Performance of Fractional Watt Ion Exchange Membrane Fuel Cells

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The effect of design and operational variables on the performance of one type of hydrogen-oxygen ion exchange membrane fuel cell has been studied. Only the results of cells based on a phenolsulfonic acid formaldehyde type of ion exchange membrane containing one type of reinforcement are described. Platinum, palladium, iridium, and rhodium are adequate electrode materials for room-temperature operation. Performance of cells with platinum gauze current collectors bonded to the cell surfaces was only slightly better than that with external contacts about 1 cm. apart.

Open circuit voltages range from 0.9 to 1.1 v. (theoretical 1.23) depending on the catalyst. The typical current at 0.5 v. is 30 ma./sq. cm. Better cells have delivered 80 ma./sq. cm. at 0.5 v. Life tests indicate that these cells can be expected to deliver a minimum of about 40 amp.-hr./sq. cm., when operated in the load range 8.5 to 230 ohm sq. cm., before failure of the electrolyte owing to pinhole formation. Current efficiency is very nearly 100%. Cell performance vs. temperature in the range 0° to 85°C. shows a maximum at about 55°C.

Hydrogen-oxygen cells based on an ion exchange membrane electrolyte were first described in 1957 by W. T. Grubb (*1*, *2*). Two years later a significant improvement in performance was reported by L. W. Niedrach (*3*). A fairly detailed account of the construction, operation, and performance of cells based on the early Grubb structure was published recently (*4*). This report is concerned with the performance of ion exchange membrane cells as it is influenced by cell construction parameters, type of electrode material (catalyst), and certain operating variables such as temperature and load resistance.

It is important to call attention at the outset to the fact that all the data have been obtained with small (1½-in. diameter) laboratory cells operating on static heads of hydrogen and oxygen or air at room temperature and pressure. Under these conditions the effects of heat generated in the cell due to ohmic losses and electrochemical irreversibilities will be negligible. Thus extrapolations of the results will give only roughly the performance of large high power-density batteries. In the latter the heat rejected by the cells leads to temperature gradients and possibly to concentration gradients, which can have profound effects on cell performance. Since temperature gradients are involved, useful results will not be obtained by simply operating the small cells at elevated temperatures. However several constructional parameters, for example electrode material and its relative amount, ion exchange resin, current collector design, etc., are studied more easily with small cells; the results may be extrapolated to larger sizes with complete confidence. Some chemical factors, for example stability of the electrolyte, can be investigated in the small cells over a range of temperature, and the results will be useful in predicting behavior of the larger cells and batteries.

EXPERIMENTAL

All of the cells discussed here have electrode areas of 11.4 sq. cm. (circular), electrolyte thicknesses of 0.06 cm., and gas space thicknesses of 0.16 cm. A reinforced sulfonated phenol-formaldehyde casting resin was used for the majority of the cells. The essence of the ion exchange membrane cell is the bonding of thin layers of electrode material (referred to as *catalyst*) to the surfaces of the membrane electrolyte. These layers have a thickness of about 0.0025 cm. Since the catalyst layers are relatively poor electronic conductors, current collectors must be provided in order to minimize the internal resistance of the cells. Thus two cell constructions were studied:

Type I. Platinum gauze current collectors are buried in the electrolyte surface (see Figure 1). This is a laboratory convenience and cannot be considered practical owing to high cost and because of manufacturing difficulties encountered with the use of gauze collectors in large-size cells.

Type II. Current collection is provided by external collectors contacting the cell at several points (see schematic diagram in Figure 2). Collectors machined from high-density graphite and molded of graphite-loaded plastic (PVC) have been used successfully. In general these collectors had twelve circular contacts 0.16 cm. in diameter equally spaced on ½- and 1-in. diameter circles. In assembling the cells the optimum contact pressure was obtained by tightening the bolts until a minimum internal resistance was reached.

Fuel cells have been operated on hydrogen and oxygen and on hydrogen and air. Usually, electrolytic grades of hydrogen and oxygen have been used. Laboratory prepared (from aqueous potassium hydroxide) electrolytic oxygen and hydrogen were used in about 25% of the cells. No significant differences in polarization performance were found between these cells and those operated on cylinder gases. However the gases prepared in the laboratory contained smaller amounts of impurities than those obtained commercially.

The basic measure of cell performance is the polarization curve. These data were obtained by placing various resistive loads across the fuel cells and measuring the voltages and currents after each had reached a steady state value. The time required to attain steady voltage and current after a change of load varied from several seconds to a few minutes, depending on the cell characteristics. Two equivalent methods were used for obtaining data.

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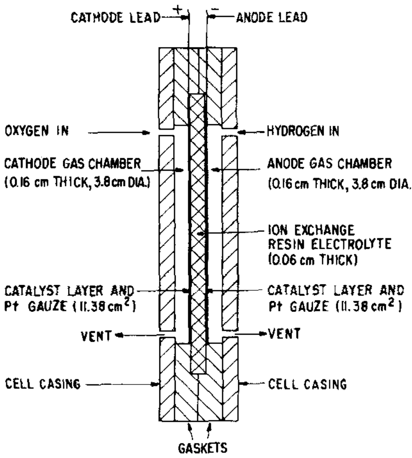

Fig. 1. Type I fuel cell.

1. A decade resistance box (0.1 Ω to 10,000 Ω) was connected in series with a d-c polyranger (serving as an ammeter) across the fuel cell. The voltage across the cell terminals was measured with a potentiometer and recorded on a graphic recorder.

2. An X-Y plotter was connected to the fuel cell such that the voltage across the cell was plotted on the Y-axis, and the current through the load circuit was plotted on the X-axis. Range settings for the Y-axis were determined by comparison with readings on a potentiometer. A current sensing resistor having a value of 0.1 ohm was placed in the load circuit, and the voltage drop across it was plotted on the X-axis. The X-range was set by use of a d-c polyranger serving as an ammeter. The load resistance on the fuel cell consisted of various 1% resistors which were placed in the load circuit for 2-min. intervals. At the end of each 2-min. interval the pen drop circuit was activated, placing a voltage-current data point on the chart. This cycle was continued until nine points were plotted, starting with the highest resistance value and progressing to the lowest.

A total of about fifty cells, including some of each type, have been placed on life test by connecting fixed resistive loads across the terminals. Periodically the voltages across the load resistances have been recorded by a twelve-point recording potentiometer. Early in the life of the cells the record was made daily. Later, as cell output became steady, the record was made at intervals of 2 weeks to a month.

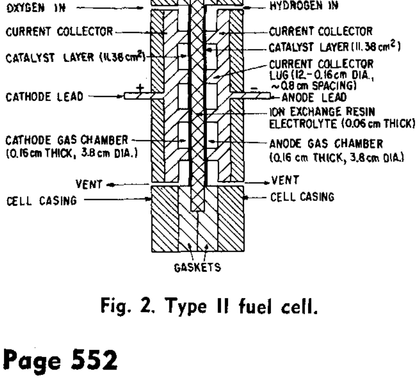

Fig. 2. Type II fuel cell.

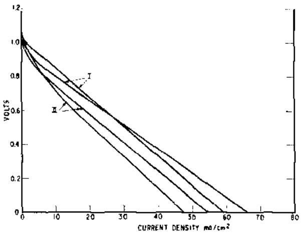

Fig. 3. Comparison of cell types at 0.0088 g./sq. cm. platinum black, t ≈ 27°C.

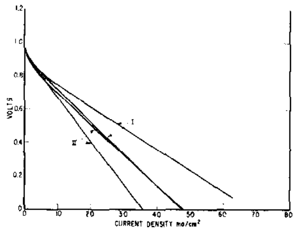

Fig. 4. Comparison of cell types at 0.0088 g./sq. cm. palladium black, t ≈ 27°C.

At similar intervals the fixed load resistors have been removed long enough to take polarization curves.

Normally the fuel cells have been operated at room temperature (25° to 27°C.) on a static head of hydrogen and oxygen amounting to a few inches of water. Both gases are nearly saturated with water vapor. The vents shown in Figures 1 and 2 are kept closed during normal operation by means of tubes immersed in water. The product water from the cells drains by gravity into the water pool which seals the vent tubes. At intervals of about 1 week the vent tubes have been opened for several seconds to 1 min. in order to purge the accumulated inerts from the gas chambers. As a rule a purge has preceded polarization data taking.

Only cells of Type I have been operated on hydrogen and air. Here a very thin plastic is used for the casing on the air side. Access of air to the electrode is provided by a 0.3- to 0.5-cm. diameter hole in the center. Product water which accumulated in the cell has been drained periodically.

Variables other than the cell structure, studied in connection with their effect on the cell performance and life, were

1. Catalyst loading. Several different catalyst surface concentrations or loadings ranging from 0.003 g./sq. cm. to 0.022 g./sq. cm. were investigated. No specific efforts have been made to adjust loading for the differences in specific gravity among the various catalysts.

2. Catalyst. Most experiments were confined to platinum and palladium electrodes. Preliminary results are reported for iridium, rhodium, and ruthenium.

3. Ion exchange resin. Most experiments were confined to the phenol-formaldehyde resin previously mentioned. However some modifications of this resin were studied in a preliminary manner.

4. Load resistance. The effect of various fixed resistive loads on the lifetime and on the cell performance was studied.

5. Operating temperature. Preliminary experiments have been carried out on the effect of temperatures in the range of 0° to 85°C. Cells were immersed in an ice bath, and polarization curves were taken as above. As the ice melted and the bath temperature slowly increased, data were taken yielding polarization curves for temperatures between 0° and 27°C. Cell performance at elevated temperatures up to 85°C. was studied by immersing cells in a constant temperature water bath. Gases were saturated with water vapor by bubbling them through water held at the same temperature as the cells. Some of these tests were continued for periods up to 1 month to obtain some indication of cell life at high temperatures.

A sufficient number of experiments have been carried out so that all of the results reported in the following section are based on observations of two or more cells, unless otherwise noted.

RESULTS AND DISCUSSION

Polarization Phenomena

The theoretical open-circuit voltage for the reaction

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O_{(liq.)}$$

is 1.23 v. at 25°C. The voltage is attained, for unit activity of the reactants and the products, when one has both a reversible hydrogen and a reversible oxygen electrode. In the case at hand the oxygen electrode is far from reversible. The hydrogen electrode on the other hand is nearly reversible; in the current density region reported here all electrode polarization may be attributed to the oxygen electrode.

When current is drawn from the cells, the voltage drop with current increase follows a logarithmic (Tafel) relationship associated with the fact that the electrode kinetics are governed by an activation process. This logarithmic activation polarization reaches a saturated value at current densities in the region of 10 ma./sq. cm. The straight-line portion of the polarization curve is associated with the ohmic drop in the cell. The important contributions to resistive losses are listed below.

1. Membrane resistivity, which is equal to about 11.5Ω-cm. for pure standard resin and to about 25 to 30Ω-cm. for the membrane.

2. Catalyst layer lateral resistance, which is equal to about 1 ohm/sq. of 0.078 g./sq. cm. palladium black, and to about 8.5 ohms/sq. of 0.0039 g./sq. cm. of palladium black. For the same loadings using platinum black the resistance values are approximately three times as large.

3. Contact resistance (pressure dependent).

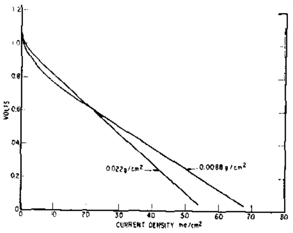

Fig. 5. Performance comparison of various platinum black loadings in type I cells at t ≈ 27°C.

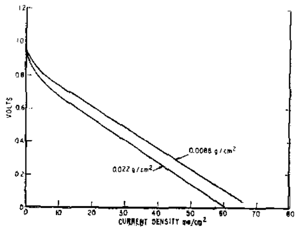

Fig. 6. Performance comparison of various palladium black loadings in type I cells at t ≈ 27°C.

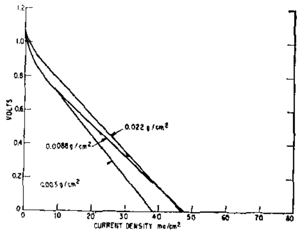

Fig. 7. Performance comparison of various platinum black loadings in type II cells at t ≈ 27°C.

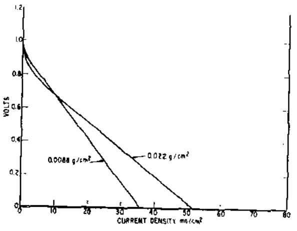

Fig. 8. Performance comparison of various palladium black loadings in type II cells at t ≈ 27°C.

4. Current collector resistance (usually not significant).

Another effect, which may be important in the linear portion of the polarization curve, is the extent of catalyst surface coverage by adsorbed fuel or oxidant.

Diffusion limitations are characterized by a steep drop in the polarization curve at the higher current densities. Usually such a limitation has not been encountered with the cells discussed here, unless by accident the electrode surfaces have become masked by a barrier film, for example a resin or water film.

Fuel-Cell Efficiency

All of the polarization phenomena discussed above lead to corresponding losses in efficiency. The free-energy efficiency of a fuel cell is defined as

$$\text{Eff} = \frac{\int_0^{\theta} Ei d\theta}{n'FE^{\circ}}$$

Any voltage or current loss results in an efficiency loss in the operating fuel cell. Thus an open-circuit voltage which is less than E° results in a voltage efficiency of E/E°.

Comparison of Cell Structures

Typical polarization curves for the two cell structures with electrodes consisting of 0.0088 g. platinum/sq. cm. are shown in Figure 3. Each curve is representative of the time-average performance of several cells, each taken over several months. The open-circuit voltage (O.C.V.) obtained with platinum black electrodes is in the range 1.06 to 1.11 v. For any given cell the open-circuit voltage is usually constant to ± 0.01 v. The 95% confidence limits for the current variation from cell to cell at a given voltage for a given cell type are approximately ± 15%. Differences in performance between the types are not great; however cells having the platinum gauze current collectors (type I) show slightly better performance, probably due to the reduced contact and catalyst layer resistances. In some early type II cell assemblies these resistances totaled several tenths of an ohm, resulting in markedly decreased performance.

Figure 4 reports similar representative average polarization curves for the two cell types using 0.0088 g./sq. cm. of palladinum black catalyst. Note that the general performance for the palladium cells is nearly the same as for corresponding platinum cells shown in Figure 3, except for the reduced open-circuit voltages (0.96 to 0.99 v.) These are quite reproducible and for a given cell do not vary more than about 1% over long periods of time (months).

Catalyst Loading

The time-average performance of cells is not sensitive to variations in catalyst loading in the range 0.0088 g./sq. cm. to 0.022 g./sq. cm. While one might expect a greater effect, it is possible that the lower amount is enough to nearly saturate the available resin surface. That is, almost the maximum possible development of the three-phase contact line (in reality a zone of finite width) is achieved at the smallest catalyst loading. Since the site of the electrochemical reaction is the three-phase region, additional catalyst loading would not greatly enhance the performance. The electrical resistance of the catalyst layer however would be decreased, and this would be expected to show up as a performance increase in type II cells.

Effects of catalyst loading on the performance of various types of cells are summarized in Figures 5 through 8. Figures 5 and 6 show typical time average performance curves for type I cells with platinum black and palladium black catalyst, respectively. These results are interpreted to mean that there is no large effect of catalyst loading. In the section on results of life tests this point is discussed further. In other experiments it has been found that the performance of type I cells is unaffected by catalyst loadings in the range 0.022 g./sq. cm. to 0.066 g./sq. cm.

Type II cells typically show slightly better time-average polarization behavior at the higher catalyst loadings, as shown in Figures 7 and 8; however these differences are generally not greater than experimental scatter. Extension of the range of catalyst loading down to 0.003 g./sq. cm. of platinum black in the type II cells would be expected to show greater differences in cell performance per unit change in catalyst loading, and such is the case as shown in Figure 7. The practical lower limit on catalyst loading is a function of the type of current collector used. Thus the effect of a change in catalyst loading on performance is a function of cell type, catalyst type, and current collector characteristics. Based on the results of the present experiments it does not appear that a catalyst loading above about 0.025 g./sq. cm. is especially advantageous. Greater loading may be needed under very adverse current collector design conditions, in which case the additional catalyst will be acting as a current conductor rather than as a catalyst per se.

Catalyst

The catalysts upon which most of the present work is based are platinum and palladium; however all of the remaining platinoid elements were considered (iridium, rhodium, ruthenium, osmium). Since platinum and palladium serve very well as a reversible hydrogen electrode, but not nearly so well as an oxygen electrode, the main interest was in testing various catalysts to find a better oxygen electrode material. Therefore the experiments were performed with platinum or palladium electrodes on the hydrogen side and various other materials on the oxygen side. Most of the experiments performed were of rather short duration (a few weeks), and only limited life test data are available for comparison with platinum results, which may be adopted arbitrarily as a standard. There is no indication so far that iridium or rhodium will show life performance inferior to platinum or palladium. Studies were made for the most part with the type I cell structures, and the catalyst loading was determined empirically as the minimum amount necessary to give a loading which appeared continuous and homogeneous on visual inspection. The resulting variation in catalyst loading should have little effect on cell performance as discussed above. Results are summarized in Figure 9. No great effort was expended in determining the best cell-production techniques for use with rhodium and iridium (each catalyst has different bonding properties). These results then appear quite encouraging, and it is not unreasonable to hope that the performance for iridium and rhodium cathodes could be equivalent to the better platinum and palladium cathode performance.

Resin Type

Attempts have been made to improve the fuel-cell performance by altering the composition of the ion-exchange resin. The properties of the resin which one can easily measure do not necessarily give an adequate index of the performance of a hydrogen-oxygen fuel cell produced therefrom. In addition to the obvious properties such as water permeability, physical strength, and electrolytic resistivity, the bonding properties of the resin to the membrane reinforcing material and to the catalyst play a strong role in determining fuel-cell performance. Figure 10 shows typical time-average performance curves of cells produced from standard resin (1.5 formaldehyde:phenol), a resin with a reduced amount of crosslinkage (1.2 formaldehyde:phenol), and a modified resin produced by adding glycerin to the standard liquid casting resin. Both of the modified resins had electrical resistivity values lower than that of the standard resin. The 1.2 formaldehyde:phenol resin had a specific resistivity of about 8.5 ohm-cm., and the glycerol modified resin had a specific resistivity of about 14 ohm-cm., compared with about 19 ohm-cm. for the batch of standard resin used in these experiments. The curves in Figure 10 however show that the standard resin cell performed better than the glycerol modified resin, although not so well as the reduced cross-linkage resin. Even though the 1.2 formaldehyde:phenol resin did show superior performance in the fuel cells, it was not adopted for general use because of its rather poor strength and flexibility properties. Also the bonding properties of this resin were markedly inferior to those of the standard resin. Recently more elaborate resin modifications have been carried out but have not been fully tested at this time. These resins will be the subject of a separate paper.

Life Tests Under Fixed Resistive Loads

Fixed operating loads were placed on about fifty cells of various types and catalyst loadings, with mainly platinum and palladium. The various loads had values between ¾ ohm and 20 ohms and were, in nearly all cases, left unchanged for a given cell.

Variations in cell performance with time usually manifest themselves in a change of slope of the polarization curve. Sometimes however a change in shape also occurs, but this shape change usually lies in the region below 0.5 v. and is of minor interest as a practical long term operating point, since the voltage and fuel efficiency would be low. Since all polarization curves discussed here pass through a point at approximately 1.0 v. and zero ma./sq. cm., the most accurate and sensitive picture of the polarization curve behavior with time is obtained by using the current density at 0.5 v. as an index. Conveniently the maximum power point also occurs in the region of 0.5 v. Other indices of performance are the operating voltage and operating current density under fixed load (at constant temperature and pressure). Accordingly the life test results are presented as a series of plots of current density at 0.5 v., operating voltage, and operating current density vs. time and ampere-hours of charge per square centimeter passed through the cell. Unless otherwise noted, all life test curves include data from more than one cell.

Figure 11 is typical of the performance of most cells. The curve of current density at 0.5 v. reflects much more sensitively the changes in the cell than do the operating voltage or the operating current-density curves. These curves allow one to reconstruct approximate polarization curves as a function of time, following the general shape shown in Figures 3 through 10.

The initial (rising) portion of the current density at 0.5 v. curve may be interpreted as reflecting an electrode conditioning or activation process. This effect has been found in nearly all of the cells tested. The maximum in the curve nearly always occurs earlier than 10 amp.-hr./sq. cm. The falling portion of the curve may be associated with resin degradation and is a long-term effect. The general shape of the life test curve is consistent then with a composite of two logarithmic contributions: the first, activation of the electrodes, and the second, a degradation of the resin, finally reaching a plateau somewhere after about 20 amp.-hr./sq. cm.

The resin degradation may be an oxidation of low molecular-weight materials in the resin. Evidence of the resin degradation is found in the straw-colored washings which are carried from the cells by the product water. Eventually brown precipitates form in the cell-washing collectors. This discoloration varies in intensity from one cell to another but continues over long periods of time and does not appear to stop as long as the cell is operating. In addition it is probable that the resin is suffering a desulfonation (loss of sulfonic acid groups), as is evidenced by the presence of sulfuric acid in the cell washings (pH ≈ 3-4, gradually becoming pH ≈ 5), even after the cell has been washed in running distilled water for a few days prior to operation. Finally, when cell failure does occur, it is not due to a

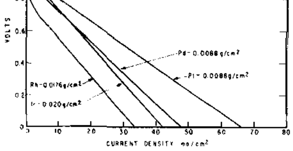

Fig. 9. Performance comparison with various catalysts in type I cells at t ≈ 27°C.

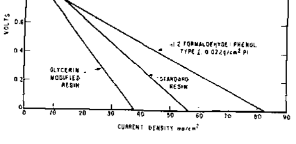

Fig. 10. Performance comparison with various resins at t ≈ 27°C.

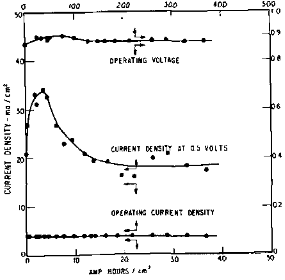

Fig. 11. Life test of type I cells with 0.0088 g./sq. cm. platinum black on 20 ohm continuous load.

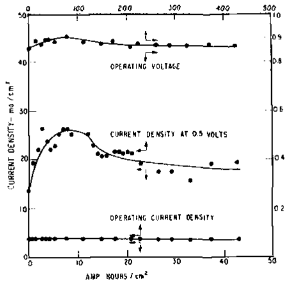

Fig. 12. Life test of type I cells with 0.002 g./sq. cm. platinum black on 20 ohm continuous load.

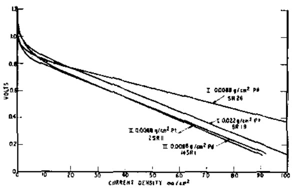

Fig. 13. Best polarization curves for the two cell types.

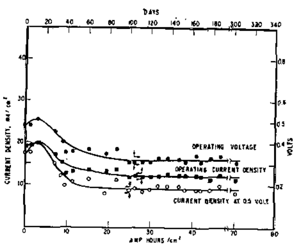

Fig. 14. Life test of type I cells at 0.0088 g./sq. cm. palladium black on 2 ohm continuous load.

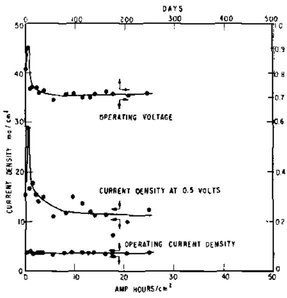

Fig. 15. Life test of type I cell with 0.0088 g./sq. cm. palladium black on 20 ohm continuous load.

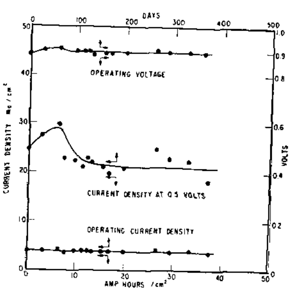

Fig. 16. Life test of type II cells with 0.0088 g./sq. cm. platinum black on 20 ohm continuous load.

malfunctioning of either electrode but is due to the formation of a pinhole in the resin. Although all the cells reported here used the same reinforcement, the tendency toward pinhole formation has been found to be a strong function of reinforcing material.

Figures 11 and 12 refer to type I cells with platinum catalyst, 0.088 g./sq. cm. and 0.022 g./sq. cm. respectively. The cells have been operating on 20-ohm loads. Comparison of the two sets of curves indicates that the effect of catalyst loading appears only late in the operating life of a cell. The initial portions of the curve of current density at 0.5 v. do not seem to be strongly influenced by catalyst loading and are sensitive to electrode activation processes and amount of free acid in the membrane. Plateaus in the current at 0.5-v. curves on the other hand are reached only after 15 to 20 amp.-hr./sq. cm. The height of the plateau is a function of catalyst loading. Thus Figure 12 shows a plateau at about 20 ma./sq. cm. for a loading of 0.022 g./sq. cm., while Figure 11 indicates a plateau of about 15 ma./sq. cm. for a catalyst loading of 0.0088 g./sq. cm.

The data which were used to arrive at the time average performance curves, shown in Figures 3 through 8, averaged in the maxima shown in the life test curves. For example by reexamining Figures 11 and 12 one finds that the time averages of the two are quite nearly the same, yielding very similar time average polarization curves as indicated in Figure 5. All of the comparisons made in Figures 3 through 8 are subject to similar limitations, and the life test curves should be consulted for comparisons at specific points in the life of a cell. As an illustration Figure 13 shows polarization curves of some of the best performing fuel cells, two of each of the types. These data were collected at the maxima of the life test curves (see Figures 11 and 12); they are representative of the best performances obtained to date. Comparison of Figure 13 with Figures 3 through 8 brings out the changes in performance that occur during the lifetime of a cell.

Figures 14 and 15 are analogous to Figures 11 and 12, except for the palladium black catalyst. The general shape of the life test curves are the same as the previous ones, except that the peaks are displaced to the left. Generally it has been found that the life test curves which showed a peak very near 0 amp.-hr./sq. cm. were those for cells which had not been washed very thoroughly, or had not been washed at all. In such cells there was a good deal of free sulfuric acid in the membrane, which was leached away slowly by the product water causing a decrease in performance with time.

By comparison Figure 15 with Figure 14, 0.022 and 0.0088 g./sq. cm. of palladium, respectively, one can see that the plateau for the former lies slightly above that of the latter. It is likely that the palladium black cells are less sensitive to catalyst loading in this range than the corresponding platinum black cells since palladium is only about one-half as dense as platinum. Therefore palladium should (and does) form a more continuous electrically conducting electrode for a given weight of catalyst per unit area. In addition the catalyst layer in the case of palladium is more nearly saturated, and small changes in loading would not affect the cell performance as much as would a corresponding change in the platinum loading.

The life curve for a type II cell having 0.0088 g./sq. cm. of platinum black, operating on a 20-ohm load, appears in Figure 16. The characteristic peak is present at about 5 amp.-hr./sq. cm.; the curve levels off in a plateau at about 20 ma./sq. cm. Figure 17 presents the results for a type II cell of higher platinum black loading, again showing the characteristic form. Figure 18 shows the life curve for the type II cell with palladium black electrodes at a catalyst loading of 0.022 g./sq. cm operating on a 20-ohm load. Unfortunately corresponding cells at the 0.0088 g./sq. cm. level did not yield useful data because the electrodes were poisoned by the plasticizer used in the preparation of the graphite-filled plastic current collectors.

While most of the life curves presented so far have dealt with cells discharged continuously at low current densities, there is abundant evidence that life is independent of load. Figure 19 shows the performance of a type II cell (0.0088 g./sq. cm. of palladium black) on a 1-ohm load. At this point it can be stated that the operating life of these ion exchange membrane cells at room temperature on a 30-ohm load is at least 2 yr. The failures which have occurred, and which could not be explained by some malfunction of the test procedures and apparatus, have been after about 40 amp.-hr./sq. cm. independent of load. To date the maximum charge per unit area delivered by any cell has been 150 amp.-hr./sq. cm. The statements above apply to operation on static heads of hydrogen and oxygen.

Effect of Operating Temperature

The effect of ambient temperature on the polarization curves for cells with platinum and palladium electrodes was studied in the range of 0° to 85°C. Results were similar for the two types of cells as shown by Figures 20 and 21. The data shown were reproducible at each temperature and could be retraced after operation at other temperatures in the range indicated.

The open-circuit voltage increases with decreasing temperature as one would predict from thermodynamics:

$$\frac{\partial E^\circ}{\partial T} = \frac{\Delta S^\circ}{nF}$$

Since ΔS is negative for the reaction of hydrogen and oxygen to form water, the open-circuit voltage increases with a decrease in temperature.

The voltage-temperature relationships under current drain are influenced by several factors: the reversible voltage-temperature effect discussed above, the change in membrane conductance with temperature, the change in catalyst layer and contact conductance with temperature, and the change in electrode reaction rate with temperature. Except at very low current densities the last-mentioned factor is probably controlling at the oxygen electrode. As might be expected, the kinetics at the oxygen electrode become less favorable with decreased temperatures, characteristic of processes involving an energy of activation. The hydrogen electrode in this system is essentially reversible.

Note the identical effect of temperature on the shape of the polarization curves at 0°C. for both the platinum and palladium cells. The more rapid decrease in voltage with increase in current density at the higher current densities is characteristic of a diffusion type of polarization and could be due to the accumulation of a water film on the oxygen electrode at the lower temperatures. It has been observed continually that a distillation action in cells running at room temperature causes the product water to condense on the cell casing rather than gather on or drip from the electrode. Since the vapor pressure of water at 0°C. is only about 20% of the value at room temperature, it is suggested that the distillation action cannot proceed at a high enough rate to continuously remove all of the product water. As a result water accumulates on the electrode, setting up a diffusion barrier for the oxygen.

The decline in performance as the temperature was raised from about 50° to 85°C. was quite real and reversible. It appears to be associated with a gas phase concentration polarization. In this case it is probably related to the low partial pressure of oxygen in the system, particularly in the vicinity of the electrode, where the water is formed and where a somewhat higher temperature prevails.

Polarization curves like those shown in Figures 20 and 21 yield cross plots of power density vs. ambient temperature for various fixed load values. Such a plot for the cell with palladium electrodes is shown in Figure 22; that for the cell with platinum electrodes is similar. For the lighter load resistances (higher Ω-sq. cm. values) the temperature effect is quite small. As the maximum power region of the polarization curve is approached, the power output of the cell is much more temperature dependent. At very high current densities the power output is again less sensitive to ambient temperature.

As additional tests of the performance at the elevated temperatures, several cells were placed on continuous operation on 30-ohm loads at 85°C. Results are shown in Figure 23 in terms of the operating voltages on load.

The performances of the platinum cells were steady on load for the duration of the tests. In both cases equipment failures external to the cell resulted in termination of the runs. Performance of the palladium cells was erratic, and in the two cases failure was associated with the cells themselves. It was observed that the solutions draining from the palladium cells were yellow in color, and the color was associated with dissolved palladium. This was in sharp contrast to the platinum cells, where the drainings were colorless. At the elevated temperatures palladium appears to be attacked at a significant rate, and it washes out of the cell with the acid that slowly but continuously splits from the membrane. It appears likely that the major attack of this type occurs at the oxygen electrode.

Several polarization curves were taken during the lives of these cells. However, their frequency was not sufficient to establish the trends observed with the cells operating at lower temperatures. It was evident however that the general character of the polarization curves became poorer as the cells aged.

Air Operation

While most of the test work has been done with cells operating on oxygen, a few cells have been run on air. In such cases the regular cover plate on the oxygen side was replaced with a thin sheet of Mylar having a 0.3- to 0.5-cm. diameter hole in its center. This size opening permits an adequate influx of oxygen to prevent serious polarization effects, yet it prevents an excessive rate of evaporation of the water with associated dehydration of the membrane.

Polarization curves obtained in this way resembled those for operation on oxygen, although some indications of diffusion control were evident at higher current densities. This undoubtedly occurred because no attempts were made to optimize the size of the vent to the air. It was felt that this will prove to be a function of the cell structure, and the single layer laboratory cells cannot be considered prototypes of large-scale units in this regard.

Air cells have also been placed on continuous operation. One such cell ran for 219 days. During this period the load was varied from 1 to 30 ohms, and steady performances were obtained in all cases.

Current Efficiency

An important consideration in any electrochemical process is the current efficiency of the reaction of interest. In the fuel cell this is the electrochemical formation of water from hydrogen and oxygen.

One side reaction of considerable importance in cells consisting of thin

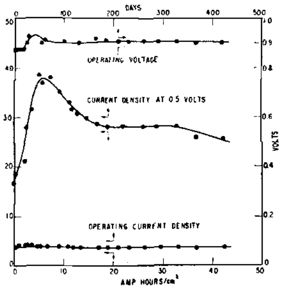

Fig. 17. Life test of type II cell (no. SR 20) with 0.022 g./sq. cm. platinum black on 20 ohm continuous load.

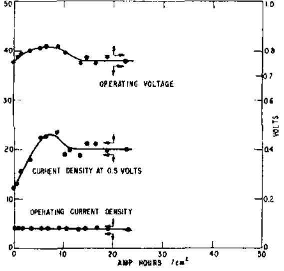

Fig. 18. Life test of type II cells with 0.022 g./sq. cm. palladium black on 20 ohm continuous load.

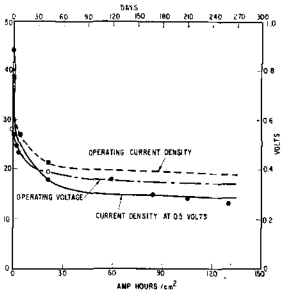

Fig. 19. Life test of type II cell (no. 14SR1) with 0.0088 g./sq. cm. palladium black on 1 ohm continuous load.

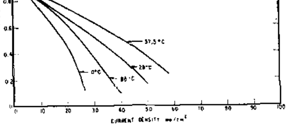

Fig. 20. Temperature effect on performance of platinum cells at 0.0088 g./sq. cm.

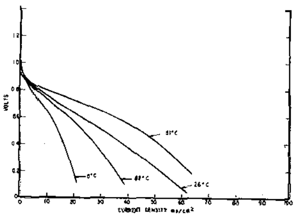

Fig. 21. Temperature effect on performance of palladium cells at 0.0088 g./sq. cm.

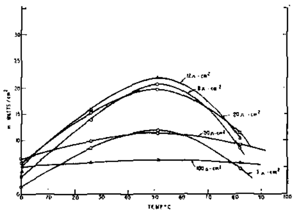

Fig. 22. Power density vs temperature for palladium cells.

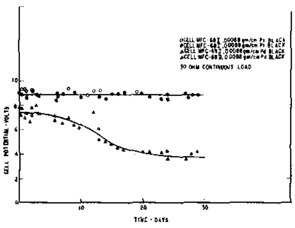

Fig. 23. Performance of type I cells on continuous load at 85°C.

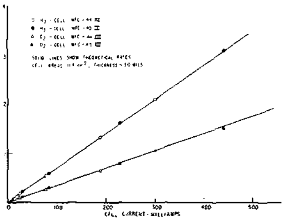

Fig. 24. Gas consumption during operation.

membranes of relatively large areas is permeation of the hydrogen and oxygen through the membrane. Preliminary calculations of the magnitude of this effect were made on the assumption that hydrogen and oxygen would have the same permeability coefficients through the membranes as through water. While these calculations indicated that this type of loss would be low, an experimental determination was felt desirable.

The experiment is relatively simple because one can safely assume that hydrogen diffusing through the membrane to the oxygen side will be completely consumed to form water at the catalytically active oxygen electrode surface. Similarly consumption of diffusing oxygen will occur at the hydrogen electrode. The net result will be a stoichiometric consumption of hydrogen and oxygen to form water. Because of the disappearance of gas on both sides as a result of reaction, the diffusion losses can be determined by simple volumetric techniques employing gas burettes.

The average rate of consumption of hydrogen due to permeation of it and oxygen through the membrane was found to be 0.0022 ml./min. as shown by measurements on two cells having membranes about 30 mils thick. Oxygen consumption was measured to be at approximately one-half the rate for hydrogen. These consumption rates are equivalent to current densities of the order of 0.025 ma./sq. cm. Such losses are low compared with the hydrogen consumption in a cell operating in the range of 3 to 30 ma./sq. cm., which would be the normal operating region for the present cells. It must be recalled however that such diffusion losses will be in effect when a cell is on open circuit.

Since it is not possible to state a priori that diffusion losses will remain constant at high current densities, it was felt desirable to determine current efficiencies for the cell under operating conditions. Again gas burettes were employed, and the volume of gas consumed was measured during cell operation at constant current for measured time intervals. The results in terms of milliliters of gas per minute under standard temperature and pressure conditions are plotted as a function of current in Figure 24 for two representative cells. The theoretical gas consumption rates are shown as solid lines.

These experiments indicate that permeation losses are the major side effects that need be considered with regard to fuel losses with a membrane cell. The magnitude of these losses will be largely determined by the operating temperature of the cell and by the thickness of the membrane. To a lesser extent they will probably be controlled by the material from which the membrane is fabricated.

SUMMARY AND CONCLUSIONS

The performance of about 100 hydrogen-oxygen ion exchange membrane fuel cells having 11.38 sq. cm. electrodes was studied. In addition to operational variables such as temperature, load current, age, and fundamental features including electrode material and membrane chemistry, two basic cell designs were investigated. In one the current was removed from the cell via a bonded platinum gauze current collector and in the other by external collectors making contact to the catalyst electrode layer.

Only small differences are found between the two cell types for a given catalyst at loadings between 0.0088 and 0.022 g. of catalyst/sq. cm. of electrode area. The time average polarization curves for cells with bonded platinum gauze current collectors lie slightly higher than those for cells with external current collectors. The differences are probably due to catalyst layer and contact resistance ohmic losses. Characteristic open-circuit voltages are 1.07 for platinum and 0.97 for palladium electrodes. Typical polarization curves show current density values of about 30 ma./sq. cm. at 0.5 v.

Various platinoid elements were tested as catalyst materials for the oxygen electrode. Osmium and ruthinium dissolved in the resin during the final curing stages. Iridium is nearly equivalent to platinum and palladium. Preliminary experiments have not proved rhodium to be inferior to the other catalysts. A few modifications of the standard resin were tested. Based on results from about ten cells a resin with reduced cross linkage (1.2 moles formaldehyde/mole of sulfonated phenol) gives higher fuel cell performance than the standard resin, while standard resin with glycerol added yields results below those characteristic of standard resin.

Life tests on about fifty cells under fixed resistive loads from 8.5 to 230 ohm-sq. cm. at room temperature indicate that a reasonable minimum life expectancy for cells of this type is about 40 amp.-hr./sq. cm. of active area. Early in the life of the cell the electrodes become activated, characterized by a performance increase. Simultaneous with the activation process a resin degradation process tending to decrease performance occurs. The combination of these effects yields a performance peak between 0 and 10 amp.-hr./sq. cm. The influence of resin degradation on cell performance decreases to the point where the current at 0.5-v. curve (life curve) reaches a plateau. This is usually maintained until cell failure due to a pinhole in the resin. Results of tests with other reinforcements indicate significant life expectancy improvements. The point of failure is not influenced by operating current density or voltage within the range investigated (based on the limited failure data available). Catalyst loading influences the plateau height of the life curve, that value being higher for higher catalyst loadings.

Temperature has a significant effect on performance under the nearly isothermal conditions prevailing in these experiments. In the range from 0° to about 55°C. performance increases with temperature. From 55° to about 85°C. the performance drops owing to dilution of oxygen by water vapor. While the results are suggestive in part of an activated process, it is possible that water films forming on the oxygen electrode under conditions of limited evaporation lead to poor performance at low temperature. Temperature effects are more pronounced near the maximum power point than at low or very high current densities. Life tests of cell performance at 85°C. with platinum electrodes showed no decrease in performance after 1 month. Palladium cells on the other hand fell off in performance, and the electrode material was found to have partially dissolved in the water product effluent.

The hydrogen-oxygen ion exchange membrane fuel cell has a practical operating current density of about 30 ma./sq. cm. and can be expected to deliver about 40 amp.-hr./sq. cm. at room temperature. Failure has been due to formation of pinholes in the membrane electrolyte. Platinoid elements insoluble in strong sulfuric acid are adequate electrode materials.

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NOTATION

C_p = specific heat at constant pressure, cal./mole °C.
E = terminal voltage of a cell, v.
$E°$ = reversible electromotive force at standard conditions. v.
F = Faraday constant, 96,517 coulombs/equiv.
$G°$ = standard Gibbs free energy, cal./mole
$H°$ = standard enthalpy, cal./mole
i = current delivered by a cell
n = number of equivalents per mole
n' = number of equivalents of fuel consumed in time θ
$S°$ = standard entropy cal./mole °C.
t = temperature, °C.
T = absolute temperature, °K.
θ = time

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Multicomponent Mass Transfer

I. Theory

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As the primary phase in the development of multicomponent mass transfer theory, equations are derived which predict the rate of mass transfer of each species from an interface to a ternary gas mixture in turbulent flow for equimolal-countercurrent transfer and for transfer with one of the three gases stagnant.

The mass transfer equations obtained, regardless of whether a film, Prandtl-Taylor, or modified Chilton-Colburn model is used, differ in form from the usual binary equations and predict qualitative as well as large quantitative differences between binary and ternary transfer.

A criterion is obtained which any consistent multicomponent mass transfer theory must satisfy, and although the ternary film and Prandtl-Taylor models satisfy this criterion, the modified ternary Chilton-Colburn model does not.

Although the essential features of binary mass transfer are fairly well understood, there is a rather startling dearth of knowledge of multicomponent mass transfer. The general differential equations which describe multicomponent mass transfer are easily obtained, at least for ideal gases, by combining the Maxwell-Stefan equations with a continuity equation for each species, but these equations are intractable in all but the simplest situations. Nevertheless the marked differences between the binary and multicomponent forms of the Maxwell-Stefan equations imply that there will be significant differences between binary and multicomponent mass transfer, whether the flow be laminar or turbulent.

In flow systems of the type commonly encountered there is an impressed flow which has velocity components parallel to and velocity gradients normal to the interface across which transfer is taking place. It is these hydrodynamic complications which make even a moderately rigorous prediction of the transfer rates in multicomponent systems difficult. The term "convective mass transfer" is used to describe these systems.

Methods based on the use of an effective diffusivity for each species in a multicomponent mixture have been proposed for handling multicomponent convective mass transfer (*7, 19, 11, 1*), but these methods will be seen to be inadequate for the types of systems studied here. (The inadequacy does not arise, except for one case, in a failure of these methods to approxi-

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