A THIN-PLATE BATTERY

SUPPLEMENT TO

Eleventh Quarterly Report
on
Molecular Circuit Development

Contract No. NOw 60-0362-c

Submitted to

U. S. DEPARTMENT OF THE NAVY
BUREAU OF NAVAL WEAPONS
Washington 25, D. C.

MELPAR INC
A SUBSIDIARY OF WESTINGHOUSE AIR BRAKE COMPANY
3000 ARLINGTON BOULEVARD FALLS CHURCH, VIRGINIA

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TO

ELEVENTH QUARTERLY REPORT

ON

MOLECULAR CIRCUIT DEVELOPMENT

Period of 15 November 1962 to 15 February 1963

Prepared by

R. T. Foley
J. Smit
H. Titus
M. Hart

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Submitted by

Melpar, Inc.
3000 Arlington Boulevard
Falls Church, Virginia

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1. INTRODUCTION

This supplement describes the technical effort of a program directed toward demonstrating the feasibility of miniaturizing the NOLC liquid ammonia activated cell. The end-object of this program is the utilization of miniaturized cells in a power source which will meet the requirements of the Bureau of Naval Weapons. Specifically, these requirements demand:

a. High energy-to-weight ratio.

b. High energy-to-volume ratio.

c. High current-density drain rates with voltage-output regulation of ±10% for six to ten minutes.

d. Rapid activation.

e. Uniformity of characteristics over the military range of operating temperature.

f. Safety and reliability of operation.

The NOLC liquid ammonia activated cell, utilizing a reducible organic compound at the cathode and a light, active metal anode, has the theoretical capability of meeting the energy requirements. The solvent for the system, liquid ammonia, satisfies the temperature requirements. The transition from a theoretical capability to a practical device, however, involves many practical difficulties. The aim of this program is to accomplish this transition. During the period of this report, the effect on cell performance of the purity and particle size of the active cathode material and the composition of the electrolyte received scrutiny. The study of multiple cell devices was continued. Several new concepts, expected to improve all performance, were also examined.

2. TECHNICAL EFFORT

2.1 Description of Technical Effort

During this reporting period, technical effort has been directed toward improving single-cell performance, constructing and evaluating multiple-cell batteries, and analyzing cell-reaction products.

The initial effort of this period was concentrated on the completion of studies started and proposed during the previous quarter. The study of m-DNB particle size was completed and a follow-up study of m-DNB purity was initiated. In addition, studies relating to electrolytic solution concentrations were begun.

Several multiple-cell, encapsulated batteries were fabricated and evaluated concurrently with the single-cell work. These units were constructed without the tab interconnectors previously used. The devices contained five-five cell series batteries linked internally in parallel. Paragraph 2.2.8 contains a complete description of these units. Fixture-activated, multiple-cell assemblies were also evaluated.

Chemical analysis of extracts of spent cells was continued during this period. The reaction products of replicate cells were studied using thin-film chromatographic techniques. In addition, various cathodic, anodic, and electrolytic materials were evaluated to determine their effectiveness in cell systems. The details of these studies, as well as the pertinent data, are given in subsequent sections.

2.2 Results of Technical Effort

Cell and battery performances are evaluated on the basis of the peak output voltage, the times required for the voltage to drop to 80 percent and to 50 percent of peak value, the energy produced and charge transported during these two time intervals, and the total charge transported to cutoff. The cutoff time is not fixed, but usually occurs after the voltage has dropped below 50 percent of its peak value. The energy-weight ratio is also determined for single cells. This determination is made on the basis of the energy produced during the 80 percent and 50 percent time intervals. The single-cell weight used consists of the spacer weight, the weight of the cathode (carbon and m-DNB), the weight of anode consumed (this includes corrosion loss), and a calculated weight of electrolyte required in the cell as determined by the free volume between the cell anode and the stainless steel cathector. The basis of evaluation is essentially arbitrary, although it has been chosen with ultimate power source design requirements in view.

2.2.1 Particle Size and Ammonia Purity

During the tenth quarterly report period, an improvement in cell performance was noted with the use of a different supply of NH_3. For identification, this ammonia, obtained from the Matheson Co., Inc., was designated supply "B." This supply was analyzed for water content by means of a molecular sieve material and found to contain 0.93% water. To remove this water, the supply was passed through a molecular sieve material before use (this dried supply was designated "C"). Test cells were run using supply "C" against standard cells having m-DNB of random and 150 - 200 (0.0041-0.0029 inch diameter) particle size. These results are given in table I. A comparison, using the average of five runs, between cells having m-DNB of particle size 150-200, and using supplies "B" and "C" ammonia, is given below.

TABLE I

Meta-dinitrobenzene Particle Size

Cathode weight 0.80+0.03 grams. Electrolyte concentration 34% NH_4SCN by weight in NH_3. Ammonia supply "B" having been passed through a molecular sieve. External load 1.01 ohms. 0.006-inch-thick magnesium anode perforated. Activated under equilibrium vapor pressure solution. Cell thickness 0.018±0.001 inch.

Cell No.	m-DNB Particle Size	Peak Voltage (volts)	Time to 80% Peak Voltage (sec.)	Time to 50% Peak Voltage (sec.)	Watt Hours Produced to 80% of Peak Voltage	Watt Hours Produced to 50% of Peak Voltage	Coulombs Transported to 80% of Peak Voltage	Total Coulombs Transported	Total Cell Weight (Grams)	Watt Hours Per Lb. to 80% of Peak Voltage
562	Random	2.02	147	250	0.122	0.174	254	488	1.87	29.7
563	Random	1.98	216	317	0.183	0.230	374	557	1.84	45.1
564	Random	1.96	298	394	0.265	0.310	545	747	1.94	62.1
565	Random	1.93	356	494	0.264	0.311	566	834	2.08	55.4
566	Random	1.97	291	471	0.265	0.346	533	830	2.04	57.0
568	Random	1.86	246	495	0.168	0.246	383	644	1.91	40.0
569	Random	1.96	260	358	0.236	0.281	470	625	2.02	53.0
571	Random	1.86	45	316	0.037	0.176	77	484	1.89	8.9
572	Random	1.88	281	374	0.240	0.280	494	645	2.00	54.5
573	Random	1.99	277	393	0.255	0.312	506	705	1.98	58.5
567	150-200	1.93	295	520	0.245	0.346	519	854	2.00	55.7
575	150-200	1.97	268	351	0.249	0.289	493	630	1.91	59.2
576	150-200	1.95	261	456	0.226	0.318	472	787	1.89	54.3
577	150-200	1.94	294	532	0.262	0.340	519	735	2.01	59.2
578	150-200	2.00	232	310	0.223	0.261	439	568	1.96	51.5

Ammonia supply	Watt hrs/lb to 80% peak voltage	Time to 80% peak voltage (sec)	Peak voltage (volts)
"B"	51.4	256	1.90
"C"	56.0	270	1.96

Because significant improvement is achieved in all three categories, it is evident that the molecular sieve treatment removes some substance or substances deleterious to the system. All tests are now conducted using ammonia-filtered just before use.

2.2.2 Meta-Dinitrobenzene (m-DNB) Purity

Several experiments were conducted in an attempt to correlate cell performance with DNB purity. A series of five single-cell runs were made for cells using cathodes made from each of the three grades of m-DNB: technical, reagent, and recrystallized* material. The results are given in table IIA. An analysis of the runs gives the following results:

Grade of DNB	Average cathode efficiency	Watt hrs/lb to 80% peak voltage	Time to 80% peak voltage (sec)	Peak voltage (volts)
Reagent	28.4	56.0	270	1.96
Technical	29.0	45.8	228	1.92
Laboratory purified	20.7	34.6	177	1.88

It can be seen that the reagent-grade material performed in a manner superior to the other two grades, especially to the highly purified material. An attempt has been made to identify the impurity, the removal of which increases the melting point

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*Recrystallized to constant melting point of 92-93°C with methanol.

TABLE II

A. Meta-Dinitrobenzene Purity

Cathode weight 0.80±0.03 grams. Electroyte concentration 34% NH_4SCN by weight in NH_3. Ammonia Supply "B" having been passed thru a molecular sieve. Particle size (150→200). External Load 1.01 ohms. 0.006-inch-thick magnesium anode perforated. Activated under equilibrium vapor pressure of solution. Cell thickness 0.018±0.001 inch.

Cell No.	Grade of m-DNB	Peak Voltage (volts)	Time to 80% Peak Voltage (sec.)	Time to 50% Peak Voltage (sec.)	Watt Hours Produced to 80% of Peak Voltage	Watt Hours Produced to 50% of Peak Voltage	Coulombs Transported to 80% of Peak Voltage	Total Coulombs Transported	Cell Weight (grams)	Watt Hours Per lb. to 80% of Peak Voltage
589	Purified	1.84	165	399	0.128	0.209	292	604	1.99	29.2
590		1.96	234	333	0.202	0.248	434	601	1.82	50.4
591		1.85	174	294	0.139	0.182	291	498	1.85	33.9
592		1.82	144	249	0.105	0.146	244	480	1.89	25.2
593		1.93	168	270	0.132	0.173	298	452	1.79	34.3
601	Technical	1.81	204	540	0.146	0.270	354	757	1.84	36.0
602		1.88	243	555	0.191	0.315	424	966	1.92	45.2
603		1.99	207	339	0.189	0.251	386	704	1.88	45.6
604		2.03	216	306	0.204	0.249	416	585	1.92	48.2
605		1.91	270	405	0.233	0.282	486	706	1.93	53.9

* Reagent grade found in Table I. (150→200)

B. Picric Acid Cathodes

External Load 1.01 ohms. Cell weight 1.82±0.02 grams. Electrolyte concentration 34% NH_4SCN by weight in NH_3. Activated under equilibrium vapor pressure. Ammonia supply "B" passed through a molecular sieve. Cell thickness 0.018±0.001 inch. 0.006-inch-thick magnesium anode perforated.

Cell No.	Grade of m-DNB	Peak Voltage (volts)	Time to 80% Peak Voltage (sec.)	Time to 50% Peak Voltage (sec.)	Watt Hours Produced to 80% of Peak Voltage	Watt Hours Produced to 50% of Peak Voltage	Coulombs Transported to 80% of Peak Voltage	Total Coulombs Transported	Cell Weight (grams)	Watt Hours Per lb. to 80% of Peak Voltage
615	Picric Acid Cathode	1.54	20	300	0.012	0.082	26	364	50.9	3.0
617	Picric Acid Cathode	1.66	30	222	0.020	0.087	78	364	54.6	4.9

of the "recrystallized" grade over that of the reagent grade. As yet, it remains an unidentifiable, water-soluble, yellow material. Further efforts will be directed toward characterizing the impurity and establishing its role in battery performance.

2.2.3 Effect of Electrolytic Salt Percentage on Battery Performance

With the substitution of NH_4SCN for KCNS as electrolytic salt in the carbon-DNB-magnesium cell, investigations were initiated to determine the most favorable salt-to-solvent ratio. Standard cells were tested using varying percents of NH_4SCN to NH_3.* The results are given in table III. Averaged results for each concentration are tabulated below.

%NH_4SCN to NH_3	Peak voltage	Time to 80% peak voltage	Watt hrs/lb to 80% peak voltage
30%	2.02	200	43.3
33%	1.77	157	24.7
34%	1.96	270	56.0
35%	1.86	260	47.2
40%	1.60	204	24.7
45%	1.36	27	2.4

This evidence indicates superior performance at the 34 percentile range. However, there are several incongruities in these results, e.g., the high peak voltage at 30% and the low watt-hr/lb. figure for the 33% run. It is clear that further investigations must be conducted in this area.

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* i.e., $\left(\frac{\text{weight } NH_4SCN}{\text{weight } NH_3}\right) \times 100$

TABLE III

Electrolyte Concentration

Cathode weight 0.80±0.03 grams. Ammonia supply "B" having been passed thru a molecular sieve. External Load 1.01 ohms. 0.006-inch-thick magnesium andoe perforated. Activated under equilibrium vapor pressure of solution. Cell thickness 0.018±0.001 inch. Reagent grade m-DNB. Total cell weight 1.95±0.15 grams. Particle size m-DNB (150 200).

Cell No.	Concentration NH_4SCN by Weight to NH_3	Peak Voltage (volts)	Time to 80% Peak Voltage (sec.)	Time to 50% Peak Voltage (sec.)	Watt Hours Produced to 80% of Peak Voltage	Watt Hours Produced to 50% of Peak Voltage	Coulombs Transported to 80% of Peak Voltage	Total Coulombs Transported	Current Density (ma/cm^2)	Watt Hours Per lb. to 80% of Peak Voltage
579	30%	2.07	186	285	0.183	0.238	346	510	68.3	42.5
581		1.96	213	494	0.183	0.285	380	680	64.8	41.2
587	33%	1.80	201	513	0.138	0.248	297	736	59.5	31.8
588		1.74	114	468	0.072	0.196	171	603	57.4	17.6
583	35%	1.96	258	360	0.231	0.278	459	611	64.6	54.0
586		1.76	261	579	0.171	0.284	417	880	58.1	40.4
580	40%	1.59	380	509	0.201	0.242	525	735	52.5	45.4
582		1.62	27	402	0.017	0.147	40	494	53.5	3.9
584	45% *	1.35	24	912	0.010	0.169	39	766	44.5	2.1
585		1.36	30	732	0.012	0.126	40	629	44.8	2.6

* 34% Found in Table I. (150→200).

2.2.4 Effect of the Presence of Water on Battery Performance

A brief study of the effect of various amounts of added water on the performance of the magnesium-DNB cell was conducted. Water, ranging from 0.1 to 9 percent by weight of water to weight of NH_3 was added to the electrolyte solutions. The results (table IVA) indicated that, to obtain the highest peak power output, the system should be anhydrous. However, after six minutes of discharge time, the power output is the same within experimental error (figure 1). This phenomenon will be evaluated further in the laboratory. It may be that an electrode reaction product is removed from the surface of the electrode by the added water, allowing the maintenance of a high-voltage output.

Attempts were also made to remove all water from the cathode matrix by drying over P_2O_5 for some time. The results (table IVB) gave no evidence of performance improvement.

2.2.5 Exploratory Cells

All data for cells in this section are given in table V.

a. Experimental Methods of Cathode Preparation

1. Solvents for preparing the slurry: To keep water out of the system, the cathode matrix was prepared from slurries containing acetone and liquid ammonia. Cells 570 and 574 had cathodes made from acetone slurries and cell 599 had a cathode matrix prepared from a liquid ammonia slurry (table 1A). The solubility of DNB in acetone caused the loss of some of this material during pressing of the cathode material, and the performance of the cells with cathodes so prepared indicated that nothing was to be gained by this method of preparation.

TABLE IV

A. Water Addition to Electrolytic Solution

Cathode weight 0.80±0.03 grams. Ammonia supply "B" having been passed thru a molecular sieve. External Load 1.01 ohms, 0.006-inch-thick magnesium anode perforated. Activated under equilibrium vapor pressure of solution. Cell thickness 0.018±0.001 inch. Reagent grade m-DNB. Total cell weight 1.95±0.15 grams. Particle size m-DNB (150→200). Electrolyte concentration 34% NH_4SCU by weight in NH_3.

Cell No.	Percentage Water to NH_3 in Electrolytic Solution	Peak Voltage (volts)	Time to 80% Peak Voltage (sec.)	Time 50% Peak Voltage (sec.)	Watt Hours Produced to 80% of Peak Voltage	Watt Hours Produced to 50% of Peak Voltage	Coulombs Transported to 80% of Peak Voltage	Total Coulombs Transported	Current Density (ma/cm^2)	Watt Hours Per Lb. to 80% of Peak Voltage
609	8.69	1.29	441	1098	0.151	0.276	510	1183	43.0	35.7
610	5.46	1.44	357	949	0.165	0.208	479	660	47.6	38.6
611	2.09	1.82	317	423	0.200	0.241	491	768	60.5	47.7
612	5.46	1.50	351	447	0.177	0.203	487	600	49.6	42.3
613	1.00	1.83	23	354	0.016	0.170	39	552	60.3	3.9
614	0.45	1.91	192	360	0.158	0.240	406	635	63.0	38.0
616	0.18	1.71	363	654	0.216	0.316	550	900	50.5	50.5
618	0.09	1.99	227	432	0.208	0.291	418	702	65.6	49.1

B. Drying of Cathode Matrix

Cathode weight 0.80±0.03 grams. Ammonia supply "B" having been passed thru a molecular sieve. External Load 1.01 ohms. 0.006-inch-thick magnesium anode perforated. Activation under equilibrium vapor pressure of solution. Cell thickness 0.018±0.001 inch. Reagent grade m-DNB. Total cell weight 1.95±0.15 grams. Particle size m-DNB (150→ 200). Electrolyte concentration 34% NH_4SCN by weight in NH_3.

620	Dried over P_2O_5	1.95	183	326	0.154	0.220	314	528	64.3	37.1
621	Dried over P_2O_5	2.01	210	303	0.194	0.238	380	543	66.3	47.9

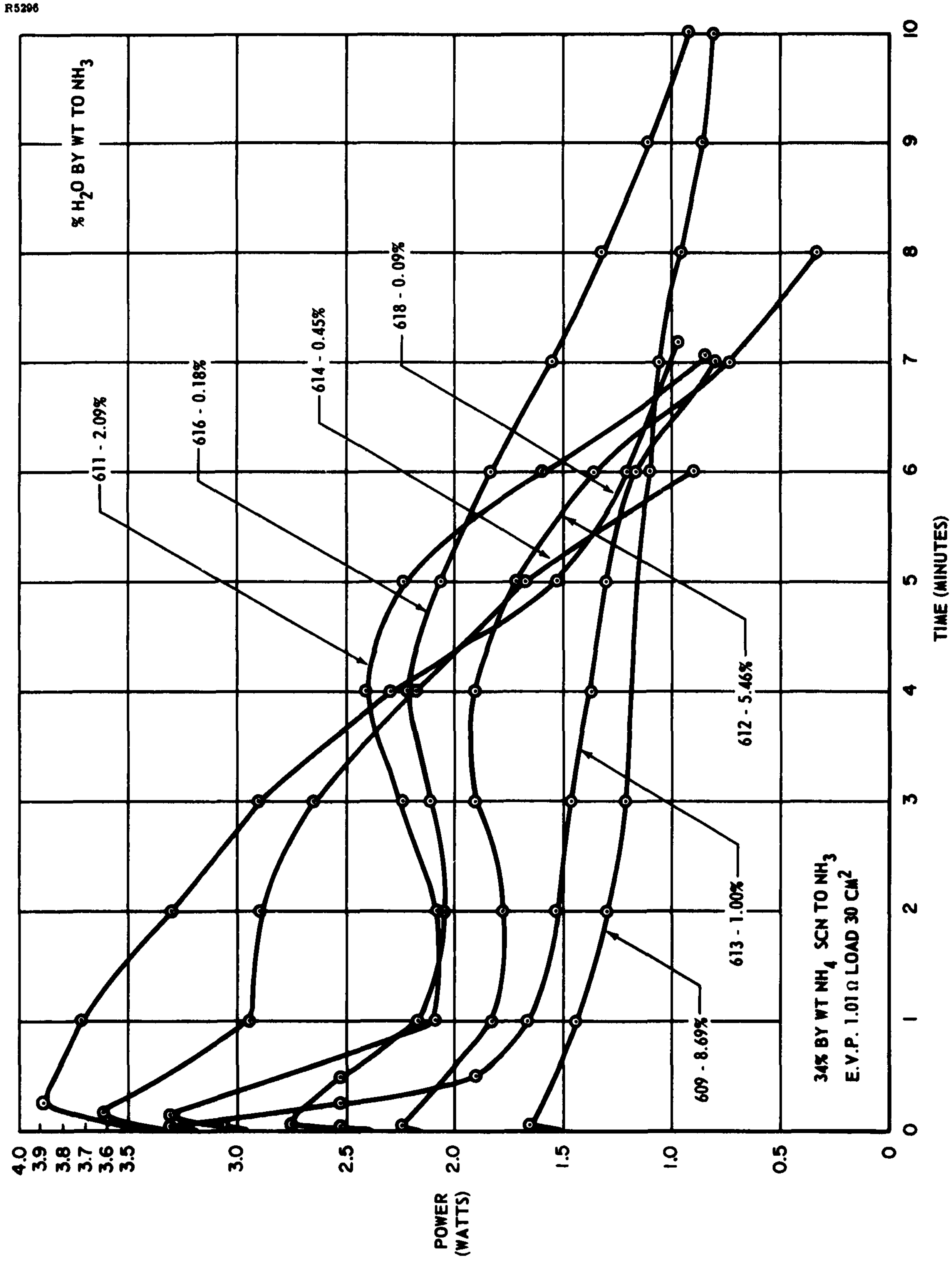

Figure 1. NH_3-H_2O Series

TABLE V

Exploratory Cells

A. Experimental Cathode Mixes

Ammonia supply "B" passed through a molecular sieve. Cell thickness 0.018±0.002 inch. 0.006-inch-thick magnesium anode perforated. External load 1.01 ohm except where noted. Electrolyte concentration 34% by weight in NH_3. Activated under equilibrium vapor pressure.

Cell No.	Type of Cathode	Peak Voltage (volts)	Time to 80% Peak Voltage (sec.)	Time to 50% Peak Voltage (sec.)	Watt Hours Produced to 80% of Peak Voltage	Watt Hours Produced to 50% of Peak Voltage	Coulombs Transported to 80% of Peak Voltage	Total Coulombs Transported	Watt Hours Per Lb. to 80% of Peak Voltage
597	Graphite treated with HNO_3: 200 ohm Load; 167 Peak Voltage; 10 sec. to 80%; 552 sec. to 50%.								
597	Acetylene Black treated with HNO_3: 200 ohm Load; 2.02 Peak Voltage; 363 sec. to 80% Peak Voltage; 1404 sec. to 50% Peak Voltage								
599	DNB Deposited by Evaporation of Ammonia Solution	1.81	159	324	0.124	0.184	277	544	31.5
600	Cathode Matrix Prepared with HNO_3 in Place of H_2O	Very short life; Beyond reasonable calculations.							
570	Cathode Matrix Prepared with Acetone in place of H_2O	1.86	29	408	0.025	0.184	46	553	6.1
574	Cathode Matrix Prepared with Acetone in place of H_2O	1.81	183	390	0.135	0.215	300	644	31.9
606	Adsorption of Cathode Material on Carbon	1.68	57	357	0.037	0.130	91	509	10.6
607	Adsorption of Cathode Material on Carbon	1.45	58	162	0.034	0.061	105	269	8.0
608	Adsorption of Cathode Material on Carbon	1.93	47	180	0.039	0.087	78	358	10.3
619	Adsorption of Cathode Material on Carbon	1.92	99	339	0.080	0.186	168	570	18.9
620	Adsorption of Cathode Material on Carbon	1.99	186	289	0.167	0.216	346	532	44.4

B. Magnesium - Lithium Alloy

Activated under equilibrium vapor pressure; External Load 1.01 ohms. Electrolytic concentration 34% NH_4SCN by weight in NH_3. Cell thickness 0.018±0.001 inch. Ammonia supply "B". 150-200 Reagent Grade m-DNB.

Cell No.	Type of Cathode	Peak Voltage (volts)	Time to 80% Peak Voltage (sec.)	Time to 50% Peak Voltage (sec.)	Watt Hours Produced to 80% of Peak Voltage	Watt Hours Produced to 50% of Peak Voltage	Coulombs Transported to 80% of Peak Voltage	Total Coulombs Transported	Watt Hours Per Lb. to 80% of Peak Voltage
557	Plain Anode	1.59	20	510	0.0123	0.135	40	506	3.0
560		1.95	292	516	0.258	0.354	516	895	61.4
561	Perforated Anode	1.93	170	459	0.145	0.254	300	646	33.6

C. Electrolytic Solutions

Cell thickness 0.018±0.001 inch. 0.0006 inch Magnesium anode perforated. Reagent grade m-DNB. Particle size 150-200.

Cell No.	Electrolyte	External Load (ohms)	Activation Pressure (PSI)	
554	NH_4NO_3 - NH_3	1.01	E.V.P.	Low Peak Voltage - Negligible Results
555	NH_4NO_3 - NH_3	1.01	E.V.P.	Low Peak Voltage - Negligible Results
623	NH_4SCN - CH_3CN	500	50	Peak Voltage 0.46 volts - Negligible Results
624	NH_4SCN - CH_3CN	500	50	Peak Voltage 0.76 volts - Length of Run 90 hours with slow voltage deterioration

2. Carbon treated with nitric acid: Nitric acid was adsorbed onto carbon black (cell No. 598) and on graphite (cell No. 597) to determine if this nitro group would perform as a cathode material. The acetylene black, which would have adsorbed more acid, did actually have a higher potential and a longer life. When nitric acid replaced water in the formation of the slurry for the cathode matrix, the resulting cell (No. 600) performed very poorly.

3. A small amount of nitrocellulose has been considered as a binder for the cathode matrix, so it was informative to discover if this material would contribute any energy to the output of a cell. The energy contribution of this material is demonstrated by cell No. 607.

4. Adsorption of DNB on carbon: Because the particle size of DNB was found to be significant in the performance of the ammonia battery*, it was of interest to investigate the performance of DNB adsorbed onto carbon black and graphite from a solution of DNB in acetone. The type of carbon and the concentration of the acetone solutions are given below:

Cell No.	Type of Carbon	Concentration of DNB in Aceton
606	Graphite and Carbon Black	3 gm/100 ml
608	Carbon Black	3 gm/100 ml
619	Graphite and Carbon Black	Saturated Solution
620	Carbon Black	Saturated Solution

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* A Thin-Plate Battery, Supplement to Tenth Quarterly Report on Molecular Circuit Development.

Cells 606, 608, and 619 contained no ammonium thiocyanate in the cathode matrix, while the cathode matrix for cell No.620 was prepared in the usual manner, except for the omission of DNB.

It is interesting to note that the performance of cell No. 620 was quite similar to that of cells using DNB particles smaller than 200 mesh, both as to peak voltage and energy output to 80 percent of peak voltage.

B. Magnesium-Lithium Alloys

In continuance of a test series initiated during last quarter, three cells employing anodes composed of a Mg-Li (LA 141) alloy* were fabricated and tested. The alloy contains 14 percent lithium, 1 percent aluminum, with the balance magnesium.

This material was shaped into 30 cm^2 anodes and tested against the standard 0.8 gram cathode. One of the cells tested (No. 561) utilized an anode perforated with 350 one-sixteenth-inch holes. The other two anodes were solid faced. Only one run (560) compared favorably with the standard magnesium anode.

C. Experimental Electrolytes

The use of an ammonium nitrate - liquid ammonia electrolyte, 34 weight percent in ammonium nitrate (cell Nos. 554 and 555), caused the cell's output to be quite disappointing. It has been suggested that this is caused by an oxide formation on the magnesium anode.

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*Obtained from Brooks-Perkins Co.

2.2.6 Chemical Analyses

The extracts of a series of cells were analyzed for their main components using thin-film chromatographic techniques*. These cells were all prepared, activated, and discharged under replicate conditions. The analyses were initiated by preparing standard solutions of compounds thought to be present in the extracts. The standards used were m-dinitrobenzene, m-nitroaniline, m-phenylenediamine, p-nitroaniline, and diphenylamine in ethyl acetate solution. Samples of each of the five reference solutions, the battery extract, and a mixture of the m-dinitrobenzene, m-nitroaniline and m-phenylenediamine were then spotted in a straight line about 2 cm from the bottom of chromatoplates. These chromatographic plates were fabricated on glass slides (6" x 6") and contained a 1/4-inch adsorbent layer of a 2:3 mixture of aluminum oxide and silica gel. After spotting, the plates were subjected to an eluting solvent to produce separation. The separations were produced using either an 8% ethyl acetate solution or a 45% H_2O, 45% methanol, 10% ethyl acetate solution. In the final step, spot color reaction was obtained by spraying the plates, first with a 1% solution of Na-glutaconic aldehyde enolate followed by a solution of 10% $SnCl_2$ in concentrated HCL. Chromatograms prepared as described show the presence of m-dinitrobenzene, m-nitroaniline, and traces of m-phenylenediamine. In addition, there appears to be at least two and possibly more unknown constituents in

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*This technique will be reported in detail in a subsequent report.

large quantity in the extract. Approximately 7.5 mg of these unknowns have been collected through separations by column chromatography. This material will be prepared in pellet form for infrared analysis. A nitrogen analysis will give support to any information obtained from the infrared spectra.

2.2.7 Multiple-Cell Evaluation, Fixture-Tested

Three types of multiple-cell assemblies were fabricated and fixture tested. These multi-cell assemblies can be characterized as being bimetal series, laminate series, and laminate series-parallel batteries. The unit cell characteristics of all assemblies are similar to the characteristics of the standard single cell, except where noted. The bimetal series battery assembly contained a nickel-plated 0.006-inch thick magnesium electrode. The cathode matrix was prepared on the nickel surface of this electrode. The completed electrode is a bimetal anode-cathode combination. This combination was placed between a standard cathode and a standard magnesium anode in the test picture. The final assembly was a two-cell series battery. The inter-cell spacing was 0.017 in. to 0.018 in. in the two devices fabricated. The discharge characteristics of the units and of all other fixture-tested units are given in table VI. The peak closed-circuit voltage in both cases was low and the time to 80% of peak voltage short. (Runs BF-2 and BF-3.)

The laminate series battery assembly contains electrodes formed by spot welding 0.006 inch thick magnesium discs to 0.0015-inch thick stainless steel discs. The cathode matrix was prepared on the stainless steel surface of this combination. The laminated anode-cathode combination was placed in the test

TABLE VI

Fixture Tested Batteries

Electrolyte concentration 34% by weight NH_4SCN to NH_3. Reagent grade m-DNB (150 → 200) particle size.

Battery No.	Type of Battery and Electrical Rating	External Load (ohms)	Peak Voltage (volts)	Cell Thickness (inch)	Current Density (ma/cm^2)	Time to 80% Peak Voltage (sec.)
F-B.1	4 Volt -2 Amp: Series	2.0	3.84	0.018	64.0	186
F-B.2	4 Volt -2 Amp: Series (Ni plated Magnesium)	2.0	2.66	0.017	44.2	45
F-B.3	4 Volt -2 Amp: Series (Ni plated Magnesium	2.0	2.78	0.018	46.4	108
F-B.4	10 Volt -4.5 Amp: Series Parallel	3.3	5.75	0.018	Negligible Results	
F-B.5	10 Volt -4.5 Amp: Series Parallel	3.3	6.00	0.040	Negligible Results	
F-B.6	10 Volt -1 Amp: Series	10.2	8.90	0.018	Negligible Results	
F-B.7	10 Volt -1 Amp: Series	10.2	9.30	0.040	31.0	515
F-B.8	10 Volt -1 Amp: Series	10.2	9.60	0.040	31.4	542
F-B.9	10 Volt -1 Amp: Series		Instrument Failure			
F-B.10	10 Volt -1 Amp: Series	10.2	9.65	0.040	31.6	500

fixture as described above. The inter-cell spacing was 0.018 inch. A two-cell series battery fabricated in this manner produced 1.92 volts per cell at a current density of 64 ma/cm^2 when activated with a 34% by weight NH_4SCN in NH_3 electrolytic solution (Run BF-1). The time to 80% of peak voltage was slightly over 3 minutes. A five-cell series battery fabricated in the same manner, except that four laminate combinations were used, produced little output at a cell spacing of 0.018 inch. However, when the cell spacing was increased to 0.040 inch, a similar device operated for a total of 515 seconds to 80% peak voltage at a current density of 31 ma/cm^2 (Run BF-7). Peak voltage for this assembly when discharged across 10.2Ω was 9.30 volts or approximately 1.86 volts/cell. Runs BF-8 and BF-9 verified this result. Laminate 5-cell series assemblies with internal parallel connections did not produce measurable outputs at either 0.018-inch or 0.040-inch cell spacing.

2.2.8 Multiple-Cell Evaluation, Self-Contained

Many practical difficulties have been encountered in the evolution from a theoretical to a practical battery unit. The principal problem involves the transition from the fixture-contained to the self-contained or encapsulated battery unit.

The initial attempt at self-contained battery units was the fabrication and production of six 28-volt, 3-amp, battery packages. Four of these were sent to NOL, Corona, for testing in July 1962, and two were tested in Melpar's laboratory. A description of the preparation of these batteries appears in the ninth quarterly report of this series. Although none of the battery units reached full output, they all did activate and discharge to some extent. An analysis of the test data revealed the following facts:

One of the batteries achieved a peak voltage under load of 10 ohms of 23.2 volts. Energy output to 80% of peak voltage was low in all the battery units, however case failure in the units deteriorated possible performance.

A second group of three 28-volt, 3-amp, batteries was sent to NOL, Corona, for testing in September 1962. A description of these batteries appears in the tenth quarterly report of this series. Severe problems in activation were noted with the composite unit of battery cells.

Six 10-volt, 3-amp, batteries have been prepared during this reporting period. They embrace a different design from the earlier 28-volt, 3-amp, battery packs.

Five packs of five series cells each were stacked in parallel, giving the electrical requirement. The series connections were made by spot welding 0.0015-inch stainless steel cathode substrates to 0.006-inch magnesium sheets. The parallel connections were made through two "S"-shaped designs fabricated of 0.0015-inch thick stainless steel. In one case, the flat areas in the "S" were the stainless steel substrates of the positive connection. In the other, magnesium sheets spot welded to the stainless steel formed the negative connection. The leads were 1/4-inch diameter stainless steel tubing (wall thickness 0.063 inch) soldered to the positive and negative connections.

The feed passage was a 1/4-inch hole in the battery center. The four feed passages of the earlier batteries were used for tie down spots of the 0.050-inch-thick epoxy end plates.

One-tenth-inch, Nylon-coated stainless steel bolts, threaded on both ends, were inserted into the passages. Nuts were placed on the bolts and tightened, allowing measurement of accurate cell thickness. This assembly was then inserted into an epoxy case (wall thickness of 0.075 inch) and fixed into place with epoxy cement. One-eighth-inch diameter Nylon tubing was inserted into the 1/4-inch stainless steel tubing leads for feeding purposes.

Four of these batteries have been tested in Melpar's laboratory and evaluated. Peak voltages under load not exceeding 5.7 volts and short life to 80% peak power were obtained. These results left much to be desired.

When the batteries were sectioned for close observation, it was noted that the major problem appeared to be electrolyte wetting of the plates, very likely being caused by a limited cell thickness. Another difficulty may have been the design of the series-parallel internal circuitry. Further investigations will be designed to eliminate these problems.

3. CONCLUSIONS AND RECOMMENDATIONS

The average energy output to 80% of peak voltage of single cells has been increased to 0.24 watt-hours. This corresponds to a net cell energy/weight ratio of 56 watt hours/lb. By comparison, the output at the end of the previous reporting period was 0.22 watt-hours, or 51 watt hours/lb to the same voltage regulation factor. The improvement was achieved through the use of molecular sieve-treated ammonia. No improvement in cell performance, however, was obtained through the use of a purified grade of m-DNB; rather, the converse was true. Optimum performance, on a single-cell basis, is achieved at this time from cells having the following makeup:

a. Anode -0.006 inch thick, perforated, AZ31B, magnesium.

b. Cathode -0.8 grams of 45% by weight reagent grade m-DNB, particle size 150-200 screen, 45% by weight carbon mix, and 10% by weight NH_4SCN.

c. Solution - 34% by weight NH_4SCN in filtered NH_3.

d. Cell spacing and area - 0.018 inch and 30 cm^2 respectively.

The addition of small amounts of water to the electrolytic solution generally depresses cell performance. The nature of the discharge curves, however, is such that more detailed studies must be undertaken.

Series multiple cell battery assemblies can be activated and discharged using an electrolytic solution which is common to all cell plates. At this time, however, there is some difficulty in achieving satisfactory operation using the thinner intercell spacings. A high-voltage level, approximately

1.9 volts/cell, has been established at current densities of 30 ma/cm^2 using a cell spacing of 0.040 inch. It is clear that the problem lies in the activation of the electrode material.

Much fixture testing of multiple-cell assemblies must be undertaken to establish the best method of activating a close-packed plate assembly. This problem is pertinent to encapsulated devices and is probably the cause for the low performance levels achieved by certain units tested and described in paragraph 2.2.8.

4. PROGRAM FOR NEXT QUARTER

Attention during the next quarter will be given mainly to the fabrication and evaluation of multiple-cell assemblies, both fixture-held and encapsulated. The net single-cell performance is now at a sufficient level at high current densities to warrant concentrating on the investigation of these assemblies. It is desirable now to obtain in the individual cell of a multiple-cell assembly the discharge characteristics of the standard single cell.

Although a series multiple-cell assembly can be discharged satisfactorily at this time utilizing a common electrolytic solution, it is necessary to sacrifice cell thickness. The problem now is to reduce cell thickness and maintain cell performance. The solution to this problem will be sought in a modification in plate geometry and a change in electrolyte feed pass geometry. The effects of modification will be analyzed first in fixture tests. Several encapsulated devices will then be fabricated for evaluation using the geometry which produces optimum performance in the fixture tests.

Prepared by: RTFoley
R. T. Foley
Project Scientist

J Smit
J. Smit
Principal Investigator

MI Hart
M. I. Hart
Senior Scientist

H H Titus
H. H. Titus
Chemist

Submitted by:
C. Feldman
Section Head
Physical Electronics

Approved by:
P. E. Ritt
Vice President-Research