FUEL CELL
RESEARCH & DEVELOPMENT

RESEARCH ON COMPACT FUEL CELL POWER SUPPLIES

PROGRESS REPORT NUMBER 3

NOVEMBER 30, 1960 - JANUARY 30, 1961

CONTRACT NO. DA-19-129-QM-1705

U.S. ARMY

QUARTERMASTER RESEARCH AND ENGINEERING COMMAND

NATICK, MASSACHUSETTS

AIRCRAFT ACCESSORY TURBINE DEPARTMENT

GENERAL ELECTRIC

52

RESEARCH ON COMPACT FUEL CELL POWER SUPPLIES

BY

AIRCRAFT ACCESSORY TURBINE DEPARTMENT
FUEL CELL LABORATORY

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LYNN, MASSACHUSETTS

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INTRODUCTION

This is a technical progress report of a research program directed toward improvement of the Ion Exchange Membrane Fuel Cell concept. This work is conducted by the General Electric Company under contract No. DA-19-129-QM-1705 with the U.S. Army Quartermaster Research and Engineering Command. The objective of this program is to:

> "Initiate research studies to establish those factors which currently contribute the high energy losses of the ion exchange membrane and establish approaches for minimizing such losses to achieve substantially greater power densities per unit weight of cell."

In this series of reports, progress is reported on work directed toward the above objective. In addition, progress is reported on certain related work being conducted at the Aircraft Accessory Turbine Department. This is made possible by virtue of the similarity of the objective of this contract with that of other work being conducted concurrently. The Work Plan for the total work reported is given in section 0.4 of this report. Guidance and approval of the direction of the work under this contract is given by Mr. L.A. Spano - Chief, Advanced Projects Office, Quartermaster Research and Engineering Command, Natick, Massachusetts.

These progress reports are issued on a bi-monthly basis and special summary reports will be issued as indicated. The reader should recognize that this is a progress report covering a particular period of time. The experiments reported are factual, but not necessarily complete, and any conclusions made must be considered tentative until a summary report is issued. Comments and suggestions on these reports are most welcome.

SUMMARY

Contact resistance between the various current-collector materials and the metallic-black electrodes is nearly inversely proportional to superficial contact area which is consistent with electrode-surface roughness controlling the contact. Advances have been made in the computer-integration of component geometry and specific resistance into cell internal-resistance, and some comparison between experimental and calculated values of internal cell resistance has been made. A correlation between ionic conductance of four different ion-exchange polymers and their other measured properties shows "PKA" values to be a better prediction-indicator of conductivity than ion-exchange capacity. When studying the amount of crosslinking versus the conductivity in a given polymer system, conductivity varies along with ion-exchange capacity. Seven new reinforcing materials for membranes were evaluated with no improvement over existing materials. Nine carbon-catalysts, impregnated with platinum, were used in cell assemblies as the oxygen electrode. To date, in acidic systems, loadings as high as 0.4 mg./cm^2. of dispersed platinum gave electrode polarizations of no better than off 0.7 volts from 1.2 volts at 20 ma./cm^2. Initial work on both the electrolysis and chemical methods of external hydrogen generation are reported.

The work is on schedule for the joint-contract program.

0.3 STATEMENT OF WORK

A. SCOPE:

The Contractor shall, commencing on October 1960 and continuing through 2 October 1961 furnish necessary services, labor, materials, tools, equipment and supplies, and will furnish his best efforts to do what is deemed necessary to:

Initiate research studies to establish those factors which currently contribute the high energy losses of the ion exchange membrane and establish approaches to minimizing such losses to achieve substantially greater power densities per unit weight of cell. The principal effort under this contract should include but not be limited to a study of the factors that impede the conduction of electronic and ionic charges. Investigation of resins, membrane and catalyst formulations and their incorporation into a cell should be conducted to achieve maximum performance.

B. REPORTS:

Reports shall be submitted in accordance with the following:

1. The Contractor shall submit ten (10) copies of bi-monthly reports within fifteen (15) days following the end of each reporting period, indicating progress of work to date and significant developments. These quarterly reports shall include:

   a. An estimate of the percentage of work completed to date.

   b. An estimate of the percentage of costs incurred to date.

   c. A statement that to the Contractor's best knowledge the funds remaining unexpended are sufficient to complete the work called for by the contract, or a revised estimate setting forth the costs required to complete the contract and the reason(s) for the contemplated excess.

2. Upon completion or termination of the contract, the Contractor shall furnish fifty (50) copies of a complete final report or summary report which shall consolidate all findings, notes, data, computations, test procedures, evaluation of all data, test results, principles and techniques relative to the objective indicated herein.

REPORTS (Cont'd):

The Contractor shall include specific conclusions and recommendations concerning work done and detailed information and recommendations relative to further work that may be required. All reports shall be identified with Project No. 7X80-01-New. The final report shall be submitted within thirty (30) days after the expiration or termination date of the contract. Reports shall be of a paper bound brochure type using commercially available bond paper. All reports shall be submitted to the responsible Project Officer, Chemicals & Plastics Division HQ QMR & E Center, Natick, Massachusetts.

PRIORITY RATING: DD C9E CERTIFIED UNDER DMS REGULATION #1 IS ASSIGNED TO THIS CONTRACT.

PLACE OF PERFORMANCE: CONTRACTOR'S PLANT, WEST LYNN, MASSACHUSETTS.

0.4 WORK PLAN

REGULATED, COMPACT FUEL CELL POWER SUPPLIES

General Objective

Conduct a research and development program to achieve the capability of designing compact, lightweight and reliable, regulated fuel cell power supplies.

Research Approach

Task I

Studies of Contributions to and Efforts to Minimize Electronic and Ion Impedances

A. Quantitative studies of contributions to electrical losses in present cells.

1. Separate ohmic losses from electrochemical irreversibilities by use of an adaptation of the Kordesch-Marko bridge and other electronic techniques.

2. Determine magnitude of various contributions to ohmic impedance by independent measurements of electrode-layer resistance, current-collector resistance, contact resistance, and electrolytic conductivity of the membranes. Establish apparent ohmic resistance attributable to electrolytic conductivity of the membranes by other methods, including multi-frequency A.C. bridge measurements and driven-cell D.C. resistance with two hydrogen electrodes.

B. Minimization of Electrolytic Conductance Losses

1. Investigate ion exchange resin formulations with varying exchange capacities, ionization constants and water content with regard to their effect on cell performance.

2. Investigate the effect on cell performance of membrane thickness along with varying the amount and distribution of resin and reinforcing material.

3. Evaluate various reinforcing materials from the standpoint of cell performance, strength, compatibility, and ease of membrane manufacture.

C. Minimization of Electronic Losses

1. Investigation of catalyst impregnated carbon electrodes to minimize electrode layer resistance.

2. Evaluate various carbon blacks with different catalyst loadings and physical properties with regard to cell performance and life.

Task II

Study of the Internal Generation and Storage of Hydrogen Fuel

A. Studies at the Electronics Laboratory, HMED, Syracuse, of palladium and other absorbents.

B. Provision of data by the AAT Laboratory on the electrolysis characteristics of membrane fuel cells, including details of supplying the water required for such operation.

Task III

Study of the External Generation and Storage of Hydrogen and Oxygen

A. Electrolytic methods:

Engineering work leading to the development of a prototype model of a small high pressure electrolyzer. The initial design concept is that of a compartmented vessel for simultaneous generation and containment of hydrogen and oxygen in quantities sufficient for operation of a fuel cell for a specified duty cycle. Included will be studies of pressure reduction methods including minimum weight regulators of conventional design.

B. Chemical Methods:

Studies of various chemical systems for minimum volume and cost hydrogen generators. The size will be set by the required duty cycle.

Chemical Methods (Cont'd)

Noxious reaction products are to be avoided. Feasibility of the process using the best of the chemical system(s) will be demonstrated by constructing a laboratory model generator including pressure regulators as required.

1.0 TASK 1A Quantitative Studies of Electrical Losses in Present Cells

1.1 Separation of Ohmic Losses from Electro-Chemical Irreversibilities.

Progress Report #2 described a completion of this separation within the scope of this work.

1.2 Magnitude of Ohmic Resistance

The methods of determining ion-exchange polymer resistance, catalytic electrode resistance, membrane resistance, and contact resistance were described in Progress Report #1 and Progress Report #2. Also described in Progress Report #2 were the elements of a computer program which will eventually in its final form correlate the individual ohmic resistances of the cell components with the cell assembly resistance for specified cell geometries. In Progress Report #2, contact resistance was presented as specific experimental data since it was not known whether the area or perimeter of the contact surface was the predominant correlating parameter. This section of the present report describes contact resistance data best correlated by superficial contact area. Also described are the initial correlations obtained from the elementary computer program. Finally, in this section of the report, a summary is given indicating the part that the fuel-cell components contribute to the total cell ohmic resistance.

1.2.1. Contact Resistance

In Progress Report #2, some discussion was presented concerning the data obtained on contact-resistance measurements. The reader should be familiar with this material. The data was presented as experimentally taken, with no attempt to correlate contact resistance with contact area, contact perimeter, etc. It was then felt that contact resistance might be a function of both parameters, but which parameter was dominant, if any, was yet to be studied.

In general, the case of contact resistance in the fuel cell can be shown by Figure 1 on Page 1-3. The current flows through the catalytic electrode, turns, and travels through the contact area. Depending on the relative magnitudes of the electrode thickness and the contact member as well as their conductivities, it was considered that a large part of the current could flow through a small area near the outer edge of the contact member, giving a pronounced "periphery" effect to contact resistance. On the other hand, the macro-current-flux could be approximately uniform flowing into both members, showing a simple inverse area relationship to the contact resistance.

To evaluate the two possibilities, titanium contact members, two inches wide, were made of different thicknesses so that the contact area could then be changed directly by using various thicknesses. The length of the leading edge could be changed by cutting down the width of the cell under the contact member, and choosing a member of the right thickness to keep the total contact area constant.

Table I, Page 1-4, shows the results of the contact resistance measurements of titanium contacts to the catalytic electrode. The last two columns show a contact resistivity based on:

1. The Contact Area
2. The Contact Leading Edge

It can be seen that there is a wide scatter of ten to one in values of contact resistivity based on the assumption that the leading edge alone contributes to contact resistance. When a contact resistivity is calculated on an area basis alone, the resistivities fall within a more reasonable error band (about 100%). It was, therefore, concluded that for the thickness of catalytic electrode studied, contact resistance is a more direct function of area at constant pressure. This means that the catalytic electrode acts as a "plenum chamber", and the current flow is restricted only by the small percentage of any contact area where the contact member and the catalytic electrode correctly touch. These facts are consistant with a concept of a rough electrode surface touching only at points.

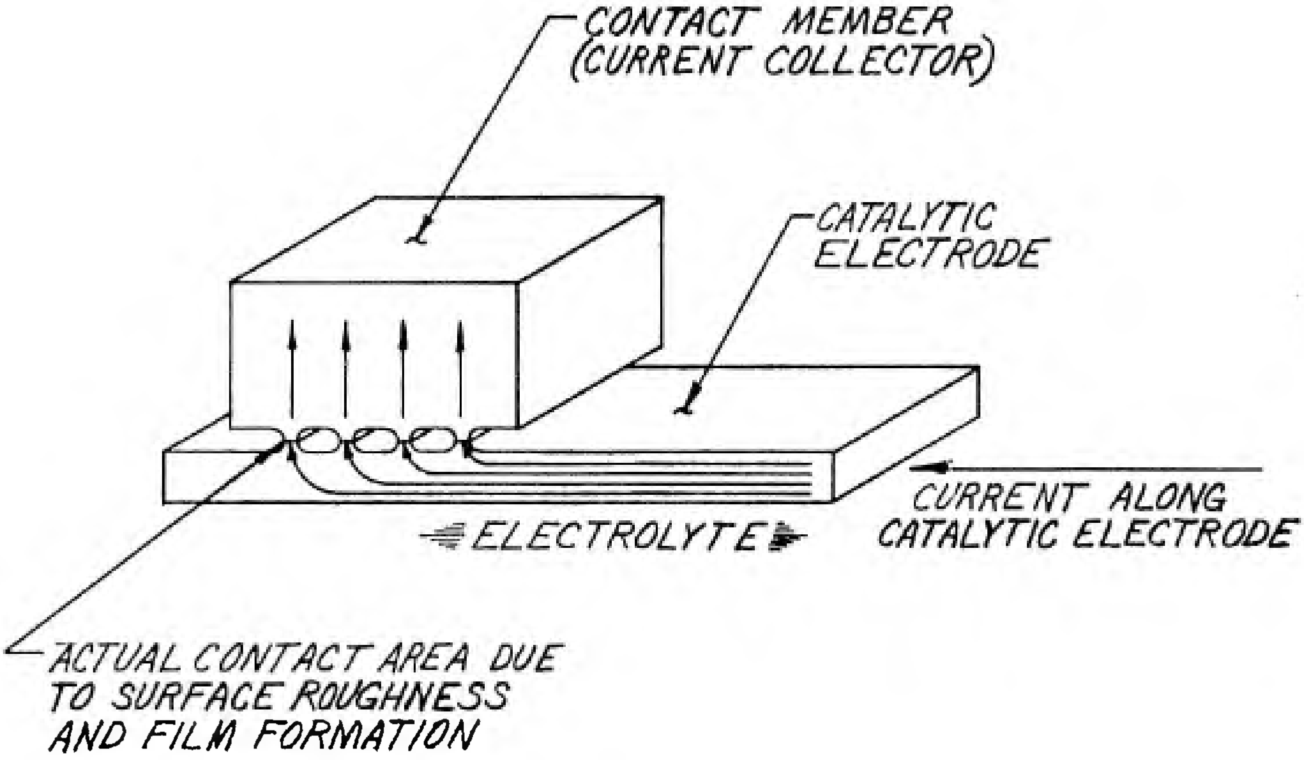

FIGURE 1

MODEL: EXPLAINING CONTACT-RESISTANCE

TABLE I - CONTACT RESISTANCE VS CONTACT AREA

Results of Contact Resistance Measurements Using Titanium Contacts against a Catalytic Electrode containing .0375 g Pt + .0375 g Pd per square inch or 0.0375 g Pd per square inch.

Dimensions of Contact Area						
Width (in.)	Length (in.)	Contact Area (in.^{2})	Contact Loading (psi)	Contact Resistance (ohms)	Contact "Resistivity" (ohm-cm^2)	Leading Edge Basis Contact "Resistivity" (ohm-cm)
.250	1.00	.250	20	.033	5.31 X 10^{-2}	8.38 X 10^{-2}
.125	2.00	.250	20	.058	9.35 X 10^{-2}	29.5 X 10^{-2}
.125	1.00	.125	20	.081	6.52 X 10^{-2}	20.6 X 10^{-2}
.060	2.00	.120	20	.085	6.59 X 10^{-2}	43.0 X 10^{-2}
.020	2.00	.040	20	.182	4.70 X 10^{-2}	92.4 X 10^{-2}
.250	1.00	.250	40	.018	2.90 X 10^{-2}	4.56 X 10^{-2}
.125	2.00	.250	40	.019	3.06 X 10^{-2}	9.65 X 10^{-2}
.125	1.00	.125	40	.034	2.74 X 10^{-2}	8.64 X 10^{-2}
.060	2.00	.120	40	.033	2.56 X 10^{-2}	16.7 X 10^{-2}
.020	2.00	.040	40	.162	4.18 X 10^{-2}	82.2 X 10^{-2}
.250	1.00	.250	60	.011	1.77 X 10^{-2}	2.80 X 10^{-2}
.125	2.00	.250	60	.010	1.61 X 10^{-2}	5.08 X 10^{-2}
.125	1.00	.125	60	.020	1.61 X 10^{-2}	5.08 X 10^{-2}
.060	2.00	.120	60	.026	2.02 X 10^{-2}	13.2 X 10^{-2}
.020	2.00	.040	60	.130	3.36 X 10^{-2}	66.0 X 10^{-2}
.125	1.00	.125	100	.013	1.01 X 10^{2}	3.30 X 10^{-2}
.060	2.00	.120	100	.013	1.01 X 10^{-2}	6.60 X 10^{-2}
.020	2.00	.040	100	.066	1.71 X 10^{-2}	33.5 X 10^{-2}

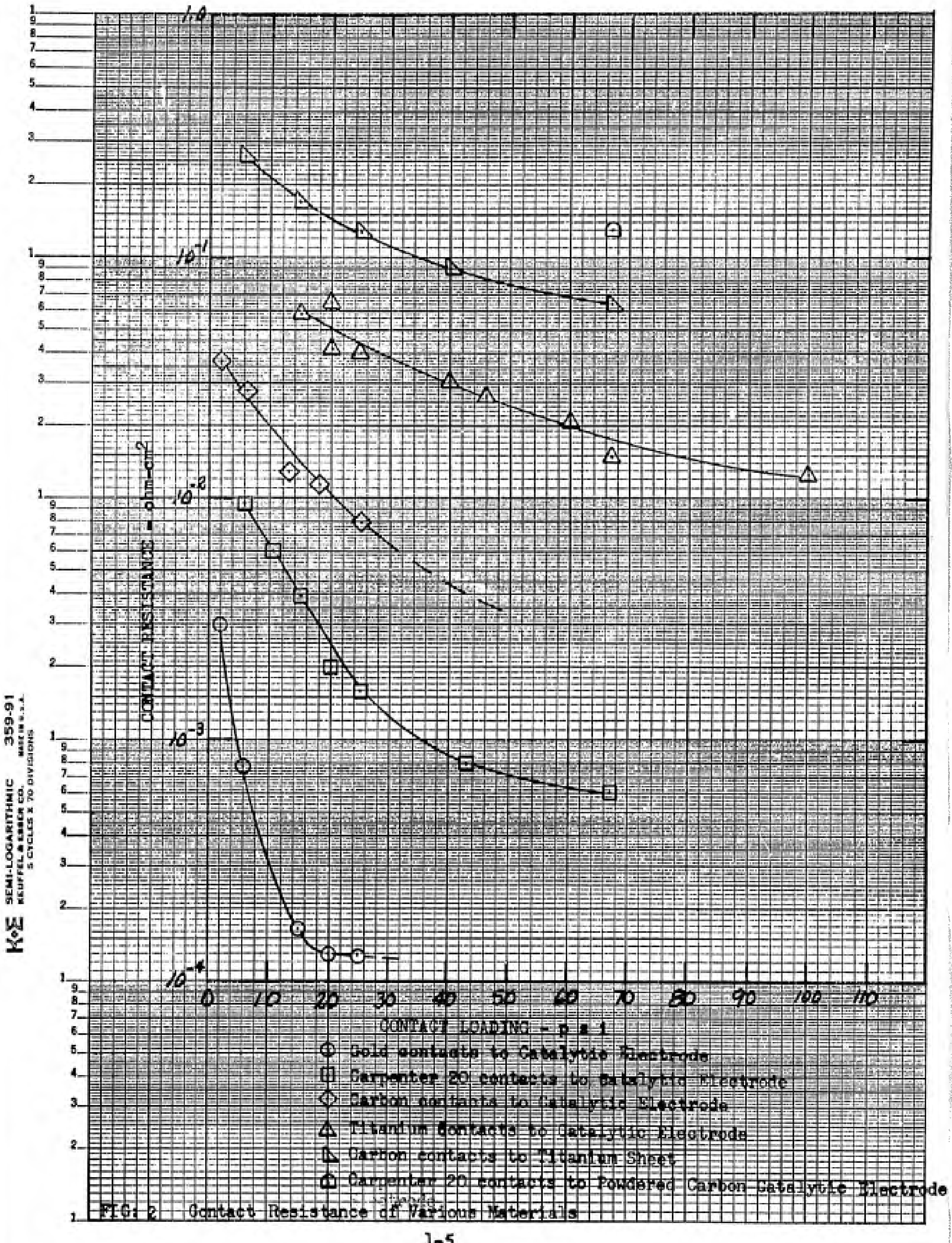

FIG. 2 Contact Resistance of Various Materials

The contact resistance data previously taken with titanium-carbon, and Carpenter 20 Stainless Steel and gold contact members was replotted as a contact resistivity.

In Progress Report #2, the data for carbon contacts and Carpenter 20 Stainless Steel contacts showed a band of resistances. In this report, the lower portion of the band has been deleted for clarity and to show the maximum probable contact resistances with these materials. Note the very low contact resistance between the 1/2 mil-thick gold plate and the electrode surface. This low value may be partially explained by the "softness" of gold and the general freedom of gold surfaces from oxide films.

In a fuel cell using titanium current collectors, the apparent contact area would be set at about 5% of the total catalytic electrode area. Assuming a membrane resistance of 3 ohm-cm^2 for a typical cell, the contribution of contact resistance amounts to 20% of the membrane resistance at a contact loading of 40 psi, and 8% of the membrane resistance at 100 psi. The contact loading in an actual fuel cell can be about 200 psi, which means that the contact resistance is lower than 8% of the membrane resistance for this combination of catalytic electrode surfaces and titanium current collectors.

The work reported here on contact resistance has served to quantitatively characterize the effect of various surfaces in contact as well as to indicate that resistance values are nearly inversely proportional to contact area on the present platinum and palladium black catalytic-electrodes. Also, a simple method of determining contact resistance values has been demonstrated for possible use with future collector-electrode combinations.

1.2.2 Computer Correlations

A 704-IBM computer program was adopted to determine cell assembly resistance from individual specific ohmic resistances of cell components for various geometries that might be used in a cell. This first attempt at a satisfactory numerical-solution was described in Progress Report No. 2.

Using this program, which had only one "node" in the catalytic layer, values were calculated for a 3.5 inch by 4 inch fuel cell having a current collector consisting of parallel ribs, 0.1 in. wide, 3.5 in. long, and 0.8 in. centers. These values were then compared with experiments on such cells. In the experiments, the current-collector resistance is negligible due to the thickness of the solid current collector used. The contact resistance was negligible since the collector was gold-plated and the contact resistance of gold vs platinum or palladium black has been shown to be negligible.

To aid in this first comparison, cell assembly resistances were computed for membrane resistances of 1.58, 3.16, 6.32 and 12.64 ohm-cm^2 plus catalytic electrode resistances of 0.1, 0.3, 0.5, 0.8, 1.3 and 5.0 ohms/ "square" (specific resistivity/thickness) for a given set of cell geometry previously sited where the total cell thickness was made up of 3 mils of electrode on each side of 23 mils of membrane, and the contact and current collector resistances were taken as zero. Table II, Page 1-8, and Figure 3, summarize the data obtained by the computor. Cross-plots of Figure 3 can be used to determine cell assembly resistance if membrane resistance and catalyst resistance are known. For example, if a cell has a catalytic electrode resistance of 0.40 ohms/square and membrane resistance of 1.88 ohms-cm^2 by entering the graph we find cell assembly resistance equal to approximately 2.00 ohm-cm^2.

It may be observed that the curves of constant cell assembly resistance are a constant distance apart at all points when measured along a line normal to the curves. This allows an accurate interpolation for the correlation of points which do not fall directly on a curve.

Unfortunately, this computer program cannot be readily compared with the cells previously tested and described in previous reports, because these cells had catalytic electrode areas which do not satisfy the boundary conditions of the computer program. The present computer program requires, as a matter of convenience, that the length of the catalytic electrode be exactly the same as the rib length, and that the width of the catalytic electrode overhang the outer ribs by exactly one half the distance between the ribs.

TABLE II

CATALYTIC ELECTRODE CONTRIBUTION TO CELL ASSEMBLY RESISTANCE

CURRENT COLLECTOR GEOMETRY
0.1" WIDE PARALLEL RIBS ON 0.8"CENTERS
RIBS 3.5 " LONG.

	MEMBRANE RESISTANCE OHM-CM2											
	1.58			3.16			6.32			12.64		
Catalytic Electrode Resistance * (ohm/square	Computed Catalyst Resistance (ohm-cm^2)	Total Cell Resistance (ohm-cm^2)	Percent Resistance Contributed by Catalyst	Computed Catalyst Resistance (ohm-cm2)	Total Cell Resistance (ohm-cm^2)	Percent Resistance Contributed by Catalyst	Computed Catalyst Resistance (ohm-cm2)	Total Cell Resistance (ohm-cm^2)	Percent Resistance Contributed by Catalyst	Computed Catalyst Resistance (ohm-cm^2)	Total Cell Resistance (ohm-cm^2)	Percent Resistance Contributed by Catalyst
.1	0.020	1.60	1.3	0.028	3.19	0.9	0.048	6.37	0.8	0.086	12.71	0.7
.3	0.120	1.70	7.2	0.086	3.25	2.6	0.064	6.38	1.0	0.106	12.73	0.8
.5	0.224	1.80	12.3	0.187	3.35	5.6	0.116	6.44	1.8	0.118	12.74	0.9
.8	0.370	1.95	19.0	0.346	3.51	9.9	0.277	6.60	4.2	0.156	12.78	1.2
1.3	0.596	2.10	27.4	0.593	3.75	15.8	0.541	6.86	7.9	0.386	13.01	3.0
5.0	3.43	3.43	54.0	2.138	5.30	40.4						

* ohm/square= $\frac{\rho}{t}$

Where ρ =ohm-cm (specific resistivity)
t =thickness of catalyst

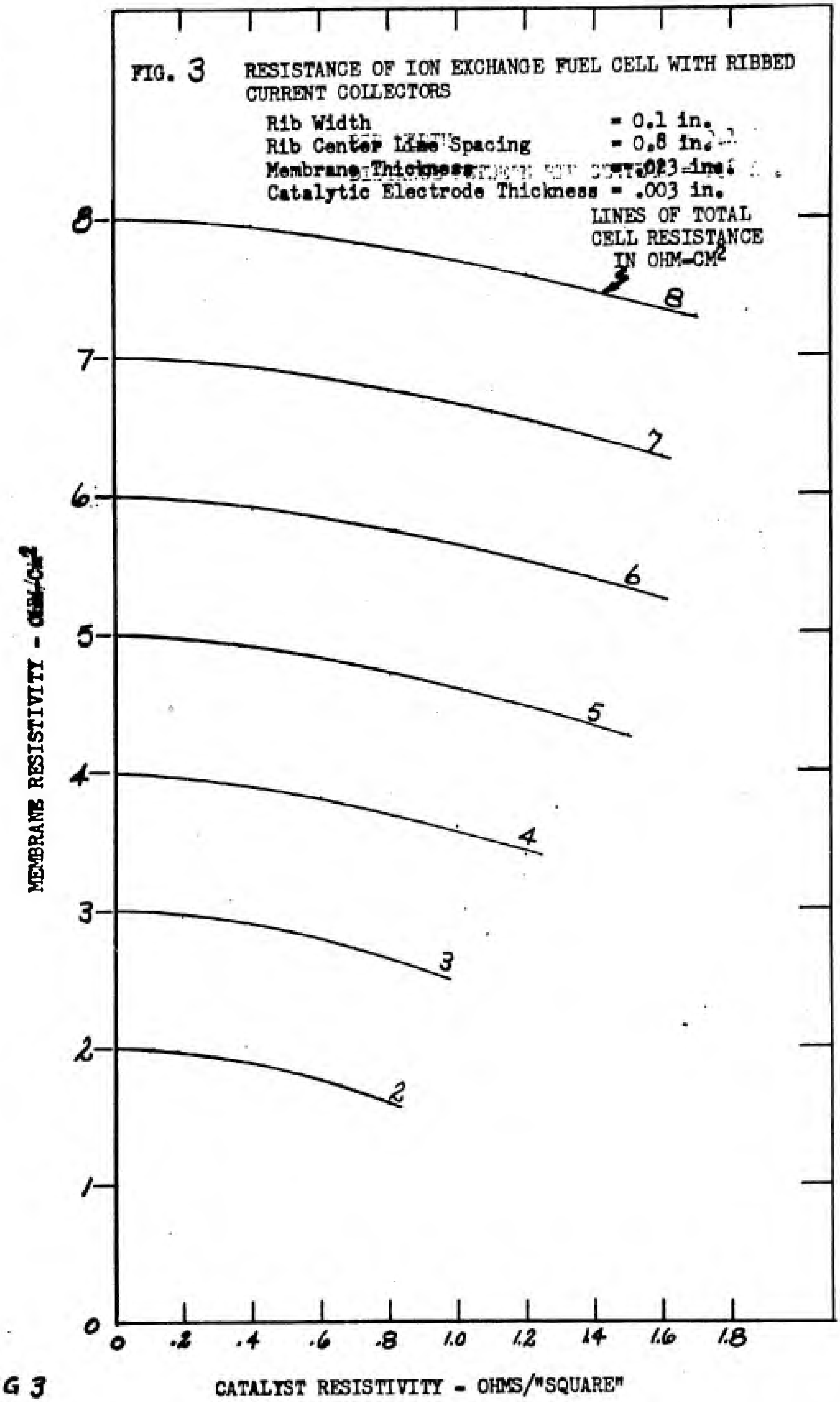

FIG. 3 RESISTANCE OF ION EXCHANGE FUEL CELL WITH RIBBED CURRENT COLLECTORS

Rib Width = 0.1 in.
Rib Center Line Spacing = 0.8 in.
Membrane Thickness = .023 in.
Catalytic Electrode Thickness = .003 in.

FIG 3

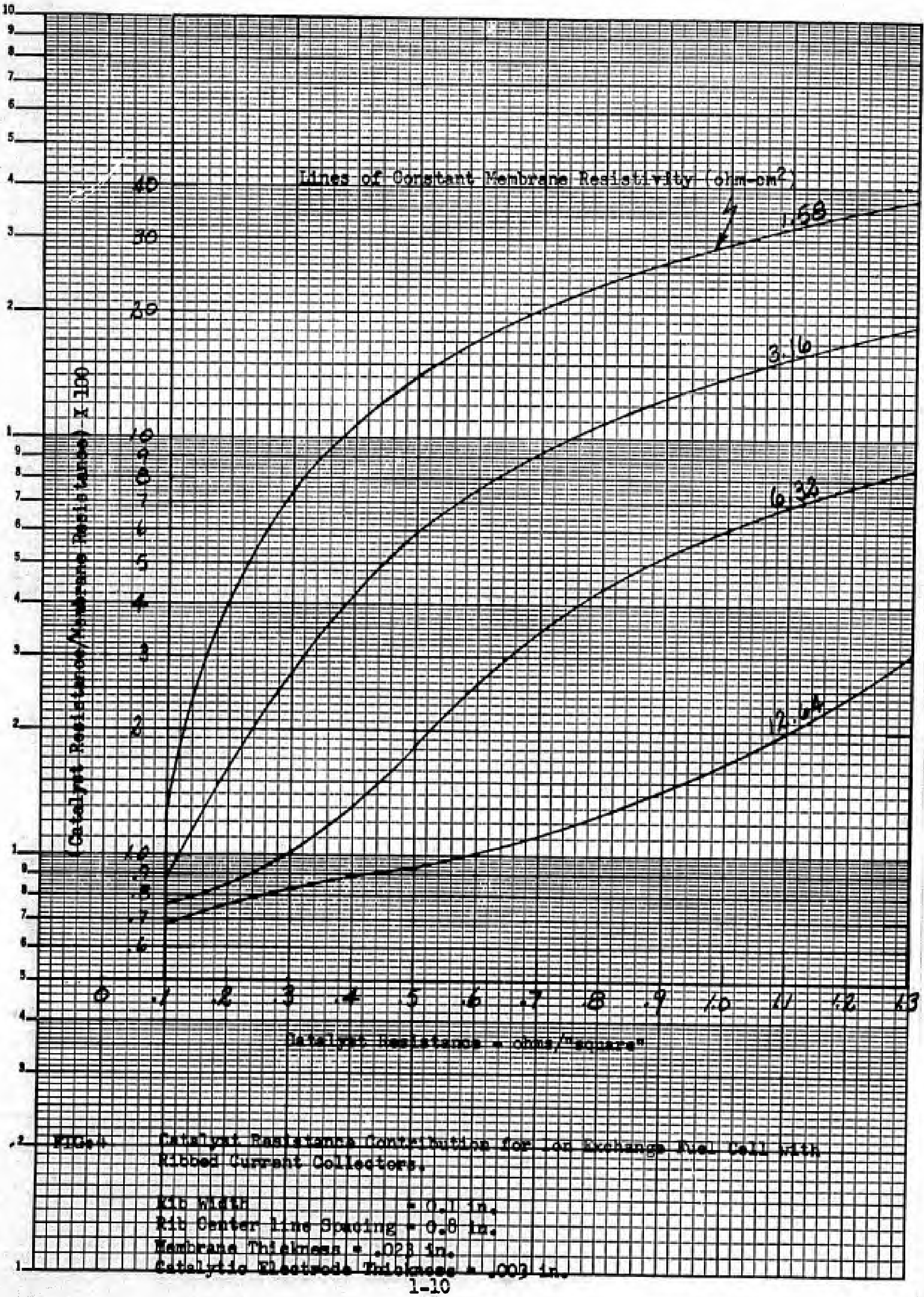

FIG. 4 Catalyst Resistance Contribution for Ion Exchange Fuel Cell with Ribbed Current Collectors.

Rib Width = 0.1 in.
Rib Center line Spacing = 0.8 in.
Membrane Thickness = .028 in.
Catalytic Electrode Thickness = .003 in.

Rib Width = 0.1 in.
Rib Center Line Spacing = 0.8 ins.
Membrane Thickness = .023 in.
Catalytic Electrode Thickness = .003 in.

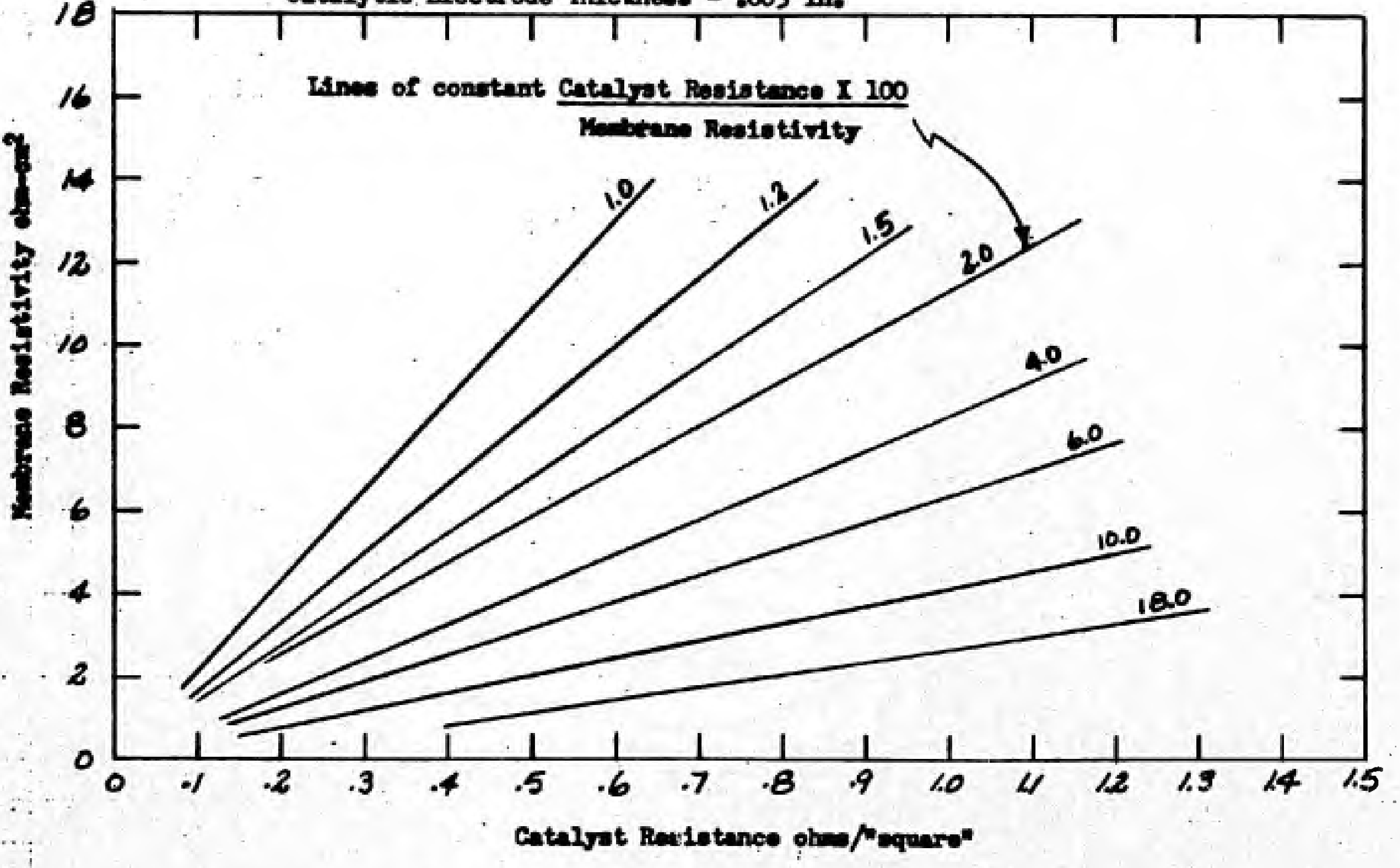

FIG: 5 Cross Plot of Fig. 4 Catalyst Resistance Contribution for Ion-Exchange

For the current collector geometry this requires catalytic electrodes 3.5 in. by 4.0 in. whereas previously described cells had catalytic electrodes 4.35 in. by 4.35 in. Thus, the catalytic electrode resistance could be expected to be a much greater percentage of cell assembly resistance in the previously cited cells where there was not the equivalent number of contacts per catalytic electrode area.

By referring to Table III (Progress Report #2) it can be seen that the average percent of total resistance contributed by the 4.35 in. by 4.35 in. catalytic electrode was 16.6% whereas for the same cells with catalytic electrodes of the proper geometry 3.5 in. by 4.0 in. the contribution would be substantially less as can be seen by referring to Table II or Figure 3.

In order to properly compare the computer results with actual cells, four 12 in. by 12 in. cells were made up so that different combinations of membrane resistance and catalytic electrode resistance would be obtained. The 12 in. by 12 in. cells were then cut into two identical portions measuring 5.0 in. by 5.0 in. The catalytic electrode was then scraped to a 3.5 in. by 4.0 in. size so that its geometry conformed to that required by the initially selected computer program. This special cell manufacture provided four different cell types (two of each kind for a total of eight cells) for which individual ohmic resistances and cell assembly resistance were measured. The measured cell assembly resistance was then compared to the cell assembly resistance obtained from the computer program. Table III, Page 1-13, shows the results of this comparison. It can be seen from Table III that the ohmic losses contributed by the catalytic electrode for the four cells is so small that we are essentially comparing the accuracy of our measurements and the reproducibility of the cell manufacture instead of checking the computer program. It is planned to compare another series of cells prior to the next reporting date. The next series will be cells which have low membrane resistance and a high catalytic-electrode resistance so that the percent contributed by the catalytic electrode will be substantially greater than the error band of the measurements. These new cells will give a better idea of how well the simplified "one-node" program predicts cell-assembly resistance.

TABLE III

COMPARISON OF MEASURED CELL ASSEMBLY RESISTANCE WITH COMPUTED CELL ASSEMBLY RESISTANCE

Cell No.	O_2 Side Catalytic Electrode Resistance (ohms/square)	H2 Side Catalytic Electrode Resistance (ohms/square)	Measured Membrane Resistance (ohm-cm^2)	Kordesch Marko Cell Assembly Resistance (ohm-cm^2)	Computed Cell Assembly Resistance (ohm-cm^2)
COM 1A	0.23	0.41	3.74	3.57	3.81
COM 1B	0.25	0.37	3.20	3.62	3.37
AVE COM 1	0.24	0.39	3.47	3.60	3.59
COM 2A	0.57	1.05	3.08	3.52	3.43
COM 2B	0.41	0.57	3.30	3.78	3.44
AVE COM 2	0.49	0.81	3.19	3.65	3.44
COM 3A	0.19	0.69	7.33	8.68	7.42
COM 3B	0.40	1.13	6.45	6.49	6.70
AVE COM 3	0.21	0.58	7.19	7.85	7.27
COM 4A	0.34	0.87	6.33	6.88	6.51
COM 4B	0.40	1.13	6.45	6.49	6.70
AVE COM 4	0.37	1.00	6.39	6.69	6.61

If the current computer program does not describe with the sufficient accuracy the variations in total cell assembly resistance after changes in cell construction, a more complex program will be tried. A possible second program might have two layers of node-points in the numerical-solution-network in both the catalytic-electrode layer and in the ion-exchange polymer membrane.

1.2.3 Magnitude of Ohmic Resistances

Having established methods and correlations for determining the magnitudes of various ohmic resistances, a Table on Page 1-15, containing a summary of some generalizations has been included so that the percentage of the total cell resistance contributed by each of the individual components can readily be compared. Table IV separates the cell assembly resistance into the four types of contributing resistances and indicates the percent of cell assembly resistance contributed by each. The values are approximate and cannot be used directly for calculating specific cases.

At present, Table IV indicates the areas of importance in the optimization of individual components.

The following conclusions can readily be drawn from the investigation of internal resistance up to this point in the work.

1. Stainless steels such as Carpenter 20 or mil-thick impervious gold-plate should be used as a contact material against the present noble-metal-black electrodes so that contact resistance is kept to a minimum.

2. In the present General Electric ion-exchange fuel-cell using noble-metal-blacks as electrodes, the main internal resistance is in the membrane which is made up of ion-exchange-polymer and reinforcing. Task IB of this report shows that much can be accomplished in this area toward cutting the internal resistance of the present cell.

3. When new catalyst-support or carrier materials are being evaluated as electrode structures, careful consideration must be given to their specific resistance as well as to the spacing of current collector contacts if minimum internal cell resistance is to maintained. Our work shows that this problem is more important than the previous estimations had led us to believe. The use of these new electrodes is essential to the necessary cost-reduction program for materials used in this cell.

TABLE IV

MAGNITUDE OF THE OHMIC-RESISTANCE CONTRIBUTIONS OF VARIOUS COMPONENTS TO TOTAL CELL ASSEMBLY INTERNAL RESISTANCE

Resistive Component	Approximate Percent of Cell Assembly Contributed
I Current Collectors	
A. 1/8 inch or thicker	NEGLIGIBLE
B. 5 mil thick C-20 or Titanium	1% - 30%
II Catalytic Electrode	
A. 0.0375 g. Pt + 0.0375 g. Pd/in^2 or 0.0375 g. Pd/in^2	1% - 10%
B. 0.0185 g. Pt + 0.0185 g. Pd/in^2 or 0.0185 g. Pd/in^2	2% - 20%
C. High loadings of carbon	20% - 54%
III Contact Resistance	
(Contact Area equals 5% of Catalytic Electrode Area)	
A. Gold vs Platinum or Palladium Blacks	NEGLIGIBLE
B. C-20 vs Platinum or Palladium Blacks	0 - 1%
C. Titanium vs Platinum or Palladium	4% - 25%
D. Gold) C-20) vs Carbon Catalytic Electrode Titanium)	20% - 80%
IV Membrane Resistance	100% - (I + II + III) (above)

2.0 TASK IB - Minimization of Electrolytic Losses

As previously reported work shows, in the present low-resistance fuel cells, the electrolyte and any required membrane reinforcing are the major contributions to the internal resistance. TASK IB of the work statement was designed to reduce this electrolyte resistance in two phases. The first phase consists in finding what conductivity improvements can be made in the cation-exchange polymer; the second phase consists of minimizing the percent of reinforcement volume needed in the membrane to yield satisfactory membrane properties of strength, resistance to failure on drying, etc.

In this progress report, a generalized correlation of ion-exchange-polymer ionic-conductivity with two frequently measured properties of ion-exchange polymer systems will be discussed. This correlation work based on data measured for four different ion-exchange-polymer systems shows that a large improvement in polymer ionic conductivity can be realized if different presently-known polymers can be used in constructing a cation-exchange-membrane fuel cell. This correlation also indicates, in terms of other ion-exchange-polymer properties, the requirements for satisfactory operation in a cation-exchange fuel cell of low internal resistance.

Also in this section of the report are given data concerning new reinforcing materials, so that once an improved ion-exchange polymer system is developed optimization of the reinforcing may proceed quickly.

2.1 Investigation of Ion-Exchange-Polymer Formulation

In evaluating phenolsulfonic-formaldehyde ion-exchange-polymers against other polymer systems to obtain a low ionic-resistance system, a brief literature survey indicated that little comparable data on ionic conductivities were available for membranes leached (equilibrated) in distilled water, when the cation-exchange polymer is completely in the acid form. In 1958, Dr. W. T. Grubb of the General Electric Laboratory reported (1)* on ionic migration and also evaluated the literature (2, 3, 4, 5, 6, 7)*, concerning ionic transport. The literature and his work were mostly concerned with the effect of changing the migrating ionic specie, its transport mechanism, and the lyosphere of solvent necessary rather than comparison of the ion-exchange polymers in acid form.

* See literature reference Appendix A

From electrochemical principles, it might be concluded that hydrogen-ion conductivity would be proportional to the active hydrogen-ion concentration in the hydrated ion-exchange-polymer network. This porton activity or "free hydrogen-ion concentration" can be measured for an ion-exchange polymer by the standard technique of evaluating "PKA". Also, it was generally thought that high ion-exchange-capacities would increase conductivities when the free-hydrogen-ion concentration (the antilog of minus the PKA) is made up of the product of the ion-exchange-capacity, or number of sites, times the equivalent degree of ionic dissociation at the sites. Finally, it was considered that the dependence of ionic conductivity on the amount of water-solvent present in the polymer should be demonstrated.

Four different cation polymer systems, - polyacrylic acid, polystyrene-sulfonic acid, polyvinyl-phosphonic acid and the condensation product of formaldehyde and para-phenolsulfonic acid, were prepared. The polyacrylic acid was polymerized in benzene from acrylic acid using a trace of benzoyl peroxide as a catalyst. For our work the purchased sodium salts of polystyrene-sulfonic acid were converted to the well-leached acid.form. The phenol-formaldehyde-sulfonic-acid polymers were prepared by reacting melted crystals of pure para-phenol-sulfonic acid with various amounts of formalin solution (37 wt. % formaldehyde stabilized with methanol.) The polyvinyl-phosphonic acid was prepared from purchased bis-2 chloro-ethyl-vinyl phosphate by polymerizing again with traces of benzoyl peroxide for 72 hours at a bulk temperature of 125°C, followed by hot hydrolysis at 50°C in basic solution and finally ion-exchanged with a pure acid resin to generate the phosphonic acid.

While ion-exchange capacity and "PKA" were measured by standard techniques, the ionic conductivity (reciprocal resistance) was measured by an a.c. bridge. The applicability of this measurement for resistance to ionic transport has been substantiated by prior work on this contract as well as by the literature (3)*. Our ionic conductivity measurements were taken by the variable-cell-length method described in Progress Report No. 1 where the ion-exchange polymer is in solid form.

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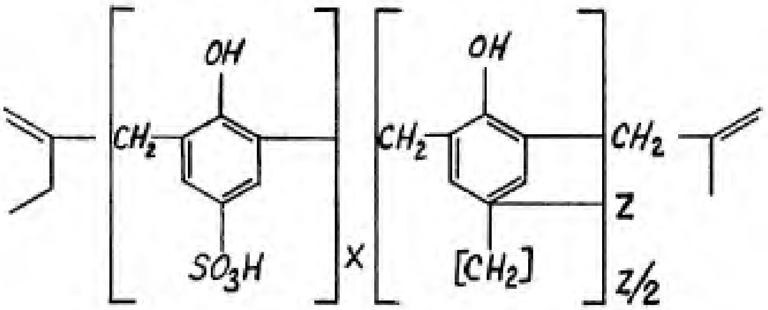
* See Appendix A

Tables V and VI contain the results of this preliminary investigation. Under the double column in Table V entitled "ION-EX. CAPACITY" are given both theoretical and measured values of the polymer's ion-exchange capacity. These theoretical values for the formaldehyde-phenylsulfonic-acid polymers were calculated using the experimentally measured value of ion-exchange capacity to determine the "molecular-weight" of the "mer" unit according to a simple model where the difference between the value of 5.37 meq/gm. for the linear polymer and the actual measured value of capacity were taken as an indication of the amount of crosslinking caused by some of the excess formaldehyde available at ring sites where the sulfonic-acid groups were hydrolyzed off. Hence for the phenol-formaldehyde polymers, one "mer" is assumed to equal:



$$X + Z = 1$$

$$X = \frac{\text{Meas. Ion-Ex. Cap.}}{5.37}$$

$$Z = \frac{5.37 - (\text{meas. I. E. Cap.})}{5.37}$$

Then "mer" weight = $(186.2)X + (112.1)Z$
"mer" weight = 112.1 + 13.8 (Meas. I. E. Cap.).
And meq./g of polymer = 1000 (X) / (mer. wt.)
meq./g of polymer = 186.2 (Meas. I. E. Cap.) / (mer. wt.).

For the other polymers, theoretical ion-exchange capacities were calculated assuming that the linear molecular-polymer structure determines the "mer" unit.

TABLE V

PROPERTIES OF CATION-EXCHANGE POLYMERS IN ACID FORM

POLYMER FORM USED	ION-EX. Theory meq./gm.	CAPACITY Meas. Val. of polymer	MEASURED "PKA" VALUE	IONIC CONDUCTANCE at 92.5% Rel. Humidity milli-Ohm^{-1} cm^{-1}	Ohm^{-1}cm^{-1} gm/equiv.**	PERCENT SULFUR CONTAINED Theory Wt. percent of Polymer	Meas. Val.
linear polyvinylphosphonic acid (one proton off only)	9.26 (first proton only	7.22	2.43	0.84	0.12	-	-
linear polystyrenesulfonic acid	5.45	2.99	0.50	140.	46.	-	-
crosslinked polyacrylic acid	-	-	6.00	0.07	0.0056	-	-
linear polyacrylic acid	13.9	12.5	5.70	0.10	0.008	-	-
1.15 moles HCHO per mole p-phenolsulfonic acid	3.75***	3.13	2.14	68.*	21.6*	12.0***	8.6
1.25 moles HCHO per mole p-phenolsulfonic acid	3.55***	2.90	2.22	44.*	15.3*	11.4***	7.4
1.40 moles HCHO per mole p-phenolsulfonic acid	3.08***	2.40	2.29	35.*	14.4*	9.9***	6.9
1.55 moles HCHO per mole p-phenolsulfonic acid	2.77***	2.10	2.40	29.*	13.9*	8.9***	6.4

* - Measured at 100% Relative Humidity

** - This is an approximation to an equivalent conductance: equals (reciprocal ohm-cm) divided by equivalents (I.E. Cap.) per gram of solid resin instead of equivalents per cc. of solid resin.

*** - Assumed mol. wt. of "mer" unit based on I. Ex. Cap. found signifying amount of crosslinking caused by some excess formaldehyde bridging at sites of hydrolyzed-off SO_3H groups. Linear value = meq./gm.

TABLE VI

CHANGE IN IONIC-CONDUCTIVITY OF HYDRATED-SOLID ACID-FORM CATION-EXCHANGE POLYMERS WITH RELATIVE HUMIDITY

POLYMER FORM	IONIC-CONDUCTIVITIES* WHEN POLYMER IN EQUILIBRIUM WITH CITED REL. HUMIDITIES			
	100%	92.5%	79.3%	70.8%
linear polystyrene-sulfonic acid (Prelim. Data)	-	140	51	41
linear polystyrene-sulfonic acid plasticized with 16.7 wt. % glycerol	-	137	79	40
1.50 moles HCHO per mole** p-phenolsulfonic acid	74	69	55	40

* - Values given in milli-ohm^{-1}cm^{-1} as determined by an A.C. bridge.

** - Values determined prior to this contract. Average of many values. <u>Best</u> cure-time conditions.

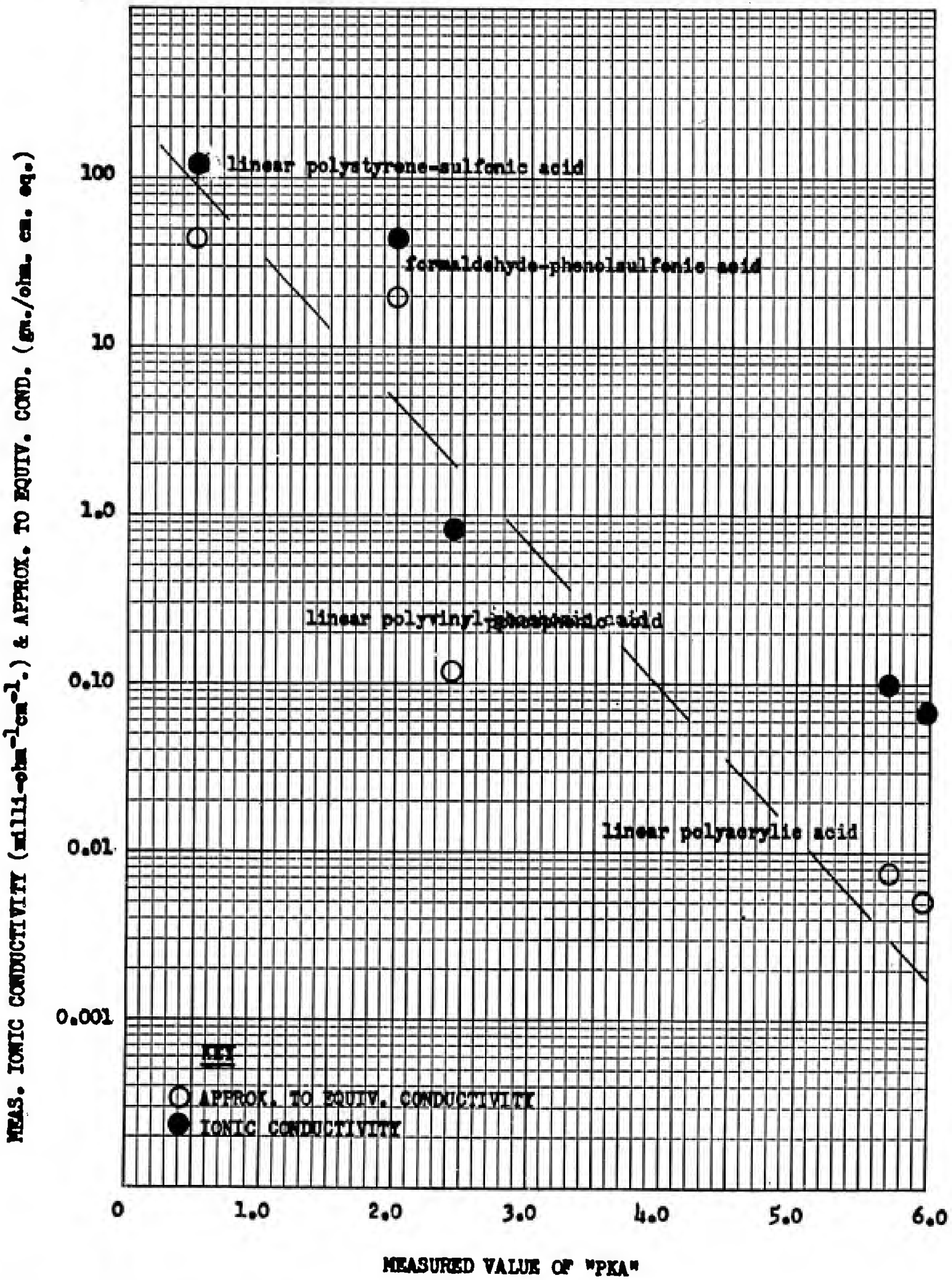
Also in Table V in the double column entitled "IONIC CONDUCTANCE" is given ionic conductance determined from the well-leached acid-form of the solid polymer using an a.c. bridge. Values appear both as specific conductances and as an approximation nearly proportional to equivalent conductance. While equivalent conductance can be defined as specific conductance divided by concentration, expressed in equivalents per volume of solution, here such a number might be very inaccurate because no independent evaluations of milli-equivalents per cubic centimeter in the hydrated solid ion-exchange polymer have been made to date. At present, the equivalent-conductance approximations have been calculated by using measured values of ion-exchange capacity instead of equivalents per volume of polymer. The last double column in Table V contains a comparison between theoretical percent sulfur contained in phenolic polymers and the actual amount found by measurement. Theoretical values were obtained by multiplying the theoretical ion-exchange capacities by 3.21 to account for the equivalent weight of sulfur and the change in units from milli-equivalents to percentage.

Several preliminary conclusions can find support in the values given in Table V. First when comparing <u>different</u> polymer structures containing different ionizable groups, a measured "PKA" value can be used to give a very rough prediction of ionic conductivity. Conductivities of different polymers are NOT related to ion-exchange capacity to any great extent. Thus the effect of changing the number of possible ionized sites over the small range of interest, say from 1 to 10 meq./gm. of polymers, cannot compare with the very large effect on "free-hydrogen-ion" concentration induced by changing ionizing groups where the degree of dissociation possible can easily be varied over a range exceeding 1000 times, as indicated in the variation of the antilog of the "PKA." As seen in Figure 6, the ionic conductivity (or the approximation to equivalent conductivity) is correlated to some degree by the "PKA" measurements. The scatter in the correlation is partly explained by the effect of different polymerization conditions, impurities, etc.

Assuming that the value of "PKA" is the main variable available in the literature to predict ionic conductivities of polymers leached with distilled water and in the acid form, one can conclude that only polymers containing the sulfonic groups are worth considering for acid-cells of low internal resistance.

FIGURE 6

IONIC-CONDUCTIVITY VERSUS "PKA" FOR SOLID CATION-EXCH. POLYMER IN ACID FORM



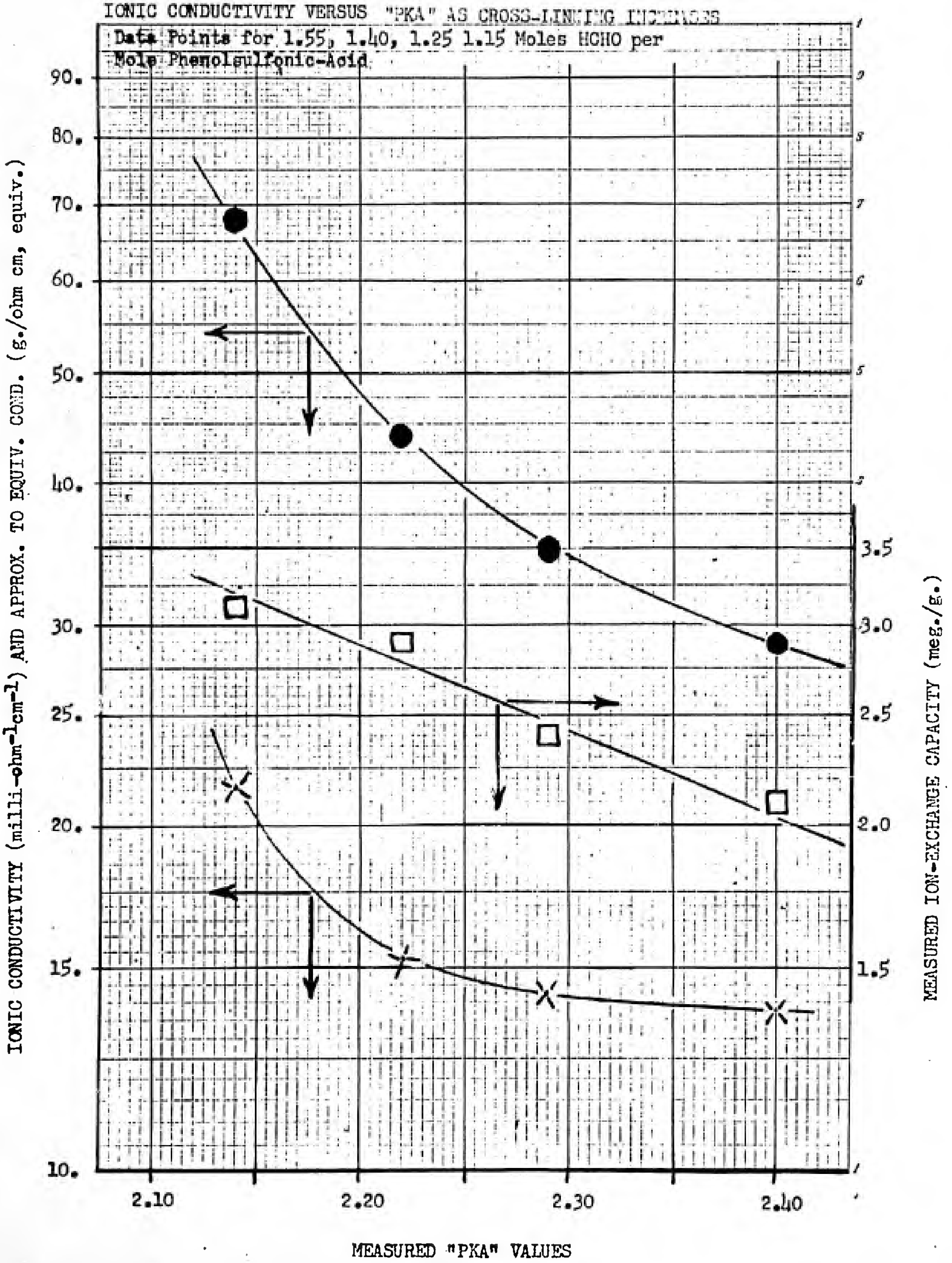
The obvious polymer systems possessing both improved physical properties and higher conductivities than the formaldehyde-phenolsulfonic-acid system are polyvinylsulfonic-acid and polystyrene -sulfonic acid systems. The manner in which these polymers would be crosslinked and attached correctly to the catalytic-electrode structures is not known at present. Also the thermal stability limit of at least one of these new systems in the presence of water, acid, oxygen, and a good catalyst is in question. Other work in our laboratory, not part of this contract, is continuing on these two acid-polymer systems. Any significant accomplishments will be reported at later dates.

Another conclusion, from evidence in the data presented in Table V, concerns the variation in ionic conductance in a given polymer system when the ion-exchange capacity is decreased while the type of ionizing-group is kept constant. This effect was accomplished in the formaldehyde-phenolsulfonic-acid system by inducting more crosslinking with excess formaldehyde. A correlation of measured ion-exchange capacity and ionic conductivity versus measured "PKA" values appear in Figure 7.

Note in Figure 7 how the decrease in ion-exchange capacity, - I.E.C., is directly reflected in an increase in "PKA". This type of relationship would be consistant with the hypothesis that the "free-hydrogen-ion" concentration, as approximated by minus the antilog of "PKA", is equal to the product of I.E.C. and the percent dissociation at each site. However, this relationship is not quantitatively shown by the data if one assumes only the number of sites are being varied as crosslinking is increased. Note as the I.E.C. varied in Figure 7 from 3 to 2 meq. per gram, a factor of 1.5, the antilog of "PKA" increases by a factor of 2 instead of 1.5. This discrepancy can easily be explained. First one can assume the degree of dissociation possible at each site has also changed with the amount of crosslinking. Secondly the amount of data used to determine correlation is slight and thus experimental error may account for the discrepancy. And finally an explanation may be found in the approximate nature of the hypothesis. While the hypothesis is qualitatively useful, it only describes the situation to a very approximate degree in a quantitative sense. However, the data shown in Figure 7 illustrates that where only one ionizable group and polymer system are concerned, the change in ionic conductivity is principally a function of the amount of ion-exchange capacity.

One more fact should be noted from the data presented in Table V. The ratio between measured I.E.C. and the theoretical values calculated for the formaldehyde-phenolsulfonic-acid, according to the simple model for the "mer" unit, extend from 84 percent to 76 percent.

FIGURE 7



IONIC CONDUCTIVITY VERSUS "PKA" AS CROSS-LINKING INCREASES

Data Points for 1.55, 1.40, 1.25 1.15 Moles HCHO per Mole Phenolsulfonic-Acid

These percentages indicate that the suggested polymer only partly may be explained by the structure model, or that the I.E.C. measurements do not accurately take into account all of the sulfonic-acid groups because of some structural hindrance. Evidence against the latter possibility may be found in the independent analysis for the percent sulfur contained in the polymer. The ratio between measured percent sulfur and theoretical percent sulfur, which is based on the "mer" model, runs about 65 to 72 percent. The discrepancy between sulfur analysis and I.E.C. acid-titration is only about 10%. This is a slight difference because the sulfur analysis requires an estimation of polymer molecular weight. Thus it can be concluded some evidence exists for believing a good correlation ion-exchange capacity and percent sulfur exists. This may indicate no solvated protons are trapped in the polymer during the I.E.C. caustic titration. If this is the conclusion, then sulfonic acid groups are being hydrolyzed off during the acid cure process, indicating that the phenolic polymer does not possess the best life for high temperature operation over 150°F.

Also during this reporting period, a small amount of work on the change in ionic conductivity with the amount of solvent present in the solid ion-exchange polymer was done. The effect reported in Table VI has been demonstrated prior to this contract many times for the formaldehyde-phenolsulfonic-acid system. The values presented for polystyrene-sulfonic-acid in Table VI are preliminary, while those for the phenolic polymer represents data for polymers with an optimized cure-cycle. General agreement between the A.A.T. Department Laboratory and the General Electric Research Laboratory exists on these phenolic values. This small amount of data on the effect of water content serves to illustrate the well-known fact that ionic conductivity is proportional to the amount of solvent present. This is especially true when polymers are in the acid-form and the solvent is such a strong dipole as water.

2.2. Effect of Membrane Thickness and Reinforcement on Cell Performance.

No work was done during this reporting period. After presenting the data given in Progress Report No. 2, it was planned to wait for improved resin formulations before initiating any more work on the effect of membrane thickness on cell performance.

2.3 Evaluation of Reinforcing Materials

Several new reinforcing materials have been evaluated in an attempt to optimize the membrane-electrolytic resistance and "dryout strength" characteristics. Work was based on phenolic polymers. Table VII, Page 2-12, includes the evaluation data obtained on the cells made from these materials:

1. A porous polyethylene with 80% voids of a 100-125 micron pore sizes from E.S. Reeves Company.
2. A heavy-weight dacron felt from National Felt Company.
3. A heavy-weight polypropylene felt from National Felt Company.
4. A natural rubber battery separator 45 mils thick with 60% voids - U.S. Rubber Company.
5. A 50% wool - 50% rayon non-woven blend from National Felt Company.
6. Two (2) tissue-glass sheets obtained from American Machine and Foundry Company.
7. A dacron-wool woven cloth from Waumbec Mills.

Table VIII, Page 2-13, lists the reinforcements evaluated to date with the pertinent characteristics of each. Table VIII would indicate that none of these new materials approaches the required 1.00 - 2.50 ohm-cm^2 membrane resistance with the present polymer used. The best resistances were obtained with the dacron and polypropylene felts. These are especially promising as the materials evaluated were exceptionally heavy in weight as indicated by Table VIII. It is hoped that this resistance may be substantially lowered with lighter materials having the capacity to hold more ion-exchange polymer. The porous polyethylene material did not fail in the dryout test. This is probably due to the poor impregnation, indicated by the membrane's very high resistance and low-percent polymer pickup.

TABLE VII

EVALUATION OF REINFORCING MATERIALS

CELL #	THICKNESS INCHES X 10^3	REINFORCEMENT PLY 1-PLY2-PLY 3	MEMBRANE RESISTANCE OHM-CM^2	MULLIN BURST psig	4 X 4 FRAMED DRY OUT 40% R.H.	% RESIN
1	.025	DN-POLYETHYLENE-DN	18.13	275	NO FAILURE	
2	.030	DACRON FELT	5.46	350	60 MIN. PINHOLE	51
3	.030	POLYPROPLYENE FELT	5.67	450	120 MIN. PINHOLE	12
4	.055	RUBBER SHEET	12.36	20	10 MIN. CRACKED	
					VERY BRITTLE	44
5	.025	WOOL/RAYON	17.10	NIL	NO DATA TOO BRITTLE	69
6	.025	DN-TISSUE GLASS-DN	TOO WEAK TO HANDLE			
7	.025	DN-TISSUE GLASS-DN	TOO WEAK TO HANDLE			
8	.027	234 Waumbec 234	6.18	350	790	
9	.025	429 Waumbec 429	6.30	270	60	
BEST RESISTANCE TO DATE	.025	234	1.72	under 100	under 20	80
PREVIOUS BEST DRY-OUT	.030	234	6.90	265	200	55-60

TABLE VIII
REINFORCING MATERIALS

MATERIAL	GRAMS/IN^2	THICKNESS	DESCRIPTION
Wool/Rayon	0.41	0.037	50% Wool - 50% Rayon Non-woven Fabric
Dacron Felt	0.19	0.250	Dacron Non-woven Fabric
Polypropylene Felt	0.30	0.250	Polypropylene Non-woven Fabric
234	0.055	0.024	Dynel Non-woven Fabric
424	0.055	0.006	Dynel Non-woven Fabric
Tissue Glass #1	0.019	0.009	Glass Tissue Non-woven
Tissue Glass #2	0.067	0.026	Glass Tissue Non-woven
DN	0.031	0.005	Dacron Woven Fabric
Waumbec	0.092	0.015	70% Dacron-30% Wool Woven Fabric
Porous Polyethylene	0.053	0.016	80% Void volume, 7100 micron pores-polyethylene material
Rubber Separator	0.39	0.045	60% Void volume - natural rubber battery separator
429	0.030	0.005	Dynel Non-Woven Fabric

Since this particular material is 80% void by volume with pore-size greater than 100 microns, it is extremely doubtful that this type of porous polyethylene shows much promise unless an improved method of impregnation is used.

The wool-rayon blend, the natural rubber separator, and the "tissue-glass" are poor choices because they are physically weak and have high resistance. Resistance will not be evaluated for the "tissue-glass" because it fell apart. Several other materials are being considered and will be evaluated. Most of these are wool-dynel non-woven blends, and special glass weaves. It should be noted that wool is attacked by the polymer. However, the polymer does not adhere to the presently-used orlon or dynel as well as desired. Since the polymer does adhere to the wool, probably by chemical attack, wool blends seem advantageous for easy impregnation, adherence, and possibly higher percent polymer pickup.

The use of wool may become necessary in place of orlon, dynel, dacron, or glass fibers which will require the development of chemical pretreatments for easy impregnation. If this is the case, it is estimated that only about five weight percent of the reinforcing need be wool to aid impregnation.

3.0 TASK 1C Minimization of Electronic Losses

Since, as previously described in Section 1.2.2 of this report, the contribution of the resistance of the present expensive catalytic-electrode to the present cell-assembly resistance is only approximately 5%, the major problem is not one of minimization of the small electronic losses of the present metallic catalytic electrode, but rather one of minimizing the cost of the electrodes while not substantially increasing the electronic or contact resistance.

The complete development of low-cost catalytic electrode structure is beyond the scope of the present contract. However it was hoped to achieve sufficient work on these contracts in this area to clearly define some of the electrode requirements quantitatively. First efforts will be directed toward a preliminary evaluation of various forms of carbon catalyst supports.

In a simplified statement of the situation, it may be said that the catalytic electrode serves at least, the following four purposes:

1. Furnishes sites for fuel (hydrogen <u>or</u> oxygen) adsorption;
2. Promotes catalytically the electrochemical reactions;
3. Has a contact area with the electrolyte so that the ions produced or used by the electrochemical reactions can migrate to or away from the electrode;
4. Has sufficient electron-conductivity to allow electrons to migrate through the structure.

Unless one is prepared to assume high mobility of the absorbed species or ions on the electrode surface at low temperatures, the actions denoted by Numbers 1, 2, and 3 above must occur at approximately the same places on the electrode, namely around the catalytic site. If electrons can be transferred from the catalytic sites to an electron-conducting substrate without appreciable interface resistance, then a much less expensive material can be used for the bulk of the electrode.

Since carbons are much poorer electron conductors than platinum or palladium blacks, it is understandable that some performance sacrifice will have to be made in reducing the cost, alternately, that the electrode thickness must be increased with the possibility of introducing diffusion limits. It should also be noted that materials other than carbon may be used provided, of course, that they are compatible with the present acid system.

None of the electrode materials or cell structures reported here were prepared on this contract. The work was accomplished on general development funds available to the AAT Laboratory. Only the evaluation of the cells was performed on funds from contracts for which this progress report is being written.

Table IX and Figure 8 show the results obtained on various cells which had standard hydrogen side catalysts of 0.0375 g/in^2 of palladium black. The oxygen side catalysts were various carbons or other compatible materials treated with platinum or palladium compounds.

One cell, (ACP), contained pure platinum on the oxygen side. This platinum was spongy rather than being a platinum-black type, and was investigated as an alternate platinum type. The oxygen catalyst loadings were arbitrarily selected as close to the maximum loading as would satisfactorily adhere to the membrane using the present construction techniques.

Referring to Table IX, it can be seen that the contact-resistance of the gold-plate versus the platinized materials was very high as predicted earlier in the contact resistance section. It is also obvious that the electronic resistances of these materials was at least five times greater than that of the standard platinum or palladium. The sum of the high contact resistances and the high catalytic electrode resistances resulted in very high cell resistances. However, Figure 8 indicates that the electrochemical irreversibilities are also affected by the decrease in the amount of platinum. All curves shown in Figure 8 are those attributed to electrochemical irreversibilities only (the ohmic losses are indicated in the section above the curves). Even the spongy-platinum, (ACP), had a higher resistance and larger electrochemical loss than the standard platinum-black catalytic-electrode.

TABLE IX
RESULTS OBTAINED WITH VARIOUS OXYGEN-SIDE CATALYTIC ELECTRODES

Data obtained with standard Hydrogen side catalyst (5.8 mg. palladium per square cm.
Gold plated 0.1" wide parallel ribs on 0.8" centers.
Active catalyst area 103 cm.^{2} (4 X 4 inch.)

Cell No.	O_2Side Catalyst	Total Electrode Loading mg./cm^2	Kordesch Mark Cell Assembly Resistance (OHM-CM^2)	Measured Contact Resistance (OHM-CM^2)	Measured Catalytic Electrode Resistance (OHM-CM^2)	Calculated Membrane Resistance (OHM-CM^2)*	Measured Open Circuit Voltage
S-1	Stackpole Carbon 3039 Platinized with Chloroplatinic Acid	7.7	6.8	0.3	9.9	1.85*	0.874
S-3	Tungsten Carbide Platinized with Ammonium Chloroplatinate	47.	17.0	72.5	16.0	1.85*	0.867
S-4	Stackpole Carbon 3039 Platinized with Colloidal Platinum.	12.	4.0	.01	4.7	1.85*	About 0.775
S-5	Titanium Carbide Platinized with Chloroplatinate	25.	27.0	72.5	Over 20	1.85*	0.775
ACP	Decomposed Ammonium Chloroplatinate	14.	5.2	nil	3.0	3.60**	1.01
S-7	10% Platinum Black on Battery Carbon	4.6	9.1	1.2	12	1.85*	0.97
S-8	10% Platinum Black on Coke	31.	13.5	4.0	Over 50	1.85*	1.03
S-9	10% Platinum Black on Acetylenic Carbon Black	3.9	9.2	1.0	20.0	1.85*	0.979
S-10	10% Palladium Black on Shawinigan. Carbon Black	3.1	11.0	0.6	Over 30	1.85*	0.982
Std.	Standard Plat. Black	17.	2.1	nil	0.48	1.85*	1.07

* Because of high contract-resistances involved, the method of measuring membrane resistance with an A. C. Bridge directly is not accurate. Recommend these calculated values.

** This membrane is of different construction than the others listed in this table. 3.60 OHM-CM^2 is normal for the construction.

Curves below were obtained from data using Kordesch-Marko bridge. All curves show only the results obtained from interruption of current.

Symbol	Cell Number	Cell Resistance (ohm-cm^2)
⬡	Standard Cell	2.1
⊙	S-1	6.8
⊡	S-3	17.0
◈	S-4	4.0
△	S-5	27.0
◺	S-7	9.1
◗	S-8	13.5
⌂	S-9	9.2
◉	S-10	11.0
⌂	ACP	5.2

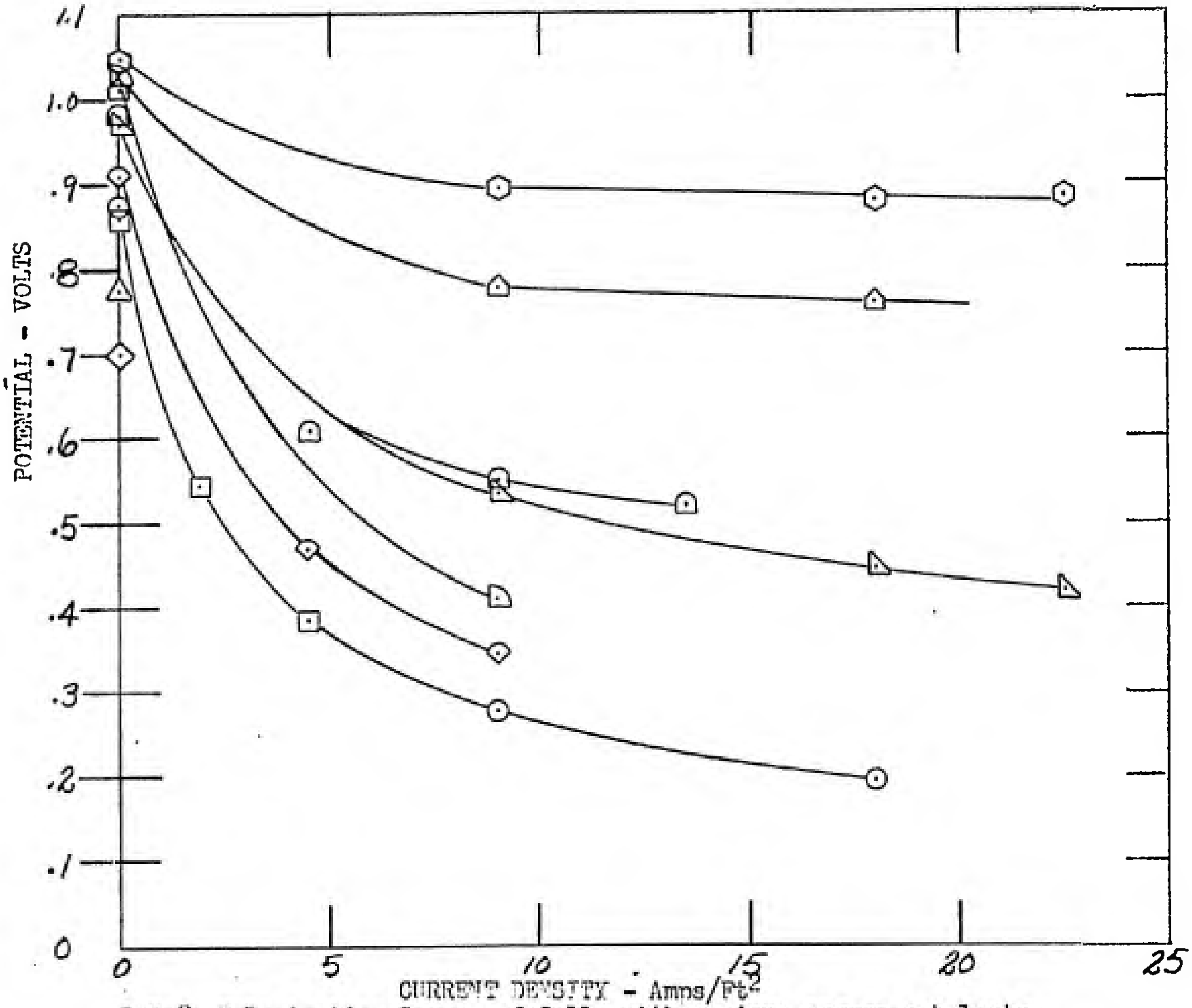


FIG:8 Polarization Curves of Cells with various oxygen catalysts.

Cells S-7, S-8, S-9, and S-10 utilized carbon materials obtained from Dr. Niedrach of the General Electric Research Laboratory. These materials, platinized by the Englehard Industries, gave close to the standard open circuit voltage whereas cells S-1, S-3, S-4, and S-5 resulted in lower open circuit voltages.

The data presented herein is quite preliminary and insufficient to draw any real conclusions other than to point out observations which were earlier stated in a previous section of this report. The largest obstacle to cost reduction in the catalytic electrode seems to be that of obtaining low electron-resistances, both in the catalytic electrode itself and in the electrode-current-collector contact-area, which are equivalent to those obtained with pure platinum and/or palladium metallic blacks.

4.0 TASK II Internal Generation and Storage of Hydrogen Fuel

4.1 TASK IIA Palladium and Other Absorbents for Hydrogen

This work will be accomplished by the General Electric Heavy Military Electronics Department at Syracuse, New York and will be reported under separate cover by the above department.

4.2 Electrolyses by Ion Membrane Fuel Cells

Work to be initiated at a later date.

5.0 TASK III External Generation and Storage of Hydrogen and Oxygen

5.1 Electrolytic Methods

The literature study which was undertaken is essentially complete. Electrolytic generation of hydrogen has been developed in Germany to the extent that commercial units with a dry hydrogen capacity of 580 ft^3 /hr. (S.T.P.) are in operation. These units operate at a pressure of 450 psi. Recently, in this country, the M.G. Treadwell Company has developed for the U. S. Navy a method of producing hydrogen and oxygen at pressures up to 3000 psi in an electrolytic apparatus.

The separating membrane, which is perhaps the most vulnerable portion of the electrolyzer, is normally made from asbestos cloth. This cloth is being used in the 450 psi units. The method of separation in the treadwell electrolyzer has not as yet been determined. However, information is being sought about this problem and when obtained will be reported on at a later date. Since the use of asbestos cloth as a membrane material requires that the pressure differential between the gases be nil, a suggestion has been made that perhaps a "thick porous plug" would better serve as a separator. However, it is believed that obtaining a suitable membrane or separator will require a much more thorough investigation.

The preliminary materials selection for the electrolyzer is as follows:

Vessel -	- Nickel or Monel metal
Electrodes	- Nickel or Monel metal.
Electrolyte	- 25 to 30% aqueous solution of potassium hydroxide.

It is expected that sizing of an electrolyzer and preliminary sketching of its configuration will be accomplished during the next work period.

5.2 Chemical Methods of Generating Hydrogen

Preliminary sizing and cost estimates are based on a 12 watt-hr. duty-cycle which will require 0.003 lbs.*, or 0.54 cubic feet* (S.T.P.) of hydrogen. No attempt has been made to describe the weight, cost, and details of the complete generator design as a complete system. Final comparisons will depend upon the experimental results which will be obtained during subsequent reporting periods.

TABLE X contains the preliminary estimates of reactant weights and costs. This information is based on using 35 wt.% H_2SO_4 as the liquid reactant. The values are probably slightly conservative as the 35% H_2SO_4 is only necessary where minus 65° F. freezing points are required. Using more dilute non-volatile acids or pure water, will slightly reduce the weights and volumes of the reactant systems. In some cases the lower level of acid concentration may be set by reactivity requirements unless catalysts are included. The equations for the reactions given in TABLE X are also based on 35 wt.% H_2SO_4 except in the case of lithium hydride and calcium hydride which do not require acid for their reactions to occur. In these instances, equations are given for both 35% acid and pure water. The actual acid concentration will not be known until experimental data is available.

Since the weights and costs of the chemical-reactants are small, the weight and cost of the total generator system will be the determining factor in selecting the optimum system based on cost. Figure 9 shows the relative volumes of chemical reactants required to complete the 12 watt-hour duty-cycle. The actual system-volume for the chemical storage and reaction will be somewhat larger as some added volume is required for solid-chemical expansion and gas-liquid foaming which occur during reaction. The final hydrogen-source selection will be based on ease of handling, reliability, adiabatic-reaction temperature and logistics, as well as the cost, weight and volume of the total system.

Initial experimental data will be obtained in laboratory glassware and emphasis will be placed on determining the following:

* These values include a safety factor of approximately 100% as exact cell efficiencies, fuel utilization factors etc. will not be known until further work has been accomplished.

1. Reaction temperature in a given reactor
2. Gas temperature leaving a given reactor
3. Minimum acid concentration for reactivity, etc.
4. Purity of gas produced
5. Percent of reaction water carried out with gas
6. Actual hydrogen delivered versus theoretical hydrogen possible
7. Optimum method of mixing reactants; excess of any chemical needed

The above experimental program will be started in February and data will be presented in Progress Report No. 4.

TABLE X
COMPARISON OF POSSIBLE HYDROGEN GENERATION SYSTEMS FOR 12 WATT HOURS OPERATION

Hydrogen Source	Total lbs. of reactant for 12 watt hours operation*	Cubic Inches of total reactants for 12 watt hrs. operation*	Expected cost of reactants for 12 watt hrs. operation	BTU/12 watt hrs. evolved
$NaBH_4$	.04	0.77	$0.25	-49
Al	0.10-0.17	1.9-3.4	neg.	-187
CaH2	.07	1.5	$0.10	-70
LiH	.08-0.13	2.1-3.5	$0.10	-72

* These values include stoichiometric acid or water needed according to equations given.

EQUATIONS USED

$4NaB_4 + 1H_2SO_4 + 10H_2O \rightarrow Na_2\ SO_4 + Na_2\ B_4O_7 + 16H_2 + 3H_2O$ (35% acid)*

$12\ Al + 3H_2SO_4 + 30H_2O \rightarrow Al_2\ (SO_4)\ 3 + 10\ Al\ (OH)_3 + 18H_2$ (35% acid)*

$5\ CaH_2 + H_2SO_4 + 10H_2O \rightarrow CaSO_4\ 2H_2O + 4Ca\ (OH)_2$ (35% acid)*
or
$CaH_2 + 2H_2O \rightarrow Ca\ (OH)_2 + 2H_2$ (0% acid)

$12LIH + H_2SO_4 + 10H_2O \rightarrow LI_2SO_4 + 10LOH + 12H_2$ (35% acid)*
or
$LIH + H_2O \rightarrow LIOH + H_2$ (0% acid)

Systems are shown approximately to scale (Height of all cylinders is 2.0 inches.)

Inner cylinders show design volumes. Outer cylinders show volumes for 50% excess reactants.

Systems are designed to deliver .003 lb. or .54 Ft^3 of H_2 gas.

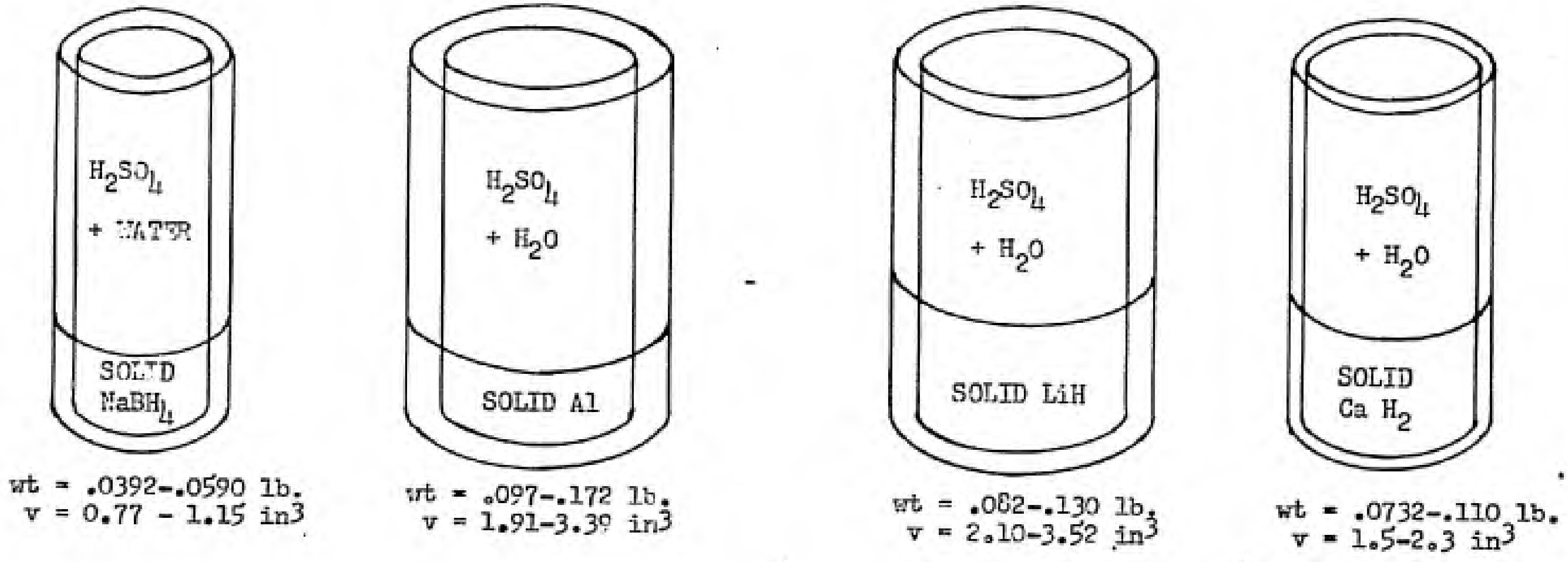


FIG:9 Relative Sizes of Chemical Systems for Generating Hydrogen

Appendix A

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