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NSAR 60-56

Third Quarterly Progress Report
January 1 to March 31, 1960

OR
Contract DA-36-039-80-78955
Task No. 3-99-09-401
to

U.S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

Report No. 3

STUDY OF ENERGY CONVERSION DEVICES

R.E. Shearer
T.A. Ciavariello
S.J. Veccharella

29 April 1960

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MSA Research Corporation

Subsidiary of Mine Safety Appliances Company

Callery, Pennsylvania

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STUDY OF ENERGY CONVERSION DEVICES

R.E. Shearer
T.A. Ciarlariello
S.J. Veccharella

The purpose of this contract is to develop a cyclic or
continuous thermally regenerative galvanic cell.

29 April 1960

MSAR Job No. XA-720203

Approved by:


J.W. Mausteller

MSA Research Corporation
Callery, Pennsylvania

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I PURPOSE

It is the purpose of the research and development work under this contract to develop a practical electrochemical device which converts thermal energy into electrical energy by means of electrochemical formation of suitable compounds followed by their thermal decomposition and recombination on a cyclic and continuous basis. Special consideration is to be given to the ionic hydrides.

Feasibility is to be judged on ability to give a power output of at least 10 watts per pound, to have a current density of at least 100 A/sq ft at an operating voltage above 0.3V per single cell.

II ABSTRACT

Studies on hydrogen electrode materials for ionic hydride cells showed that double porosity micrometallic materials gave improved current densities over thicker single porosity materials and that while platinum showed beneficial catalytic activity, it failed mechanically both in pure form and as an electroplate on micrometallic nickel. Analysis of pressure drop measurements showed that less than 1% of the pores permitted gas to pass into the molten salt and indicated the desirability of a much more uniform pore size to improve current density.

Measurements of solubility of lithium hydride in fused salt solvent and of decomposition pressures of hydride solutions were made and showed promise for attainability of reasonable hydrogen pressures at practical decomposition temperatures with even low recirculation rates. Hydride content of a melt of LiCl, NaCl, CsCl and RbCl in approximate eutectic proportions saturated with LiH at 315-320°C was found to be 0.8%. Decomposition pressure of a 4.2 wt % solution of LiH in the eutectic of LiF and LiCl was found to be 605 mm at 1065°C and that of a 0.35% solution was about 145 mm at 1100°C.

Measurements of hydride cell resistance values were made with use of a second gas electrode as a reference electrode. These data, together with analysis of pressure relationship in the system and operational data on an earlier model, formed the basis of a new system design.

III CONFERENCES

On January 25, 1960, a conference was held at MSA Research Corp. in Callery, Pennsylvania, to review the program under the contract, to discuss the Second Progress Report, and to plan the program for the future. It was agreed that the emphasis would be shifted from basic work to design and operation of closed-cycles systems by the end of February. In attendance were Dr. Herbert Hunger, U.S. Army Signal Research and Development Laboratories and from MSA Research Corp. Messrs. C.B. Jackson, J.W. Mausteller, R.E. Shearer and R.C. Werner.

On March 3, 1960, a conference was held at Wright Air Development Division, Dayton, Ohio so that Signal Corps and Air Force representatives could compare programs of MSA Research and Thompson-Ramo-Wooldridge on regenerative fuel cell work to be sure that there was no duplication of effort. In attendance were: from WADD - Captain E.F. Redden, Messrs. J. Cooper, R. Cooper and R.H. Retz; for Signal Corps - Messrs. H. Hunger, D. Linden, and J. Murphy and for MSA Research Corp. - Messrs. T. Ciarlariello, C.B. Jackson, J.W. Mausteller and R.E. Shearer.

IV FACTUAL DATA

Cell with Reference Electrode of Double Porosity Material

A cell was assembled with a sodium electrode and two gas electrodes in the eutectic of lithium chloride-lithium fluoride. One gas electrode was of 0.062 in. thick double porosity nickel with 5 and 15 micron pores and with an area of 0.55 sq in., the other of 0.125 in. thick single porosity nickel (65 micron pores) with an area of 0.25 sq in. The sodium electrode area was 0.99 sq in. Cell temperature was held at 540°C. A peak emf of 0.62V was observed. After the emf had fallen to 0.40V, current was drawn for 1-1/2 hr from the larger gas electrode under a potential of 0.30V. Results are as follows:

time (min)	0	10	65	70	90
current (amp)	0.52	0.50	0.50	0.48	0.48

After this loading, open circuit potential had fallen to 0.38V. The polarization voltage or the decrease in voltage from open-circuit potential between the sodium electrode and each of the gas electrodes was now measured with current drawn from the double porosity electrode.

current (amp)	0.31	.50
ΔV (double porosity)	.05	.095
ΔV (single porosity)	.01	.03

With an open circuit voltage of 0.32V, the load was placed on the single porosity electrode with the following results:

current (amp)	0.50	0.68
ΔV (single porosity)	0.22	0.28
ΔV (double porosity)	0.03	0.05

The above data show that there is a significant voltage drop other than at the gas electrode and that the drop across the electrolyte and at the metal electrode must be taken into consideration in cell design.

Additional data were also taken to evaluate the effect upon current density by use of double porosity material. With approximately equal open circuit voltages in each of the gas electrode circuits, current was drawn from the two electrodes with the results shown in Table 1.

Table 1 - Current Obtained Using Double and Single Porosity Material

<u>Load Voltage</u>	<u>Current Density (A/sq ft)</u>	
	<u>Double Porosity</u>	<u>Single Porosity</u>
0.30	39	16
0.22	114	96

These data show a significant advantage for the thinner double porosity material. Channelling of gas is reduced with this material, making effective area a larger percentage of actual area. Furthermore, plugging of the electrode was not experienced with double porosity material in contrast with the considerable plugging obtained with single porosity material of even larger pore size.

Pressure Drop in Micrometallic Elements

The pressure drop resulting from the flow of hydrogen gas and argon gas through a micrometallic filter into molten salt was measured. The micrometallic filter consisted of a 1/8 in. thick, 3/4 in. diameter, Grade D nickel micrometallic immersed 1-3/16 in. into a LiCl-KCl eutectic melt at 380°C. The pressure difference across the micrometallic filter was measured with a mercury manometer, and the hydrogen flow was measured by a low flow rate rotameter. Figs 1 and 2 shows the pressure drop results graphically.

The pressure drop can be considered to be the sum of three pressure drops. One pressure drop consists of the hydrostatic head exerted by 1-3/16 in. of molten salt. The second pressure drop consists of the pressure required to overcome the molten salt-solid nickel surface tension. The third pressure drop is the pressure drop of the hydrogen flowing through the micrometallic filter element.

The hydrostatic head of 1-3/16 in. of molten salt is small. This pressure drop is about 4.65 mm of mercury and is small compared to the pressure drops measured in Figs 1 and 2. The pressure drop due to surface tension is quite important. This pressure arises because the salt tends to wet the nickel and fill the pores of the micrometallic filter. In order for hydrogen to flow through the filter pores, the gas must displace liquid from the pores. The

pressure required to do this will depend on the pore diameter and the hydrogen/molten salt/nickel interfacial tensions. Figs 1 and 2 show that at zero gas flow rate with the electrode immersed in 1-3/16 in. into the melt, a pressure of 46.5 mm Hg was required for argon to displace the salt and 31.5 mm Hg was required for the hydrogen to displace the molten salt. Subtracting 4.65 mm for the hydrostatic head of the molten salt then gives 41.9 ~~psi~~ for the argon pressure and 26.8 mm for the hydrogen pressure.

The pressure drop due to gas flowing through the micrometallic filter can be found by measuring the slope of the lines given in Figs 1 and 2. Since even at current densities of 450 amperes/sq ft, the gas flow rate is small, this pressure drop is small. The argon pressure drop is 0.58 psi/cu ft/min and the hydrogen pressure drop is 0.31 psi/cu ft/min across a plate with an area of 1 sq ft.

These figures can be compared with the expected pressure drops of 7.1×10^{-4} psi/cu ft/min for hydrogen and 1.98×10^{-3} psi/cu ft/min for argon¹. The difference between the observed and the expected pressure drops is due to the effects of surface tension. Since higher pressure is required to displace the salt from the smaller pores, at low pressure differences the small pores will be sealed off with liquid and only the largest pores will be open. Comparison of the observed and expected pressure drops yields the percent of the flow area which is available. It can be seen that only 0.228% of the flow area is open for hydrogen and 0.342% for argon flow.

Use of a micrometallic plate with a constant pore size would be highly advantageous. This would give an increased current density and a reduction in the pressure drop. Since the pressure drop is quite small, this reduction would not be important. However, the increased current density would be a very significant advantage. The plate with a uniform pore size would have a significant increase in bubble sites - each pore would be releasing hydrogen bubbles. The increased number of bubbles would then give an increased effective surface area and thereby give an increased current.

Figs 1 and 2 show some scatter at the low gas flow rates. This scatter can be attributed to a partially plugged micrometallic filter element. It takes a much higher pressure to eject molten salt from a pore after the salt has penetrated into the pore.

¹Micro Metallic Corporation PSS Release No. 212.

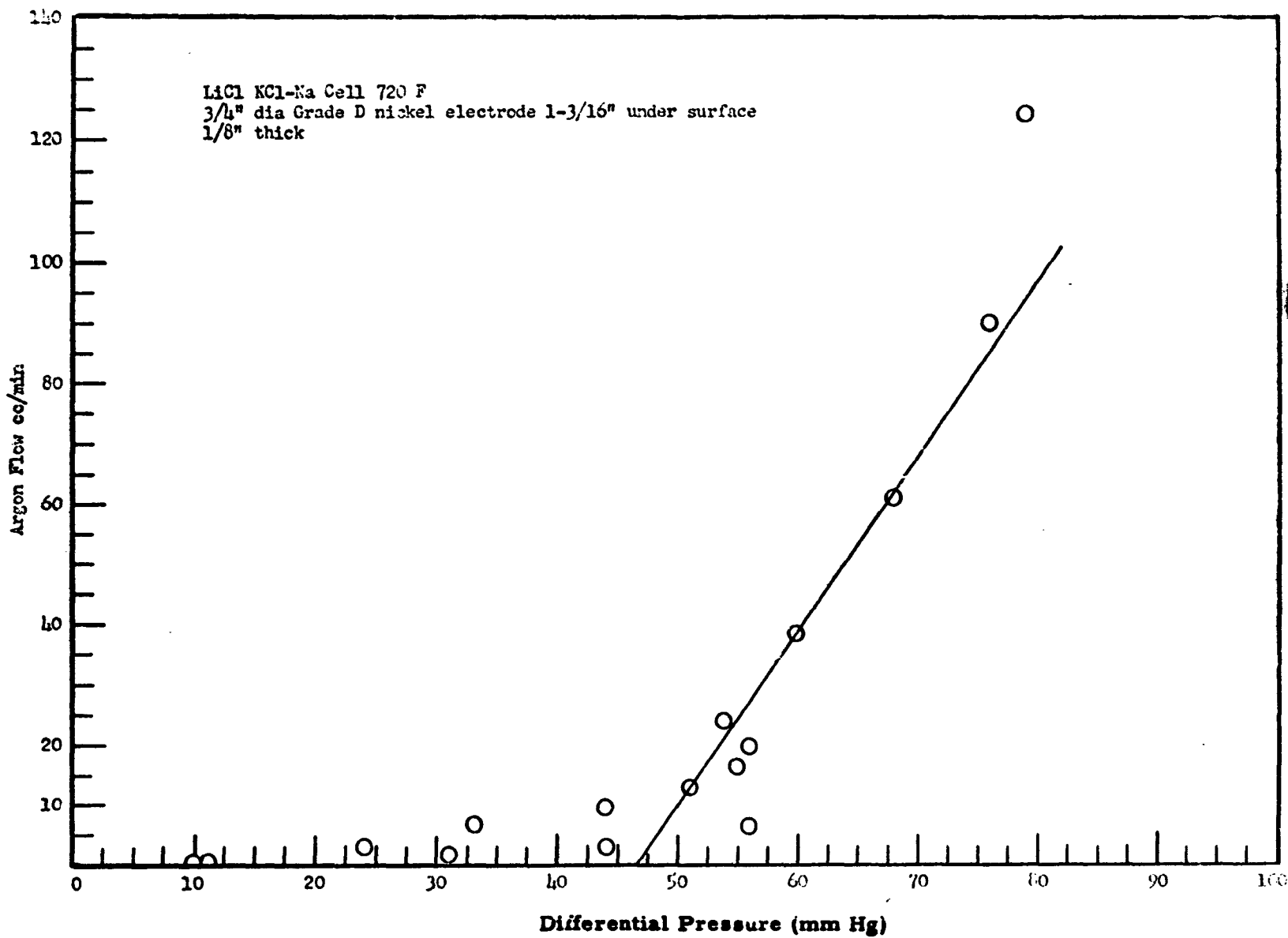


Fig 1 - Differential Pressure Across Micrometallic Vs Argon Flow

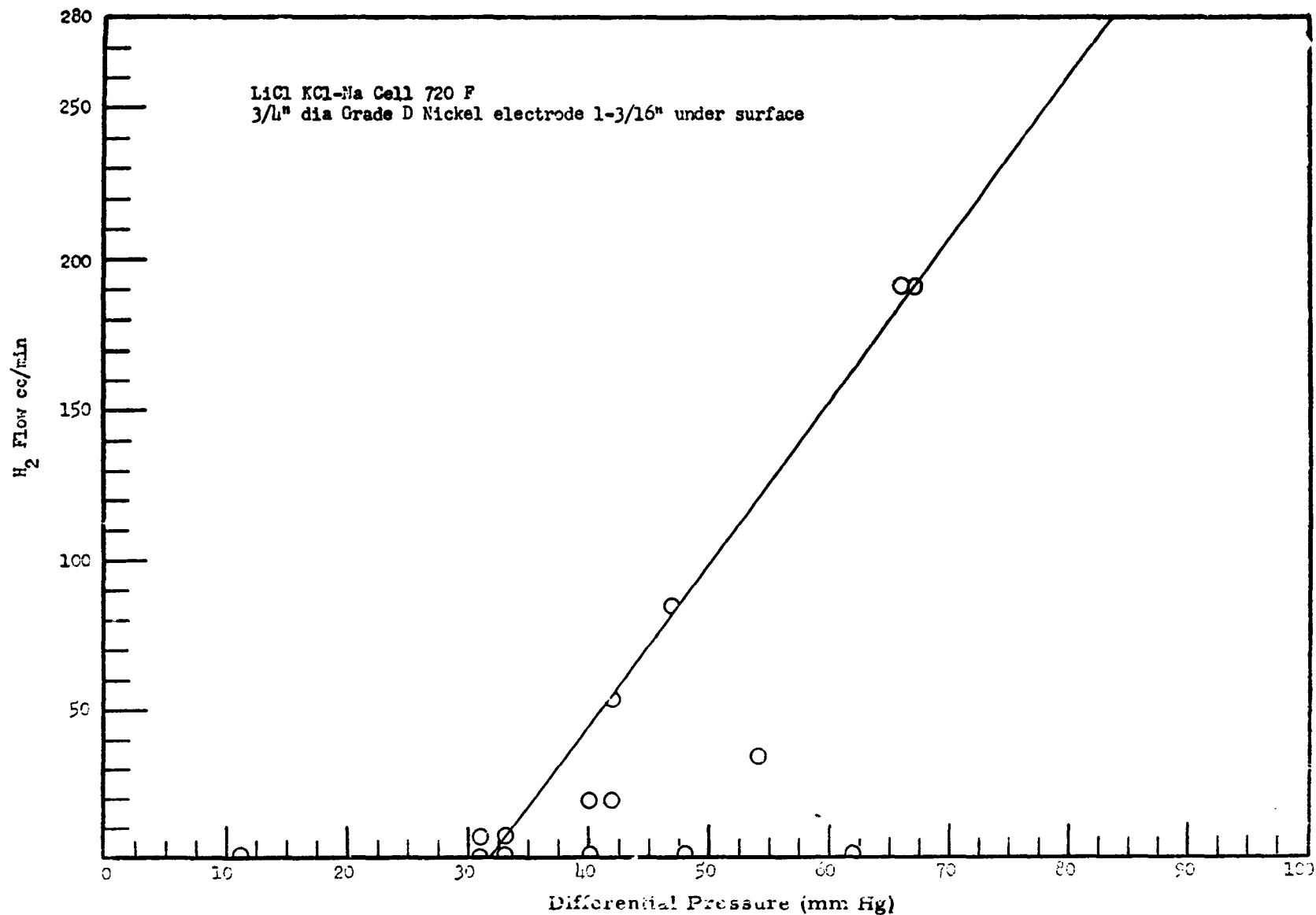


Fig 2 - Differential Pressure Across Micrometallic Vs Hydrogen Flow

Design of New Closed Cycle System

A new closed cycle system has been designed based on an analysis of pressure drops through the system and on results of work with earlier designs.

The new system shown in Fig 3 is similar to the previous system but contains the following differences:

1. The regenerator is lowered to provide sufficient hydrostatic head to overcome the effects of surface tension on the hydrogen electrode.
2. A barrier is provided between the hydrogen and metal electrodes to prevent hydrogen from bubbling through the electrode and impinging on the metal electrode.
3. The metal electrode is insulated from the cell wall. As before, the hydride is removed from the cell in solution form and carried to the regenerator. The liquid metal leaving the regenerator then floats upward to rejoin an insulated pool of liquid metal.

Calculations were made on pressure drops in a system delivering 2 amperes and consuming 32 cc/min of hydrogen.* About 0.6 psi is required to overcome surface tension, 0.1 psi to overcome pressure drop in the micrometallic filter and 0.2 psi to overcome the hydrostatic head of immersion of the electrode in the molten salt. The total pressure difference required is then 0.9 psi. This difference can be provided by lowering the regenerator about 6 in. This design will operate with a 6 in. differential in liquid level between the cell and the regenerator. There is provided sufficient flexibility to operate with any difference between 0 and 12 in. that might be required and to incorporate pumps for either gas or liquid phases if desired.

Use of Platinum in Gas Electrodes

Because of low current densities obtained in a number of cells with lower-melting solvents, the need for catalysts became apparent. Platinum is an excellent catalyst for industrial hydrogenation, but in hydrogen at high temperature it can disintegrate. Manufacturers' representatives have asserted that this difficulty could be avoided by cooling in an inert atmosphere after use at elevated temperatures. Consequently, a platinum electrode was handled in such a way, but no data were obtained because the electrode disintegrated in short order.

* @ 800°C

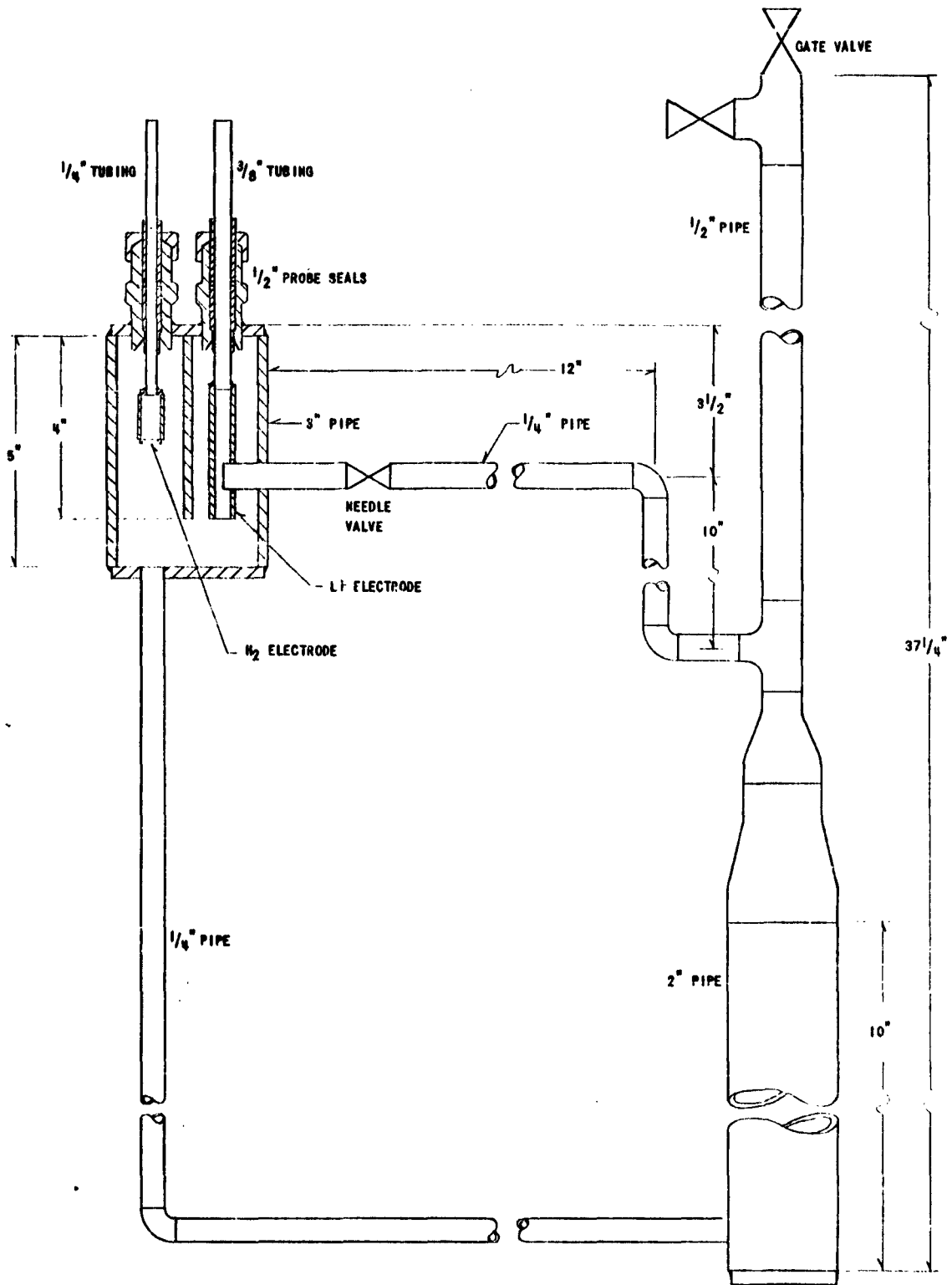


Fig 3 - Regenerative Fuel Cell

In the hope that a micrometallic nickel base would offer a good support for electroplated platinum two such bases were plated in a 'Platinex III' plating solution in accord with directions of the manufacturer, Sel-Rex Corporation.

One plated electrode was used in a cell with a sodium anode and a LiF-LiCl solvent. An equilibrium current density of 330 A/sq ft was obtained from this cell at a potential of 0.17V compared with 67 and 123 A/sq ft in previous work with stainless and nickel electrodes respectively. Steady-state current density at 0.30V was 208 A/sq ft. Upon cooling the cell and subsequent inspection of the electrode, it was found that the plated micrometallic element had disintegrated, and it is not known just how much of the surface had disintegrated while current measurements were being made.

The second platinum-plated micrometallic electrode was used in a cell with a lithium anode and a solvent composed of a mixture of the chlorides of rubidium, cesium, sodium and lithium. Open-circuit voltage was only 0.32V and apparent current density only 9.0 A/sq ft at 0.13V. Again upon inspection of the electrode, it was found to have partially disintegrated so that it is not known how much platinum, if any, was on the electrode during current measurements.

While there is some indication of beneficial effect upon current density of a platinum catalyst, its mechanical strength under operating conditions is unsatisfactory. Since palladium is a catalytic material comparable to platinum and since a palladium-silver alloy is reported² to have good mechanical strength in high temperature hydrogen, an electrode of this material will be used in further work. Because of the high rate of diffusion of hydrogen through films of this alloy and because of possibilities in zero-gravity applications, the alloy will be used in the film form.

Dissociation Pressure of Lithium Hydride in Fused Salts

In order to determine the hydrogen pressures likely to be developed in the regenerator of a closed cycle system, a bomb was made of 3 in. Type 304 stainless steel pipe with wall thickness of 0.22 in. It was fitted with a mercury manometer and was heated in a Kanthal furnace controlled with a General Electric Company millivoltmeter-type temperature controller. Temperatures were measured with a chromel-alumel thermocouple in a thermowell immersed in the melt. The bomb was charged with lithium chloride and lithium fluoride in eutectic proportions (80 mole % of the former) as described below, then with various amounts of lithium hydride, pressures determined at various temperatures.

² Hunter, James B., U.S. Patent 2,773,561, 'Silver-Palladium Film for Separation and Purification of Hydrogen', December 11, 1956.

After introduction of the fluoride and chloride salts, they were vacuum dried overnight at 200°C and a pressure of 1 mm of mercury, then just below the melting point until no more moisture was collected in a trap in the exit line. The salt was then melted under vacuo, then heated to 815°C with pumping overnight. After cooling, a quantity of Class V lithium hydride furnished by Lithium Corporation of America was introduced into the bottom of the bomb. The charge was melted under a cover of hydrogen above atmosphere pressure and then hydrogen was bubbled through the melt to insure mixing. This apparently gave rise to dissolving of hydrogen in the melt; for an apparent decomposition pressure of 50 mm was measured at 540°C, compared with a pressure of less than 1 mm for pure hydride at this temperature. The system was then pumped off at 540°C until the hydrogen pressure held at 1 to 2 mm. There had been indications of the possibility of diffusion losses of hydrogen through the stainless steel^{3,4}. Reference 1 gives the following values for diffusion of hydrogen under a pressure of 760 mm through .020 in. thick Type 304 stainless steel at various temperatures.

temperature (°C)	400	500	600	700	800	900
cc (STP)/cm ² /hr/mm	0.0047	0.019	0.066	0.19	0.44	0.76

Reference 2 gives the rate at 970.9°K through 0.01 in. thick Type 347 stainless steel for various pressures of hydrogen as follows:

pressure (cm)	1	4	9	16	25	36
cc (STP)/cm ² /hr/mm	.011	.03	.049	.068	.088	.16

In the case in one run on the 4.2% LiH solution after 5 cycles of heating evacuating and cooling, pressure at 1065°C fell from 625 mm to 584 mm in 44 min. To minimize these effects of pressure drop with time, readings were taken as soon as apparent equilibrium had set in, generally in 5 to 10 min after reaching a given temperature. Good reproducibility of results were obtained both upon varying temperature upward or downward and upon successive runs. Fig 4 shows results of two successive runs together with a curve showing the average of the two runs corrected for vapor pressure of the fused salt solvent. The correction factor was determined as the sum of the products of vapor pressure of each component⁵ by its mole fraction. Corrected values for this solution as well as for the 4.2 wt % solution correspond with products of mole fraction and decomposition pressure of pure hydride up to 850°C⁶. After the second run was made, a sample of the solution was analyzed and was found to contain 0.35% LiH by weight.

³Flint, P.S., 'The Diffusion of Hydrogen through Materials of Construction' KAPL-659, December 14, 1951.

⁴Randall, D. and Salmon, O.N., 'Diffusion Studies of Type 347 Stainless Steel to Hydrogen and Tritium' KAPL-904, March 17, 1953.

⁵Smithells, C.J., Metals Reference Book, p 615, Vol. II Interscience Publishers, 1955.

⁶Hurd, D.T., Chemistry of the Hydrides, John Wiley and Sons, 1952.

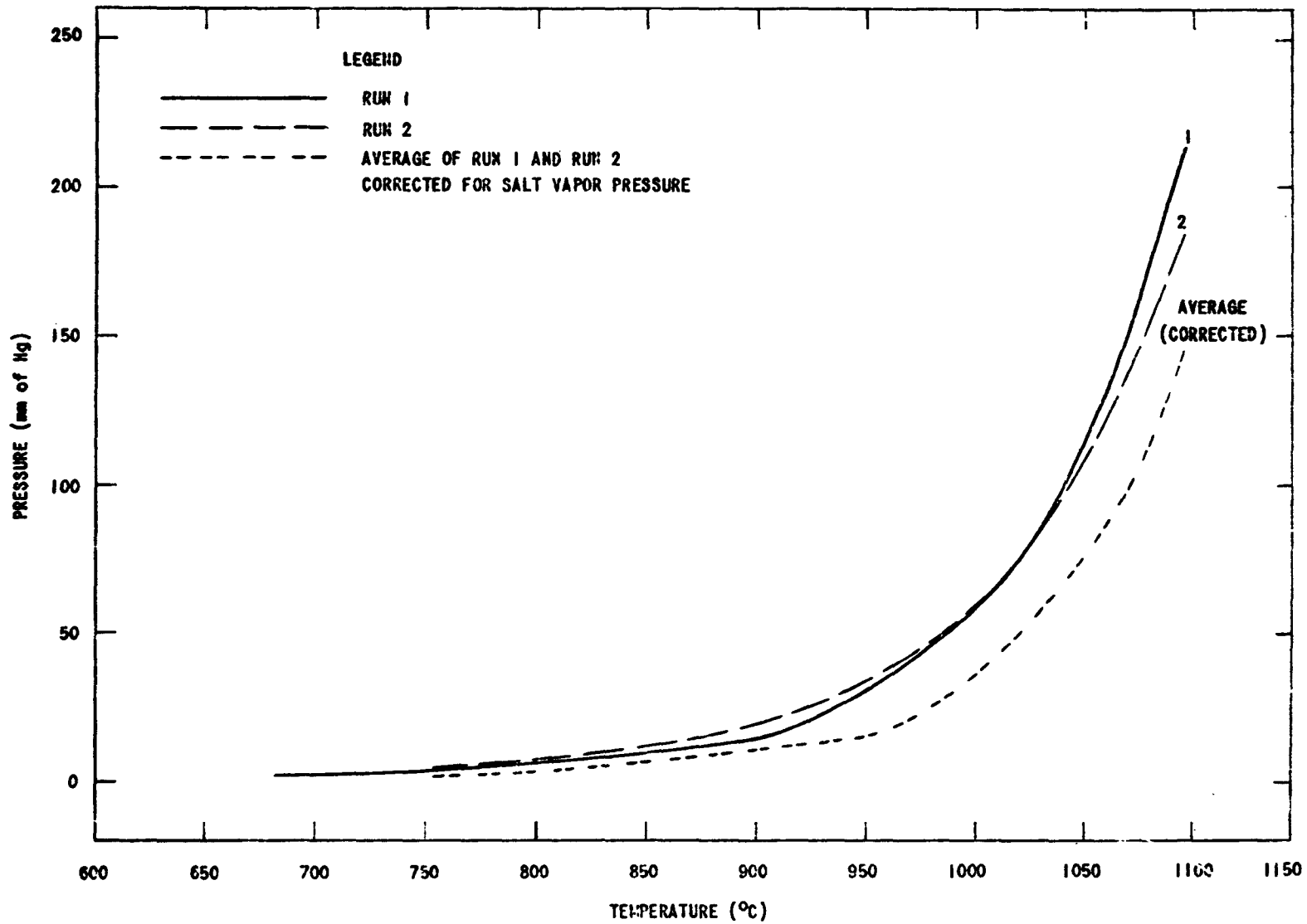


Fig 4 - Dissociation Pressures of 0.35 wt % LiH in LiCl-LiF Eutectic

A similar set of experiments was run on a solution containing 4.2 wt % LiH. Results are shown in Fig 5. In this case no hydrogen was introduced into the melt prior to or during mixing, which was done under argon. Mass spectrographic analysis of the gas in the decomposition vessel at room temperature at the end of the experiment revealed only a trace of argon and pure hydrogen as the only other gas.

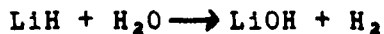
Calculations of effect upon emf of the hydride cell were made for hydrogen pressures developed at some attainable regeneration temperatures compared with a pressure of one atmosphere. They show that emf would be lowered by about 0.12 volt for pressure developed from the 0.35 wt % LiH solution at 1100°C and 0.07 V from the 4.2 wt % solution at 1020°C.

Solubility of LiH in Fused Salts

To determine the solubility of lithium hydride in the quaternary salt solvent, a mixture consisting of 28.5 wt % LiCl, 3.1% NaCl, 30.5% RbCl and 38.9% CsCl was melted down, mixed and cooled to room temperature. Total weight was 700 g. To this were added 70 g of LiH, and the mixture was heated to 680°C to melt the hydride and to permit it to dissolve. The solution was then cooled to cell operating temperature (316°C), allowing excess LiH to freeze out. A sample of the melt was taken from the bottom of the container.

The sampling of the molten salt was accomplished using a device consisting of a solid 3/16 in. stainless steel rod and a 1/4 in. tube of similar material. The tube was crimped shut at one end and a slot cut in the wall of the tube about 1/2 in. to 3/4 in. above the crimped end. The rod was inserted inside the tube and pushed down to the crimped end, thus covering the slot, and the tube with the rod inside was lowered into the salt to the desired sampling depth. The rod was raised in the tube to just above the slot to allow the liquid salt to flow inside, then lowered slightly again to cover the slot. The rod and tube were withdrawn from the melt and the end of tube containing the sample, after having been cleaned free of salt on the outside, was sawed off into a flask.

Analysis was made for hydride content by a gas evolution method based on the reaction:



Hydride content was found to be 0.8%. With this hydride content and an assumed 30% decomposition in the regenerator, a circulation rate of about 210 g of solution per minute would supply 100 amperes.

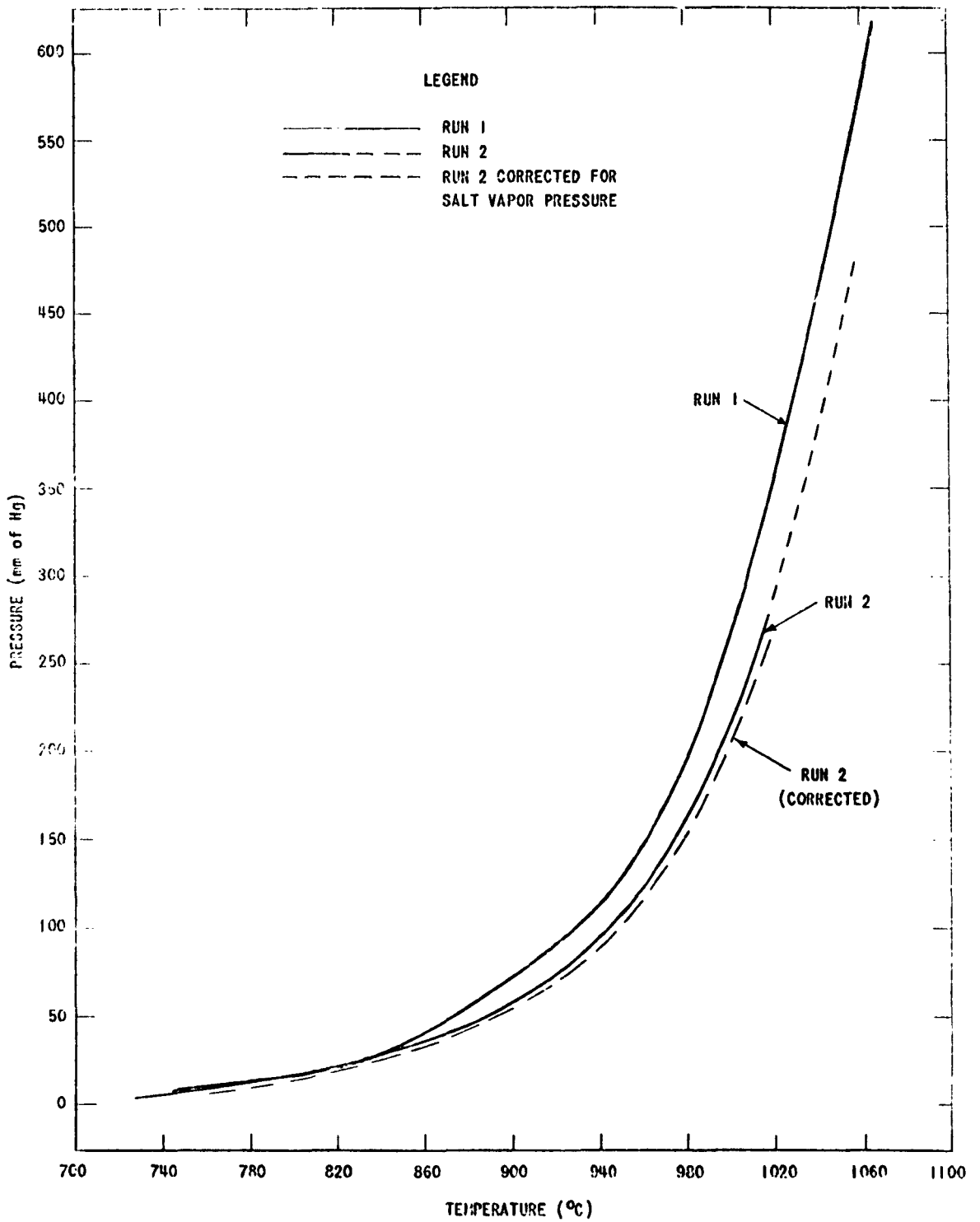


Fig 5 - Dissociation Pressure of 4.2 wt% LiH in LiCl-LiF Eutectic

V CONCLUSIONS

Gas electrodes of pure platinum and of platinum-plated micrometallic nickel exhibited poor mechanical strength under the conditions used in tests on the hydride cells although evidence of beneficial catalytic effect was obtained.

Solubility measurements of lithium hydride in the quaternary eutectic of the chlorides of lithium, sodium, rubidium and cesium show a hydride content of 0.8% at 316°C; and this should be adequate for maintaining reasonable current densities at the gas electrode with a low recirculation rate to the regenerator if adequate decomposition pressures and suitable activation are attained.

Decomposition pressure measurements of solutions of lithium hydride in the eutectic of the fluoride and the chloride of lithium show the ability to attain reasonable hydrogen pressures at temperatures in the range of 1000 to 1100°C.

Use of a gas electrode of double-porosity micrometallic nickel has given higher current densities than use of thicker material of single porosity, with values of 114 and 96 A/sq ft having been obtained under identical conditions.

Measurements of various segments of cell resistance show that the combination of IR drop across the electrolyte plus anode polarization contributes significantly to internal cell losses in addition to the contribution of the gas electrode.

Analysis of pressure drops across the gas electrode shows that the drop due to the hydrostatic head of molten salt is small compared with that due to surface tension, that with a single porosity micrometallic element only a small proportion of pores pass gas at the low flow rates used.

VII IDENTIFICATION OF PERSONNEL AND
DISTRIBUTION OF HOURS

1. T.A. Ciarlariello	89 hours
2. J.C. King	226
3. J.W. Mausteller	40
4. J.B. McDonough	12
5. R.E. Shearer	166
6. S.J. Veccharella	506
7. R.C. Werner	24
8. Hourly	252
9. Misc. salaried	<u>83</u>
	1,398 Total

John B. McDonough

Mr. McDonough received his B.S. degree in Science from Pennsylvania State University in 1954. He received a B.S. in Chemical Engineering from the same university in 1955. At the present time he is attending Carnegie Institute of Technology doing graduate study in Chemical Engineering under a MSA scholarship. He was employed by Standard Oil of Ind. from 1955-1956. He was employed by the Allegheny County Sanitary Authority for a period during 1956 and then in November, 1956, as a test engineer by MSA Research Corporation.

VI PROGRAM FOR NEXT INTERVAL

The newly-designed closed-cycle system will be completed and put into operation. Operational data will be taken; and if satisfactory performance is obtained, long-term operation will be initiated. Open circuit voltages, current densities on various loads, hydride contents of solvent at various stages and effect of regenerator temperature will be determined.

Additional designs will be made as dictated by performance data on operational systems; and operation of systems based on these additional designs will be initiated as time permits.

Supporting effort of a more basic nature will be maintained as needed. In particular, study of the catalytic and mechanical properties of palladium-silver alloy as gas electrode material will be made. Also decomposition pressure measurements at various temperatures will be made on the solution of the eutectic of the chlorides of lithium, sodium, rubidium and cesium saturated at cell temperature (315-320°C) with lithium hydride.

A cell with the formulation $H_2(T_1)/LiH-LiCl-LiF/H_2(T_2)$ will be built and operational data taken. In this cell, the two hydrogen electrodes will be at different temperatures, with high temperature electrode giving rise to decomposition and the low temperature electrode to formation of lithium hydride. This is the lithium hydride version of the molten salt thermocell⁷; and the experiment will establish whether the high temperature electrode will in fact operate as a hydride decomposition electrode.

⁷ Sundheim, B.R. and Rosenstreich, J., 'Molten Salt Thermocell', J. Phys. Chem. **63**, p 419-422 (1959).