UNCLASSIFIED

AD NUMBER

AD402683

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 31 JAN 1963. Other requests shall be referred to US Army Electronics Research and Development Agency, Fort Monmouth, NJ.

AUTHORITY

Army Elect Rsch Dev Agen, 31 Jan 1975

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 402 683

Reproduced by the DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA. VIRGINIA



UNCLASSIFIED

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.



¢

402 683

RESEARCH ON AMMONIA BATTERY SYSTEM 63-33

OCTOBER 1, 1962 THROUGH DECEMBER 31, 1962 REPORT NO. 10 SECOND QUARTERLY PROGRESS REPORT



SINCE 1843

PICHER



I STATE THE

ASTIA AVAILABILITY NOTICE

والمستعلم والمستعلم

.

Qualified requestors may obtain copies of this report from ASTIA. ASTIA release to OTS not authorized.

~ ~

RESEARCH ON AMMONIA BATTERY SYSTEM

1 7 7 OCTOBER 1, 1962 THROUGH DECEMBER 31, 1962 REPORT NO. 10 SECOND QUARTERLY PROGRESS REPORT

CONTRACT NO. DA-36-039-sc-89188 (Continuation of Contract No. DA-36-039-sc-85396)

RESEARCH ON AMMONIA BATTERY SYSTEM

REPORT NO. 10 SECOND QUARTERLY PROGRESS REPORT

OCTOBER 1, 1962 THROUGH DECEMBER 31, 1962

CONTRACT NO. DA-36-039-sc-89188 (Continuation of Contract No. DA-36-039-sc-85396)

DEPARTMENT OF THE ARMY PROJECT NUMBER 3A99-09-001

Signal Corps Technical Guidelines for PR&C 60-ELE/R-4905 dated March 7, 1960

The object of this contract is to perform research to establish the feasibility of the liquid ammonia system in galvanic cells and develop the use of this system in batteries.

U. S. ARMY ELECTRONICS RESEARCH AND DEVELOPMENT AGENCY FORT MONMOUTH, NEW JERSEY

> THE EAGLE-PICHER COMPANY COUPLES DEPARTMENT P. O. BOX 290 JOPLIN, MISSOURI

> > PREPARED BY: D. J. Doan, Project Supervisor L. R. Wood, Project Engineer

<u>REVIEWED BY:</u> J. F. Dittmann, Engineering Supervisor

APPROVED BY: E. M. Morse, Engineering Manager

DATE OF REPORT: January 31, 1963

TABLE OF CONTENTS

I.

1

5

	ABSTRACT	
	PURPOSE	
	CONFERENCES	
Ι.	INTRODUCTION	35
11.	 FACTUAL DATA A. Multicell Units Automatic Activation Efficiency Study Cell Design B. Hardware Corrosion Study Cold Activation Problem Low Rate and Screening Tests AC Impedance Measurements Interpretation 	36 36 39 43 45 53 53 53 56
III.	CONCLUSIONS	58
IV.	PROGRAM FOR NEXT INTERVAL	59 59 59
v.	IDENTIFICATION OF KEY PERSONNEL	60
	Appendix	
	Abstract Card	
	Distribution List	
	TablesNo. X- Battery DataNo. XI- Coil Rupture DataNo. XII- Single Cell Calendering DataNo. XIII- Cell DescriptionNo. XIV- Cell Width Reduction Study	38 42 44 46 48
	Figures No. 15 - Complete NH ₃ System with Curved Squib-Holder No. 16 - Cold Activation Variation No. 17 - Straight and Curved Squib-Holders No. 18 - Battery No. 120, 9-Cell Unit, Activation Curve No. 29 - Test Cell with Small Vexar and Corrugated Anode No. 20 - 14 Multicell Unit Block No. 21 - Ammonia Battery Activation Data No. 22 - Activation Data on BA-472'U, 100° F Ambient	37 40 41 47 50 52 54 55

ABSTRACT

Γ

<u>.</u>

From continued investigation into the defining factors involved on cold activation, the conclusion is reached that cathode electrode fabrication and processing variables are causing the variance of 0.5 second to about 3 seconds. Separator development has resulted in increasing capacity and permitting use of thinner cells, both of which result in approximately doubling the energy per unit weight to a maximum of 4.51 watt-hours per pound.

PURPOSE

The purpose of this contract is to carry on research and development on the use of liquid ammonia as an electrolyte solvent with various cathode and anode materials, toward determining the applicability of the system generally in batteries. Specifically, the program will include the following investigations:

A. A comprehensive study of possible cathode materials for use with conventional anodes, such as: magnesium and zinc immersed in liquid ammonia electrolytic solutions. Cathodic materials of possible use in liquid ammonia systems fall into several classes which include oxides, both inorganic and organic, reducible inorganic salts and metallic nitrides, which are the "oxides" of the nitrogen system. Studies shall include measurement of E.M.F., electrode voltage as a function of discharge current density and temperature, determination of reaction products, effect of local action on electrode potential and coulometric capacity and effect of contaminants in liquid ammonia on electrode properties. Desirable characteristics of cathodic materials include: (1) ability to maintain good cell voltage level under high and low rate discharge conditions over a wide range of temperature (-65° F to +165° F); (2) stability in electrolyte for long periods of time over a wide temperature range; (3) small temperature coefficient of voltage, and, (4) ease of fabrication into practical electrode structures.

B. Investigation of liquid ammonia electrolyte systems will be undertaken for optimum performance of new ammonia battery systems. Acid, neutral and alkaline solutions are to be investigated. Mixed salts can be used to import desirable electrolyte properties. The physical and chemical properties of the salts and solutions will be investigated including such measurements as solubility, vapor pressure and conductivity as functions of temperature and concentration. Determination of stability and interaction with other cell components will also be made.

Studies will be made to establish cell design information best suited to achieve optimum performance throughout the temperature range of -65° F to $+160^{\circ}$ F. The investigations should provide practical design information which can be used for future battery development.

The Power Sources Division of USAELRDL has performed much work in this area and is continuing with its studies. Since this Division is monitoring the present contract, it is important to state that the contractor will maintain close liaison and will be prepared to cooperate with their suggestions through conferences, etc., toward accelerating and any altering of the plans of the contract effort. This, of course, may be brought about by the bringing to light of information by both laboratories and by changes as to emphasis on certain type batteries, etc. The contractor will obviously assume full responsibility for the quality of the contract effort.

CONFERENCES

On November 24, 1962, a conference was held with USAELRDL at Fort Monmouth, attended by Mr. Howard Knapp of the Signal Corps, and Mr. L. R. Wood and Dr. D. J. Doan of The Eagle-Picher Company. The details of the work to date were discussed and reviewed. The following was agreed on for the current effort to be stressed:

A. High Rate Application

(1) In the battery development, stress should be placed on consistent activation and capacity, regardless of voltage (cells) of the battery.

(2) Perform single cell tests as required in problemsolving for the units under (1).

(3) Continue effort toward concentrating the cell structure.

B. Low Rate Application

(1) Investigate S, M-DNB and PbO2.

(2) Investigate possible procedures for drying electrolyte, Pb-Na, NaNH₂, MgSCN, MgC**10**₄, and molecular sieve.

(3) Continue investigation of gassing from magnesium to find a system (electrolyte and type magnesium, etc.) that will gas a minimum.

(4) Proceed with fabrication of complete cells and multicell units as the research and development indicates.

I. INTRODUCTION

The general direction of the effort has been outlined in the "Conference" section of Report No. 9, or the First Quarterly Progress Report of the current contract. Primary effort was devoted to battery investigation, separator development leading toward concentration of the cell structure. At the latter part of the interval, a number of nitrides and carbides were received. A number of borides are still on order with a promise of delivery. These are scheduled for screening tests for high and low rate performance.

A paper has been prepared for presentation at the Fifth Ammonia Battery Symposium, January 29-30, 1963, at Plymouth Meeting, Pennsylvania.

II. FACTUAL DATA

3

A. Multicell Units

As designated in the program for this interval, considerable effort was directed toward automatic multicell operation. Improvement of cell design to increase energy per unit weight of the system has been of paramount interest and significant advancement has been made in this area.

Hardware design remains basically unchanged although development of a curved squib-holder and use of 0.625 inch diameter electrolyte reservoir has reduced battery length approximately one inch. Current units are 5.2 inches long, 4.25 inches in diameter, and weigh 1450 grams. Figure No. 15 shows a completed unit with curved squib-holder and large coil. Progress in cell design has permitted use of additional cells, thus increasing the voltage per unit volume.

Maximum high rate (270 MA/in.^2) energy output obtained was 4.51 watt-hours per pound. Minimum activation time recorded was 0.45 second. Specific data concerning multicell operation is shown in Table No. X.



COMPLETE NH₃ SYSTEM WITH CURVED SQUIB-HOLDER

TABLE NO. X

|

į

0

.

BATTERY DATA

BATT.	.TW	1425	1421	1450	1502	1556	1539	1598	1607	1682	1682	1585	1542
WATT-HRS. PER LB.	TO 80% PLV	2.70	1.97	0.05	2.18	1.36	4.51	3.63	4.1	3.28	3.63	2.39	3.77
THEO.	MIN,	85.2	83.5	84.3	94.6	93.2	94.8	93.8	95.1	93.2	94.0	94.2	93.4
TOTAL AMP.	MIN.	42.55	30.5	7.6	36.0	24.4	83,09	80,84	82.0	64.1	68.5	20.0	75.35
TOTAL MIN.	T0 807	18.5	13.0	3.0	15.0	9.0	30.5	29.5	31.0	26.5	19.0	8.5	25.0
30%	75	50.0	36.5	E0*5	38.1	25.2	86.63 87.73	86.1	86.4	68.8	73.0	21.2	80.5
3 FF. TO 80% MA/1n. ²	145	50.0	36.5	e0.e	38.1	25.2	86.63	82.1	84.7	68,8	73.0	21.2	80.5
% EFF. MA/	270	50.0	36.5	9.03	38.1	25.2	83.0	74.2	79.5	68.8	50.5	21.2	66.4
OCA OCA		11.0	9.5	2.5	11.1	6.9	11.4	11.0	11.7	11.0	19.5	32.2	14.0
MAX. ACZ	-Ohms-	1.6	1.8	36.8	3.6	ł	1	ł	ł	I	8	18.7	1.0
MAX. AMPS		2.49	2.49	2.60	2.56	2.76	2.65	2.47	2.55	2.51	2.79	2.42	2.62
PEAK LOAD	VOLTS	12.6	12.7	12.7	12.5	13.1	12.6	11.75	12.4	11.9	19.0	27.0	13.1
1.9 V. CELL		4.0	1.17	2.67	6.8	3.7	>3.5	30.0	30.0	15.0	2.5	60.0	3.6
	to 90% PLV	3.8	1.17	2,67	5.0	4.4	73.5	10.0	17.0	4.2	2.3	4.0	4.4
ACT. TIME -Seconds-	to 80% PLV	6*0	0.45	1.40	2.20	2.40	1.0 *	4.2	10.0	2.9	0.82	2.6	2.6
ACT.		-25	-54	- ⁵	-54	-54	-54	-54	-54	\$	-54	-54	-54
BATT. ACT.		111	112	113	114	115	116 86	117	118	119	120	121	122

* Activation measured visually on Weston voltmeter.

1. Automatic Activation

Variations in cold activation times remain a problem in multicell operation. Prior work on this variation indicated intercell leakage and electrolyte location in the reservoir as primary factors. Complete analysis of the problem has been delayed since the program calls for a transition from 12 to 28 volt units, which would probably necessitate re-evaluation of the same problem. Average cold activation time variation due to the heretofore described factors is one to three seconds. The extreme variations reported in Table No. X are assumed to be a result of using experimental gas generators fabricated by Eagle-Picher personnel. Use of the curved squib-holder necessitated fabrication of special generators. Figure No. 16 shows cold activation curve variations resulting from use of special experimental generators. Battery No. 118 was known to be 0.25 gram deficient on propellant and the diaphragm rupture lag time indicates the importance of this factor. Battery No. 120 was tested using a standard U.M.C. gas generator to verify the activation observations.

Laboratory work has been initiated to establish the necessary corrections in curved squib fabrication. Squib-holders are presently made from coil sections cut to proper length. Figure No. 17 compares the earlier model and current "banana" type holders. Tests regarding rupture strength of curved holders are shown in Table No. XI. These values apply also to electrolyte reservoirs which demonstrate the possibility of reducing wall thickness and thus, weight of the coil since 3000 psi is sufficient to withstand activation and operation pressures.

359-12	2 V V V V V V V V V V V V V V V V V V V
10 X 10 TO THE '2 INCH	KEUFFL & ESSER CC.
U Y	

-

••••		1.1	111+1	詚	11			FI H		睈								ΠF				4							III
<u>;</u>]+;							刞	田	田	山			iii:	Ħ						144						1	即		鬪
				围										Ī#							111								
	Ľij	E									辯															2			<u> </u>
-		0	.i.†1											Щ		#											HI,		
· · ·	<u>;</u> ;;	y N											¥.		ų.											5			Æ
.:;:	- 1	ter	; <u>[</u>]]						Į.				ð																
		Bat		F			. 1					-++	1	- H	ti E	H			iii		1		F +				H.		H.
•	11	::	, i-										3			늰	19												冊
:;;!	! : 14				411			11					. 11			111										0	Ht.		H
1,1							1	1:5		11. 11.1.			3	H.	T	1													
1.11	rii		1:11						1				: H													0			
<u>`</u> ~							[];;;										1.7										iii.		H
				Va											. 1	.11	: 1		1									;#j	
No.	Ξ.		in] : :									11								<u>FI</u>				ψ	
5				1.						:: <u>.</u>	,	T											spu		111		E.	115	
tt		•	[;;;;		A					. ;.						;	,11,			<u>.</u>		T.	U U	tii		1111			
Å			1	1:1:		X							· · ·]:	ļ.		1						Š.	97	
									. :			: :						::	 . • .	<u>.</u>	1.		2			Γ.	<u>B</u>	9	
							N	1 .						-									ej :			1.111			
										1	1						.:				1					α.		ICI	
;								ļ: N	1	•				:		:		T	1		TT.		3					P	it
			di-	T :						1.1]										8						
		. '				1.											; *			-			ptu				•••••		
										· :'.				T									1.1						
					. :																						1		
								:. :		i • : •	1			; ; ;		È.			<u> </u>			; †	q	11		40. 			
		 										,							1				H				÷	. l , l ,	
4		-, !			: ;				••• •••	• •						μį	TT:						N					1	
•		:.				11			!	• †										: :							1		
				Þ		:11	1.1.1			÷;;;		[i.!	Tii	1 -			1			- 1	1	1			N			· · · ;	
								. .		- 11							1.1												
; . <u>.</u>		::;		5		1						. [.].		: ':		ĮĮ.		: 											
				80	.::+:			FIT.					1						1					T			i ii		
							ETT	11.1		11				F E	1												ŧμ		H
					111		1. + + [] 		11						tt			ttitt	;*tt	LH'		即日		i i i		: 4
ě				¢		40			9	ļŗ	1-1		¢.							閸				囲	¢				
	• • •											1111	H.:			in l			;		箭油	t in	.						
	 												Ща	A TI	1									盯					
			Ē			HE.						臣	11										詌						
				Battery Wo. 112		Battery Wo. 112 890% P. U.V.																							

- 40 -



Ī

I

Ţ

.....

STRAIGHT AND CURVED SQUIB-HOLDERS

FIGURE NO. 17

TAB	LE	NO.	XI

*

PART NO	DESCRIPTION	0.D. -in	I.D. -in,-	RUPTURE -psi-
1	Coil section	0.625	0,569	6800
2	Coil section	0.625	0.569	6700
3	Coil section	0.625	0.569	6750

COIL RUPTURE DATA

2, Efficiency Study

Significant improvement of multicell efficiency has been accomplished. This improvement resulted from control of active material diffusion through control of separation porosity. Observation had been made that many of the battery end voltages had been reached along with the development of some noise and substantial open circuit voltage at 30 to 50% efficiency. It was reasoned that this may be due to migration and galvanic precipitation of silver on the magnesium. Undisturbed growth would, of course, cause a shorting condition. Single cells have always been higher in efficiency and did not show (when Vexar is used) the shorting. It is reasoned that preventing some boiling or disturbance in single cell testing is difficult. This silver bridging is readily broken. Therefore, a better index of effectiveness of separation is the amount of silver deposition present under various conditions. Table No. XII shows laboratory work from which the calendaring technique was derived. Optimum results were obtained in cells containing three layers of Pellon pressed at 300° F for 10 seconds under 22,000 pounds total pressure.

Incorporating this technique into battery operation resulted in considerable efficiency gain as shown in Table No. X (Battery Nos. 116 - 120).

XII
g
TABLE

ł

1

1

SINGLE CELL CALENDERING DATA

	TEMP. CAVITY -°F- WIDTH	300 0.5 in.	300	300	300	•	300	300	300	300	•	300	300
ROCES	PRESSURE -	22,000 3	8,000 3	22,000 3	22,000 3	0	1,500 3	22,000 3	22,000 3	22,000 3	0	3,000 3	22,000 3
CALE	TIME	10	10	10	10	0	10	10	10	10	0	10	10
PELLON	LAYERS/ CATHODE	H	2	e)	n	7	2	en	ς	n	1	7	1
END	B S		1.48	2.18	2.10	2.10	1.70	2.27	2.30	2.24	2.25	2.30	2.24
OL.NIM	80% PLV	13.0	25.0	20.0	21.0	21.0	19.0	26.0	25.0	23.5	23.0	25.0	13.0
MAX.	AMPS	1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.60	1,70	1.70	1.70
PLV		2.10	2.10	2.05	2.08	1.96	2,10	2.10	1.98	2.00	2.00	1.98	1.98
Z EFF. TO	80% PLV @ 270MA/in ²	38.2	74.0	59.0	62.0	62.0	56.0	72.5	74.0	65.2	68,0	74.0	38.2
THEOR.	AMP. MIN.	57.5	=	2	=	:	:	=	:	:	11		5
TEST	TER. (F)	-30	=	=	=	=	=	=	2	=	=	:	2
CELL	.0N	1015	1016	1017	1018	1019	1020	1021	1022	1023	1024	1025	1026

.

- 44 -

3. Cell Design

Previous experimental work indicated the necessity of using 0.5 inch wide cell cavities. Development of the calendering technique, however, has evidently decreased premature and unpredictable shorting. Reduction of cell cavity width was therefore attempted in Battery No. 120. (Cell designs for batteries are shown in Table No. XIII.) This unit was of standard size but contained additional cells. Activation was very good (Figure No. 18) and efficiency was only slightly low. The unit delivered 3.63 watt-hours/pound at the high rate.

Table No. XIV shows further laboratory work toward cell width reduction. Cell Nos. 998 through 1001 were pilot runs preparatory for Battery No. 120 previously discussed. Cell Nos. 1002 through 1004 were designed with reduced Vexar width and tested in 0.250 inch cavities. The efficiencies obtained from this design were significantly low due apparently to electrolyte limitation between the cathodes. Normal swelling of cathodes prohibited gas evolution regardless of the presence of small Vexar.

TABLE NO. XIII

. |

1

CELL DESCRIPTION

BATTERY NO.		CATHODE PELLON THICKNESS THICKNESS -in	VEXAR THICKNESS -in	CATHODE BACKING CATHODE THICKNESS EDGE -in	CATHODE EDGE SEALENT	ANODE THICKNES: -1n	CELL S VOID	TOTAL CELL THICKNESS -in
116 through 119	ل و يا	.024	.200		Silicone Rubber	.010	.196	
120	•068	•024	.200	•002	Silicone Rubber	.010	•046	.350



.

Ś

- 47 -

TABLE NO. XIV

C

CELL WIDTH REDUCTION STUDY

÷

	ANODE	Plain	Corrugated														
SEPARATORS	WIDTH VEXAR -in	• 100	.100	.100	. 100	.025	.025	.025	None	.015	.015						
	NO. PELLON LAYERS	ß	n	ñ	ñ	n	m	e	n	Ś	ñ	n	ñ	4	4	ñ	3
CELL	WIDTH -in-	•350	.350	.350	•350	.250	.250	.250	.250	.250	.250	.250	.250	.250	.250	.250	.250
END	N	2.3	2.3	2,3	2.25	2.3	2.3	2.14	2.3	2.25	2.32	2.30	2.15	2.25	2.20	2.25	2.28
MIN.	TO CUTOFF	29.0	26.0	30.5	30.0	19.0	24.5	19.0	15.5	19.5	19.5	16.0	21.0	18.5	30.0	29.5	30.0
MAX.	AMP.	2.3	2.3	2.3	2.3	2.71	2.45	2.3	2.42	2.45	1.08	1.08	1.08	2.3	2.3	1.08	1.08
PLV		2.00	1.94	2.1	2.0	2.0	2.05	2.00	2.00	2.00	2.00	2.06	2.14	2.10	1.97	2.12	2.14
Z EFF. TO	80% PLV CUTOFF	63.5	61.0	74.3	71.5	48.8	0.09	47.0	38.0	46.7	52.0	43.0	50.0	0.09	73.5	0.67	80,5
THEOR.	AMP. MIN.	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0	94.0	40,3	40.3	40.3	94.0	94.0	40.3	40.3
CELL	NO.	866	666	1000	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010	1011	1012	1013

- 48 -

Cell Nos. 1005 through 1009 were assembled without Vexar and with corrugated anodes. The corrugation would permit gas evolution channels even though the anode and cathode made contact along the anode ribs. Efficiencies were sub-standard and it is assumed that shorting through the Pellon separation was responsible, even though open circuit values did not indicate this. Examination of discharged cells revealed silver build-up through the Pellon in areas adjacent to the anode ribs. Addition of an extra Pellon thickness improved efficiency approximately 15%, although voltage levels were inconsistent and multicell activation would very likely be impaired. Cell Nos. 1010 and 1011 were used for these observations. Cell Nos. 1012 and 1013 were assembled in 0.250 inch cell cases using small Vexar to prevent shorting, and corrugated anodes to allow gas evolution. Results were considerably better than previous thin cells and equalled results of 0.5 inch cases. Efficiency to 90% peak load voltage was 69.0% and 67.0% in Cell Nos. 1012 and 1013, respectively. Figure No. 19 shows Cell No. 1013 after discharge.

Projecting these results into multicell operation, it would be possible to fabricate a 24-volt system using the present hardware dimensions. With only slight changes in cell block and case, it would be possible to produce a 28-volt unit with energy output in the order of 7 to 8 watt-hours per pound.



Figure No. 20 shows the 28-volt, 14-cell unit fabricated as a result of single cell tests. This unit (No. 121) proved sub-standard in regard to efficiency. Data recorded during discharge included pressure and A.C. impedance which indicated the premature voltage drop was due to boiling of the electrolyte from the cells. Open circuit readings remained normal for the 14-cell unit which further indicates electrolyte limitation.

It is theorized that excessive heat was generated by the additional cells (increased cathode active material), and that the reduced cell volumes contribute to faster boiling. To establish the validity of this theory, Battery No. 122 was fabricated using the 0.250 inch cell design with only six cells in the 14-cell case. Each cell was separated by one cell width, thus limiting excess heat build-up in any one cell. Although it may be possible to obtain good operation from the 14-cell unit by pre-ammoniation, it was deemed necessary to first establish that the 0.250 cell design would function satisfactorily in multicell operation.



14 MULTICELL UNIT BLOCK

- 52 -

1

B. Hardware Corrosion Study

Storage of liquid NH3-KSCN for prolonged periods of time will be important with regard to materials used for battery fabrication. Current batteries are mild steel and stainless steel, depending on availability of components, and is of little significance at this stage of development.

Storage coils were fabricated, however, to study dependability over extended time periods. These coils were mild steel and identical to battery reservoirs in all respects. Storage coils at -65, +165 and +70° F since September 7, 1962 remain satisfactory with no loss of electrolyte. These coils are checked by weight periodically.

C. Cold Activation Problem

Reviewing the problem variance in the activation time found on batteries has led to one possible explanation. The pressure information has been obtained from Battery No. 122 in comparison with parallel data for the silver-zinc BA-472/U battery shown in Figure Nos. 21 and 22, respectively. A new responsive transducer made these data possible. Assuming slower activation batteries behaved similar to No. 121, then filling on activation cannot be the cause. This has been verified by impedance measurements made on Battery No. 104 reported in the First Quarterly Progress Report of the current contract. Therefore, plate activation for D.C. production is varying somewhat. Attempts will be made to isolate and confirm this cause by single cell tests.

D. Low Rate and Screening Tests

No effort has been possible during the current quarter on either of these projects. Additional work is planned, however, for the next quarter.



i

- 54 -



1

- 55 -

E. AC Impedance Measurements Interpretation

It is deemed of sufficient interest to detail current thinking on the interpretation of AC impedance and its relation to the DC discharge. It is hoped that the difficulty outlined herein will generate comments that will lead to a more definitive method.

At one time, it was believed that AC impedance (using the resonant frequency) could be used as the ohmic component for DC circuit. This has been expressed by Drs. Ernest Yeager and John Yeager (Enlarged Abstracts, Theoretical Division, Electrochemical Society, Indianapolis meeting, pp. 5-8, April 30-May 3, 1961). In the present application to ammonia batteries, the conclusion is now reached that this is not the case. At the moment of activation (as well as during steady state discharge), two possible paths exist for the passage of the 10,000 cps measuring current (across a single cell 0.5 ampere at 0.030 to 0.050 volt).

(1) An electronic conducting path at both electrodes that may or may not be necessarily involved in DC producing mechanism;

(2) The surface area that is specifically involved in DC producing mechanism.

It has been assumed that these two surfaces are equal and are identically the same. If the theory of solution mechanism of the non-electronic conducting cathode material (AgC1 and HgSO4) is correct, it is obvious that the conducting ammonia electrolyte being introduced into the cell will result in low conductivities utilizing the electronic conducting surfaces only. If the solution-ion formation step is rate controlling and is appreciably slow, the DC voltage rise under load may be also much slower than the AC impedance change to a steady state value. If the ultimate DC discharging surface is substantially equal to the initial electronic conducting surface, the impedance will remain equal after the DC mechanism has become operative. It is believed safe to predict that the surface involved for the AC impedance will remain equal after the DC mechanism has become operative. It is believed safe to predict that the surface involved for the AC impedance include all the DC surface being utilized, but the converse is not necessarily true. This has actually been observed in batteries where both have been measured simultaneous. The AC impedance has been normal and equal to the steady state value, while the DC voltage (under load) has only reached a small fraction of its normel and steady state value. By the same reasoning, it is concluded that the AC surface, or path, does not necessarily equal the "DC path" and surface during discharge. That is, the cathode electrode may be depleted in active material and the "DC path" may be shrinking in area which obviously should change the DC ohmic resistance, while the AC path would be substantially unchanged, as would also be the resonant impedance. This, of course, leads immediately into concentration and diffusion polarization considerations which involve separate and additional treatment beyond the simpler ohmic resistance and ohmic polarization.

From this reasoning, it is concluded that AC resonant impedance measurement cannot be safely used to monitor the DC ohmic resistance of cells. It is probably a low value as compared to the true ohmic resistance for the actual DC path.

~

•

III. CONCLUSIONS

(1) Initial trials with a "curved" gas generator for this battery indicate a slower ignition and propelling action.

(2) Mechanism of cathode discharge has been theorized as being an initial solution followed by an ion-electron interchange at the electronic surface. The solution ion stage is subject to simultaneous diffusion loss of cathode ions by migration from the electronic conductor surface and ultimate precipitation on the anode.

(3) Based on the processes outlined in (2) above, controlled decreasing percesty in the separator has resulted in approximately doubling the capacity of batteries.

(4) Following this line of reasoning further, the cell geometry has been modified to permit thinner cells without serious loss of capacity. This results in the possibility of doubling the number of cells per unit.

(5) Explanation is presented to explain why single cells discharge longer without shorting than battery operation. That is, the single cell bridging of the silver galvanically precipitated is readily broken, while in the battery, this is not the case.

(6) Based on a series of observations relative to the filling and activation of the -50° C battery, the conclusion is reached that plate fabrication and processing create the observed differences in activation times.

IV. PROGRAM FOR NEXT INTERVAL

A. High Rate Application

1. In the battery development, stress should be placed on consistent activation and capacity, regardless of voltage (cells) of the battery.

2. Perform single cell tests as required in problem-solving for the units under (1).

3. Continue effort toward concentrating the cell structure.

4. Investigate gas generator design and holders for economical space accomodation in the battery.

5. Investigate in more detail single cell activation as a function of fabrication and processing variables.

B. Low Rate Application

1. Investigate S, M-DNB and PbO2.

2. Investigate possible procedures for drying electrolyte, Pb-Na, NaNH₂, MgSCN, MgClO₄, and molecular sieve.

3. Continue investigation of gassing from magnesium to find a system (electrolyte and type magnesium, etc.) that will gas a minimum.

4. Proceed with fabrication of complete cells and multicell units as the research and development indicates.

V. IDENTIFICATION OF KEY PERSONNEL

Ī

÷

Following is a list of key personnel who worked on this project during the second quarter, their job titles, and the number of hours contributed:

NAME	TITLE	MAN-HOURS
Doan, D. J.	Project Supervisor	321
Wood, L. R.	Project Engineer	504
Dittmann, J. F.	Engineering Supervisor	34
Witherspoon, S.	Senior Engineer	249
Sieglinger, G. F.	Senior Engineer	52
Morse, E. M.	Engineering Manager	29
Hodges, K.	Technician	126
	TOTAL	1,315

APPENDIX

1.

Ì

]___

Ι

Ι

I

I

I

Unclassified 1. Cold activation 2. Increased capacity 3. Thinner cells 4. Doubled unit weight	Unclassified 1. Cold activation 2. Increased 3. Thinner 3. Thinner 4. Doubled energy per unit weight
 AD Accession No. The Eagle-Picher Co., Joplin, Mo. RESEARCH ON AMMONIA BATTERY SYSTEM D. Doan, L. Wood Report No. 10, Second Quarterly Progress Report, Contract No. DA:36:039-sc951396, DA 7: 31, 1962, 2004 and proceeder 31, 1962, 2004 and proceeder 31, 1963, 26 pp, illustrations, Lables. From continued investigation into the defining factors involved in cold activation, the conclusion is reached that cathode electrode fabrication and processing variables accounds. Separator development has resulted in increasing capacity and permitting use of thinner cells, both of which result in approximately doubling the energy per unit weight to a maximum of 4.51 watthours per pound. 	 AD Accession No. The Eagle-Picher Co., Joplin, Mo. RESEARCH ON AMMONIA BATTERY SYSTEM D. Doan, L. Wood Beport No. 10, Second Quarterly Progress Report, Contruct No. DA.36:039-cs93183 (Continuation of Contract No. DA.36:039-cs93183 (Continuation of Action of Contract No. DA.36:039-cs93183 (Continuation of A.36:039-cs93183 (Continuation of Activation, the conclusion is tradied in increasing capacity and permitting the second that cathode electrode fabrication and processing variables are causing the veriance of 0.5 second Second Separator development thas resulted in increasing capacity and permitting the second that cathours per pound.
Unclassified 1. Cold activation 2. Increased capacity 3. Thinner eells 4. Doubled unit weight	Unclassified 1. Cold activation 2. Increased capacity 3. Thinner cells 4. Doubled energy per unit weight
ADAccession NoAccession NoThe Eagle-Picher Co Joplin. Mo. The Eagle-Picher Co Joplin. Mo. RESEARCH ON AMMONIA BATTERY SYSTEM D. Doan, L. Wood Report No. 10, Second Quarterly Progress Report, Contract No. DA.36-039-sc89188 (Continuation of Contract No. DA.36-039-sc89188 (Continuation of tables. From continued investigation into the defining fac- tors involved in cold activation, the conclusion is reached to actor desclopment the second to about 3 seconds. Separatofor development use of thinner cells, both of which result in approxi- mately doubling the energy per unit weight to a maximum of 4.51 watt-hours per pound.	ADAccession NoAccession NoThe Eagle-Picher Co., Joplin, Mo. RESEARCH ON AMMONIA BATTERY SYSTEM D. Doan, L. Wood Beport No. 10, Second Quarterly Progress Report, Contract No. DA.36039s-c893198 (Continuation of Contract No. DA.36039s-c893198 (Continuation of Contract No. DA.36039s-c893198 (Continuation of Contract No. DA.36039s-c8935396), DA Froj. No. 3A99-09-001, October 1, 1962 to December 31, 1962, Date of Report January 31, 1963, 26 pp, illustrations. It contract No. DA.36039s-c895396), DA Froj. No. 3A99-09-001, October 1, 1962 to December 31, 1962, Date of Report January 31, 1963, 26 pp, illustrations. Terom continued investigation into the defining factors involved in cold activation, the conclusion is reached that cathode electrode fabrication and processing variance of 0.5 second second cond. Separator development has resulted in increasing capacity and permitting use of thinner cells, both of which result in approximately doubling the energy per unit weight to a maximum of 4.51 watt-hours per pound.

Г

DISTRIBUTION LIST CONTRACT NO. DA-36-039-sc-89188

2

	No. of <u>Copies</u>
Commanding Officer, U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey Attention: Logistics Division (For Project Engineer)	18
Commanding Officer, U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey Attention: SELRA/P	1
Commanding Officer, U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey Attention: Director of Research/Engineering	1
Commanding Officer, U.S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey Attention: File Unit #1	1
Commanding Officer, U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey Attention: Technical Document Center	1
Commanding Officer, U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey Attention: Technical Information Division (For retrans- mittal to accredited British and Canadian Government Representatives)	3
OASD (R&D), Rm. 3E1065, Attention: Technical Library The Pentagon, Washington 25, D. C.	1
Chief of Research and Development, OCS, Department of the Army, Washington 25, D. C.	1
Commanding General, U. S. Army Electronics Command, Attention: AMSEL-AD, Fort Monmouth, New Jersey	3
Director, U. S. Naval Research Laboratory, Attention: Code 2027, Washington 25, D. C.	1
Commanding Officer and Director, U. S. Naval Electronics Laboratory, San Diego 52, California	1
Air Force Cambridge Research Laboratories, Attention: CRZC, L. G. Hanscom Field, Bedford, Massachusetts	1
Rome Air Development Center, Attention: RAALD Griffiss Air Force Base, New York	1
Commanding General, U. S. Army Electronics Research and Development Activity, Attention: Technical Library, Fort Huachuca, Arizona	1

No. ot <u>Copies</u>

Commanding Officer, Harry Diamond Laboratories, Atten-	
tion: Library, Room 211, Bldg. 92, Connecticut Ave.	
& Van Ness St., N.W., Washington 25, D. C.	1
Commanding Officer, U. S. Army Electronics Materiel Sup-	
port Agency, Attention: SELMS-ADJ, Fort Monmouth, N. J.	. 1
Deputy President, U. S. Army Security Agency Board, Arling	2-
ton Hall Station, Arlington 12, Virginia	1
Commander, Armed Services Technical Technical Information	
Agency, Attention: TISIA, Arlington Hall Station, Arlin	
ton 12, Virginia	10
Chief, U. S. Army Security Agency, Arlington Hall Station	•
Arlington 12, Virginia	2
Commander, Aeronautical Systems Division, Attention: ASA	PRL.
Wright-Patterson Air Force Base, Ohio	1
Air Force Cambridge Research Laboratories, Attention: CR	KL-R.
L. G. Hanscom Field, Bedford, Massachusetts	1
Headquarters, U. S. Army Materiel Command, Research and	
Development Directorate, Attention: AMCRD-DE-MO,	
Washington 25, D. C.	1
Commanding General, U. S. Army Electronics Command,	
Attention: AMSEL-RE-A, Fort Monmouth, New Jersey	1,
Commanding General, U. S. Army Combat Developments Command	4.
Attention: CDCMR-E, Fort Belvoir, Virginia	1
Commanding Officer, U. S. Army Communications and Electron	aics
Combat Development Agency, Fort Huachuca, Arizona	1
Director, Fort Mommouth Office, U. S. Army Communications	and
Electronics Combat Development Agency, Fort Monmouth, N.	
Air Force Systems Command, Scientific/Technical Liaison O	ffice
U. S. Naval Air Development Center, Johnsville, Pennsylv	
Corps of Engineers Liaison Office, U. S. Army Electronics	Ree
search and Development Laboratory, Fort Monmouth, N. J.	1
Marine Corps Liaison Office, U. S. Army Electronics Reseat	rch
and Development Laboratory, Fort Monmouth, N. J.	1
AFSC Scientific/Technical Liaison Office, U. S. Army Elect	tronics
Research and Development Laboratory, Fort Monmouth, N.	
Power Information Center, Moore School Building, 200 Sout	h
Thirty-Third Street, Philadelphia 4, Pennsylvania	1
· · · · · · · · · ·	-

÷

T

•··· ·

. .

No. of <u>Copies</u>

Dr. Sidney J. Magram, Physical Sciences Division, Army Research Office, 3045 Columbia Pike, Arlington, Va.	1
Dr. Ralph Roberts, Head, Power Branch, Office of Naval Re- search, (Code 429), Department of the Navy, Washington 25, D.C.	1
Mr. Bernard B. Rosenbaum, Bureau of Ships (Code 340), Depart- ment of the Navy, Washington 25, D. C.	1
Mr. George W. Sherman, Aeronautical Systems Division, Attention: ASRMFP, Wright-Patterson Air Force Base, Ohio	1
Dr. John H. Huth, Advanced Research Projects Agency, The Pentagon, Room 3E157, Washington 25, D. C.	1
Lt. Col. George H. Ogburn, Jr., Auxiliary Power Branch (SNAP), Division of Reactor Development, U. S. Atomic Energy Commi- sion, Washington 25, D. C.	1
Mr. Walter C. Scott, National Aeronautics & Space Adminis- tration, 1520 "H" Street, N.W., Washington 25, D. C.	1
Institute for Defense Analysis, 1666 Connecticut Avenue, N.W., Washington 25, D. C., Attention: Dr. Szego & Mr. Hamilton	1
University of California, Berkeley, California, Attention: Dr. C. Tobias	1
G. & W. H. Corson, Inc., Plymouth Meeting, Pennsylvania, Attention: Dr. J. Minnick	1
Livingston Electronics Division, G. & W. H. Corson, Inc. Essex Falls, New Jersey, Attention: Mr. C. Smiley	1
Melpar, Inc., 3000 Arlington Blvd., Falls Church, Virginia, Attention: Dr. J. F. Ambrose, Research Director	1
Commander, Naval Ordnance Laboratory, Corona, California, Attention: Technical Library (Spindler)	1

ş

Ţ