

UNCLASSIFIED

AD

2	3	4		4	8	2
---	---	---	--	---	---	---

Reproduced

Armed Services Technical Information Agency

ARLINGTON HALL STATION; ARLINGTON 12 VIRGINIA

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

UNCLASSIFIED

MSAR 60-12

8 days

Second Quarterly Progress Report
October 1, 1959 to December 31, 1959

on
Contract DA-36-039-SC-78955
Task No. 3-99-09-401

to
U.S. Army Signal Research and Development Laboratory

AD No. 237 482
ASTIA FILE COPY

STUDY OF ENERGY CONVERSION DEVICES
Report No. 2

31 January 1960

MSA Research Corporation

Subsidiary of Mine Safety Appliances Company

Callery, Pennsylvania

ASTIA
RECEIVED
APR 6 1960
RECEIVED
TIPDR
C

FILE COPY
Return to
ASTIA
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA
XEROX
A-60-2-5

**BEST
AVAILABLE COPY**

MSAR-60-12

Second Quarterly Progress Report
October 1, 1959 to December 31, 1959
on
Contract DA-36-039-SC-78955
Task No. 3-99-09-401
to

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

STUDY OF ENERGY CONVERSION DEVICES
Report No. 2

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

31 January 1960

This report prepared by: R. E. Shearer
R. E. Shearer

Approved by: J. W. Mausteller
J. W. Mausteller

MSA Research Corporation
Callery, Pennsylvania

TABLE OF CONTENTS

	Page No.
I PURPOSE	1
II ABSTRACT	2
III CONFERENCE	3
IV FACTUAL DATA	4
Reference Electrodes	6
Calculations of Theoretical EMF	6
Screening Studies on Various Batch-Type Cells	8
Operation of Li-LiF-LiCl/H ₂ Regenerative Cell	14
V CONCLUSIONS	19
VI PROGRAM FOR NEXT INTERVAL	20
VII IDENTIFICATION OF PERSONNEL AND DISTRIBUTION OF HOURS	21
VIII APPENDIX I	22
Determination of Alkali Metals in the Chloride Eutectic	22
APPENDIX II	25
Sampling Techniques in Liquid Metal Systems	25

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 formation of suitable compounds followed by the electrochemical recombination of the decomposition products 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 lb, to have a current density of at least 100 A/sq ft at an operating voltage above 0.3V per single cell.

II ABSTRACT

Thermal differential analysis was made of several alkali halide systems in search of low-melting solvents for the ionic hydride cell. As a result of this work, a mixture was found which melted in the range between 284°C and 288°C and which had the composition 28.5% LiCl, 3.1% NaCl, 30.5% RbCl and 38.9% CsCl. This was used as a solvent in screening studies for a thermally regenerative cell.

A cell has been designed and built incorporating a second hydrogen electrode for use as a reference for comparison with other electrodes.

Calculations of theoretical emf's of the lithium hydride cell have been made for several operating temperatures and revealed a degree of irreversibility in operation of the closed cycle lithium hydride cell.

Screening studies were made to find promising low-melting solvents including one of borohydrides of alkali metals, one including iodides and one of quaternary chloride system above. The quaternary chloride system shows promise for voltage with 0.55V having been obtained with a LiH cell but the systems including the borohydrides and the iodides did not under conditions of the experiment. At the slightly elevated temperatures of the borohydride cell, activation energy for the hydride ion appears too great for stainless steel and nickel as catalysts. Study of other catalysts is indicated. Alkali metal iodides seem to have been decomposed at cell temperature.

Exploratory work with alternate anode materials for the hydride cell and with alternate cathode gases showed promise for sodium as an anode and no promise for nitrogen as a cathode gas under conditions of the experiment, showing need for catalytic studies if the nitride cell is to be pursued.

Non-regenerative operation of a closed-cycle hydride system showed need for redesign of the cell to reduce irreversibility in the cell operation. Low cell voltages and low current density as compared with earlier batch-type cells were observed. Use of dual porosity gas electrode material is indicated as possible means of restoring current densities to earlier values and redesign will take this factor into consideration. Regenerative operation was undertaken both under an argon cover gas and under vacuo. Peak emf's of the order of only 5 to 10 mv were obtained; and rise and fall in emf were observed to follow freezing and melting of salt in pipes connecting regenerator and cell, giving rise to alternate formation and dissipation of a pressure head of hydrogen. This shows the need to analyze pressure relationships in the system; and redesign should include results of such analysis.

III CONFERENCE

On November 13, 1959, a conference was held at MSA Research in Callery, Pennsylvania, to discuss the First Quarterly Progress Report and the program proposed therein. In attendance were Dr. Herbert Hunger, U.S. Army Signal Research and Development Lab. and as representatives of MSA Research: Messrs. C.B. Jackson, J.W. Mausteller, R.E. Shearer and R.C. Werner.

Among the types of data suggested to be of interest in future work were:

1. Distribution coefficients of metal hydrides between the liquid metal and solvent phases.
2. Data obtained from use of a second or reference gas electrode.
3. Catalytic effect of nickel or platinum as gas electrode material.
4. Theoretical emf's as compared with actual.
5. V-A data at equilibrium conditions.
6. Regenerative data with the cell under vacuum rather than an inert atmosphere.

IV FACTUAL DATA

Differential Thermal Analysis¹ and Solvent Composition

As was mentioned in the First Quarterly Progress Report under this contract, the differential thermal analysis apparatus was modified by elimination of the sand reference material and by making direct contact between the reference thermocouple and the metal block in the reference material well. This resulted in sharp breaks in the thermal analysis curves as is shown in Fig 1, which shows the results of analysis of the system KBr-KF-KI. The salt mixture was made up by the addition of 5 wt % KI to the binary eutectic consisting of 40 mol % KF and 60 of KBr melting at 580°C. It is apparent from the thermal analysis curve that the ternary eutectic temperature is about 566°C or 14°C less than the binary eutectic temperature. This decline in solvent melting point was not considered to offer sufficient promise for this potassium salt system as a hydride cell solvent and further work was abandoned.

The First Quarterly Progress Report cited a reference to a quaternary eutectic of the chlorides of rubidium, cesium, potassium and lithium. A similar one with a melting point of 275°C has been reported with the potassium salt replaced with sodium chloride. The eutectic compositions were not reported; and since analytical procedures are less difficult in the absence of potassium and since there is only a 5°C difference in melting point, it was decided to determine the approximate composition of the eutectic of the chlorides of Rb, Cs, Na and Li as a prospective solvent in a hydride cell. This was done by melting a mixture of the chlorides in the following weight ratios: LiCl 58, NaCl 2, RbCl 20, CsCl 20. These were melted down, frozen, ground to a powder and remelted by slowly raising the temperature. The first liquid appearing was vacuum filtered off through an Ace Disc Filter of porosity A. The recrystallized material was analyzed by flame photometry as is discussed in APPENDIX I. The composition in weight percentages was found to be as follows: 28.5 LiCl, 3.1 NaCl, 30.5 RbCl and 38.9 CsCl. When a new mixture was made to duplicate this composition it was found to melt in the range of 284 to 288°C. This mixture was made with 'Trona' RbCl lot number 6728 assaying 97.38% RbCl and containing 1.82% KCl as a major impurity. The cesium chloride going into the mixture was Trona lot number 6799 assaying 95.95% CsCl and containing 1.67% RbCl as the major impurity.

¹ Stravrolakis, J.A., Encyclopedia of Chemical Technology, Vol. 13
pg 932-940, Kirk, R.E. and Othmer, D.F., editors.

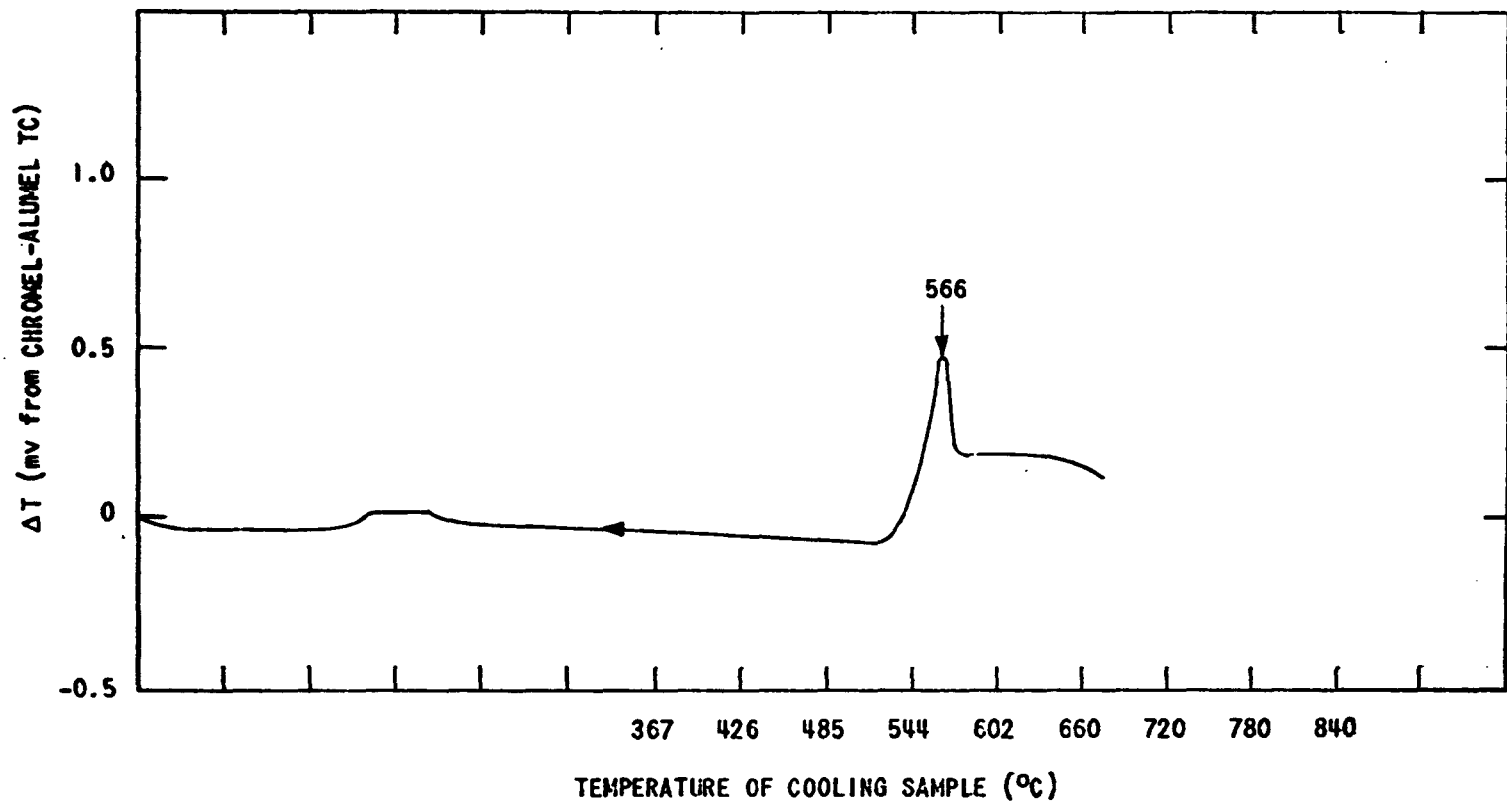


Fig 1 - Differential Thermal Analyses Curve for the System KI-KBr-KF

Reference Electrodes

For use as a tool in optimizing cell performance by study of individual electrode characteristics, a new cell has been designed incorporating a second gas electrode for use as a reference against which other electrodes could be compared. This is shown in Fig 2. Construction of this cell was in progress at the writing of this report and should be completed for use during the third quarterly report period.

Calculations of Theoretical EMF

Calculations of standard emf for the lithium hydride cell at various temperatures were made on the basis of thermodynamic data.

ΔF_T° was determined from the relationship:

$$\Delta F_T^\circ = \Delta H_T - T\Delta S_T^\circ$$

ΔH_T° was determined from the relationship:

$$\Delta H_T^\circ = \Delta H^\circ(298) + \int_{298}^T \Delta C_{pd} T - \Delta H'(Li)$$

where $\Delta H'(Li)$ is the heat of fusion of lithium which melts at 180°C. The value for $\int_{298}^T C_{pd} T$ is that of lithium hydride less half that

of hydrogen and less that of lithium. The value for that of lithium hydride was determined from the area under the curve of a plot of values obtained from AEC Report Number NYO-8022 entitled 'A Survey Report on Lithium Hydride: Supplement 1954-59' and written by Charles E. Messer and Thomas R.P. Gibb, Jr. These values are, in cal/mole-deg, 8.2 at 298°K, 11.2 at 500 and 13.5 at 800. The value ΔH° at 298°K, which is -21.61 kcal/mole, is that given by NBS Circular 500. Values for hydrogen and lithium were obtained from Thermodynamic Properties of the Elements by Stull and Sinke. These values for the function of lithium above its melting point include the value of the heat of fusion. Interpolations were made between nearest tabulated values in some cases.

ΔS_T° was obtained from the relationship:

$$\Delta S_T^\circ = \Delta S_{298}^\circ - \Delta S_m(Li) + \int_{298}^T \Delta C_p \ln T$$

These values were obtained from the area under the $\frac{C_p}{T}$ vs T curve for LiH, from Circular 500 values of S_{298}° for ΔS_{298}° , from Stull and Sinke for entropy changes of Li and H₂.

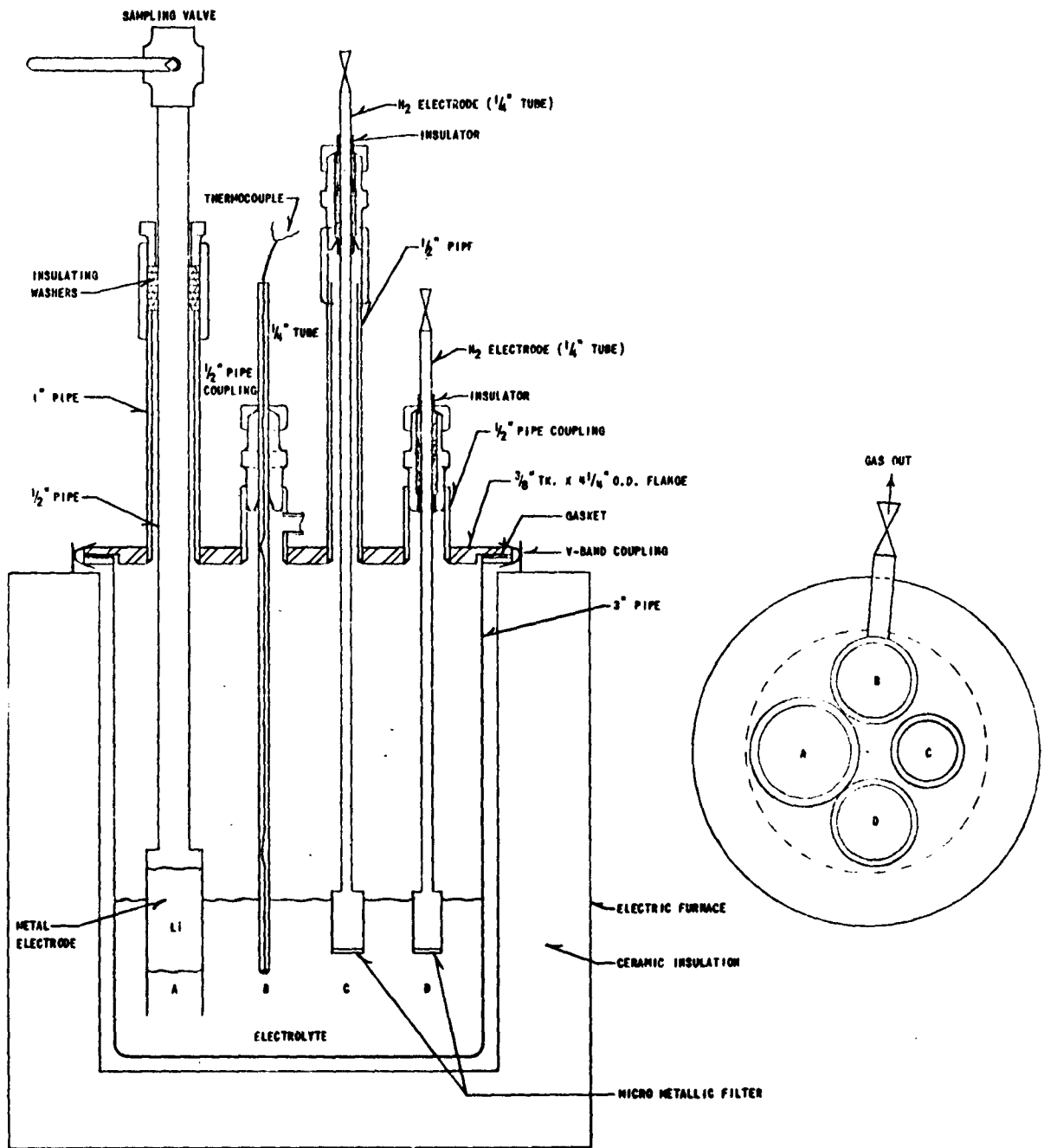


Fig 2 - Hydride Cell With Reference Electrode

In calculating actual emf's activity coefficients were assumed to be one in the absence of any reliable data. This may be the source of considerable error since some dimerization of certain molten salts² as well as covalency especially of LiF^{3,4} has been reported. Standard states of LiH and Li were assumed to be pure liquid and of H₂ gas at one atmosphere. Liquid LiH was assumed because of its being in solution; and zero free energy change was assumed for the solution process of LiH.

Results of calculations for a number of temperatures are given below:

Temp (°C)	230	502	688
E° (V)	0.581	0.364	0.202

Taking these values of E°, calculations were made to determine actual emf on the assumption of activity coefficients of one and using a nominal value of 5 wt % of lithium hydride in the solvent and 12% in the liquid metal. These composition values are the approximate values found in earlier work with batch-type LiH cells. The results are tabulated below:

Temp (°C)	230	502	688
EMF (V)	0.631	0.446	0.304

When these values are plotted and the resultant curve extrapolated to zero emf, a temperature of almost 1125°C is indicated for a decomposition pressure of one atmosphere of hydrogen. This suggests the possibility of a real materials problem for the system with a cell temperature of 775°K.

Screening Studies on Various Batch-Type Cells

General

- a. Various Hydride Systems - Because of the desirability from a thermodynamic standpoint of obtaining higher voltages at lower operating temperatures at a given activity, a number of different solvent systems with lower melting points were studied. Details given on the following pages.

²Foster, L.M., 'Constitution of Molten Salts', Paper presented before Pittsburgh Section, Electrochemical Society.

³Janz, George J., Constitution of Fused Salts, Technical Note No. 1 ARDC, Contract No. AF49(638)-50 Project Chem. 40-45 May, 1957.

⁴Ibid, Technical Note No. 11, August 1959.

Similarly, because of possible beneficial catalytic effect of gas electrodes made of nickel, a series of tests involving nickel electrodes was run, details again being given below. Similar study of the catalytic effect of platinum is being planned. Because of possible desirability of use of hydrides with lower decomposition temperatures, screening studies included work with cells of hydrides of sodium and potassium.

- b. Alternates to Hydrides - in evaluating alternates to ionic hydrides as means of meeting the objectives of the present contract, consideration was given basically to ionic nitrides.

Free energy data and decomposition temperatures of pure ionic nitrides are given in the following table:

<u>Compound</u>	<u>Ba₃N₂</u>	<u>Sr₃N₂</u>	<u>Ca₃N₂</u>	<u>Li₃N</u>	<u>Mg₃N₂</u>	<u>Na₃N</u>	<u>K₃N</u>
- $\Delta F_f^{\circ 2}$ (kcal) ¹	73.4	77.0	93.2	37.3	96.2	--	---
E ^{o 2}	0.53	0.56	0.67	0.54	0.69	--	---
Td (°K) ³	1270	1300	1170	1113	1300	548	628

¹ Quill, L.L., ed., The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, McGraw-Hill 1950.

² at 298°K

³ Kirk, R.E. and Othmer, D.F., editors Encyclopedia of Chemical Technology, Vol. 9, pg 347.

These data suggest the possibility of development of an efm by the formation in solution in fused salt solvents of ionic nitrides and the possibility of thermal decomposition of the solute into its elements. The following section discusses some experiments performed to screen nitrides for feasibility.

Individual Cell Data

Na/LiF-LiCl/H₂ Cell

- a. Stainless Steel Gas Electrode - In order to determine the feasibility of a sodium hydride cell having low sodium ion activity, an assembly was made of a sodium electrode and a hydrogen electrode of Grade C micrometallic stainless steel with the eutectic of the fluoride and chloride of lithium as solvent. After elimination of spurious voltages, a maximum open circuit voltage of 0.43v was obtained at 520°C, leveling off to 0.34v. With the cell in this condition, current was drawn giving a density of 67 A/sq ft at 1/2 open circuit voltage.
- b. Nickel Gas Electrode - Since the above is well below a practical level, a Grade D nickel micrometallic electrode was substituted for the stainless steel one in an effort to increase current density. After elimination of the newly introduced spurious emf, an open circuit voltage of 0.28v was obtained at 520°C. At this point a sample of the electrolyte was taken and was found to contain about 2-4% NaH and 3-6% Na. At 0.175v, current density was found to be 123 A/sq ft, which is greater than that with the stainless steel electrode. After further energy drain from the cell, the open circuit voltage fell to 0.22v as the hydride content rose to 5% and the sodium content held to this same value.

These values show marginal promise of optimizing cell performance to obtain current density of at least 100 A/sq ft at a cell operating voltage above 0.3v; and in the absence of more promising prospects, this cell can be reactivated for optimization studies.

Na/LiF-LiCl/N₂(Ni) Cell

The cell which has been used to screen the Na/LiF-LiCl/H₂ system was further used to test the feasibility of the system Na/LiF-LiCl/N₂ (Ni) containing 5% NaH and 5% Na in the solvent. Maximum voltage obtained was only 0.06v and the current density at 0.03v was only 56 A/sq ft. These values show little promise for a galvanic system based on the conditions of the test. However, since the standard free energy is in the range of -35 to -40 kcal/mole, judging from lithium nitride, and since the decomposition temperature of pure Na₃N is 275°C, the ionic nitrides cannot be completely discounted; and exploratory studies will be continued with lower melting solvents, with different cathode materials and especially with consideration of different catalysts.

Li/LiCl-KCl/H₂ Cell

The eutectic of the chlorides of lithium and potassium (41 mole % LiCl) was considered as a possible advantageous solvent in a lithium hydride cell, having both a relatively low melting point (352°C) and low lithium ion activity. The question about the stability of lithium metal in a melt containing KCl was judged to be satisfactory, since calculations⁵ of standard free energy values showed that of KCl to be -93.3 kcal/mole and that of LiCl to be -88.8 at 237°C and -81.6 and -80.2 respectively at 737°C.

With a cell operating temperature of 357°C, a peak open circuit voltage of 0.385v was obtained. Considerable difficulty was encountered in cell operation in that the gas electrode became plugged frequently. It has now been established that this difficulty is encountered most frequently with use of E grade 'micrometallic' porous stainless steel and can be minimized with use of the coarser C grade material.

With finding of the relatively poor open-circuit voltage of this cell and of more promising systems elsewhere, work on this particular cell was halted, at least temporarily, so that efforts could be concentrated in more promising areas. With increased current densities since having been obtained by use of Grade D nickel micrometallic gas electrode material as compared with use of Grade C stainless material and with minimizing gas stoppage, it is in order to reactivate this cell with different electrode materials.

M/LiBH₄-KBH₄/H₂ Cell

- a. Stainless Steel Gas Electrode - Potassium Anode -
As part of the program of screening low melting fused salt systems as possible solvents for the alkali metal hydride cell, a cell was assembled with the low-melting eutectic of the borohydrides of lithium and potassium as solvent, a porous stainless steel gas electrode and a potassium anode. The reported eutectic composition of 54 wt % LiBH₄-46% KBH₄ failed to melt at the reported temperature of 102°C, but melted rather at 120°C. Thermodynamic data were not available to indicate which alkali metal might be stable in the solvent, so potassium was arbitrarily chosen as the anode metal. Voltages as high as 1.6v appeared across the electrodes with argon rather

⁵ Quill, L.L., ed. Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, McGraw-Hill 1950.

than hydrogen passing to the gas electrode; and such spurious voltages could not be reduced below a value of .08v even with extended short-circuiting of the electrodes and passage of hydrogen. When hydrogen was substituted for argon terminal voltage increased by only .02v.

- b. Stainless Steel Gas Electrode - Lithium Anode - Similar results were obtained with lithium as the anode material. Current densities of the order of only 2.9 A/sq ft were obtained at maximum power output with passage of hydrogen gas and only 0.6 A/sq ft, from the spurious emf with argon gas. With such a slightly elevated operating temperature it seems that the required activation energy demands use of metals with greater catalytic activity such as nickel or platinum.
- c. Nickel Gas Electrode - Lithium Anode - When the stainless steel gas electrode in the above cell was replaced by a nickel electrode, spurious voltages appeared with argon gas and could not be eliminated even after long periods of drawing short-circuit current and passage of hydrogen gas. Current densities of the order of only 2 A/sq ft were obtained. With such poor prospects for this cell, work was discontinued. Use of a platinized electrode is indicated as a next step with this particular solvent.

Li/LiBH₄-KBH₄/N₂ (Ni) Cell

As part of the overall program of determining the feasibility of a nitride cell, the cell assembled for screening the system M/LiBH₄-KBH₄/H₂ (nickel) was fitted up with a nitrogen supply. Spurious voltage of 0.1v with argon was observed, and no increase above this value was obtained when nitrogen was passed to the gas electrode. With this failure to obtain galvanic cell action, work was abandoned on this particular system. Again catalytic effects need to be studied further.

Li/CsCl, LiCl, RbCl, NaCl/H₂ Cell

As part of the overall program of finding the optimum solvent for the lithium hydride system, the low melting mixture of the chlorides of cesium, rubidium, lithium and sodium described under 'Differential Thermal Analysis and Solvent Composition' was made as a solvent for use in the lithium hydride

cell. The weight ratios were 285 parts of LiCl, 390 parts CsCl, 305 parts RbCl and 30 parts NaCl. It was necessary to raise the temperature to 340°C to get complete melting of the rather non-homogeneous physical mixture; and initial tests on the cell were made at this temperature. After elimination of the usual spurious emf, hydrogen was passed to the gas electrode which was made of micrometallic stainless steel of porosity 'C' and the emf rose to 0.57v in 10 minutes and held at that value for 20 minutes. Current was then drawn at a density of 1.25 A/sq ft under a potential of .46v for 15 minutes and then at 2.3 A/sq ft under a potential of 0.285v for an hour. The open circuit emf after this loading was 0.48v.

While open circuit voltage values were at a reasonable level, current densities are considered unsatisfactory. Attempts to improve performance by use of nickel or platinum electrodes and by lower temperature operation are in order. If satisfactory performance can be obtained in this area, regeneration or decomposition pressure data and chemical composition information will be developed. If decomposition temperatures are excessively high for lithium hydride, use might be made of a sodium anode, since it should be stable in the chloride solvent at operating temperatures, judging from standard free energy of formation⁶.

LiI-LiBr-KI-KBr Eutectic as Solvent

The quaternary eutectic of LiI-LiBr-KI-KBr has been reported as melting at 230°C⁸. The composition was reported to be 36% LiI, 29% LiBr, 14% KI and 16% KBr. This adds up to only 95%, so each value was increased by 5% to make a low melting solvent for the lithium hydride cell.

In preparation of this fused salt solvent, it was necessary to prepare lithium iodide in the laboratory. The purity of the resultant salt was questionable as there appeared to be free iodine resulting from the hydrolysis of the salt. This material was combined with reagent grades of the other salts. The resultant mixture melted over the range of 330-350°C. This was placed in a

⁶Glassner, Alvin, The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K, ANL-5750 U.S. Atomic Energy Commission.

⁷Hunger, H., 'Investigation of the Hydrogen-Oxygen Fuel Cell' USA SRDL Technical Report 2001, 15 December 1958.

⁸Callery Chemical Company - Private Communication.

cell with a hydrogen electrode of porous stainless steel; and a lithium electrode was introduced. Ultimately, a spurious emf of 0.25v was obtained with argon passing through the hydrogen electrode. When hydrogen was substituted, the voltage fell off to zero and then reversed in sign with a value of 0.05v with the hydrogen electrode negative in sign and the metal electrode positive. This suggests that a HI cell had been formed from the reactions: $1/2 H_2 \rightarrow H^+ + e$ and $1/2 I_2 + e \rightarrow I^-$. Presumably the iodine had been liberated by decomposition of the iodide salts at the elevated operation temperature.

With lack of promise of this system, no further work was done.

Summary on Screening Studies

Table 1 lists the various electrode and solvent combinations screened together with results obtained. It will be seen that the borohydride and iodide eutectics and the nitride systems failed to give promising results as solvents for the hydride cell under conditions of the experiments. In the case of the borohydride solvents and the nitrogen electrode, further work with catalytic electrode might prove fruitful.

The CsCl-LiCl-RbCl-NaCl eutectic shows promise as a low melting solvent and should be studied further at lower temperatures, with catalytic electrodes and with a sodium anode. Use of a sodium anode would permit lower regeneration temperatures.

With an open circuit voltage of 0.43 in a solvent at 520°C, the sodium anode shows some promise of meeting objectives, especially when used with lower-melting solvents and if the current density can be improved by such means as catalysis.

Operation of Li/LiF-LiCl/H₂ Regenerative Cell

- a. Non-Regenerative Operation at One Atmosphere Hydrogen Pressure - First operation of the subject cell, which was shown as Fig 7 of the First Quarterly Progress Report, covered a week on load under a pressure of one atmosphere of hydrogen. During this period, samples of electrolyte were taken and analyzed for hydride content. Precision is probably not too great, as there is evidence of some concentration gradient in the cell as will be seen from the data below. Attempts to sample the lithium electrode material by immersion of tubes and by dipping with small buckets were unsuccessful, possibly because of wetting problems and of presence of lithium in only a very shallow pool. New techniques of sampling will be investigated. Standard techniques are described in APPENDIX II.

Table 1 - Summary Table of Screening Studies

Anode	Cathode		Solvent	Hydride Content (%)	Cell Temp (°C)	Max Vo.C.	Power Density at Equilibrium	
	Gas	Metal					Cathode (A/sq ft)	Volts
Na	H ₂	stainless	LiF-LiCl	low	520	0.43	67	0.17
Na	H ₂	Ni	LiF-LiCl	3-1/2%	520	0.28	123	0.17
Na	N ₂	Ni	LiF-LiCl		520	0.06	56	0.03
K	H ₂	stainless	LiBH ₄ -KBH ₄		120	0.02	---	----
Li	H ₂	stainless	LiBH ₄ -KBH ₄		140	----	---	----
Li	H ₂	Ni	LiBH ₄ -KBH ₄		140	----	---	----
Li	N ₂	Ni	LiBH ₄ -KBH ₄		140	----	---	----
Li	H ₂	stainless	LiCl-KCl		357	0.38	---	----
Li	H ₂	stainless	LiI-LiBr-KI-KBr		340	-0.05	---	----
Li	H ₂	stainless	CsCl-LiCl-RbCl-NaCl		340	0.55	1.2	0.45
Li ¹	H ₂	stainless	LiF-LiCl		570	0.72	2.3	0.28
							245	0.30

-15-

¹ Values from earlier privately supported work presented as a basis of comparison.

After the first interval of non-regenerative operation, a period of regenerative operation was set up as will be discussed in Section b below. This was followed by cooling of the regenerator and by a second brief period of non-regenerative operation of the cell as is included in the tabulation below. A third period of non-regenerative operation followed repairs to the system and recharging with salt and lithium.

Table 2 - Operational Data Under Non-Regenerative Conditions

Date	Cell Temperature (°C)	Open Circuit Voltage	Current Density at 1/2 Vo.C. (amps/sq ft)	Hydride Content of Solvent (wt %)
11-3	480	.36	57	---
11-4	480	.375	71	---
11-5	480	.375	73	1.8
11-6	510	.35	---	---
11-9	550	.325	---	4.2
11-10	490	.36	92	1.8
12-7	515	.17	---	4.5 ¹ 5.2 ² 1.9 ³
12-26	495	.24	---	---
12-29	495	.27	---	3.8-5.8

¹ from under Li

² bottom half of core sample

³ from H₂ electrode region

With the cell operating at 480°C, a solvent composition of 1.8% by weight of LiH and 1.7% of Li and an open-circuit voltage of 0.35, volt-ampere data were taken, steady values of current being recorded.

volts	0.34	0.32	0.31	0.29	0.27	0.25	0.24	0.22
amperes	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6

Both the open-circuit voltages and current densities are smaller than those obtained in early batch-type cells; and the emf's are smaller than calculated as is shown by comparing with section a above, indicating a degree of irreversibility of the cell reaction. A difference between the regenerative cell and early batch-type cells lies in the much larger area of lithium electrode in close proximity to the hydrogen electrode. This suggests that hydrogen might be electrochemically ionized to a large degree at the metal weir in contact with lithium and separating it from the hydrogen compartment. A redesign of the regenerative system to eliminate this problem is in order. Low current density may also be the result of flooding of the gas electrode; and use of electrode material with double porosity is indicated to eliminate this problem.

- b. Regenerative Operation - With a hydride content of 1.8 wt % in the solvent, the closed cycle system was put into regenerative operation under an argon cover gas at one atmosphere pressure. A peak emf of only 5 mv on open-circuit was obtained and fluctuated widely, apparently with variation in circulation rate causing changes in cell and regenerator temperatures, which were nominally 550°C and 890°C respectively. Since analyses had shown higher hydride contents in the solvent in batch-type cells, some LiH was added in bulk to the regenerator. Within 15 minutes, a peak emf of 33 mv was obtained, after which a slow decline set in. At this point, hydride precipitated in the cell, plugging the exit at the hydrogen electrode and forcing hydrogen up through lithium giving rise to chemical combination. When this was unplugged, the regenerator was cooled down for safe week-end operation. Upon reheating, the salt in the center of the connecting pipes apparently had melted and expanded before that at the ends with the result that forces building up the expansion caused rupture of the pipe and leaking of the molten salt. This occurred in spite of the fact that the contents of both the cell and regenerator were molten. Upon replacement of the connecting pipe, extra heaters were added where needed to prevent such forces developing again.

With the thought that the rate of diffusion of hydrogen through argon from the regenerator to the cell might be slow as compared with diffusion through a vacuum, the system was operated regeneratively under vacuum. A peak emf of 11 mv was obtained with the regenerator at 860°C. Rises and declines in emf were observed with freezing and melting of salt in the pipes connecting the cell

and the regenerator, showing the need of analysis of pressure relationships such as was done for the hydrogen-oxygen cell⁷. Apparently development of a pressure head is needed for hydrogen since diffusion seems inadequate. Higher regeneration temperatures likewise is needed; but work was abandoned on the subject system in favor of redesign and operation of an improved model.

⁷ Hunger, H., 'Investigation of the Hydrogen-Oxygen Fuel Cell'
USA SRDL Technical Report 2001, 15 December 1958.

V CONCLUSIONS

Iodides failed to show promise as low melting solvents for the hydride cell. Tests with alkali metal borohydrides as solvents and with nitrogen as a cathode gas failed to give acceptable results; but further work with catalysts is indicated.

The quaternary system of the chlorides of cesium, rubidium, sodium and lithium has shown promise as a low-melting solvent for the hydride cell from the standpoint of voltage; but improvements must be made in current density.

Sodium has been shown to yield an acceptable voltage as anode material in a hydride cell and may be studied if excessively high decomposition temperatures require an alternate to lithium hydride.

Irreversibility has been shown in the closed-cycle lithium hydride cell and redesign is indicated.

VI PROGRAM FOR NEXT INTERVAL

The quaternary system of the chlorides of cesium, rubidium, sodium and lithium will be used as a solvent for cells near the solvent melting point with nickel and platinum electrodes and with a reference electrode to assess catalytic effect both with a sodium anode and a lithium anode. Use of gas electrode material of double porosity will be investigated.

Decomposition pressure data will be taken on promising systems including the lithium hydride cell with the eutectic of the chloride and fluoride of lithium as solvent.

The closed cycle system will be redesigned in effort to reduce the degree of irreversibility. Design will be based in part on a detailed analysis of pressure relationships to be developed in operation and will include specification of electrode material of double porosity.

VII IDENTIFICATION OF PERSONNEL AND
DISTRIBUTION OF HOURS

1. John C. King	441 hours
2. Robert E. Shearer	205
3. Samuel Veccharella	417
4. Drafting and hourly	152
5. Other salaried	<u>64</u>
	1,279

Samuel J. Veccharella, Associate Chemist

Mr. Veccharella received his B.S. degree in Chemistry from Grove City College in 1958. During his summer vacations he worked as a technician for Callery Chemical Company; and he attended the Graduate School of Chemistry at the University of Pittsburgh during the academic year 1958-1959. In September, 1959 he was employed as an associate chemist by MSA Research Corporation.

VIII APPENDIX I

Determination of Alkali Metals in the Chloride Eutectic⁹

The method used to determine the relative quantities of the four alkali metals in the quaternary eutectic of their chlorides is one used by San Antonio Chemicals, Inc., in their analysis of 'Alkarb'. It is done by the use of a Beckman model DU spectrophotometer. The procedure given below was modified at MSA Research by elimination of the step involving the determination of potassium, which was not present in the eutectic, and by use of a hydrogen-oxygen torch in place of the oxygen-acetylene burner to reduce background.

Procedure

Preparation of Sample - Weigh 0.5000 grams of sample and place in a 400 ml beaker. Add approximately 100 ml of distilled water and several drops of methyl orange indicator. Cover the beaker with a watch glass and acidify with hydrochloric acid. Boil to remove CO₂, cool to room temperature and transfer to a 250 ml volumetric flask. Dilute to the mark and mix thoroughly.

Standard Solutions - Discussion

Standard solutions for flame spectrophotometric comparison are prepared by diluting appropriate volumes of stock solutions which have accurately known concentrations of pure salts of the individual elements. The following stock solutions are used:

potassium stock solution	0.0100 gm	K ₂ O per ml
rubidium stock solution	0.0100 gm	Rb ₂ O per ml
cesium stock solution	0.0010 gm	Cs ₂ O per ml
sodium stock solution	0.0010 gm	Na ₂ O per ml
lithium stock solution	0.0010 gm	Li ₂ O per ml

In making up the stock solutions, the following salts and conversion factors are used:

1.584 gm KCl	= 1.00 gm K ₂ O
1.235 gm Rb ₂ CO ₃	= 1.00 gm Rb ₂ O
1.195 gm CsCl	= 1.00 gm Cs ₂ O
1.886 gm NaCl	= 1.00 gm Na ₂ O
2.473 gm Li ₂ CO ₃	= 1.00 gm Li ₂ O

Note: Acidify all carbonates with hydrochloric acid before diluting to volume.

Note: Pure rubidium carbonate can be purchased from DeRewall International Rare Metals Corporation, Philadelphia, Pennsylvania

⁹ Private Communications - San Antonio Chemicals Incorporated.

In using the flame spectrophotometer for quantitative analysis, the preparation of accurate standard solutions is of prime importance since all results are obtained by comparison of the sample to the standards.

The alkali metals influence each other in their reactions in the spectrophotometer flame. For this reason, all standards must contain all of the alkali metals in very nearly the same concentration as the sample.

Standard Solutions-Preparation

Three standard solutions are required for the determination of each element. These are called 'high standard', 'low standard', and 'middle standard'. The middle standard should be near the sample composition with respect to the element to be determined. The high standard must contain more of the element sought than does the sample, and the low standard must have a lower concentration than the sample.

The elements must be determined in the following order: K_2O , Rb_2O , Cs_2O , Na_2O , and Li_2O . Make up the middle K_2O standard by adding together the correct volumes of stock solutions to make a synthetic 0.5000 gm sample of the following typical Alkarb composition:

K_2O	48.0%
Rb_2O	18.0%
Cs_2O	1.5%
Na_2O	1.8%
Li_2O	0.7%

This will require the following volumes of stock solutions, which are diluted to 250 ml and mixed thoroughly in a volumetric flask:

K_2O	stock solution	24.0 ml
Rb_2O	stock solution	9.0 ml
Cs_2O	stock solution	7.5 ml
Na_2O	stock solution	9.0 ml
Li_2O	stock solution	3.5 ml

The high K_2O standard is made up to contain 0.025 gm more K_2O (2.50 ml of K_2O stock solution) than the middle standard, and the low K_2O standard contains 0.025 gm less K_2O than the middle standard. Both high and low standards contain the same quantities of the other alkalis as the middle standard, and are diluted to 250 ml in volumetric flasks.

The K_2O must be determined according to the procedure outlined under 'Flame Spectrophotometric Technique' before making the rubidium standards.

In making the three rubidium standards, substitute the determined percent K_2O for the originally assumed value. This practice of substituting the correct value is followed with each succeeding element as it is determined. Thus the standards for the elements in lower concentration (where the effect of inaccurate standards would be greater) will be as precise as possible.

Tabulated below are the differences in percent between the three standards for each of the elements yet to be determined. The tabulated values are based upon 0.5000 gm of sample and all standards are diluted to 250 ml in volumetric flasks.

Table 3 - Composition of Standards

Standard	High Standard (%)	Middle Standard (%)	Low Standard (%)
Rb_2O	21.0	18.0	15.0
Cs_2O	2.0	1.5	1.0
Na_2O	2.3	1.8	1.3
Li_2O	1.2	0.7	0.2

Flame Spectrophotometer Technique

Details of the technique for making flame spectrophotometer comparisons are given below. These apply only to the Beckman Model DU instrument equipped with an oxygen-acetylene burner.

The spectrophotometer should be turned on to 'warm up' for 20 minutes before it is used. The exact wave length setting must be located by placing a dilute solution of the element under the capillary of the lighted burner, and slowly rotating the wave length dial until maximum intensity is obtained. Having thus located the correct setting, the wave length dial must not be moved again during subsequent manipulations with the given element.

Measure the radiation intensity of element from the three standards and the sample solution, reading one after the other until five readings have been taken for each of the solutions. Experimental technique and instrument stability should be such that the total variation in the readings, for any one of the solutions, will not exceed one scale division. The average of the five readings for each standard is plotted on graph paper vs the corresponding percent of the element. Draw a smooth curve through the points to form the calibration curve. The average of the sample readings is plotted on the curve and the percent of the element is read from the graph.

It is necessary to plot a new calibration curve for each sample since burner characteristics instrument settings cannot be duplicated from day to day.

APPENDIX II

Sampling Techniques in Liquid Metal Systems

In most cases our method of sampling has followed as near as practical the standard procedure for removing samples from liquid metal systems for oxide determination. A nickel sample bucket, 1/2 in. in diameter and about 1/2 in. deep is suspended on the end of a 1/4 in. tube through which argon can be purged. The tube is fitted through an insulated probe assembly which screws on top of the gate valve. After the space above the valve is purged with argon the gate valve is opened and the bucket lowered until an ohmmeter shows contact between the bucket and the salt. It is lowered 3/4 in. more to allow the bucket to fill, then withdrawn and the gate valve closed. Argon is purged over the sample to cool it, the probe assembly unscrewed and quickly placed over the neck of a flask. The bucket is released and the flask purged and stoppered.

To get samples from different levels in the cells several other methods were tried. A bell shaped cap was made to plug the end of a 5/16 in. tube and fastened to a small rod running up through the tube. The tube was lowered into the salt, the cap lowered to allow the salt to run up inside and the cap drawn tight as the sample was removed. More difficulty was experienced in transferring the sample to the flask as the end of the tube and the rod had to be cut off. Another method was to weld the end of a 5/16 in. tube shut, then cut holes in the sides about 1 in. up. A 1/4 in. solid rod was run down through the tube and bucket. The tube was lowered to the proper level in the salt and the 1/4 in. rod raised to about the holes, drawing salt into the bucket. After the sample is withdrawn the connecting sides of the tube are nipped off. Later these sides can be joined forming a bale and it was used as a regular sampling bucket. These last sampling methods take more time to prepare and are more difficult to keep free from oxide but permit sampling at different levels. These methods also have an advantage if there is a crust or obstruction in the way. In such cases, pressure can be applied to break through it without losing a sample bucket.