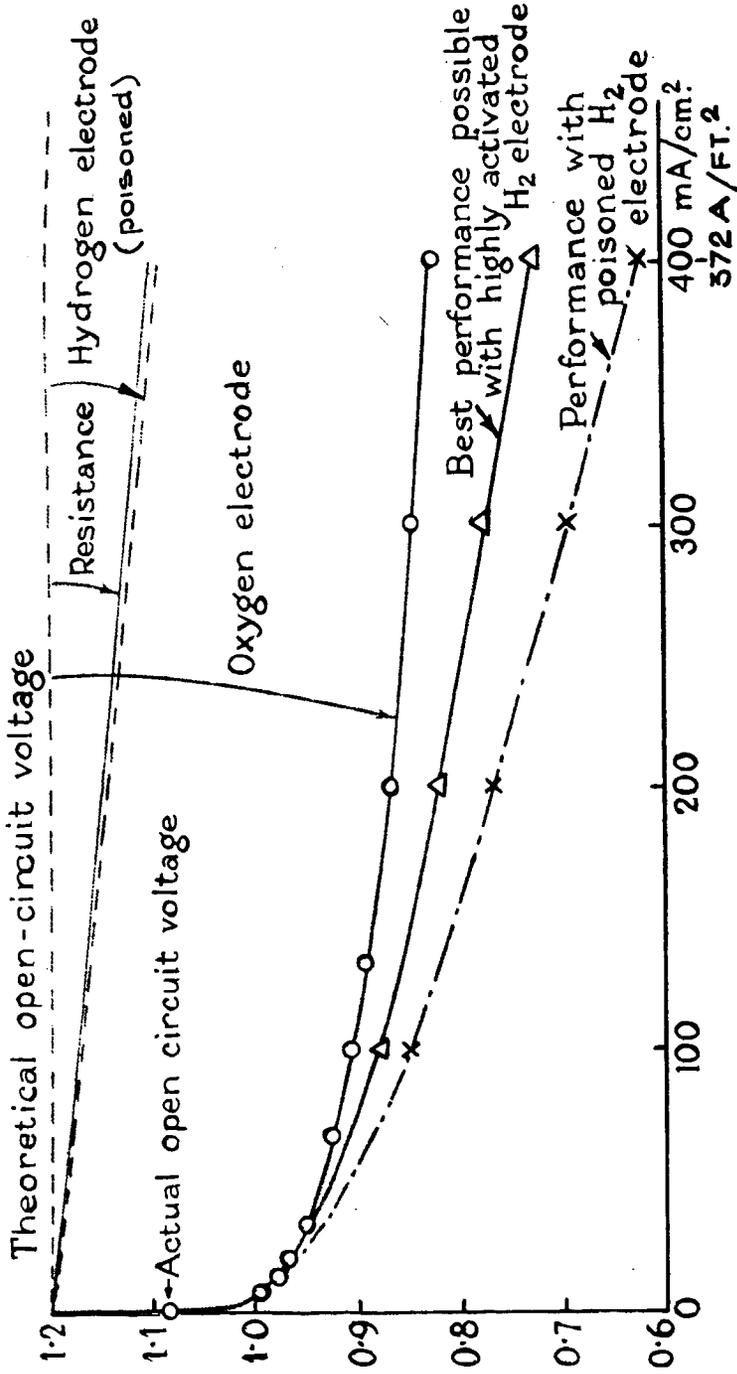
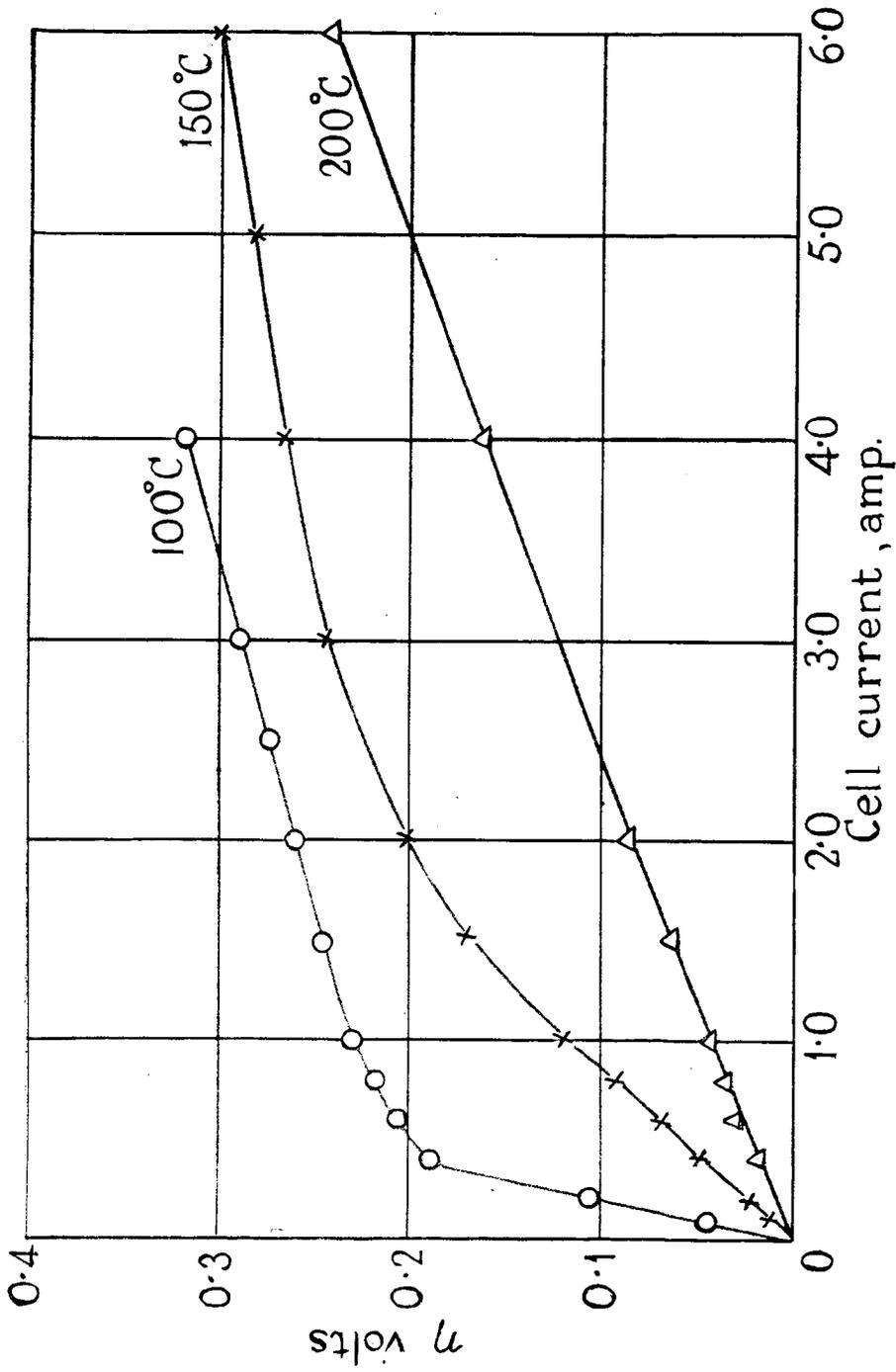


FIG. 9. PERFORMANCE OF CELL IN TERMS OF EACH ELECTRODE AND RESISTANCE 40 KOH; 200 C.; 620 lb./sq. in.



**FIG. 10. POLARIZATION OF HYDROGEN ELECTRODE AT VARYING TEMPERATURE IN 5N, KOH SOLUTION.**

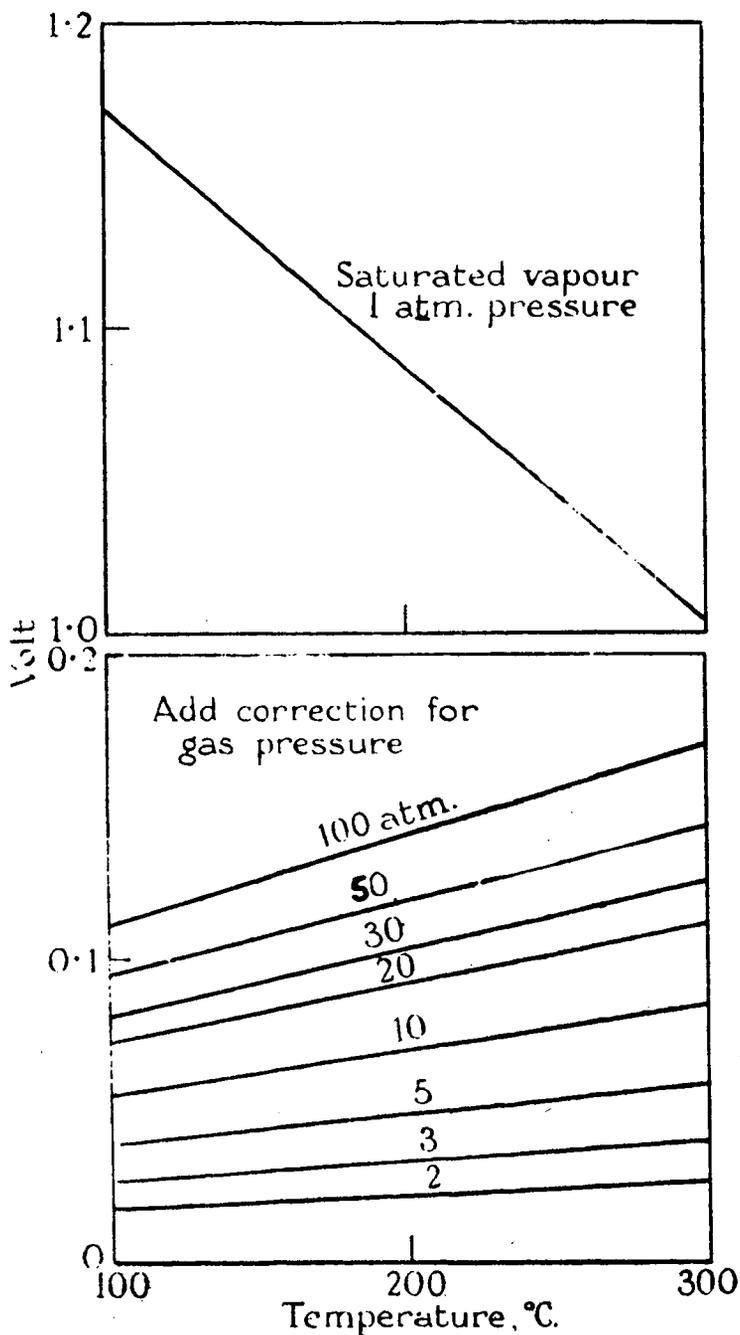


FIG. II. REVERSIBLE VOLTAGE OF HYDROGEN-OXYGEN CELL

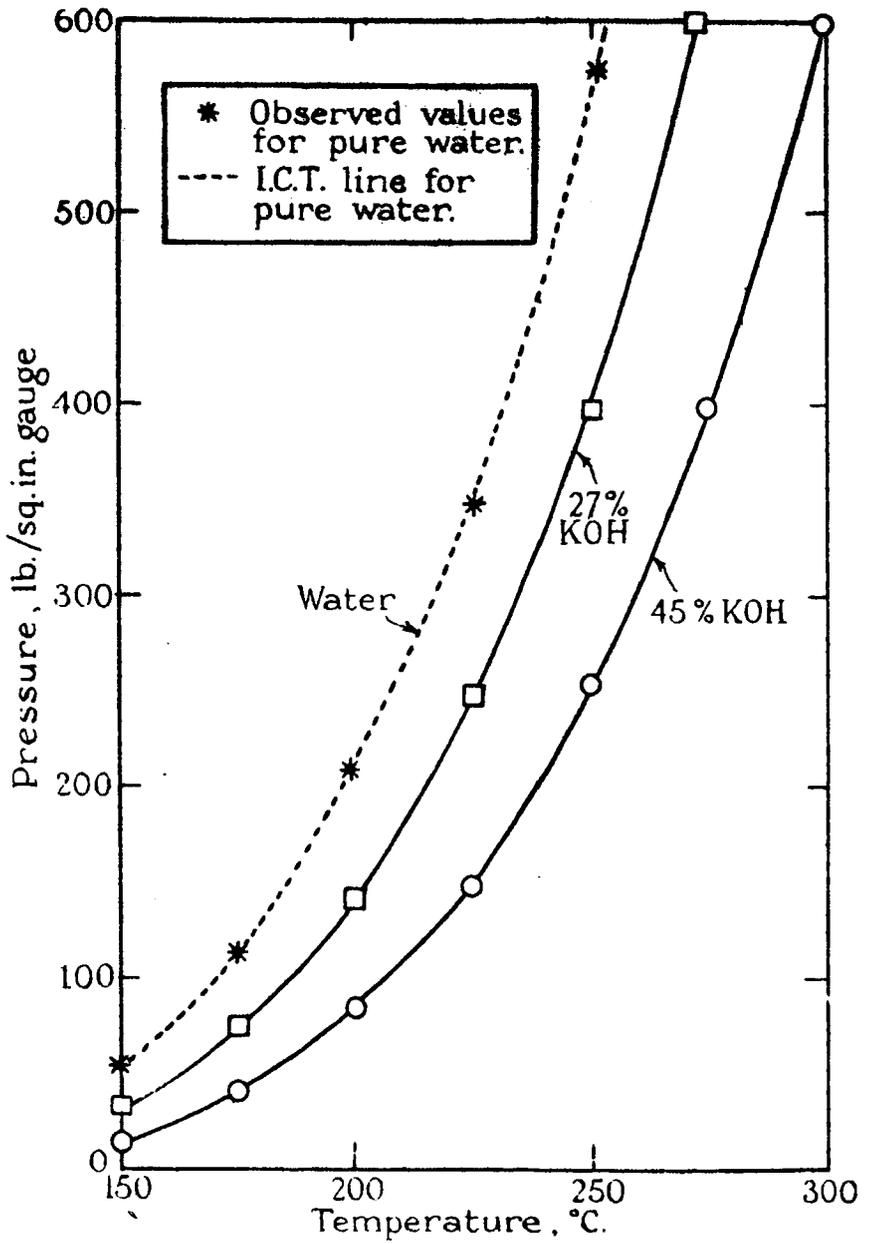
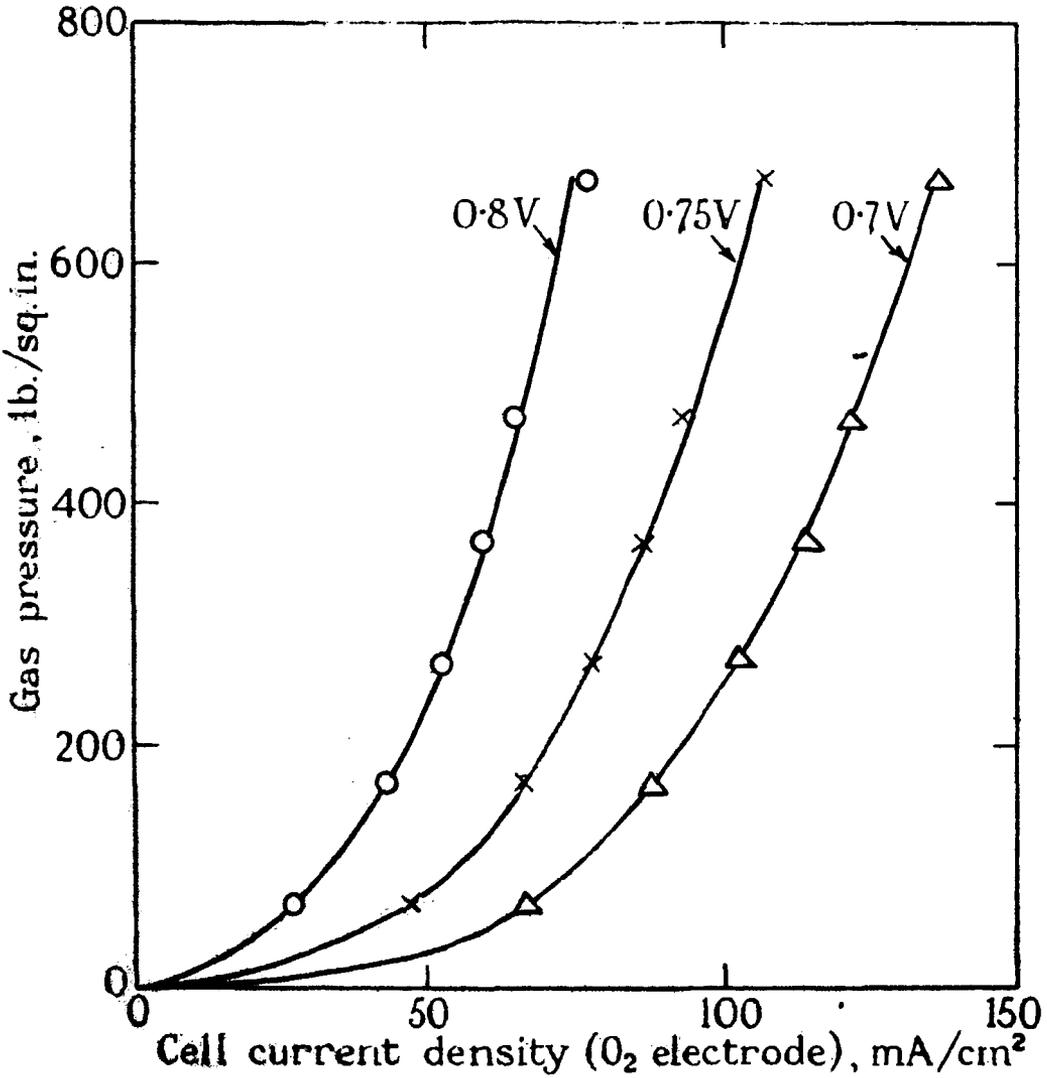
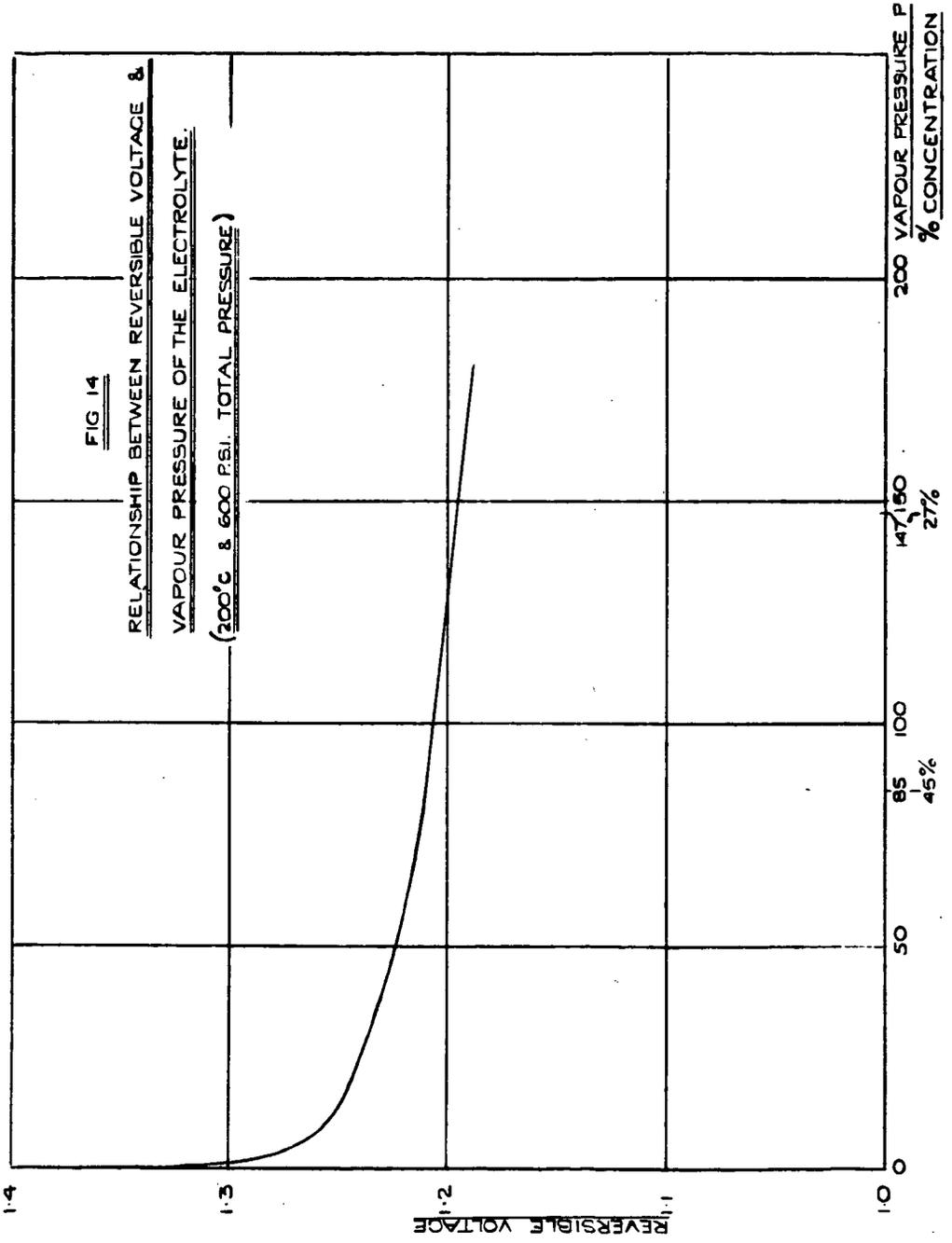


FIG. 12. VAPOUR PRESSURE OF ELECTROLYTES.



**FIG. 13. VARIATION OF CELL OUTPUT WITH GAS PRESSURE FOR VARIOUS VOLTAGES.**



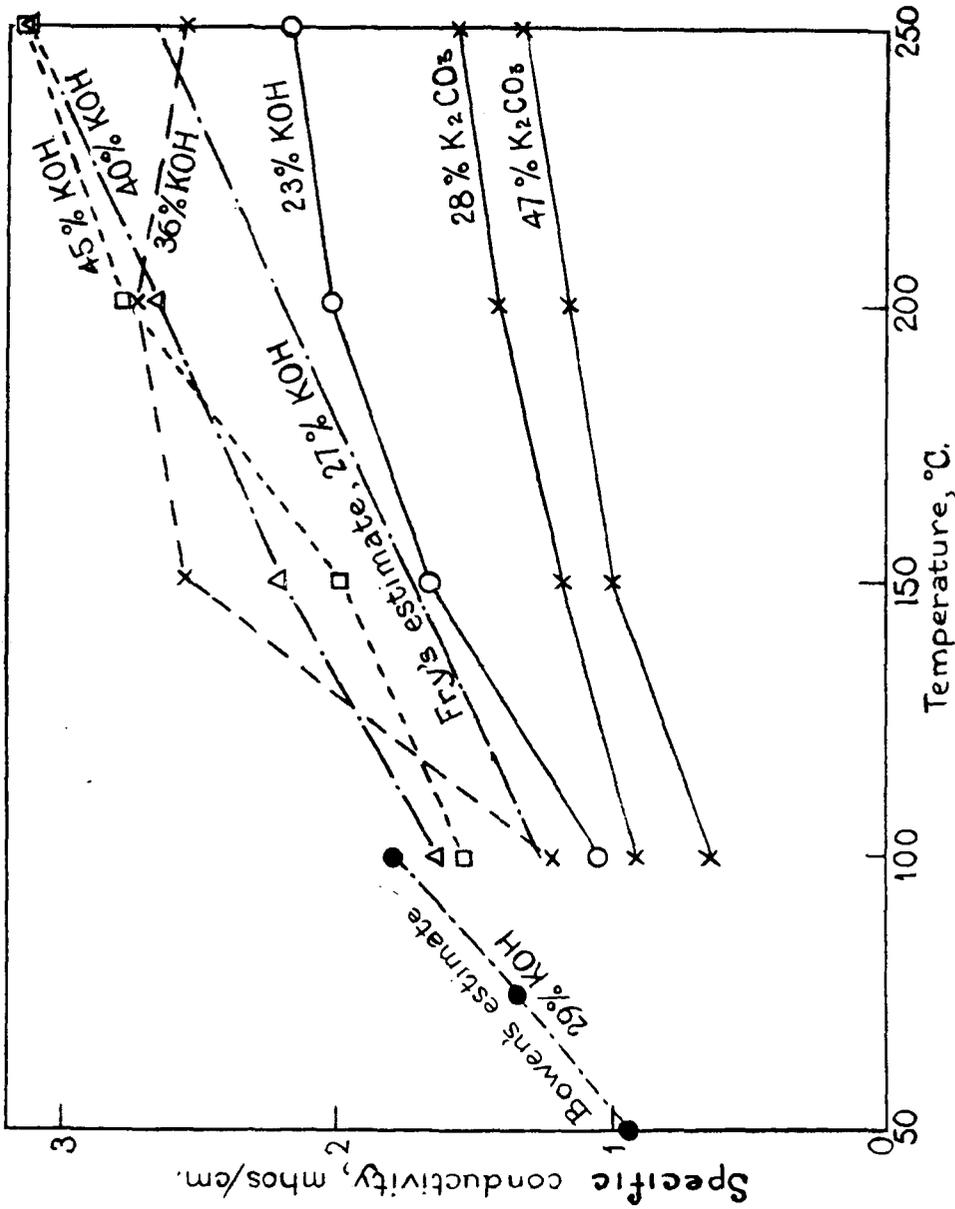


FIG. 15. VARIATION OF ELECTROLYTE CONDUCTIVITY WITH CONCENTRATION AND TEMPERATURE.

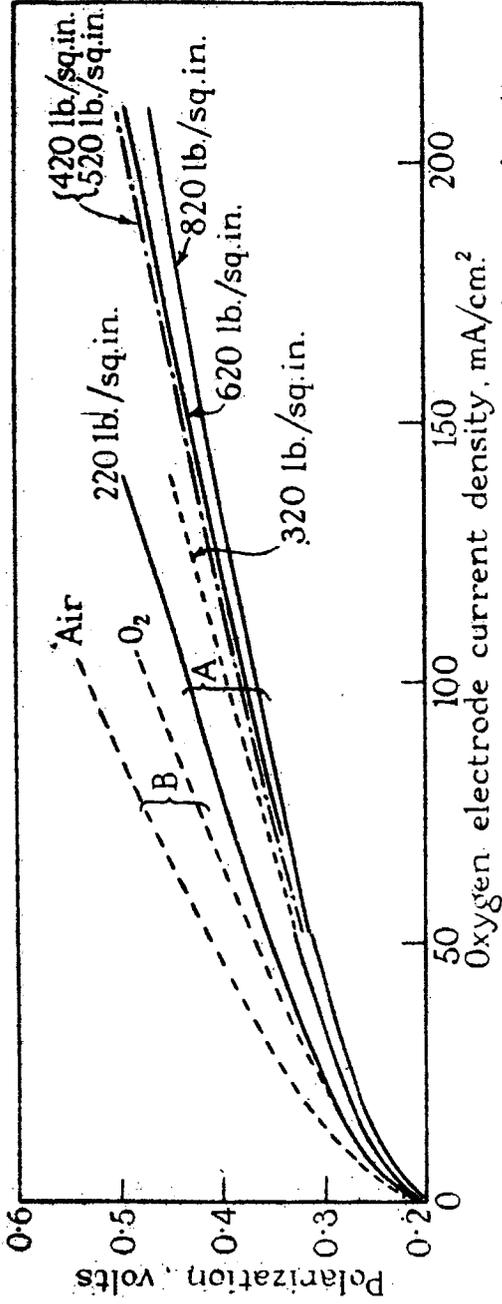


FIG. 16 THE EFFECT OF PRESSURE ON POLARIZATION AT THE OXYGEN ELECTRODE (A) 5N. KOH, 200°C. (B) 5N. KOH, 200°C. F. 183

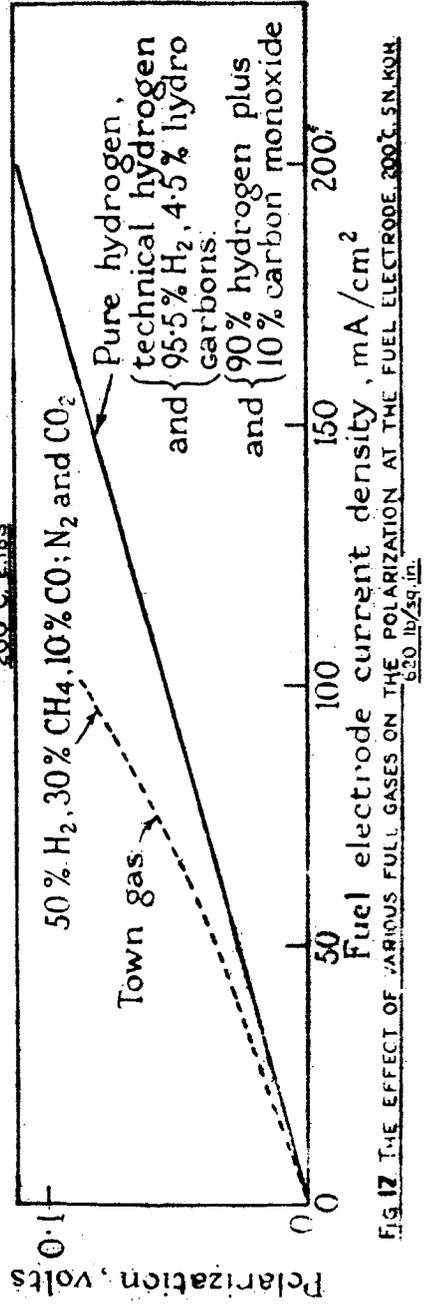


FIG. 17 THE EFFECT OF VARIOUS FULL GASES ON THE POLARIZATION AT THE FUEL ELECTRODE, 200°C., 5N. KOH, 520 lb./sq.in.

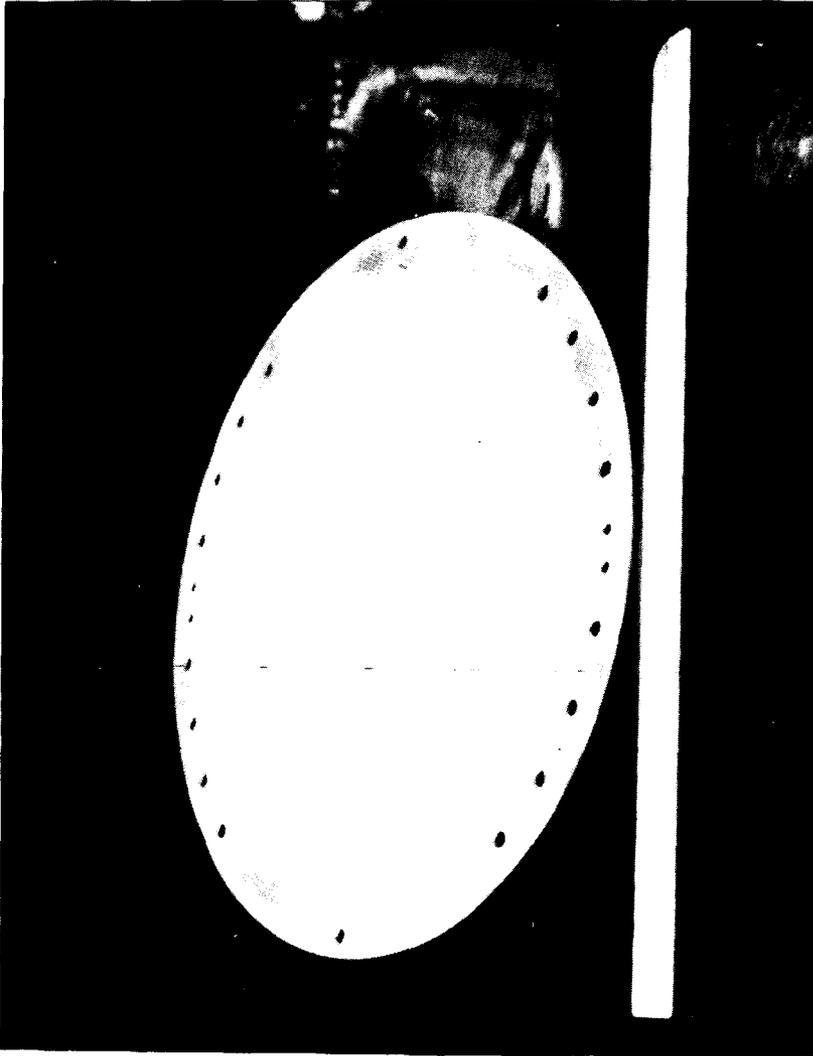


FIG. 18. ELECTROLYTE SIDE OF 10-INCH DIAMETER ELECTRODE

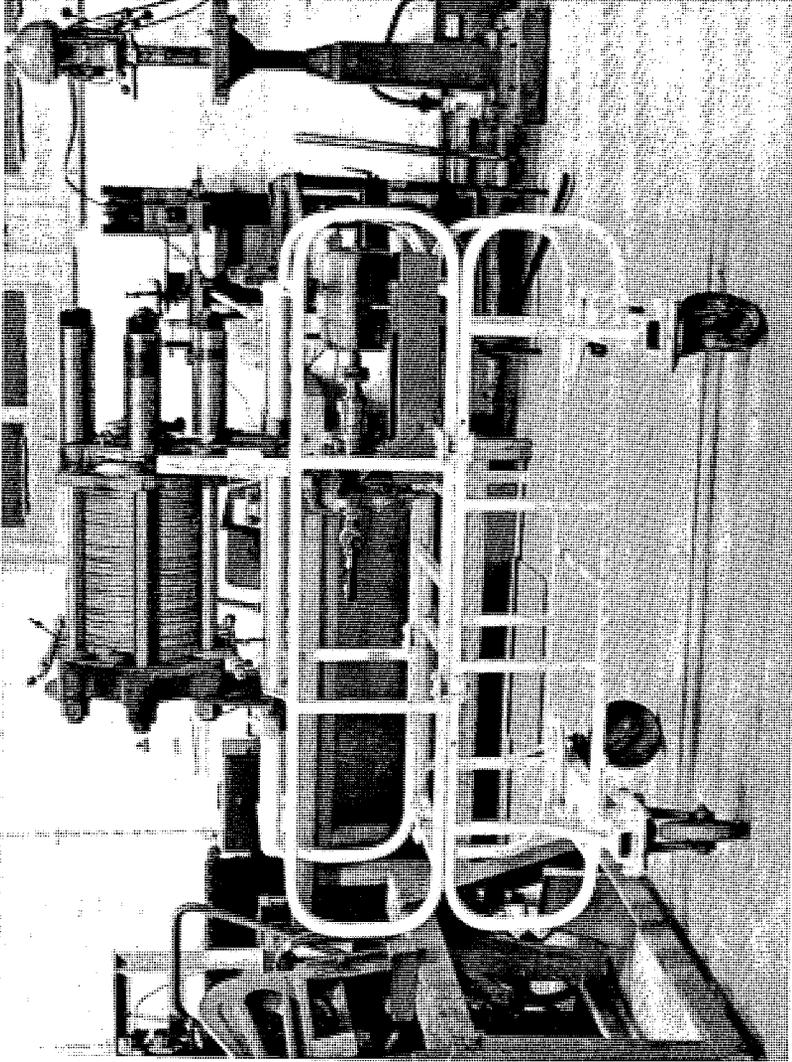


FIG. 19. 30-CELL BATTERY MOUNTED ON TROLLEY; HYDROGEN  
BLOWER MOUNTED UNDERTEATH

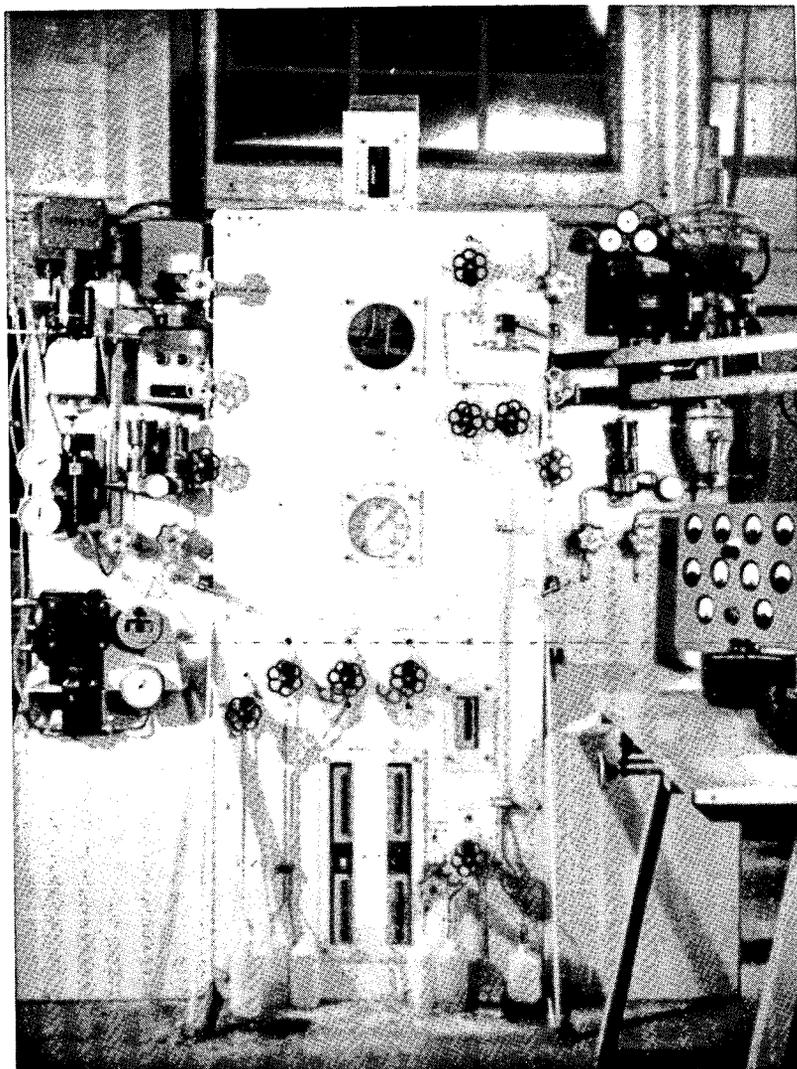


FIG. 20. CONTROL GEAR MOUNTED ON FRONT  
OF PROTECTIVE FRAMEWORK

# HYDROGEN/OXYGEN CELL (FIG 21)

## RELATIONSHIP BETWEEN WEIGHT & ENDURANCE FOR 44 KW CELL

