HYDROCARBON-AIR FUEL CELLS EMPLOYING SLURRIED MOLTEN CARBONATE ELECTROLYTES

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Fuel cells employing mixtures of molten alkali carbonates as the electrolyte have been described. These cells can be divided into three groups: those that employ a fixed ceramic matrix[1-3] impregnated with the electrolyte, a paste matrix[4-6] consisting of a mixture of fine ceramic particles and the electrolyte that is preformed, and a free electrolyte[7,8] with no matrix. In the first two groups, the ceramic-electrolyte body is the structural member and supports not only itself but also the electrodes. In the free electrolyte cells, the electrodes are the structural members and must to a great extent contain the very difficult to handle electrolyte. The slurried electrolyte cell described here takes advantage of the best of the cells mentioned above. There is no need for a pre-sintered or preformed ceramic-electrolyte body. The electrodes are the structural members. The ceramic particles serve as a separator and help contain the electrolyte. The electrolyte-ceramic slurry has no requirement for structural strength.

Cell Description

Figure 1 is a photograph of an actual test cell before operation. This unit consists of two cells connected electrically in parallel and is referred to as a 1 x 2 unit. The fuel gas supply flows between the two anodes. The unit is placed in a furnace chamber which contains the cathode gas supply. The cathodes are connected to the front plenum and the anodes to the rear plenum. The fuel gas plumbing is used for the current bus-bar, and cell voltage is measured between the leads coming from the top of the front and rear plenums. A silver wire used as a third idling electrode is placed in the ceramic electrolyte reservoir cup. Each electrode is 1 in. x 4 in. Since there are two such electrodes in parallel, there is a total geometric electrode area of 8 sq. in., or 51.6 sq. cm, of each electrode (anode and cathode) in these units. Figure 1 shows only one of the two working cathodes.

A cutaway perspective of the unit is shown in Fig. 2. The primary anodes are not only connected together at the plenum but also have a corrugated nickel screen welded between them to yield a stronger structure, provide better distribution of the gases, and to serve as a secondary electrode. In the experiments described here magnesia particles are used to form the electrolyte slurry. When the unit is assembled, dry MgO of selected particle size (depending on the electrode structure) is placed between the working cathodes and anodes. A mixture of 50 mol % Li_2CO_3 and 50 mol % Na_2CO_3 is prepared, fused, broken into pieces about 2 to 10-mesh, and placed in the electrolyte reservoir cup. The entire assembly is placed in a furnace and raised to operating temperature. At about 500°C the electrolyte begins to melt and is drawn by capillary action up the MgO-filled alumina feed tubes and into the MgO particles between the working anodes and cathodes. Once the electrolyte has saturated the MgO, the additional electrolyte in the reservoir cup merely remains there until it is needed to replace any electrolyte which may evaporate from the slurry. This feature of the unit permits very easy and rapid addition of electrolyte to the unit when it is operated continuously for extended time intervals.

Experimental

The following discussion will pertain to the performance of several of the 1 x 2 units in which the structure of the electrodes was changed. In these experiments the gas supplies were held constant. The fuel gas supply was a simulated natural gas (CH_4) reformate consisting of approximately 80% wet H_2 and 20% CO_2. Previous experience with the simulated natural gas reformate has shown that this mixture is water-gas shifted in the steel plumbing to a nearly equilibrium (> 90%) mixture of H_2, H_2O, CO_2, and CO at the operating temperature of the cell. The cathode gas supplied to the furnace chamber was 80% air and 20% CO_2.

The cells were under some load for more than 95% of the reported operating life. Operation of all the cells described was voluntarily terminated for postoperative examination while the cells were still performing at an acceptable level (>20 watts/ft^2).

The data presented here were obtained from current-voltage (E-I) curves recorded daily except for some of the week ends. These traces were obtained from the working cathode versus the working anode and from the anode and cathode individually versus the third idling electrode. The latter curves were recorded to determine total polarization of the individual electrodes. Traces were obtained using either an EAI 1110 Variplotter or a Varian F80 X-Y recorder.

Current interruption studies similar to those previously reported[1,3] for sintered matrix cells were performed. These studies continued to show that the total polarization is composed of two components, ohmic and concentration polarization. These interrupter studies also verified the 1000 cycle resistance measurements of the total internal cell resistance and determined the individual anode and cathode ohmic resistances.

Performance and polarization data as a function of operating time were presented to a 7040 computer to determine the best least mean square straight line, the standard error of the data points, and the standard error of the slope of the least means square line. The cell data treated in this manner include power density in watts/ft^2 at a fixed terminal voltage, open circuit voltage, total anode polarization, and total cathode polarization. Total anode and cathode polarization are defined as the difference between the potential versus the third idling electrode at open circuit voltage and that at the given current density. These data are discussed in detail in the following section.

Discussion of Results

Figure 3 shows two power versus hours of operation curves for 1 x 2 unit #47-47. This cell was operated at 600°C for 1100 hours before its operation was terminated voluntarily. It contains 120-mesh Ni screen primary and secondary anodes and silver-plated 120-mesh stainless steel cathodes. A secondary cathode of the same silver-plated material was also used on the cathode. (This secondary cathode can be seen on the cathodes in Fig. 10.) The MgO was sized so that it could be contained in the screens (> 120-mesh). The data points shown were selected randomly and are representative of all of the points. The solid lines are the best least mean square line at the two cell terminal voltages of 0.5 and 0.7 volt respectively. The dashed line indicates the standard deviation of the points from the line. Although the line at 0.5 volt shows a slight increase in power and that at 0.7 volt exhibits a slight decrease in power as a function of hours of operation, neither observation is statistically significant. The errors in both slopes are greater than the slopes themselves (see Table I at the end of this section). Similar treatments of the open circuit voltage,

anode and cathode polarization at current densities up to 75 ma/cm^2 also exhibit no significant slopes.

From these data it is concluded that within the limits of reproducibility of cell performance from day to day there was essentially no change in performance for 1100 hours of operation.

Cell #47-53 was another 1 x 2 unit operated at 600°C. It contained primary anodes made by sintering presieved, highly active nickel particles onto 120-mesh nickel screen. No secondary electrodes were used in this unit. The cathode consisted of sintered presieved silver particles on 120-mesh silver-plated stainless steel screen. The MgO was sized to be contained by the electrodes. Figure 4 illustrates the power at 0.5 volt as a function of hours of operation. Cell operation was voluntarily terminated after 828 hours. Notice that the initial power density of 50 watts/ft^2 is about twice that of the preceding unit. Power density remained 42 to 48 watts/ft^2 for more than 400 hours of continuous operation. The decline in performance started just after 400 hours of operation and continued to about 500 hours, when it leveled out for the next 200 hours before resuming a slower rate of decline until operation was voluntarily terminated.

Figure 5 illustrates the effects on the open circuit voltage and the total polarization of both the anode and cathode at 75 ma/cm^2. According to these data, the major cause of decline in power output of the cell was increased polarization of the cathode. There was essentially no change in the open circuit voltage during the entire operation. However, polarization on both electrodes did increase. Again notice that the cathode exhibits a distinct increase in polarization starting just after 400 hours and continuing to about 500 hours. The anode at the same time remained at worst unchanged, and at best it exhibited a slight decrease in polarization. However, the net result was a decrease in power output.

Postoperative examination of this cell showed that the sintered silver cathodes had undergone additional sintering sometime during their operating life with an accompanying decrease in surface area. The electrode appeared to be completely closed and the particles actually melted in spots. Little or no porosity remained. It is possible that a relay on the furnace temperature controller stuck, causing overheating so that the electrode continued to sinter. Some additional sintering was also observed on the nickel anodes, but these electrodes retained most of their original porosity.

Figure 6 illustrates the power at 0.5 volt versus hours of operation for cell #47-140. This cell contained 120-mesh nickel screen primary anodes and 50-mesh nickel screen secondary anodes. The cathodes were silver-plated 120-mesh stainless steel screens. The plating was heavier than that used in cell #47-47.

From 100 to 500 hours of operation power output was at a level of 35 to 40 watts/ft^2. Then it started to decline, reaching 22 watts/ft^2 at 1100 hours. The cell was terminated voluntarily after 1117 hours of operation.

The least mean square results are presented in Fig. 7 and Table I for open circuit voltage and polarization at 50 ma/cm^2 for both anode and cathode as a function of hours of operation. The order of contribution to the decline in power output of this unit are open circuit voltage, cathode polarization, anode polarization. Anode polarization, however, was higher from the start than is usually observed. This is attributed to the use of the 50-mesh nickel screen secondary electrode.

Examination of the electrodes after termination showed that the primary anode was flooded with electrolyte and had undergone appreciable oxidation. This oxidation is considered the cause for the decreased open circuit voltage, but is difficult to say which process occurred first. Previous experience with nickel anodes, however, has shown that nickel tends not to wet easily while nickel oxide does. The accompanying loss of active (for the fuel cell reaction) area may also account for the increase in anode polarization.

Several times during the operating life of this cell a small fire was observed on one of the cathodes. This fire was the result of fuel reaching the cathode. Although the fire did not cause the cell to fail, it did remove the silver plating in its vicinity. The redistribution of silver resulted in a loss of active cathode surface area, which could easily account for the increase in cathode polarization. Postoperative examination of these electrodes confirmed the silver redistribution. In many places the stainless steel screen was exposed to the electrolyte.

Silver migration on the electrodes and solubility in the electrolyte can be serious problems in any molten carbonate fuel cell. Migration can be retarded by preventing thermal and concentration gradients along the electrode. These gradients can be minimized by good heat management and gas distribution. The solubility aspects are a little more complicated. First, more silver must be present initially on the electrode than the amount required for good cathodes. Second, and more important, the solubility of silver can lead to dendrite formation, which can cause an electronic short and subsequent failure of the cell. In this respect the slurry-electrolyte system has an advantage over the other fixed matrix systems.[3,4] Fixed matrix cells provide a mechanical support for the silver dendrites through the electrolyte. The slurry system provides little, if any, mechanical support for such dendrites; consequently, it has considerably less tendency to form shorts. Reliability testing of more than 200 cells containing slurried electrolyte revealed no failures because of any type of electronic shorting. This was not the case in previous experience with fixed matrix cells.

Cell #33-1 was very similar to #47-140, but both secondary and primary anodes were constructed of 120-mesh nickel screen. Figure 8 presents the power output at 0.5 volt and the anode and cathode polarization as a function of hours of operation. The open circuit voltage was constant during this period of operation. All data points for the power output are shown. The least mean square line exhibits an increase in power output with time; however, this slope is not significant (see Table I). The cell operated at an average power density of 36-37 watts/ft^2. It should be noted that both anode and cathode polarization decreased with time and that these slopes are significant (see Table I). However, when their variations are added to the other cell variables, no significant slope for power output is obtained.

At 582 hours of operation additional electrolyte was added to the reservoir cup. The power declined in 3 hours from 42.5 watts/ft^2 to 34.5 watts/ft^2. At 602 and 625 hours of operation it had declined further to 31.0 and 29.8 watts/ft^2. At the same time the polarization at 75 ma/cm^2 for the cathode started to decrease, while that of the anode increased. These observations may be explained on the basis that the additional electrolyte increased the wetting at both electrodes. In the case of the cathode the original wetting was less than optimum, while at the anode it was more than optimum.

This cell was allowed to operate for a total of 2000 hours before it was voluntarily terminated. Power output remained above 24 watts/ft^2 for the entire 2000 hours.

These data all point to the composition and structure of the cathode as the weakest point in the present cell structure and system. Current exploratory work is aimed at appreciably reducing or overcoming this limitation. Figure 9 represents a step toward increased power performance. At 0.60 volt this cell was producing 60 watts/ft^2. At maximum power its output approached 70 watts/ft^2. The total anode polarization was 110 millivolts at 100 amps/ft^2, while the cathode polarization was 260 millivolts at the same current density. Even in this cell the cathode presents the greater problem and the more promising area for future research.

Research on new electrodes is continuing. The slurry-electrolyte cell design and construction is relatively new, and at this writing the investigations are still on the lower portion of the learning curve. In little over eight months, progress has been made from a sustained steady performance of 15 to 20 watts/ft^2 to 35 to 40 watts/ft^2. It is difficult to project what the power output of similar cells will be in the future.

Multicell Unit

A view of a 3 x 2 unit is shown in Fig. 10. This unit consists of 6 cells. Essentially, it is three 1 x 2 units connected electrically in series. These units and some similar 2 x 2 units have been operated on a mixture of H_2, CO_2, and N_2 which simulates partial oxidation of JP-4.[9,10] The CO_2 supply for the cathode is obtained by combusting the fuel gas effluent from the anodes in the furnace chamber. These units have had intermittent power output in the 40 to 60 watts/ft^2 range for short time intervals (6 to 24 hours), and 20 to 40 watts/ft^2 for hundreds of hours of operation. The cathodes employed in these units resemble those used in cell #47-47.

Figure 11 is a view of a 6 x 6 unit consisting of three parallel combinations of two 3 x 2 units in series.[9] This unit contains one square foot each of anode and cathode. Power output has been as high as 33 watts at 3.0 volt and has remained between 25 and 30 watts for longer than 500 hours of operation.

Conclusion

Fuel cells employing a magnesia alkali carbonate slurry as the electrolyte have been successfully operated for extended time intervals. Continuous operation for more than 2000 hours has been achieved. Power output in small units operating on a simulated natural gas reformate fuel has been maintained at 35 to 40 watts/ft^2 for longer than 1000 hours. Multicell units have been operated on a simulated fuel representative of partial oxidation of JP-4 at nearly the same level.

New electrode compositions and structures in the initial research stage at this time are yielding power densities equivalent to 60 to 70 watts/ft^2.

There appears to be no fundamental reason why slurried molten carbonate fuel cell systems should not achieve significantly higher power densities and longer operating periods than those reported here.

Acknowledgements

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TABLE I

Computer Results

Least Mean Square Fit of Data Presented in Figures 3-8

Unit Number Dependent Variable*	Slope watts/ft^2/1000 hrs or volts/1000 hrs	Intercept watts/ft^2 or volts	Std. Error of Slope watts/ft^2/1000 hrs or volts/1000 hrs	Std. Error of Observation watts/ft^2 or volts
#47-47				
Power 0.7 v	-0.7	17.2	1.0	1.1
Power 0.5 v	1.5	25.8	1.5	1.7
#47-53				
Power 0.5v	-34.6	52	3.7	3.0
Open circuit voltage	-0.03	0.92	0.01	0.009
Anode-polarization 75 ma/cm^2	0.12	0.15	0.03	0.02
Cathode-polarization 75 ma/cm^2	0.22	0.05	0.09	0.07
#47-140				
Power 0.5v	-19.6	44	2.9	3.0
Open circuit voltage	-0.09	1.01	0.02	0.02
Anode-polarization 50 ma/cm^2	0.06	0.16	0.02	0.02
Cathode-polarization 50 ma/cm^2	0.07	0.13	0.01_5	0.01_5
#33-1				
Power 0.5v	1.0	36	3.1	4.8
Anode-polarization 75 ma/cm^2	-0.04	0.17	0.02	0.03
Cathode-polarization 75 ma/cm^2	-0.05	0.30	0.04	0.05

*Hours of operation is the independent variable.

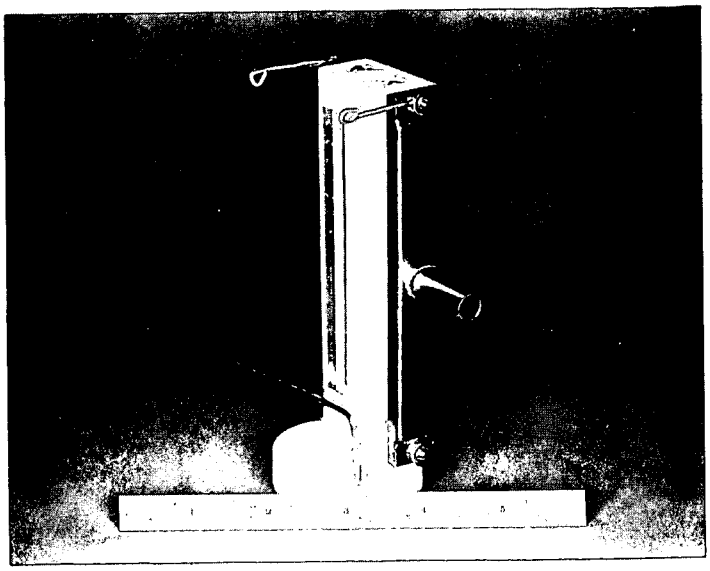

Fig. 1.-VIEW OF 1 x 2 UNIT SHOWING ONE WORKING CATHODE, THE IDLING ELECTRODE, AND THE ELECTROLYTE RESERVOIR.

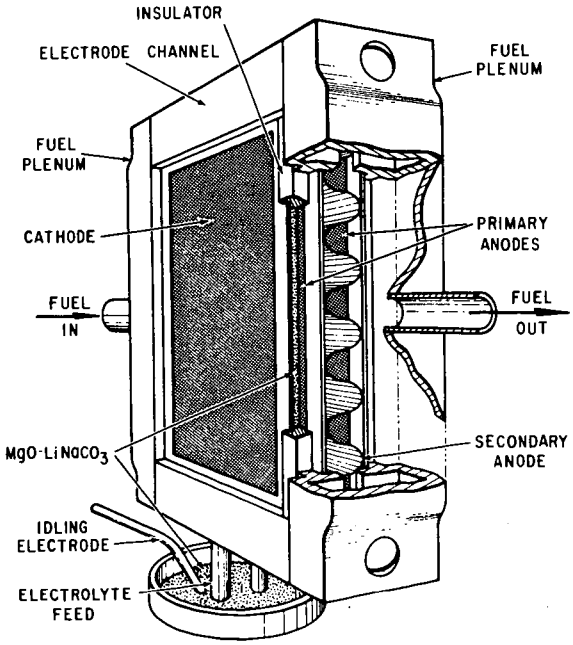

Fig. 2.-A CUT AWAY PERSPECTIVE OF A 1 x 2 UNIT.

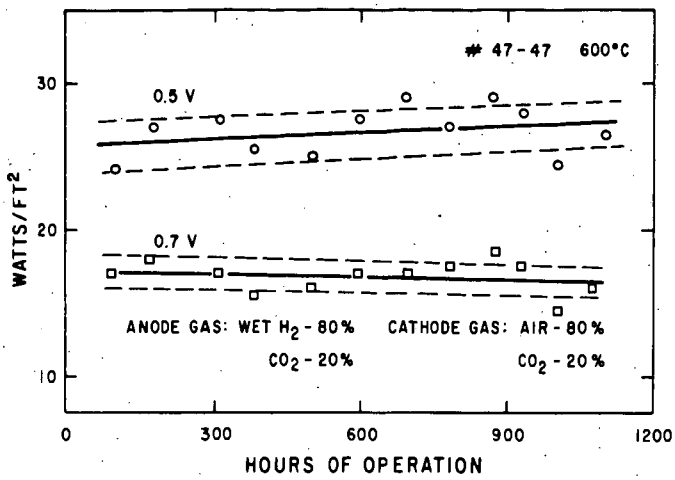

Fig. 3.-POWER OUTPUT AT CELL TERMINAL VOLTAGES (IR INCLUDED) OF 0.5 v. and 0.7 v. IS PLOTTED AS A FUNCTION OF HOURS OF OPERATION. SOLID LINES ARE THE BEST LEAST MEAN SQUARE FITS. DASHED LINES INDICATE THE STANDARD ERROR OF THE OBSERVATIONS FROM THE LINES.

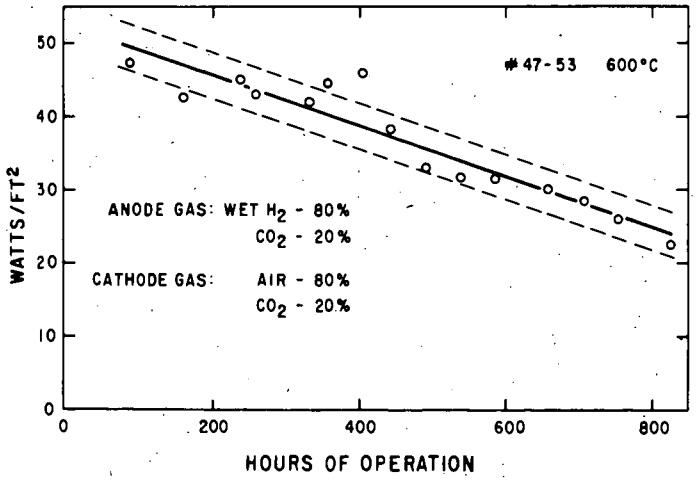

Fig. 4.-POWER OUTPUT AT A CELL TERMINAL VOLTAGE (IR INCLUDED) OF 0.5 v. IS PLOTTED AS A FUNCTION OF HOURS OF OPERATION. SOLID LINE IS THE BEST LEAST MEAN SQUARE FIT. DASHED LINES INDICATE THE STANDARD ERROR OF THE OBSERVATIONS FROM THE LINE.

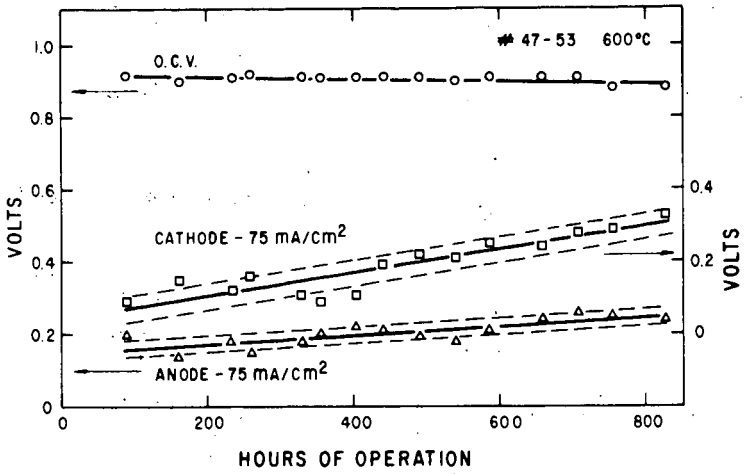

Fig. 5.-TOTAL CATHODE AND ANODE POLARIZATION INCLUDING IR AT 75 MA/CM^2 AND THE CELL OPEN CIRCUIT VOLTAGE ARE PLOTTED AS A FUNCTION OF HOURS OF OPERATION. SOLID LINES ARE THE BEST LEAST MEAN SQUARE FIT. DASHED LINES INDICATE THE STANDARD ERROR OF THE OBSERVATIONS FROM THE LINES.

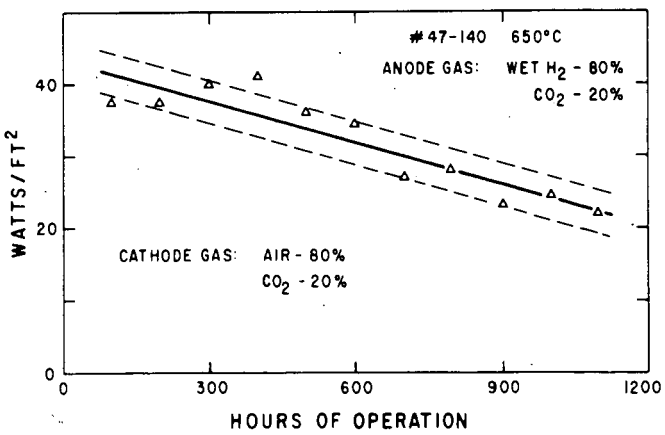

Fig. 6.-POWER OUTPUT AT A CELL TERMINAL VOLTAGE (IR INCLUDED) OF 0.5 v. IS PLOTTED AS A FUNCTION OF HOURS OF OPERATION. SOLID LINE IS THE BEST LEAST MEAN SQUARE FIT. DASHED LINES INDICATE THE STANDARD ERROR OF THE OBSERVATIONS FROM THE LINE.

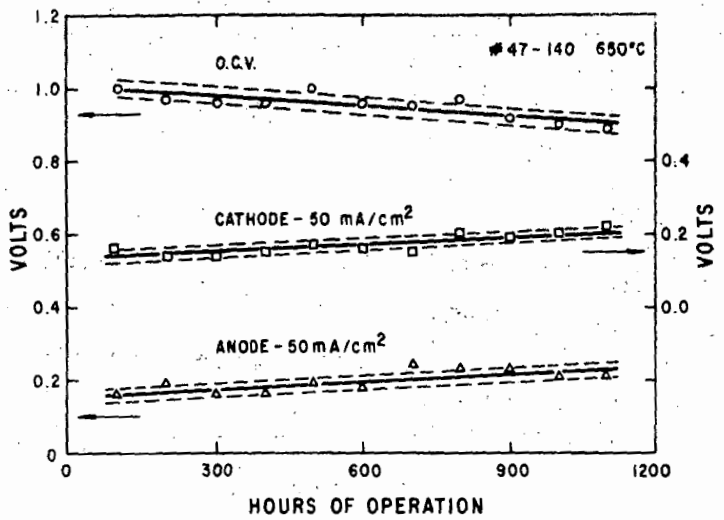

Fig. 7.-TOTAL CATHODE AND ANODE POLARIZATION INCLUDING IR AT 50 MA/CM² AND CELL OPEN CIRCUIT VOLTAGE ARE PLOTTED AS A FUNCTION OF HOURS OF OPERATION. SOLID LINES ARE THE BEST LEAST MEAN SQUARE FIT. DASHED LINES INDICATE THE STANDARD ERROR OF THE OBSERVATIONS FROM THE LINES.

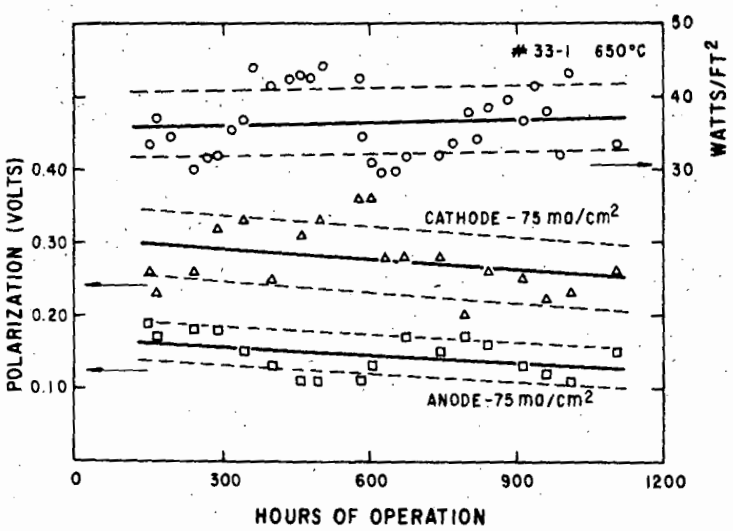

Fig. 8.-POWER OUTPUT AT A CELL TERMINAL VOLTAGE (IR INCLUDED) OF 0.5 v. AND TOTAL ANODE AND CATHODE POLARIZATION AT 75 MA/CM² ARE PLOTTED AS A FUNCTION OF HOURS OF OPERATION. SOLID LINES INDICATE THE STANDARD ERROR OF THE OBSERVATIONS FROM THE LINES.

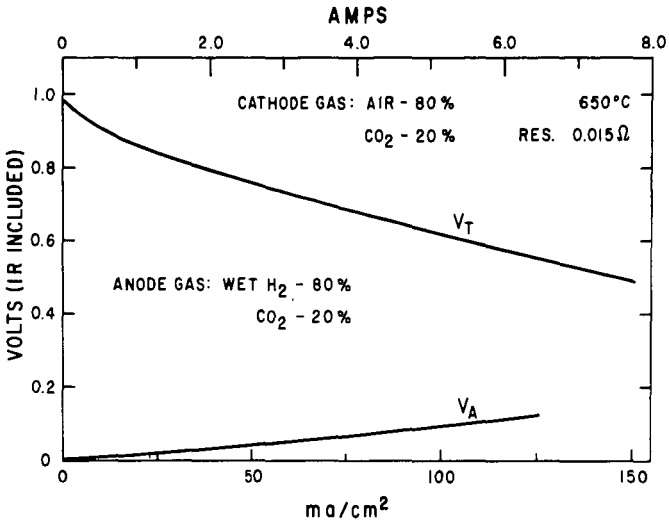

Fig. 9.-V_T IS THE CURRENT-VOLTAGE CURVE WITH IR INCLUDED. POWER OUTPUT IS 60 WATTS/FT² AT 0.6 v. CELL TERMINAL VOLTAGE. CURVE V_A INDICATES TOTAL ANODE POLARIZATION. AT 100 MA/CM² TOTAL ANODE POLARIZATION WITH IR IS 110 MILLIVOLTS.

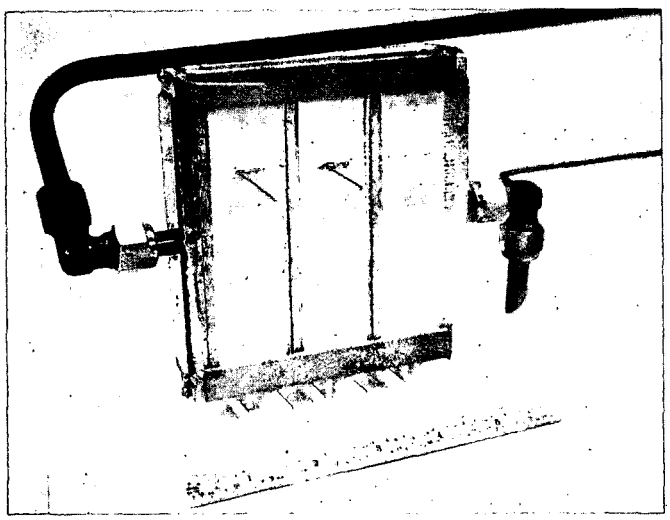

Fig. 10.-VIEW OF A 3 x 2 UNIT SHOWING HALF OF THE WORKING CATHODES.

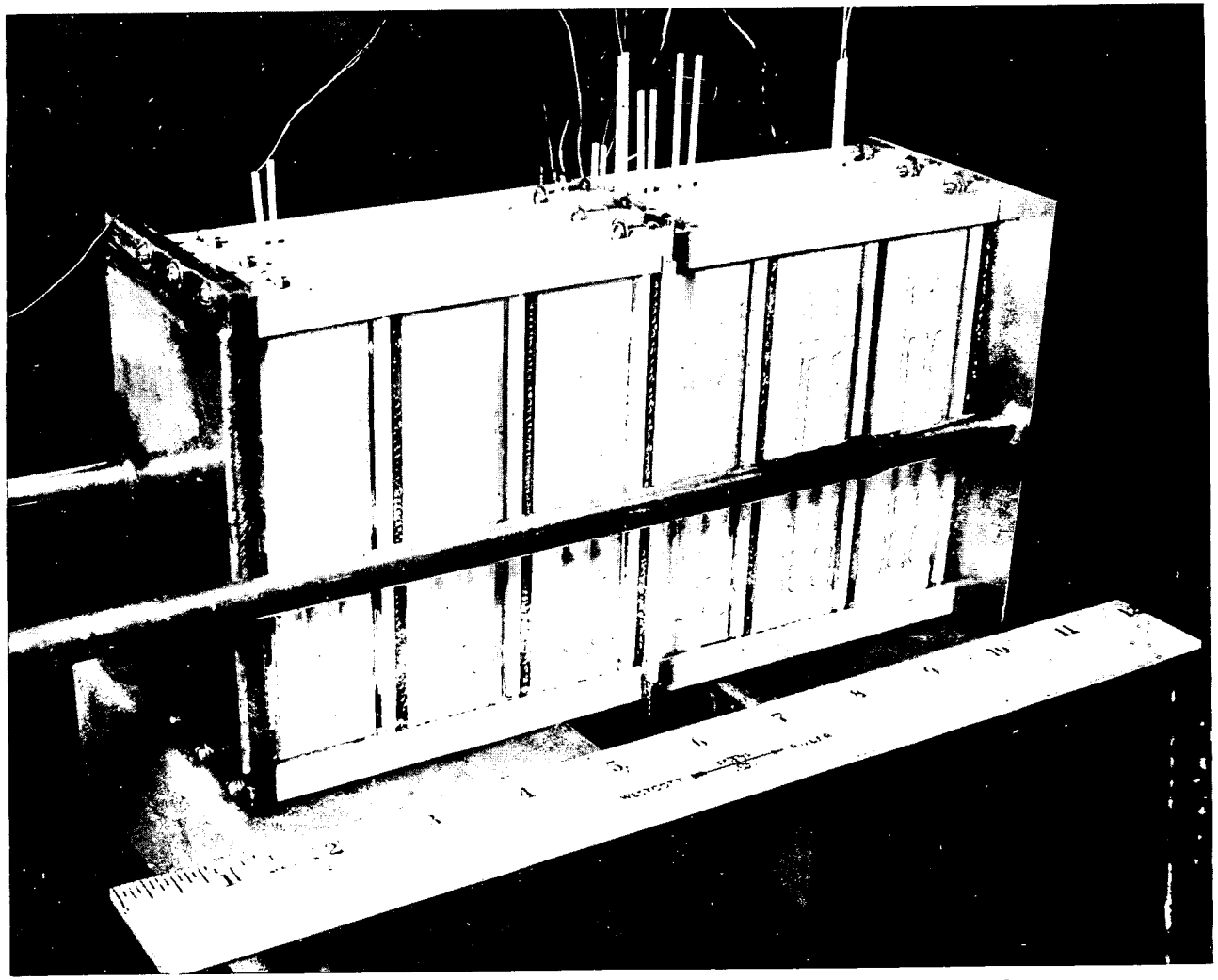

Fig. 11.-VIEW OF A 6 x 6 UNIT WITH THERMOCOUPLES ATTACHED TO SEVERAL OF THE WORKING ELECTRODES.