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DEVELOPMENT OF HIGH ENERGY DENSITY PRIMARY BATTERIES 200 WATT HOURS PER POUND TOTAL BATTERY WEIGHT MINIMUM

FINAL REPORT

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-2775

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LIVINGSTON ELECTRONIC CORPORATION

Subsidiary of G. & W. H. Corson, Inc.

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FINAL REPORT

DEVELOPMENT OF HIGH ENERGY DENSITY PRIMARY BATTERIES 200 WATT HOURS PER POUND TOTAL BATTERY WEIGHT MINIMUM

by

William F. Meyers (Principal Investigator)

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-2775

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INTRODUCTION

Statement of Work

This final report describes the research and experimentation conducted under Contract NAS 3-2775 dated May 21, 1963 of the National Aeronautics and Space Administration toward the development of high energy density primary batteries.

The objective of this research program was: "...development of high energy density primary batteries of 200 watt hours per pound of total battery weight minimum."

The scope of work expressed in the contract consisted of two phases, each divided into several tasks.

Phase I

Task A - A selective study of the literature to determine the real problems and the nature of electromotive systems which might be extended to achieve a qualitative gain in battery performance.

Task B - Study of electrolyte systems with emphasis on non-aqueous solvents.

Task C - Experimentation to determine suitable separator materials.

Phase II

Task A - Determination of compatibility of materials of construction with electrochemical system(s) emanating from work in Phase I.

Task B - Assemble experimental cells to demonstrate and evaluate available electrical energy.

BACKGROUND

From 1900 until the 1940's, flashlight and automobile batteries were of a familiar type based on the achievements of Volta, Leclanché, and Planté; but World War II demanded improved performance. This need fostered the engineering of lighter, more powerful batteries.

Until recently, nearly all batteries were based upon the same solvent—water. This unusual and distinctive solvent has the following properties:

1. Stable
2. Non-toxic
3. Inexpensive
4. Forms conductive solutions
5. Resists decomposition fairly well

However, a statistical examination of known aqueous battery performance given in Figure I-1 shows that a continuation of conventional electrochemical effort has less than one chance in a million of reaching 200 watt hours per pound in a primary battery structure.

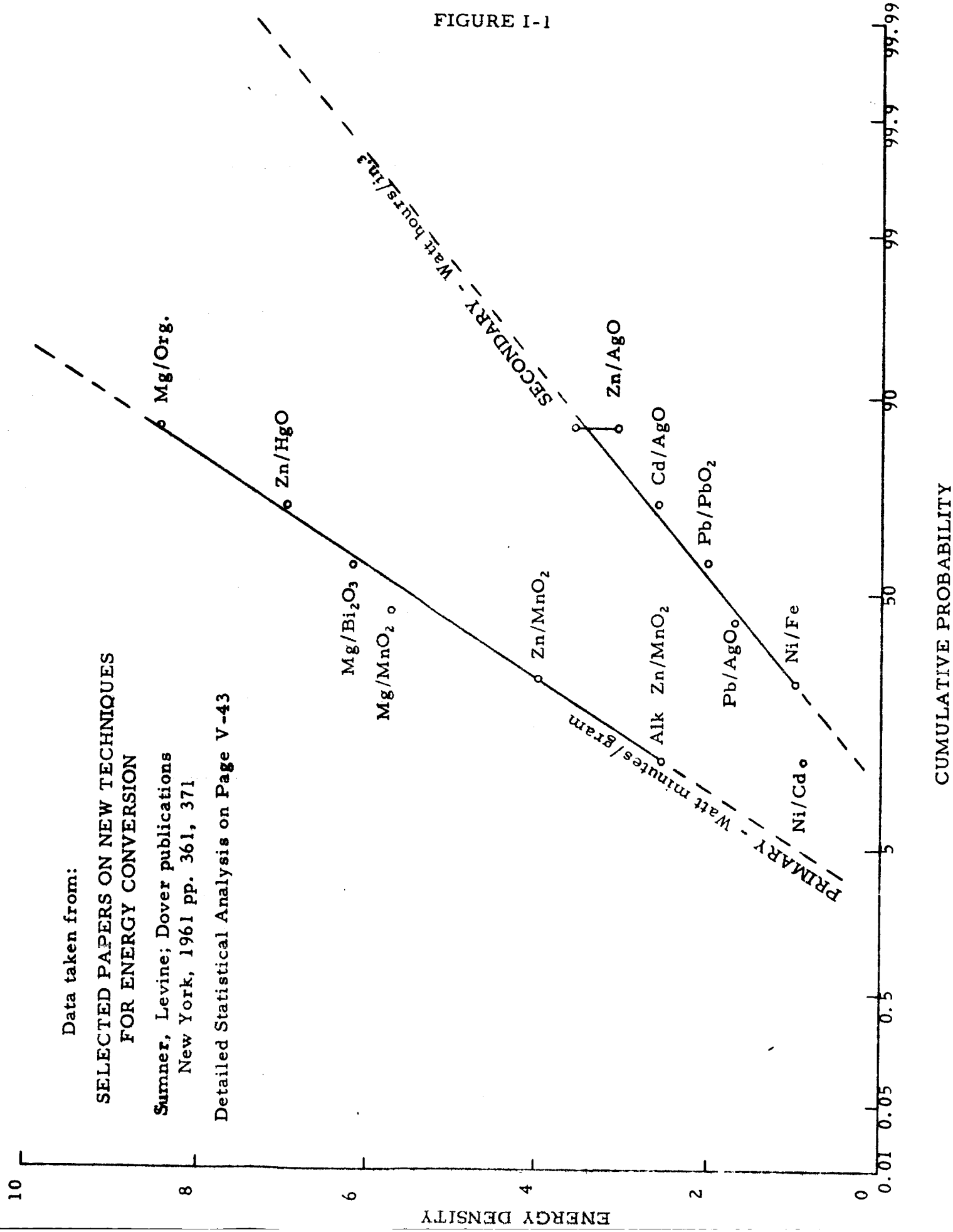
The extremes of space environment, coupled with the need for light-weight high energy batteries, demand revolutionary battery systems. From the point of view of achieving the highest energy per unit weight, the active elements (lithium and fluorine) immediately appear most desirable. In order to make such a system work, solvents must be found that can resist the violence of these light elements.

In the work described herein, we have attempted to avoid being limited by previous disciplines. Our methods have branched from the conventional, and the areas studied have been broad, ranging from new concepts for aqueous batteries to surprising combinations of electrodes, solvents, and atmospheres. Most of these combinations proved undesirable, but a few may far surpass expected aqueous performance.

Due to the great difficulty of obtaining reproducibility in electrochemistry, accepted practice is to work slowly and carefully upon restricted areas until reproducibility and, hence, reliability are obtained. This has, perhaps, led to a lack of general understanding and a welter of isolated facts which lack overall engineering utility. We have, therefore, formulated an extensive approach, realizing that the reliability of any single measurement may have been greatly affected by an obscure impurity or technique important in that particular case. This extensive approach has resulted in a large fund of

RANK-ORDER CORRELATION OF CONVENTIONAL AQUEOUS BATTERY PERFORMANCE

FIGURE I-1



data from which we hope to draw sufficient general understanding so as to focus our efforts in a more conventional and accurate fashion in areas where the probability of success is predictably high. A value of 125 watt hours per pound is presented in the data of Figure II-1, page II-3. We do not claim that even this has been reduced to predictable reproducibility, but rather that it was observed; and so the thinking evolved was practical and should provide combinations suitable for the assigned task.

Prior knowledge was used freely for the organization of the data and its practical utility. If a combination of the first law of thermodynamics—Faraday's law—and Ohm's law has proved to be useful, it matters little if the combination is also provocative.

With these points as a guiding philosophy, the Livingston Electronic Corporation approached the problem of developing a 200 watt hour per pound battery from the direction of the solvent.

SUMMARY

A detailed listing of 99 flat plate cell tests is given in the report (Table III-1, page III-3).

Cell No. 95, $Li/LiClO_4$ in Butyrolactone/$CuCl_2$, gave an energy density of about 125 (watt hours per pound of total battery weight) discharged to 80 percent of peak closed circuit volts as shown in Figure II-1, page II-3.

Similarly, Cell No. 96, $Li/LiClO_4$ in Butyrolactone/CuF_2, provided an energy density of 102 (watt hours per pound of total battery weight).

The program was initiated with a general study of the various tasks, augmented by selected reference to the literature. The references to the literature were confined to studies in the following areas: (1) non-aqueous batteries, (2) separator materials, (3) special cells, (4) materials of construction, (5) statistical, thermodynamic and engineering evaluations to determine favorable areas for high energy density battery performance, (6) non-aqueous electrolytic studies, and (7) non-aqueous theoretical electrochemistry.

This study led to the use of the first law of thermodynamics in the comparison of battery systems. An energy balance was derived permitting the calculation of a figure of merit, W, for battery electrolytes based upon physico-chemical properties which could be measured apart from battery construction. This figure of merit was defined in watt hour per pound units. The overall equation takes into account those factors which may be directly attributed to the electrolyte. Considering the phenomenal number of battery component combinations which are possible, a method of eliminating large numbers of tedious and costly experiments was desired. A method of interrelating the most significant properties of potential electrolytes into a figure of merit anticipating battery performance was evolved by a reasonable investment of effort.

The mass measurement of physico-chemical properties of electrolytes required to implement the method of evaluation was initiated by manual methods and upgraded to machine production. Computation of the data was initially done by hand and later completed by automatic data processing (Table II-3, page II-7). Nine solvents with high figures of merit were selected for more intensive consideration (see Tables II-1 and II-2).

It was decided to accelerate the study of electrochemical systems revealed by the energy balance by means of automatic cell discharge and complex recording equipment. This equipment was designed, constructed, and placed into operation during the last quarter. Details of its functions are presented in this report, and Figure II-2 is an example of a recording of a non-aqueous cell

tested with this research recorder. The advantage of this technique lies in the reliable sub-division of new and different cells into component half cells along with a rather complete presentation of such factors as resistance and polarization.

Insertion of the physico-chemical values for water into the energy balance produced an unexpectedly high figure of merit due to the ionization constant of water. Aqueous cells constructed with alkaline anolytes and acid catholytes (desalination cells in reverse) provided more than four volts until the cathode membranes failed under acid oxidation. Membranes have since been located which should be stable under acid oxidation to allow further exploration of this technique.

Since cathodes are generally the limiting factor in the majority of batteries, several approaches were examined in an effort to make available improved oxidants for electrochemical use.

Pulse catalysis of ions such as ClO_4^- was not demonstrated, but the data indicated probable kinetic benefits for reducing polarization. Some work was also done towards the use of sulfur and organic oxidants as cathode materials in liquid ammonia.

DISCHARGE CHARACTERISTICS OF Li - $CuCl_2$ CELL

CELL #95 OF TABLE III-1

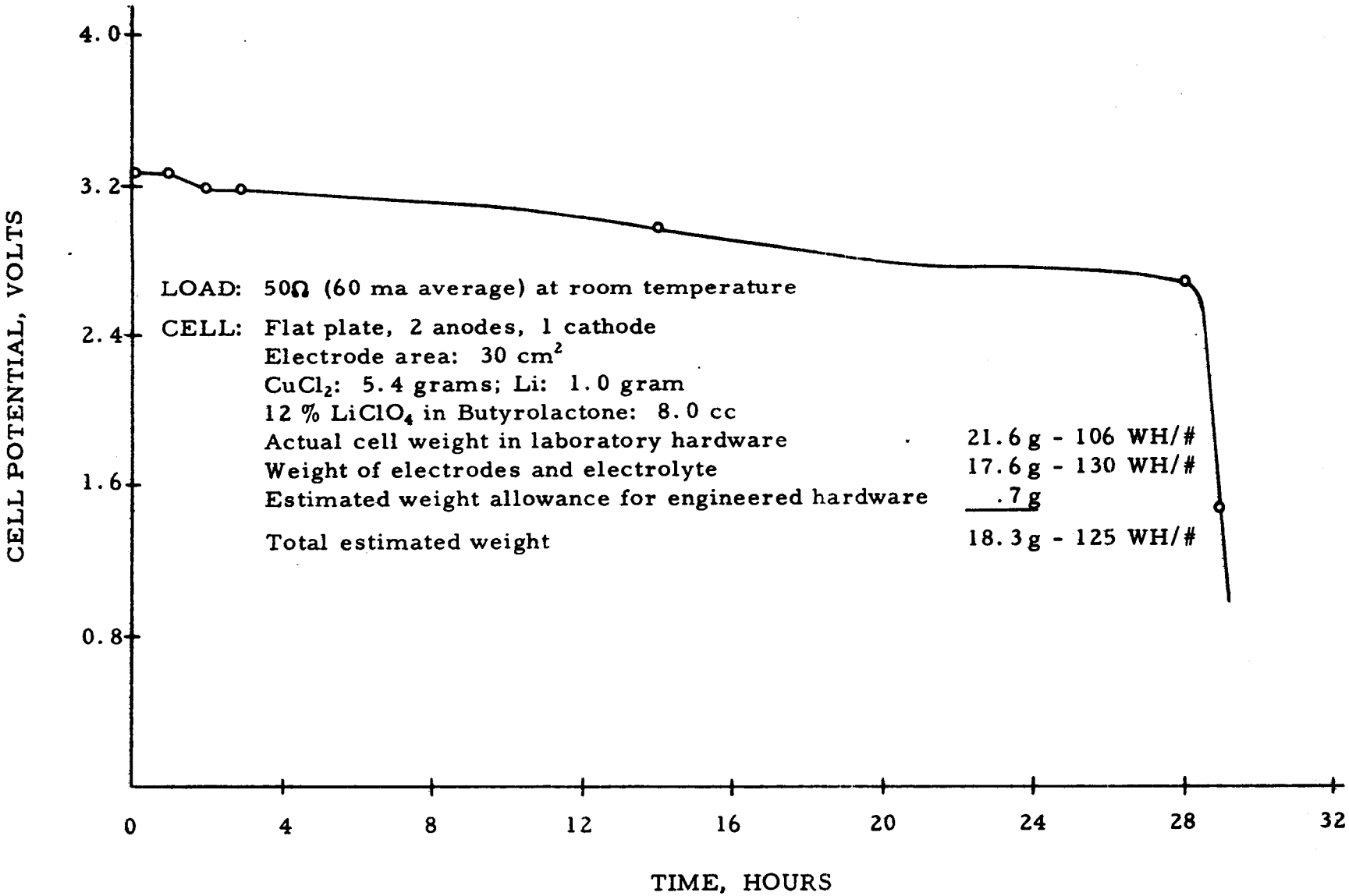


FIGURE II-1

TABLE II-1

SUMMARY OF HIGH ENERGY BINARY SYSTEMS

In the following systems, the figure of merit, "W," was greater than 500 watt hours per pound of combined net electrode reactants.

Acetonitrile

$LiCl$ - $(CH_3)_4NCl$

Butyrolactone

AlF_3 - $Al_2(SO_4)_3$ - NaI - $LiCl$ - $MgSO_4$ - $LiClO_4$

Dimethyl Sulfoxide

$AlCl_3$ - $Al_2(SO_4)_3$ - $LiCl$ - CCl_3COONa

N-Methyl-2-Pyrrolidone

LiF

N, N-Dimethylformamide

AlF_3 - $AlCl_3$ - LiF - $LiCl$ - KBr - KI - NaI - $(CH_3)_4NCl$

Propylene Carbonate

$AlCl_3$ - LiF - $LiCl$ - $MgBr_2$ - AlF_3 - $(CH_3)_4NCl$

Pyridine

$LiCl$

NOTE: The following system yielded a high value for W. Analysis of the data indicated therein is questionable.

N, N-Dimethylformamide

No Solute

TABLE II-2

SUMMARY OF HIGH ENERGY TERNARY SYSTEMS

In the following systems, the figure of merit, "W," was greater than 500 watt hours per pound of combined net electrode reactants.

Acetonitrile/Ammonia

$LiCl$ - $(CH_3)_4NCl$ - KBr

Butyrolactone/Carbon Dioxide

AlF_3 - $AlCl_3$ - $Al_2(SO_4)_3$ - $LiCl$ - KI - $KSCN$ - NaI - $(CH_3)_4NCl$

Dimethyl Sulfoxide/Sulfur Dioxide

$AlCl_3$ - $LiCl$ - NaI - CCl_3COONa

Isopropylamine/Sulfur Dioxide

$AlCl_3$ - LiF - $LiCl$

N-Methyl-2-Pyrrolidone/Carbon Dioxide

$AlCl_3$ - LiF - $LiCl$ - KBr - KI - $KSCN$ - $(CH_3)_4NCl$

N, N-Dimethylformamide/Ammonia

$AlCl_3$*- LiF - $LiCl$ - KBr - KI - NaI

Propylene Carbonate/Carbon Dioxide

AlF_3 - $AlCl_3$ - LiF - $KSCN$ - $NaCl$ - $MgBr_2$

Propylene Carbonate/Sulfur Dioxide

$AlCl_3$ - $LiCl$ - NaI

Pyridine/Ammonia

LiF - $LiCl$

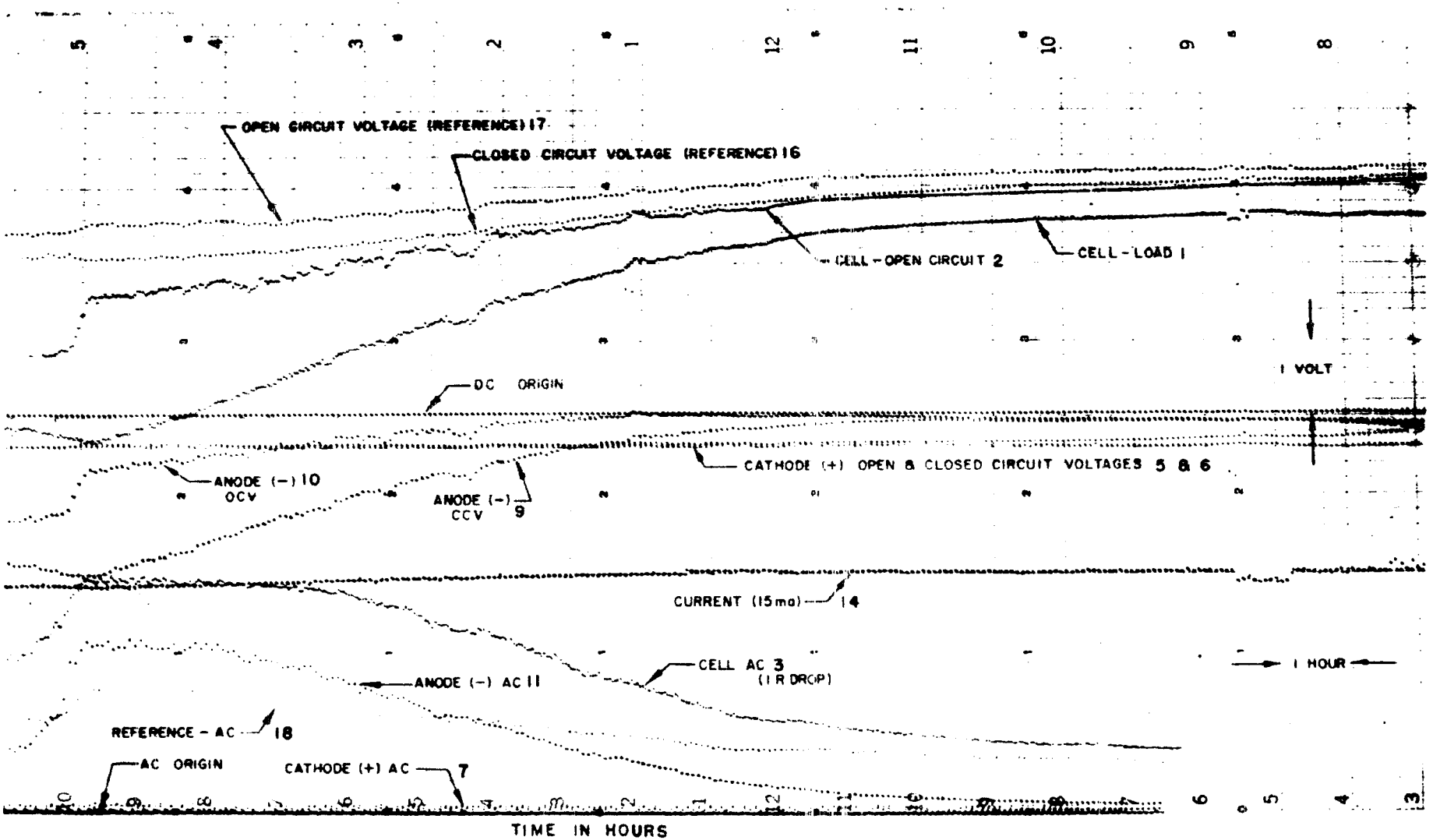
NOTE: The following system yielded a high value for W. Analysis of the data indicated therein is questionable.

Amberlite LA-1/Ammonia

$LiCl$

*see Tables II-3 and II-4, pages II-7 and II-8, 14102.13.

FIG. II-2



LIVINGSTON ELECTRONIC CORPORATION

RESEARCH CELL RECORDING No. 1

SAMPLE PAGE

COMPUTER PRINT-OUT.

TABLE II-3

N-N DIMETHYL FORMAMIDE/AMMONIA
ALUMINUM CHLORIDE

CODE	N	RK	RPK	C	D	E	W
14102.01	0	5.29	10.24	14.36	1.24	5.0	596.
14102.02	20	5.52	9.68			5.7	518.
14102.02	20	5.52	9.68	8.54	.49	4.0	646.
14102.03	40	6.23	11.36			5.3	1108.
14102.03	40	6.23	11.36	9.22	.49	5.0	1049.
14102.04	0	7.48	12.52	9.50	.45	5.5	1480.
14102.05	0	8.79	15.00	12.28	.77	5.5	1354.
14102.06	0	8.31	17.47	13.45	.95	5.5	1159.
14102.07	0	8.24	17.77	12.98	.92	5.5	979.
14102.08	0	9.01	18.40	12.07	.81	5.0	933.
14102.09	0	10.66	19.76	10.18	.60	4.5	812.
14102.10	10	10.83	8.05			5.6	463.
14102.10	10	10.83	8.05	20.68	1.95	5.5	456.
14102.11	40	13.14	18.73		E	LIMIT	EXCEEDED
14102.11	40	13.14	18.73	10.15	.30	6.0	3138.
14102.12	0	13.92	19.23	14.26	.69	6.0	2927.
*14102.13	0	13.92	18.57	10.92	.40	6.0	2973.
14102.14	40	12.93	16.88		E	LIMIT	EXCEEDED
14102.14	40	12.93	16.88	7.12	.07	6.0	3242.
14102.15	40	10.83	13.25			5.6	1488.
14102.15	40	10.83	13.25	7.26	.17	5.5	1776.
14102.16	40	9.68	13.69			5.2	1136.
14102.16	40	9.68	13.69	6.22	.11	5.0	1569.
14102.17	0	9.08	14.03	6.74	.17	5.0	1389.
14102.18	0	9.08	14.63	7.02	.19	5.0	1412.

ACETONITRILE/AMMONIA
ALUMINUM CHLORIDE

CODE	N	RK	RPK	C	D	E	W
13102.01	20	.02	.02			1.4	100.
13102.01	20	.02	.02	1.67	.05	1.0	73.
13102.02	20	.02	.02			1.4	105.
13102.02	20	.02	.02	1.79	.06	1.5	84.
13102.03	20	.02	.02			1.4	110.
13102.03	20	.02	.02	1.90	.08	1.5	99.
13102.04	20	.10	.10			1.4	83.
13102.04	20	.10	.10	1.80	.06	1.0	73.
13102.05	20	.06	.16			1.5	101.
13102.05	20	.06	.16	1.90	.06	1.5	94.
13102.06	20	.08	.14			1.5	98.
13102.06	20	.08	.14	2.03	.08	1.5	94.
13102.07	0	.20	.28	3.74	.36	1.5	70.
13102.08	20	1.31	1.33			1.3	39.
13102.08	20	1.31	1.33	1.85	.08	1.0	59.
13102.09	20	1.26	1.26			1.1	45.
13102.09	20	1.26	1.26	1.48	.03	1.0	73.
13102.10	20	14.63	15.77			.0	.
13102.10	20	14.63	15.77	.63	-.08	6.0	-3300.

COMPUTER PRINT-OUT LEGEND

Code	Code is a number which identifies the system in question. The last two digits of this code represent, in the order of their increase, the ligand pressure applied to the system. Hence, .01 represents an air atmosphere at 14.7 pounds per square inch absolute and the highest digits, the ligand at approximately 90 percent full pressure.
N	N is a code which indicates the curvature of the Tafel plot. N = 0 represents a linear Tafel plot.
RK	RK is the electrolyte specific resistance in K ohms.
RPK	RPK is the electrolyte specific resistance in K ohms under a dc voltage stress of ten volts.
P	P is the ligand pressure in pounds per square inch absolute.
C and D	C and D are the modified Tafel constants representing the Tafel slope and intercept, respectively.
E	E (Also designated as X in the Computer Program) is the cell potential at W, the maximum figure of merit in watt hours per pound. The symbol E was used in the final report in order to employ conventional terminology. However, in Fortran the same symbol has a control function meaning (exponentiation) and hence, X was used as the mathematical argument.

NOTE: Pressure readings have been omitted in certain areas due to adjustments made on the pressure transducer. Values of RK = 51.41 and 4990 represent off-scale readings on the recorder; hence, C, D, X, and W were not calculated. X = ".0" and W = "." indicated that the system in question will not yield energy.

NOTE: Dashed line through values of W indicates figures to be invalid.

NOTE: A "P" of 358 means that the recorder read off-scale.

NOTE: "X Limit Exceeded" indicates that the maximum value of the interfacial voltage was over 6.0 volts.

ELECTROMOTIVE CELL TESTS

The overall purpose of this program is to develop batteries providing increased energy density. Quite naturally, the work began with a critical examination of published literature and internal source material to provide a basis of attack. Following this, much theoretical testing and measurement was accomplished. After analysis of the entire body of data, the construction of laboratory test cells began. The battery test data is presented first, out of chronological order, as it represents the physical product of the year's work.

Cell No. 95, $Li/LiClO_4$ in Butyrolactone/$CuCl_2$, gave an energy density of about 125 [watt hours per pound of total battery weight] discharged to 80 per cent of peak closed circuit volts as shown in Figure II-1, page II-3.

Similarly, Cell No. 96, $Li/LiClO_4$ in Butyrolactone/CuF_2, provided an energy density of 102 [watt hours per pound of total battery weight].

A summary of electrochemical test results is given in Table III-1 and III-2, pages III-3 to III-12.

Table III-1 shows the results of discharge tests with flat-plate cells listing cathode material, construction, separator material, number and weight of lithium anodes, solvent, solute, discharge data, and results of cell inspection at the end of the test.

LEGEND FOR TABLE

Remarks:

1. Ball milled active material for twenty-four (24) hours
2. $LiClO_4$ added to cathode mix (1 part per 12 parts cathode material)
3. Pasted electrode (20% HCl)
4. Glass fiber in place of paper pulp in cathode mix
5. Toluene added to cathode mix

Solvent Code:

BL - Butyrolactone
AC - Acetone
DMF - Dimethylformamide
DMFA - Dimethylformamide treated with ammonia atmosphere

Solute Code:

a - Magnesium perchlorate
b - Lithium perchlorate

Separator Code:

BP - "Efficiency" blotting paper
GM - Glass filter mat
AE-30 - Whatman anion exchange membrane
MR - Microporous rubber

Anode Inspection Code:

A. O.K.
B. Moderately corroded, but appear functional
C. Severely corroded
D. Gelatinous corrosion product
E. Coherent film corrosion product
F. Powdery corrosion product
G. Corrosion of anode via cathodic oxidant
H. Definitely anode failure

Cathode Inspection Code:

A. O.K.
B. Partially wet
C. Surface copper (or other)
D. Weak construction
E. Non-functional (broken lead, etc.)

Separation Inspection Code:

A. O.K.
B. Gelatinous precipitate
C. Treeing - short circuit
D. Physical failure, but no short circuit
E. Treeing, but no short circuit

Electrolyte Inspection Code:

A. Excess and fluid
B. Excess and gelled
C. All absorbed (no excess)
D. Suspended matter

TABLE III-1

ELECTROCHEMICAL CELL TEST DATA

CATHODE						ANODE		ELECTROLYTE				DISCHARGE						INSPECTION				
Cell No.	Active Material	g. a.m. / g. carbon	g. a.m. / g. paper	Grams Mix	Separator	Number	Gram Wt.	Solvent	Solute	Volume, cc	Remarks	Initial o.c.	Load, ma	Time, hrs	Volt Initial cc	Volt Final cc	Volt Average	Anode	Cathode	Electrolyte	Separation	Cathodic Efficiency %
1	$NaBO_3$	6	6	2	BP	2	1.0	BL	a	10		2.92	5	23.5	2.2	0	1.0	C	B	A	A	
2	$NaBO_3$	6	6	2	BP	2	1.0	BL	a	10		2.91	5	21.5	2.3	0	1.0	C	B	A	A	
3	CuS	6	6	2	BP	2	1.0	BL	a	10		3.05	5	67	2.3	0	1.6	C	B	A	C	
4	CuS	6	6	2	BP	2	1.0	BL	a	10		3.2	5	71.5	2.3	0	1.6	B	B	A	A	
5	MnO_2	6	6	2	BP	2	1.0	BL	a	10		3.6	5	33	2.9	0	1.5	H	B	A	A	
6	MnO_2	6	6	2	BP	2	1.0	BL	a	10		3.5	5	25.5	2.9	0	1.3	C	B	A	A	
7	CoF_3	6	6	2	BP	2	1.0	BL	a	10		3.6	5	50.5	3.1	0	1.6	A	B	A	A	
8	V_2O_5	6	6	2	BP	2	1.0	BL	a	10		3.1	5	51.5	2.9	0	2.8	A	B	A	A	
9	CoF_3	6	6	2	BP	2	1.0	BL	a	10			10	27	2.5	0	1.5	B	B	B	A	
10	V_2O_5	6	6	2	BP	2	1.0	BL	a	10			10	21.2	3.3	0	2.5	B	A	B	A	
11	SnO_2	6	6	2	BP	2	1.0	BL	a	10			10	10	2.2	0	1.2	C	A	A	C	
12	SnO_2	6	6	2	BP	2	1.0	BL	a	10			10	10	2.2	0	1.2	C	A	A	C	
13	CuS	6	6	2	BP	2	1.0	BL	a	10	1		10	27	2.5	0	1.6	B	B	A	C	
14	CuS	6	6	2	BP	2	1.0	BL	a	10	1		10	14	2.5	0	1.3	CG	B	A	C	
15	$NiF_2 \cdot 2H_2O$	6	6	2	BP	2	1.0	BL	a	10	1		10	26	2.5	0	1.8	C	B	A	B	
16	$NiF_2 \cdot 2H_2O$	6	6	2	BP	2	1.0	BL	a	10	1		10	23	2.5	0	1.7					

TABLE III-1 Continued

ELECTROCHEMICAL CELL TEST DATA

CATHODE						ANODE		ELECTROLYTE				DISCHARGE						INSPECTION				
Cell No.	Active Material	g. a.m. / g. carbon	g. a.m. / g. paper	Grams Mix	Separator	Number	Gram Wt.	Solvent	Solute	Volume, cc	Remarks	Initial o.c.	Load, ma	Time, hrs.	Volt Initial cc	Volt Final cc	Volt Average	Anode	Cathode	Electrolyte	Separation	Cathodic Efficiency %
17	$NiF_2 \cdot 2H_2O$	6	6	2	BP	2	1.0	BL	b	10	1		10	33	2.4	0	2.0					55
18	$NiF_2 \cdot 2H_2O$	6	6	2	BP	2	1.0	BL	b	10	1		10	33	2.4	0	2.0					55
19	$NiF_2 \cdot 2H_2O$	6	6	2	BP	2	1.0	BL	b	10	2		10	12	2.8	0	1.8	C	B	C	A	
20	$NiF_2 \cdot 2H_2O$	6	6	2	BP	2	1.0	BL	b	10	2		10	18	2.8	0	1.9	C	B	C	A	
21	CoF_3	6	6	2	BP	2	1.0	BL	b	10	2		10	20	2.8	0	1.0	A	B	A	A	
22	CuF_2	6	6	2	BP	2	1.0	BL	b	3			25	5	3.2	0	2.7	B	B	A	B	
23	CuF_2	6	6	2	BP	2	1.0	BL	b	3	2		25	14.5	3.3	0	3.0	B	A	A	E	
24	CuF_2	6	6	2	GM	2	1.0	BL	b	7	2		25	12	3.2	0	2.7	B	B	C	C	38
25	CuF_2	6	6	2	BP	2	1.0	BL	b	3			25	0	3.2	0	2.8	B	B	A	E	
26	CuF_2	6	6	2	BP	2	1.0	BL	b	3			25	0		0						
27	CuF_2	6	6	2	BP	2	1.0	BL	b	3		3.4	25	1.5		0		C	A	C	C	
28	CuF_2	6	6	2	MR	2	1.0	BL	b	7	2		25	11	3.1	0	2.8	B	B	A	E	
29	CuF_2	6	6	2	MR	2	1.0	BL	b	7			25	10	3.1	0	2.6	B	B	A	E	
30	CuF_2	6	6	2	AE 30	2	1.0	BL	b	3			25	5.3	3.2	0	2.2	B	A	B	E	

TABLE III-1 Continued

ELECTROCHEMICAL CELL TEST DATA

CATHODE						ANODE		ELECTROLYTE				DISCHARGE						INSPECTION				
Cell No.	Active Material	g. a.m. / g. carbon	g. a.m. / g. paper	Grams Mix	Separator	Number	Gram Wt.	Solvent	Solute	Volume, cc	Remarks	Initial o.c.	Load, ma	Time, hrs	Volt Initial cc	Volt Final cc	Volt Average	Anode	Cathode	Electrolyte	Separation	Cathodic Efficiency %
31	CuF_2	6	6	2	BP	2	1.0	BL	b	4			25	12	3.3	0	2.8					
32	$NiF_2 \cdot 2H_2O$	6	6	1	BP			BL	b	10			10	20	2.5	0	1.7	A	B	A	A	
33	CuF_2	10.5	10.5	4	AE 30 GM	2	1.0	BL	b	6			25 15	25 11	3.2 3.0	2.5 2.3	3.0 0	B	A	C	A	
34	CuF_2	10.5	10.5	4	AE30 GM	2	1.0	BL	b	6			25	23.5	3.2	0	2.8	G	A	A	E	
35	CuF_2	6	6	2	AE 30 GM	2	1.0	BL	b	7			25 10	7.5 10	3.2 3.1	2.8 0	3.0 2.7	B	B	C	E	
36	CuF2	6	6	2	AE 30 GM	2	1.0	BL	b	7			25 10 10	3.7 3.6 38.8	2.7 2.8 3.2	2.4 2.0 2.8	2.6 2.4 0	D	B	A	E	
37	$NiF_2 \cdot 2H_2O$	6	6	2	BP	2	1.0	DMF	b	7			10	43	2.5	0	1.8	D	B	C	A	75
38	$NiF_2 \cdot 2H_2O$	6	6	2	BP	2	1.0	DMF	b	7			10	35.3	2.5	0	2.0	D	B	C	A	62
39	CuF_2	12	12	3	GM	2	1.0	CH_3NO_2	b	7	2		20	21.2	3.5	0	1.8	C	B	C	E	
40	CuF_2	12	12	3	GM	2	1.0	CH_3NO_2	b	7	2		20	13.2	3.5	0	1.5	C	B	C	E	
41	$CuCl_2$			0.9	BP	2	1.0	BL	b	5	2		20	4.4	2.7	0	1.9	GC	D	B	A	
42	$CuCl_2$			0.9	BP	2	1.0	BL	b	5	2		20	3.3	2.0	0	2.0	GC	D	B	A	
43	CuF_2	13	13	3	BP	2	1.0	BL	b	6	2		20	20.1	3.2	0	2.8	C	B	B	C	36

TABLE III-1 Continued

ELECTROCHEMICAL CELL TEST DATA

CATHODE						ANODE		ELECTROLYTE				DISCHARGE						INSPECTION				
Cell No.	Active Material	g. a.m. / g. carbon	g. a.m. / g. paper	Grams Mix	Separator	Number	Gram Wt.	Solvent	Solute	Volume, cc	Remarks	Initial o.c.	Load, ma	Time, hrs	Volt Initial cc	Volt Final cc	Volt Average	Anode	Cathode	Electrolyte	Separation	Cathodic Efficiency %
44	CuF_2	13	13	3	BP	2	1.0	BL	b	6	2		20	25.8	3.2	0	2.8	C	B	B	A	46
45	CuF_2	13	13	3	GM	2	1.0	AC	b	6	3		20	28.8	2.4	0	1.7	E	A	C	A	52
46	CuF_2	13	13	3	GM	2	1.0	AC	b	6	3		20 5	45.8 8.2	2.4	0	1.8	E	A	C	A	82
47	CuF_2	12	12	3	BP	2	1.0	AC	b	6	2	3.3	20	29	2.5	0.8	1.7	-No Inspection-				50
48	CuF_2	12	12	3	BP	2	1.0	AC	b	6	2	3.4	20	29	2.8	0.2	1.5	-No Inspection-				50
49	CuF_2	12	12	4	GM	2	1.0	BL	a	6	2		15	10.8	3.5	0	2.1	A	A	C	C	
50	CuF_2	12	12	4	GM	2	1.0	BL	a	6	2		15	7.0	3.5	0	1.5	A	A	C	C	
51	CuF_2	12	12	4	GM	2	1.0	BL	a	6	2		15	5.8	3.4	0	2.2	A	A	A	C	
52	CuF_2	12	12	4	GM	2	1.0	BL	a	6	2		15	5.4	3.5	0	2.3	A	A	A	C	
53	CuF_2	12	12	3	GM	2	1.0	AC	b	6	2		25	25.8	2.5	0	1.5	F	A	C	A	
54	CuF_2	12	12	3	GM	2	1.0	AC	b	6	2		25	40	2.5	0	1.8	F	A	C	A	91
55	$CuCl_2$	12	12	3	BP	2	1.0	AC	b	6	2		25	10.3	2.8	0	1.5	E	B	C	A	
56	$CuCl_2$	12	12	3	BP	2	1.0	AC	b	6	2		25	6.5	2.8	0	1.5	E	B	C	A	
57	CuF_2	12	12	3	BP	2	1.0	AC	b	6	2		25	32	2.3	0	1.8	F	A	C	C	
58	CuF_2	12	12	3	BP	2	1.0	AC	b	6	2		25	25.6	2.5	0	1.8	F	A	C	C	
59	CuF_2	12	12	3	BP	2	1.0	50 AC 50 BL	b	6	2		25	20	3.0	0.6	2.4	A	A	B	C	

TABLE III-1 Continued

ELECTROCHEMICAL CELL TEST DATA

CATHODE						ANODE		ELECTROLYTE				DISCHARGE						INSPECTION				
Cell No.	Active Material	g. a.m. / g. carbon	g. a.m. / g. paper	Grams Mix	Separator	Number	Gram Wt.	Solvent	Solute	Volume, cc	Remarks	Initial o.c.	Load, ma	Time, hrs	Volt Initial cc	Volt Final cc	Volt Average	Anode	Cathode	Electrolyte	Separation	Cathodic Efficiency %
60	CuF_2	12	12	3	BP	2	1.0	20 AC 80 BL	b	6	2		25	12	3.3	0	2.2	A	A	B	A	
61	CuF_2	12	12	3	BP	2	1.0	AC	b	6	2		25	0				A	A	B	A	
62	CuF_2	12	12	3	BP	2	1.0	AC	b	6	2		25	23	2.2	0.5	1.6	C	B	C	E	
63	CuF_2	12	12	3	BP	2	1.0	AC	b	6	2		100	6.5	2.6	0	0.9	C	BC	C	C	
64	CuF_2	12	12	3	BP	2	1.0	80 AC 20 BL	b	6	2		25	26.5	2.8	0	2.1	C	BC	C	A	
65	CuF_2	12	12	3	BP	2	1.0	AC	b	5	2		15	44	2.6	0	1.9	CE	BC	C	A	
66	CuF_2	12	12	3	BP	2	1.0	BL	a	5	2		15	30	3.3	0	2.7	B	AC	C	A	
67	CuF_2	12	12	3	BP	2	1.0	AC	b	5	2		210	1.5	3.0	0	2.1	CE	AC	C	A	
68	NiF_2	12	12	3	BP	2	1.0	BL	a	5	2		10	15	2.5	0	1.6	B	A	A	A	
69	NiF_2	12	12	3	BP	2	1.0	BL	a	5	2		10	15.3	2.5	0	1.7	B	A	A	A	
70	NiF_2	12	12	3	BP	2	1.0	BL	a	5	2,4		10	4.1	2.3	0	1.6	B	AD	A	A	
71	NiF_2	12	12	3	BP	2	1.0	BL	a	5	2		10	21.2	2.5	0	1.4	-No Inspection-				
72	CuF_2	6	6	5	BP	2	1.0	BL	a	3.5	2,5		25	18	3.2	1.5	2.7	B	C	A	A	
73	CuF_2	6	6	5	BP	2	1.0	BL	a	3.5	2,5		25	10	3.2	0	2.8	B	C	A	A	
74	CuF_2	6	6	5	BP	2	1.0	BL	a	3.5	2		25	18	3.2	0	2.7	B	C	A	A	
75	CuF_2	6	6	1	GM			BL	b	5			20	10	3.0	2.4	2.9	C	BC	A	A	
76	V_2O_5	6	6	2	BP			BL	a	10			10	10	2.6	0	2.2	B	B	AD	B	

TABLE III-1 Continued

ELECTROCHEMICAL CELL TEST DATA

CATHODE						ANODE		ELECTROLYTE				DISCHARGE						INSPECTION				
Cell No.	Active Material	g. a.m. / g. carbon	g. a.m. / g. paper	Grams Mix	Separator	Number	Gram Wt.	Solvent	Solute	Volume, cc	Remarks	Initial o.c.	Load, ma	Time, hrs	Volt Initial cc	Volt Final cc	Volt Average	Anode	Cathode	Electrolyte	Separation	Cathodic Efficiency %
77	V_2O_5	6	6	0.4	BP			BL	b	10			20	2.5	2.9	0	2.0	A	B	AD	B	
78	CuO	6	6	1.4	BP			BL	b	10	5		10	10	2.2	0	1.0	BD	A	B	B	
79	CuF_2	6	6	4.4	BP			BL	b	10	5		15	34	3.1	0	2.8	CD	BC	AD	AB	
80	CuF_2	6	6	0.9	What.541			BL	b	10	5		200	1.58	2.0	0	1.1	A	A	AD	A	
81	MnO_2	6	6	2.0	BP	2	1.0	DMFA	b	6								B	B	C	D	
82	MnO_2	6	6	2.0	BP	2	1.0	DMFA	b	4.5								B	B	C	D	
83	MnO_2	6	6	2.0	BP	2	1.0	DMF	b	4.5			10	43.5	2.80	0	1.32	B	B	C	A	
84	V_2O_5	6	6	2.0	BP	2	1.0	DMFA	b	6			10	16	1.50	0	1.00	F	B	C	A	
85	V_2O_5	6	6	2.0	BP	2	1.0	DMF	b	4			10	3.8	1.50	0	0.90	F	A	AD	D	
86	V_2O_5	6	6	2.0	BP	2	1.0	DMF	b	4			10	5.5	1.50	0	0.95	F	A	AD	D	
87	SnO_2	6	6	2.0	BP	1	0.5	DMF	b	6								C	BD	AD	D	
88	SnO_2	6	6	2.0	BP	2	1.0	DMFA	b	6			10	14.6	1.50	0	0.69	B	B	C	A	
89	CoF_3	6	6	2.0	BP	2	1.0	DMFA	b	6			10	8.5	1.60	0	1.22	B	B	A	A	
90	$NiF_2 \cdot 2H_2O$	6	6	2.0	BP	2	1.0	DMFA	b	6			10	15.4	1.20	0	0.55	B	B	C	A	
91	$NiF_2 \cdot 2H_2O$	6	6	2.0	BP	2	1.0	DMFA	b	6			10	19.2	2.20	0	1.00	B	B	C	A	
92	Ni_2O_3	6	6	2.0	BP	2	1.0	DMFA	b	6			10	2	0.46	0	0.24	B	B	C	A	
93	Ni_2O_3	6	6	2.0	BP	2	1.0	DMFA	b	6								B	B	C	A	

TABLE III-1 Continued

ELECTROCHEMICAL CELL TEST DATA

CATHODE						ANODE		ELECTROLYTE				DISCHARGE						INSPECTION				
Cell No.	Active Material	g. a.m. / g. carbon	g. a.m. / g. paper	Grams Mix	Separator	Number	Gram Wt.	Solvent	Solute	Volume, cc	Remarks	Initial o.c.	Load, ma	Time, hrs	Volt Initial cc	Volt Final cc	Volt Average	Anode	Cathode	Electrolyte	Separation	Cathodic Efficiency %
94	CuO	6	6	2.0	GM	2	1.0	DMFA	b	6			10	19.4	2.4	0.80	1.00	B	B	C	C	
95	$CuCl_2$	3	20	7.0	AE30 GM	2	1.0	BL	b	8			60	28	3.3	2.8	3.0	A	A	B	A	85
96	CuF_2	6	6	5.0	BP	2	1.0	BL	a	5			30	30	3.2	3.0	3.2	A	A	C	A	55
97	$CuCl_2$	2	20	10.0	What. 541	2	1.0	BL	a				60	23	3.3	2.1	2.8	B	A	B	A	54
98	CuF_2	2	20	10.0	GM	2	1.0	BL	a	5			30	26	3.2	3.0	3.2	A	A	C	A	47
99	CuF_2	2	20	10.0	What. 541	2	1.0	BL	a	5			30	24	3.2	3.0	3.2	A	A	C	A	43

TABLE III-2

PILOT CELLS UTILIZING BUTYROLACTONE SOLVENT

Cell No.	Anode	Electrolyte	Cathode	Separation	Cell Potential, Volts o.c.	10KΩ	1KΩ	.5KΩ	.2KΩ	.1KΩ	Remarks
1	Li	LiCl*	mDNB:C/Ag	Whatman 42	2.5	2.3	2.0				
2	Li	LiCl*	PbO_2/Mg	Whatman 42	3.0	2.0					
3	Mg/Li	LiCl*	mDNB**/Ag	Whatman 42	2.3	1.7					
4	Mg/Li	KCl*	PbO_2/Ag	Whatman 42	3.5						
5	Mg/Li	LiCl*	PbO_2/Ag	Whatman 42	2.8	2.0					
6	Mg/Li	$AlCl_3$*	PbO_2/Ag	Whatman 1	3.2	3.2	3.0	2.8	2.5	2.1	
7	Mg/Li	$AlCl_3$*	Ni_2O_3/Ag	Whatman 1	2.5	2.5	2.4	2.3	2.2	2.1	
8	Mg/Li	$AlCl_3$*	S:C:NH_4SCN/Ag	M 1365	2.8	2.8	2.7	2.4			Anode noticeably attacked.
9	Mg	$MgSO_4$*	mDNB:C/Ag	M 1365	0.9	0.7					
10	Mg	LiCl*	mDNB:C/Ag	Whatman 541	1.5	1.2					
11	Mg	$AlCl_3$*	Ni_2O_3/Ag	Whatman 541	1.8	1.7	1.3				
12	Mg/Li	$AlCl_3$*	Ni_2O_3/Ag	Whatman 541	2.8	2.7	2.6	2.0		1.6	
13	Mg/Li	AlF_3*	Ni_2O_3/Ag	Whatman 541	2.9	2.5	1.4				
14	Mg/Li	KI*	$HgSO_4$/Ag	Whatman 541	2.4	2.4	2.4	2.3	2.1	1.5	
15	Mg/Li	2M KSCN	$HgSO_4$/Ag	Whatman 541	2.6	2.6	2.5	2.5	2.4	2.2	
16	Mg/Li	2M KSCN	$HgSO_4$:C/Ag	Whatman 541	2.7	2.7	2.6	2.6	2.5	2.5	
17	Mg	1M KSCN	$HgSO_4$:C/Ag	Whatman 541	0.9	0.9	0.8	0.7	0.7	0.6	
18	Mg/Li	1M KSCN	$HgSO_4$:C/Ag	Whatman 541	2.7					2.5	

*Saturated Solution

**Solution

TABLE III-2 (Continued)

PILOT CELLS UTILIZING BUTYROLACTONE SOLVENT

Cell No.	Anode	Electrolyte	Cathode	Separation	Cell Potential, Volts o.c.	10KΩ	1KΩ	.5KΩ	.2KΩ	.1KΩ	Remarks
19	Mg/Li	1M KSCN	$HgSO_4$:C/Ag	Whatman 541	2.7					2.4	
20	Mg/Li	.5M KSCN	$HgSO_4$:C/Ag	Whatman 541	2.7					2.5	
21	Mg/Li	.25M KSCN	mDNB:C/Ag	Whatman 541	2.9					2.6	Anode noticeably attacked.
22	Mg/Li	.25M KSCN	mDNB:C/Ag	Whatman 42	2.9					2.4	Anode noticeably attacked.
23	Mg/Li	.25M KSCN	N_2O_3/Ag	Whatman 541	2.7		2.7	2.6		2.3	
24	Mg/Li	.25M KSCN	mDNB:C/Ag	Whatman 541	2.9					2.7	Anode noticeably attacked.
25	Mg	.25M KSCN	2,4-DNT:C/Ag	Whatman 541	0.9	0.9	0.8	0.6		0.4	Anode noticeably attacked.
26	Mg/Li	.25M KSCN	2,4-DNT:C/Ag	Whatman 541	2.9					2.4	Anode noticeably attacked.
27	Mg/Li	.25M KSCN	S:C/Ag	M 1365	2.8	2.8	2.6	2.5		2.1	Purple color on discharge.
28	Mg/Li	.25M KSCN	S:C/Ag	Whatman 541	3.2	2.7	2.6	2.5		2.1	Purple color on discharge.
29	Mg/Li	.25M KSCN	S:C/Ag	Whatman 42	2.8	2.6	2.5	2.4	2.2	2.1	Purple color on discharge.
30	Mg/Li	.25M KSCN	$CuCl_2$:C/Ag	Whatman 42	3.2	3.2	3.2			3.0	Deep purple on discharge.
31	Mg/Li	.25M KSCN	$CuCl_2$:Cu/Ag	Whatman 42	3.2	3.2				3.0	Deep purple on discharge.
32	Mg/Li	.25M KSCN $CuCl_2$*	$CuCl_2$:Cu/Ag	Whatman 541	2.7		2.6	2.6		2.2	Anode strongly attacked.
33	Mg/Li	.25M KSCN	MgO:Mg/Mg	Whatman 541	2.0	1.9	1.5				
34	Mg/Li	.25M KSCN	MgO:C/Mg	Whatman 541	2.4	2.4	2.3	2.2	2.0	1.9	
35	Mg/Li	.25M KSCN	AlF_3:C/Ag	Whatman 541	2.9	2.9	2.7	2.6	2.4	2.2	

*Saturated Solution

TABLE III-2 Continued

PILOT CELLS UTILIZING BUTYROLACTONE SOLVENT

Cell No.	Anode	Electrolyte	Cathode	Separation	o.c.	10KΩ	1KΩ	0.2 KΩ	0.1 KΩ	Remarks
36	Mg/Li	0.25M KSCN	AlF_3:C/Ag	Whatman #541	3.0	3.0	2.8	2.7	2.3	2.6V o.c. after 45 mah discharge
36A	Mg/Li	0.25M KSCN	AlF_3:C/Ag	Whatman #541	3.1		2.9	2.6	2.5	2.7V o.c. after 50 mah discharge
37	Mg/Li	$Mg(ClO_4)_2$*	$CuCl_2$:C/Ag	Whatman #541	3.8	3.8	3.6		3.4	3.0V at 20Ω load, Cu deposition on anode
37A	Mg/Li	$Mg(ClO_4)_2$*	$CuCl_2$:C/Ag	Whatman #541	3.8	3.8	3.6		3.4	2.5V at 5Ω load, Cu deposition on anode
38	Mg/Li	$Mg(ClO_4)_2$*	$CuCl_2$:Cu/Ag	Whatman #541	3.4	3.2	3.0		2.4	Cu deposition on anode
39	Mg/Li	$Mg(ClO_4)_2$*	AlF_3:C/Ag	Whatman #541	3.4	3.4	3.2	3.0	2.8	
40	Mg/Li	11% $Mg(ClO_4)_2$	CuO:C/Ag	Whatman #541	3.4	3.3	3.0	2.7	2.5	
41	Mg/Li	12% $LiClO_4$	Al_2O_3:C/Ag	Whatman #541	3.3	3.3	3.2	2.9	2.8	
42	Mg/Li	12% $LiClO_4$	Al_2O_3:Al:C/Ni	Whatman #541	2.8	2.8	2.6	2.1		
43	Mg/Li	15% KSCN	CuCl/Cu	Whatman #541	2.7	2.7	2.5	2.0		Cu deposition on anode
44	Mg/Li	12% $LiClO_4$	CuCl/Cu	Whatman #541	3.0	2.9	2.7	2.1		Cu deposition on anode
45	Mg/Li	12% $LiClO_4$	$CuCl_2$:C/Ag	Whatman #541	3.6					3.2V at 20Ω load, anode gassing strongly
46	Mg/Li	12% $LiClO_4$	$CuCl_2$:C/Ag	Gelman SA 6404	3.6	3.6	3.5	3.3	3.2	51% cathode efficiency at 100Ω load to 2.5 volts
47	Mg/Li	12% $LiClO_4$	$HgSO_3$:C/Ag	Whatman #541	3.8			3.4		Hg deposition on anode
48	Mg/Li	12% $LiClO_4$	B_2O_3:C/Ag	Whatman #541	3.4	3.4	3.3	3.0	2.8	
49	Mg/Li	12% $LiClO_4$	Ag_2O_2/Ag	Whatman #541	3.6				3.0	Ag deposition on anode
50	Mg/Li	12% $LiClO_4$	Ag_2O/Ag	Whatman #541	3.6				3.0	Ag deposition on anode
51	Mg/Li	12% $LiClO_4$	S:C/Ag	Whatman #541	3.5				3.1	

*saturated solution

During the course of the contract period, a total of about 195 electromotive cells were built and tested. Of these, about 135 were discharged at various loads in order to establish the ability of the electrode materials to quantitatively undergo discharge reactions. The remaining cells were constructed for tests of an exploratory nature, designed to indicate relative electrode potential and to demonstrate compatibility of the electrode materials with the electrolyte.

The majority of tests cells in which electrochemical efficiency was studied had (flat-plate) prismatic construction. Except for a few tests with pasted Cu plates, the cathodes used in these cells were prepared by mixing paper pulp and carbon with the active materials, and pressing the mixture onto an expanded metal support in a steel mold at pressures of 500 to 10,000 pounds per square inch. Lithium anodes were prepared by pressing the metal onto copper or nickel supports. Expanded magnesium sheet anodes were also used. The plates had geometric areas of 1.5 x 1.5 inches; the anode capacity was about 2.0 ampere-hours per plate, while that of the cathodes varied according to the weight of mix used in preparing the positive plates.

In most instances, single-positive, double-negative cells were tested, with cathode mix weights of two to four grams; this construction gave a large theoretical excess of anode material which, together with the Li anode discharge properties indicated by reference electrode measurements, allowed the cells to be considered as positive limiting for the purpose of estimating the cathodic efficiency of the various oxidants tested.

The plates and the separators (ten different separator materials were used) were assembled in polyethylene envelopes, and the latter were heat-sealed to limit contact between the electrodes and the atmosphere. After the electrolyte was introduced with a hypodermic syringe, a moderate compression was applied to the cells in a test stand to insure good contact between the separators and the plates. Discharges were generally performed at constant current; occasionally, constant resistance discharges were also employed. Following the discharge, the cells were opened and the components were inspected.

A number of cells designed to study the efficiency of cathode materials were built utilizing bobbin cathode construction. One part of the cathode material was blended with three (3) parts of graphite, and two (2) grams of the mix poured around a $\frac{1}{4}$" carbon rod to make electrodes 1" high and 0.5" in diameter. Separator paper was used as the outer support for the mix. The

cathodes were assembled with cylindrical Li anodes in glass vials equipped with rubber stoppers. Electrolyte was added to cover the electrodes, and the cells were discharged at constant current.

Pilot cells of TableIII-2used for gaining an early indication of cell potentials in various systems were built with two flat-plate electrodes. A polarization scan at various loads was obtained for the cells, but efficiency figures were usually not obtained because of the type of cathode construction used (dense pressed plates). It was also recognized that some of the open circuit potential values obtained from these tests were erroneous because the graphite which was added to the cathode mix for conductivity purposes was found to have a potential 3.5 volts positive with respect to the lithium anode in some electrolytes.

Two anode materials (Li and Mg), twenty-five cathode materials, eighteen electrolyte-solvent combinations, and ten separator materials were investigated. It was established early in the test program that magnesium has a discharge potential which is positive to lithium by about two volts in the electrolytes employed; consequently, most of the test cells were constructed with lithium anodes.

Of the cathode materials which were studied to date for electrochemical efficiency, the fluorides of copper and nickel, and copper chloride gave the most favorable results. In terms of combined active material weights, the Li-CuF_2 couple has a capacity of 211 ampere hours per pound or 740 watt hours per pound at 3.5 volts. In order to have a cell capable of delivering 200 watt hours per pound an over-all efficiency of 27 per cent would be required. Based on the component weights of the three-plate test cells, an electrochemical efficiency of about 70 per cent for the electrodes is indicated at this performance level (omitting polarization and self-discharge losses). This calculation is given in Table III-3 on page III-16.

It was recognized that cathode construction allowing constant performance and a high degree of utilization of the active material was needed to achieve weight efficiencies of 200 watt hours per pound or higher in the systems under consideration. In some cells, cathodic efficiencies in the order of 70 to 90 per cent were obtained at the 20 to 40 hour rates to 0 final voltage; however, these results were not achieved consistently.

The maximum watt hours per pound figure of 125 was obtained (See Figure II-1 on page II-3) in a Li-$CuCl_2$ cell discharging at the 28-hour rate; while 102 watt hours per pound were obtained from a Li-CuF_2 cell, (Cell No. 96, Table III-1, page III-9) to an end voltage of 80 per cent peak closed circuit voltage.

Towards the end of the program, several tests were performed in order to find means of improving the carbon-paper pulp type of cathode construction. The ratio of the materials in the mix as well as the compressing force were varied; also, additions to the electrolyte and cathode mix to facilitate wetting were evaluated. $LiClO_4$ added to the cathode formulation gave improved efficiency, but was discontinued due to the hazard of blending dry $LiClO_4$ with carbon. Further tests of this type are required in order to evaluate the numerous variables which affect the performance of any particular system.

TABLE III-3

Sample Calculation - Three-Plate Cell

Anode: Li
Cathode: CuF_2
Electrolyte: 12% $LiClO_4$ - BL

$$Li = \frac{26.8}{7} = 3.8 \text{ AH/g}$$

$$CuF_2 = \frac{26.8}{50.5} = 0.52 \text{ AH/g}$$

Material	Weight, grams
Anodes (2)	
Li	1.0 (3.8 AH)
Support (Ni)	0.2
Cathode (1)	
CuF_2	7.3 (3.8 AH)
Carbon	0.6
Paper Pulp	0.6
Support (Ni)	0.6
Electrolyte (9cc)	10.0
Separation	0.2
Envelope	0.5
Cell	21.0 = 0.046 lb.

Efficiency required at 3.5V: $\frac{200 \times 0.046}{3.8 \times 3.5} = .69$

Efficiency required at 3.2V: $\frac{200 \times 0.046}{3.8 \times 3.2} = .76$

Note: One method of specifying an appropriate cut off voltage which has been suggested is: "The cell voltage which is required to provide 200 watt hours per pound at 100% current efficiency." In this instance 2.4 volts would represent this cut off.

RESEARCH CELL AND SEPARATOR RESISTANCE MEASUREMENTS

The study of electrochemical cells is complicated by a general lack of knowledge concerning electrodes in solvents other than water. Numerous techniques are available for measuring the properties of electrodes such as half cells, interrupted or chopped loads, anode controlled cells, cathode controlled cells, etc. Normally, the application of these techniques requires the fabrication, testing, and involved analysis of many special, carefully constructed cells. We have decided to attempt to accelerate the study of the electrochemical systems revealed by the energy balance equation by means of automatic cell discharge and complex recording equipment. This equipment was designed and constructed during the third quarter. Details of its functions were presented. Figure II-2, page II-6 , is a photograph of the recording of the performance of the first non-aqueous cell tested with this Research Cell Recorder.

The application of half-cell and reference electrode techniques in varying solvents and under various atmospheric conditions is subject to practical and theoretical difficulties. One technique for overcoming many of these problems is the use of two pairs of electrodes within the same envelope. Equipment was designed and constructed to make extensive use of this approach.

The technique consists of constant average driven discharge of the cells under a cyclic loading program allowing frequent measurements of open and closed circuit voltages of the complete cell and its individual components as resolved by two reference or auxiliary unloaded electrodes. The two extra electrodes permit division of the complete cell into two half-cells and provide an index of their mutual reliability by comparison of one to the other. Frequent verification of references is necessary for sealed cells and for cells of unusual solvents. In addition, the load current may be chopped at a comparatively high frequency during the load-on half of the duty cycle to provide equally comprehensive ac measurements for cell component resistance evaluation. Since about 16 different measurements are required on a continuous basis, an automatic strip chart recording system is required.

A schematic diagram of the approach which has been formulated for this work is given in Figure III-1, page III-22 . The symbols E_2, E_3, etc. refer to the various automatic recorder functions listed in Table III-4, page III-23. A color-coded strip chart recorder was chosen as the basic instrument. The functions of this basic instrument are determined in accordance with

an external scanning system on a 52-point repetitive cycle to allow for four color coding of the 26 data channels. Alternating current data and cell current are displayed starting from the right-hand edge of the chart extending to the left-hand edge. Direct current voltages are displayed on a zero center scale to accommodate polarity reversal. Since driven discharge is used, exhaustion of one electrode need not terminate measurement of the remaining electrode and the advantages of half-cell techniques are retained. Figure III-2, page III-24, is the schematic diagram of the external stepping switch circuit used to provide this scanning sequence.

Concerning the cell discharge load current wave form, two frequencies are of basic importance. First is the basic on-off repetition rate. It is planned to use a value in the order of twenty seconds, i.e., ten seconds on, 10 seconds off. Each of the four cell terminal combinations will be scanned at the end of a load-on half-cycle and at the end of a load-off half-cycle. The load pattern will, therefore, be orthogonal; and each reading will have a comparable history. The average load current over the entire on-off cycle will be one half of the value for the fifty per cent on-period. The load-on period will also be interrupted, but at a higher repetition rate to retain polarization loss during the short but repetitive off-periods of the basic load-on period. The load-off sub-periods will be of relatively short duration compared to the load-on sub-period.

The current regulator system is of high impedance so as to hold the load current pulses relatively square and of a fixed peak and average value.

RESEARCH CELL RECORDER

The preceeding reasoning was instrumented in the following manner. A cell with its reference electrodes is detailed in Figure III-1. It is captioned "Cell Under Test" in Figure III-2 on page III-24.

Decks 2 and 3 select from cell terminals "A", "a", "C", and "c" the signal source as tabulated in Table III-4 under the heading "Signal Source."

Decks 4 and 5 select the measuring circuit supplying the recorder a signal within its coded range, but proportional to the desired measurement. This is arranged in accordance with Table III-4 under the column "Scale Type." The dc scales are zero center as indicated by an entry of $\frac{1}{2}$ under the "Scale Origin" column. Polarities were arranged so that cell output voltages read upwards from the zero center and reference to working electrodes read downwards for convenience in displaying the data. ac scales are non-polar and originate at the lower margin as indicated in Figure II-2 , page II-6.

Decks 6 and 7 control the three color presentation of the recorded data to allow for direct interpretation.

Deck 1 of the stepping switch programs the load in accordance with the column marked "load" in Table III-4 , page III-23 where 0 represents load-off and + represents load on. Figure III-3 shows the constant average current regulator providing a chopped load.

The schematic of the load control device (current control chassis) is given in Figure III-3 , page III-25 . The current delivered to the working electrodes of the test cells is fed to the stepper switch circuit via terminals Nos. 6 and 7. The high voltage present in the current control is limited at this point to ± six volts by the two 6-volt zener diodes. The two 6L6 vacuum tubes serve as grid-control rectifiers and the constant current generators simultaneously. The value of current supplied is determined by the 10 kilohm potentiometer connected to the control grids of the 6L6's, and keying is accomplished via terminals Nos. 5 and 26 leading to the stepper switch system. These terminals are alternately shorted and off-circuited by switch deck No. 1 of the stepper switch circuit. Consistency of the various wave form values are maintained by the three gaseous regulator tubes OA3, OD3, and OD3. Equality of wave form is adjusted by means of the 100 ohm potentiometer connected between the two cathodes. The 60-cycle sine input of the power

line is transformed to 270 volts rectified and, in effect, clipped to produce a series of nearly square pulses interspersed by short off-periods. It is to be noted that this output is not filtered within the circuit. Such filtering action as the cell provides serves as a measure of the internal ohmic resistance of the cell. The ac measuring circuit of the VTVM in Figure III-2 is calibrated so as to provide an equal response ac and dc when measuring a fixed resistance.

HALF CELL TESTS

Figure II-2 on page II-6 is a photograph of a recording of the first non-aqueous cell tested with this particular instrumentation.

Recorder Channel No. 2 displays the open circuit voltage of the working electrodes at the end of the load-off half cycle.

Recorder Channel No. 1 similarily displays the working electrode closed circuit voltage. Note that at the right-hand edge of the data the separation between the open circuit and closed circuit conditions is relatively small; and at the left-hand side, just prior to decay of the open circuit cell voltage, a substantial separation occurred.

Recorder Channel No. 10 displays the anode open circuit voltage (anode to anode reference voltage) and explains the sharp decline of the cell open circuit voltage.

Recorder Channel No. 9 of Figure II-2, page II-6, shows the closed circuit potential of the anode and indicates that the majority of the decline of cell voltage under load is due to losses associated with the anode.

Recorder Channels Nos. 5 and 6 confirm that the cathode resistance and polarization were negligible throughout the discharge of this cell.

Recorder Channel No. 17 serves to monitor the potential of the reference electrodes by comparing one to the other with the cell on open circuit. Channel No. 16 measures the potential of the reference electrodes when the working electrodes are drawing current. The cell current produces IR drops. In the usual configuration, the reference electrodes will be sensitive to the electrolyte portion of the IR drop; and the difference between Channels Nos. 16 and 17 will represent this decrease in the operating cell voltage.

The ac scales of Figure II-2, Page II-6, are expanded by a factor of three over the dc values in order to make them clearly legible. In additiona, the ac scales, being non-polar, may extend over the full chart width, that is, height on Figure II-2. Recorder Channel No. 3 measures the ac voltage developed between the working anode and cathode. Knowing the current (Recorder Channel No. 14), this may also be converted to an equivalent resistance figure.

The cathode ac voltage is displayed by Recorder Channel No. 7, and, as might be expected from Channels Nos. 5 and 6, is negligible.

Recorder Channel No. 11 displays the anode ac voltage, this shows the majority resistance loss in this cell is located at the anode.

Recorder Channel No. 18 displays an ac Haring voltage developed between the reference electrodes and should be comparable to the separation between Channels Nos. 16 and 17 with the physical relationships of electrodes indicated by the cell in the stepper switch circuit diagram (Figure III-2, page III-24) where the reference electrodes are located outside the working electrodes.

This convenient and direct display of the cell data in the machine-printed form facilitates rapid progress in the testing and evaluation of new and unusual cell compositions.

The test data obtained during this contract period showed that the capacity of the cells is limited by cathode polarization and an increase in the electrolyte resistance. The only exception to this pattern was found in the cell shown in Figure II-2, page II-6. In this case, the lithium anode had become strongly plated with copper causing negative capacity limitation.

FIGURE III-1

SCHEMATIC DIAGRAM OF MULTIPLE RECORDING SYSTEM TO FACILITATE 1/2 CELL STUDIES IN VARIOUS MEDIA

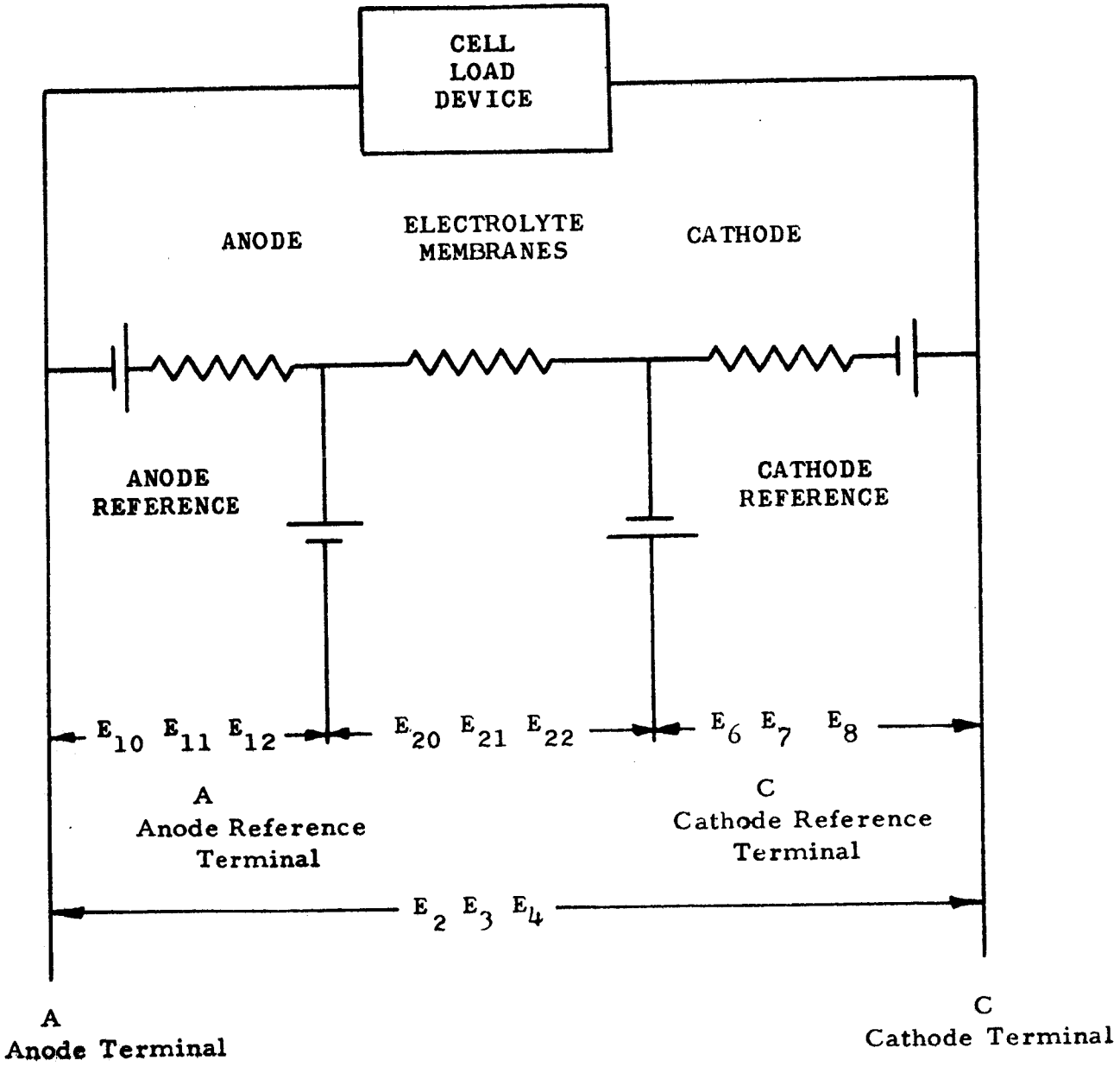


TABLE III-4

RESEARCH CELL RECORDER FUNCTIONS

Scanner Position	Recorder Channel	Load	Scale Origin	Color Code (a)	Scale Type	Signal Source
1	0	0	½	P	----	Open Circuit
2	1	+	½	R	d.c.	Cell
3	2	0	½	R	d.c.	Cell
4	3	+	0	R	a.c.	Cell
5	4	0	0	R	----	Short
6	5	+	½	G	d.c.	Cathode
7	6	0	½	G	d.c.	Cathode
8	7	+	0	G	a.c.	Cathode
9	8	0	0	G	----	Short
10	9	+	-	P	d.c.	Anode
11	10	0	½	P	d.c.	Anode
12	11	+	0	P	a.c.	Anode
13	12	0	0	P	----	Short
14	1	+	½	G	d.c.	Cell
15	2	0	½	G	d.c.	Cell
16	3	+	0	G	a.c.	Cell
17	13	0	0	G	----	Short
18	14	+	0	G	d.c.	Current
19	15	0	0	R	----	Reserved
20	16	+	½	R	d.c.	Reference Electrode
21	17	0	½	R	d.c.	Reference Electrode
22	18	+	0	R	a.c.	Reference Electrode
23	19	0	0	R	----	Short
24	14	+	0	P	d.c.	Current
25	20	0	½	P	----	Reserved
26	21	+	½	P	----	Reserved
1	0	0	½	P	----	Open Circuit

(a) R = red, G = green, P = purple

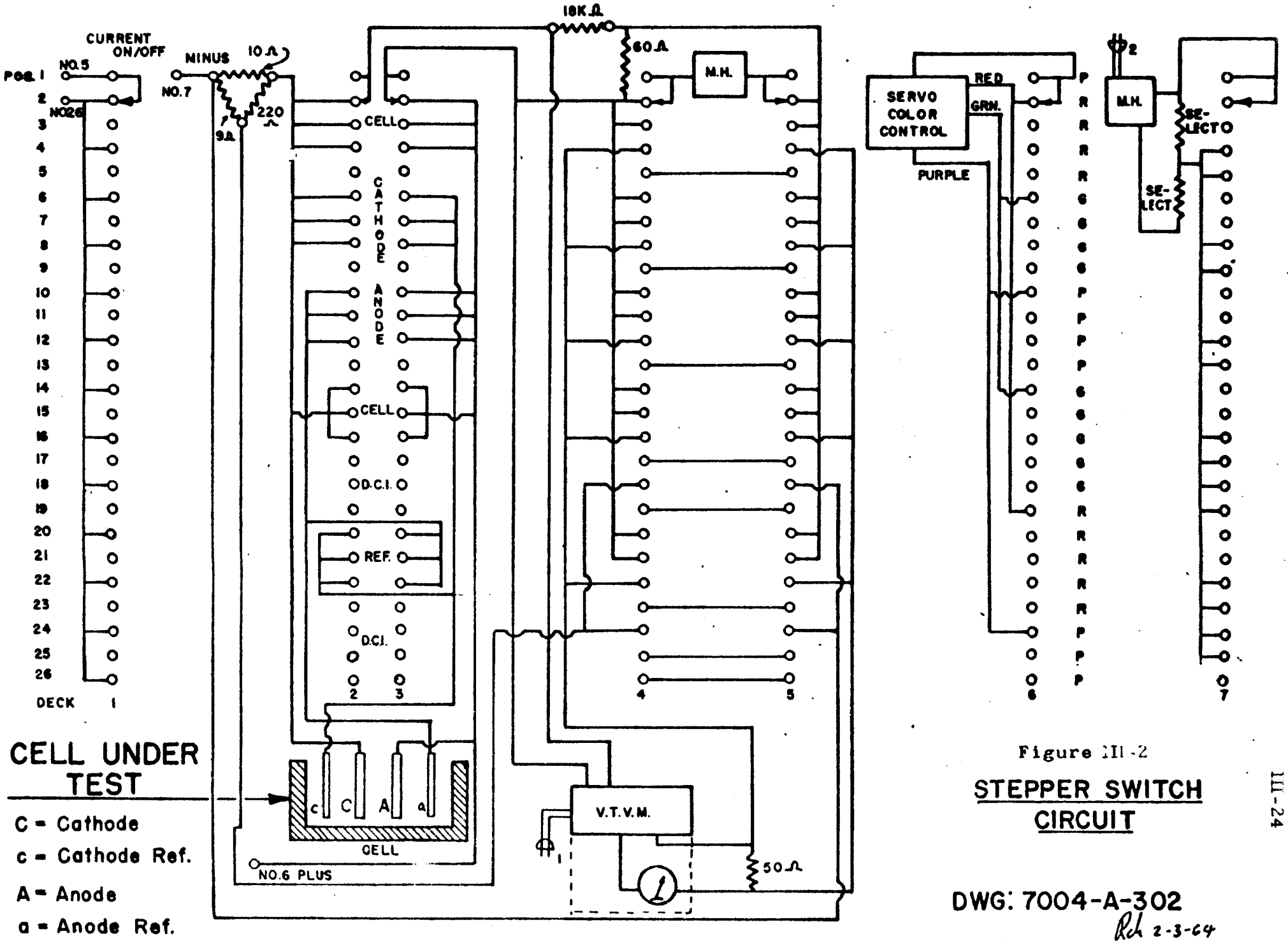
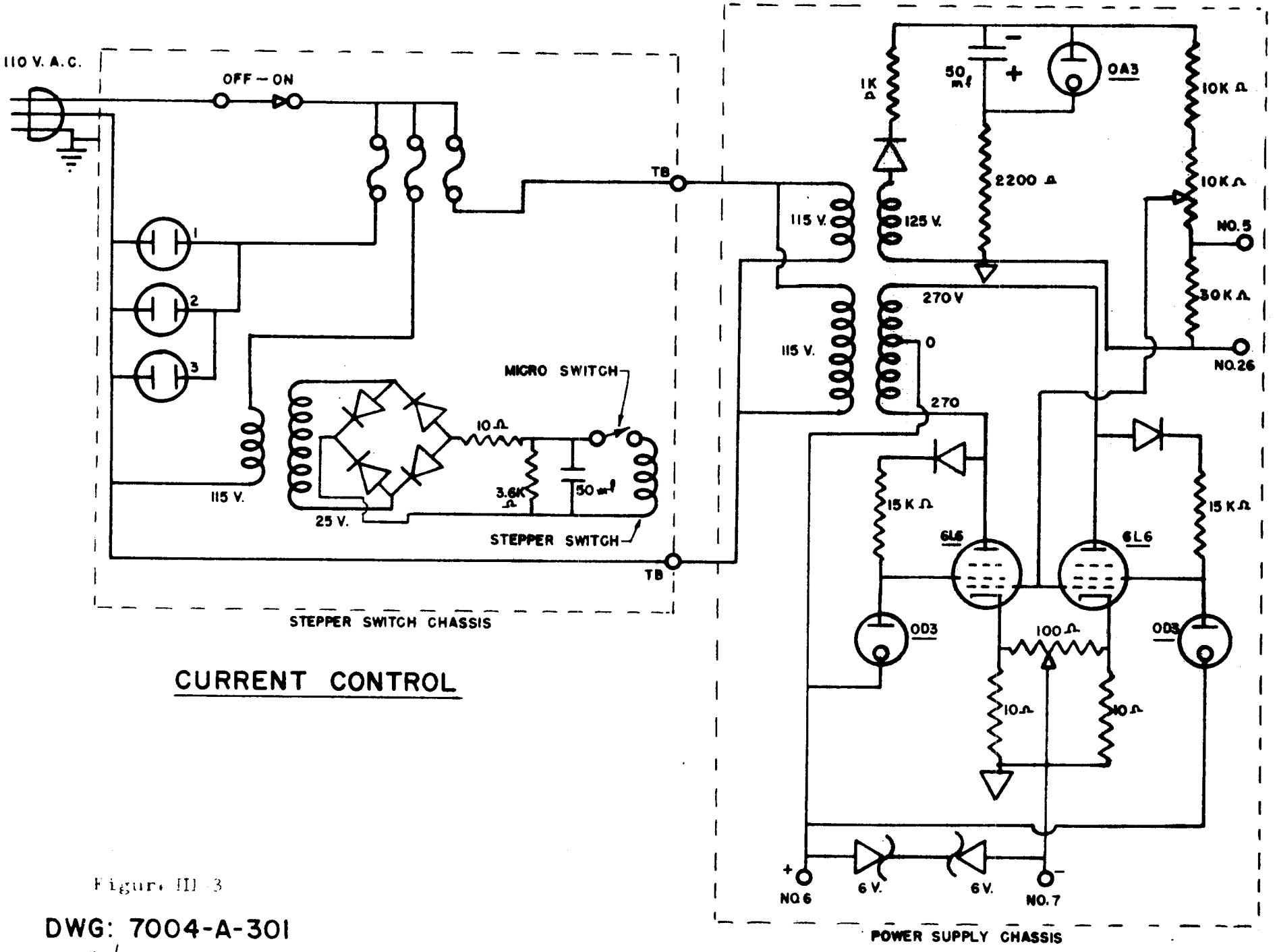


Figure III-2

STEPPER SWITCH CIRCUIT

DWG: 7004-A-302

Rch 2-3-64



CURRENT CONTROL

Figure III-3

DWG: 7004-A-301

Rch 3-2-64

PULSE CATALYSIS

The cathode of a battery is, in general, the limiting electrode. Many suitable active anodes are available. Strong oxidants, on the other hand, are noticeably absent or ineffective for one reason or other. To cite a few examples, the element oxygen is receiving considerable attention via the aqueous fuel cell. The predisposition of this element to react ineffectively and slowly to the peroxide rather than the oxide or hydroxide leads to questioning the availability of the oxygen electrode in its present state. Adding to this, the difficulties of storing oxygen in its elemental form makes oxygen even less likely as a generic cathode material in primary batteries. Sulfur, while an economical solid, has a low potential and a poly-ion chemistry even more difficult to harness than oxygen. Fluorine and chlorine, in the elemental form, present formidable engineering penalties. For this reason, it was decided to consider several unusual approaches toward the role of the cathode in high energy density batteries. One of these constitutes an electronic attempt to utilize the perchlorate and nitrate ions as a storehouse of oxidizing power. The perchlorate ion is well-known for its storagability and effectiveness as an oxidizing agent in fireworks. The nitrate ion is, perhaps, the workhorse oxidizing agent of the chemical industry. In batteries where chemical violence must be carefully restrained, the activation energies associated with unlocking the oxidizing power of the poly-anions is normally not available. However, the intrinsic impedence of the electronic devices is sufficiently greater than the electrical impedance of chemical reactions so that simple circuitry is capable of delivering what might amount to smashing blows, at least for short periods of time. For example, an efficient lithium/fluorine battery might be expected to have an open circuit potential of six volts. Since electronic circuitry can efficiently provide pulses ranging from this level of six volts up to hundreds of volts, it is reasonable to associate solid state circuitry directly with a battery for the sake of improved performance of the overall package.

The purpose of the following series of experiments was to attempt to exploit the electrochemical oxidation of polyoxygen anions. Soluble salts of anions typified by $[ClO_4]^-$ or $[NO_3]^-$ might be expected to fracture when subjected to positive voltage pulses at an inert electrode. One possibility is that three or four nascent oxygens would persist momentarily, bound to the surface of the pulsed electrode.

If this electrode were then switched into a reserve circuit where it became

the cathode with respect to an active anode, the energy return could be greater than that expended to overcome the activation of the complex ion. In order to achieve this process, two conditions must be met, namely, the anion must preferentially decompose before the solvent and the new species created at the pulse electrode must be utilized before they are lost or decay. It was anticipated that the creation of a new species at the pulsed electrode would result in a substantial increase in the voltage between the pulsed electrode and the active anode. In the systems listed in Table III-5 of this section, the majority of the pulse charge was recovered from the pulsed electrode double layer above the background potential of the cell.

The desired effect (an increase in cell voltage above normal open circuit values) was not observed in any of the aqueous systems listed in Table III-5 Therefore, in the work which may be reported to date, no evidence of decomposition of poly-anions is available.

However, in the case of the cell "A" of Table III-5 , an interesting phenomenon was observed which may be of equal importance to the original hypothesis. It was noted, following the decay of the input pulse, that the evolution of hydrogen from the platinum electrode was greatly enhanced. When the discharge of this cell was compared to the magnitude of the pulse, charge gains approaching a hundred-fold were observed. Figure III-4 of this section is a schematic of the cell and circuitry employed. "A" is an active anode, "B" is the pulsed electrode, and "C" is an auxiliary cathode.

At switch position 1, the capacitor is being charged and the active anode is under 100 ohms load with respect to the MnO_2 cathode to prevent film formation on the anode. The active anode and pulse electrode are either under 57 ohms load, referred to as Condition I, or on open circuit, referred to as Condition II.

At switch position 2, the capacitor is discharged through the cell (positive to pulse electrode, negative to the auxiliary cathode).

At switch position 3, the pulse electrode becomes the cathode with respect to the active anode and is discharged through an ammeter of 1 ohm resistance.

Coulombs input were calculated from the formula $Q = cv$, where Q = coulombs; c = capacitance; and v = voltage. Coulombic output was determined by visual ammeter readings taken at five second intervals for 25 seconds. These values were then plotted and Q output determined by integration of the area under the curve.

TABLE III-5

PULSE CATALYSIS CELLS INVESTIGATED

A. Mg/25 weight % $Mg(ClO_4)_2$; 0.1% K_2CrO_4; $Mg(OH)_2$ sat.; aqueous/Pt

B. Mg/25 weight % KNO_3; aqueous/Pt

C. Mg/25 weight % KNO_3; 10% KCL; aqueous/Pt

D. Li/12 weight % $LiClO_4$; butyrolactone/Pt

E. (Control) Mg/NaCl; aqueous/Pt

TABLE III-6

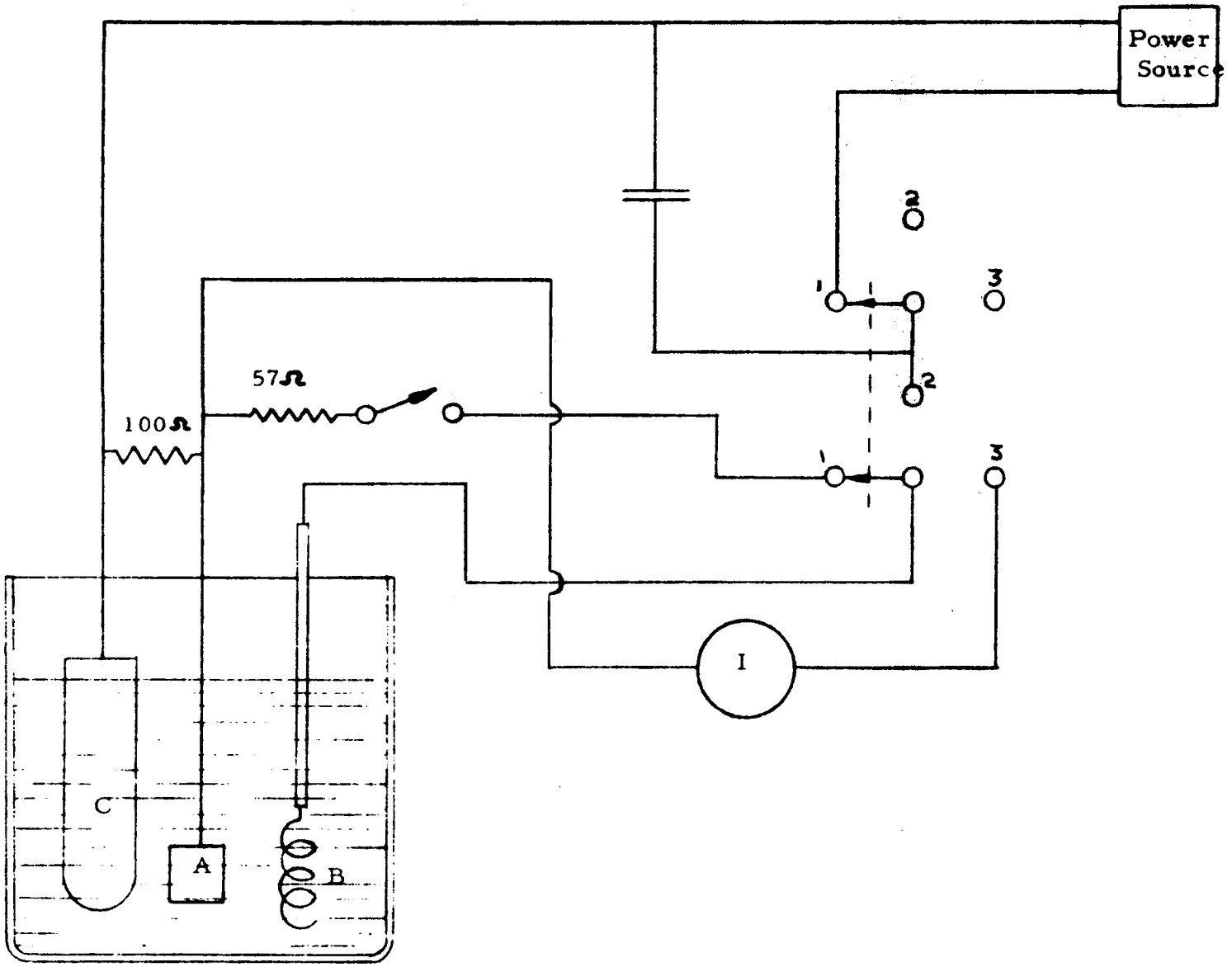
NET KINETIC CHARGE GAIN RESULTING FROM PULSE CATALYSIS IN THE AQUEOUS CELL

Mg/25 weight % $Mg(ClO_4)_2$; 0.1% K_2CrO_4; $Mg(OH)_2$ sat.; aqueous/Pt (+ pulsed)

cm^2 Pulse Electrode	Electronic µfd Capacity	µfd per cm^2	Net Q-Out/Q-In Under Condition II Capacitor Charge Voltage 20	40	60	95
2.6	50	19	48	26	71	63
2.6	130	50	97	77	36	26
0.56	130	232	82	57	34	--
2.6	650	252	22	9	6	--

Figure III-4

SCHEMATIC DIAGRAM OF THE PULSE CATALYSIS CELL AND CIRCUITRY



In each system investigated, the active couple (anode/pulse cathode) exhibited a steady state current output prior to pulsing which appeared to be dependent upon the inter-electrode distance and the area of the pulse cathode. This current was established by ammeter readings taken with the power source turned off. An arbitrary base current level, 80 ma, was then established which was higher than normal cell output of 66 ma. Thus, all current gains shown are solely due to pulsing.

Figure III-5 is a plot showing the performance of Cell A of Table III-5 immediately following the application of a pulse. The area under the curve representing Condition 2 is substantially greater than if the pulse had not been applied. A conservative figure of merit for the kinetic improvement in charge (ampere-seconds) obtained from the cell was found to be 77. The capacities per unit area of the pulse electrode and the charge voltage of the capacitor were varied and the kinetic figure of merit net Q-out/Q-in was tabulated in Table III-6 . It is significant that the largest advantages were observed with relatively low electronic voltage and capacity slightly larger than the theoretical figures for electrode double layers. Thus, if this technology could be utilized to improve or regulate an operating battery system, the feed-back energy required should be reasonable.

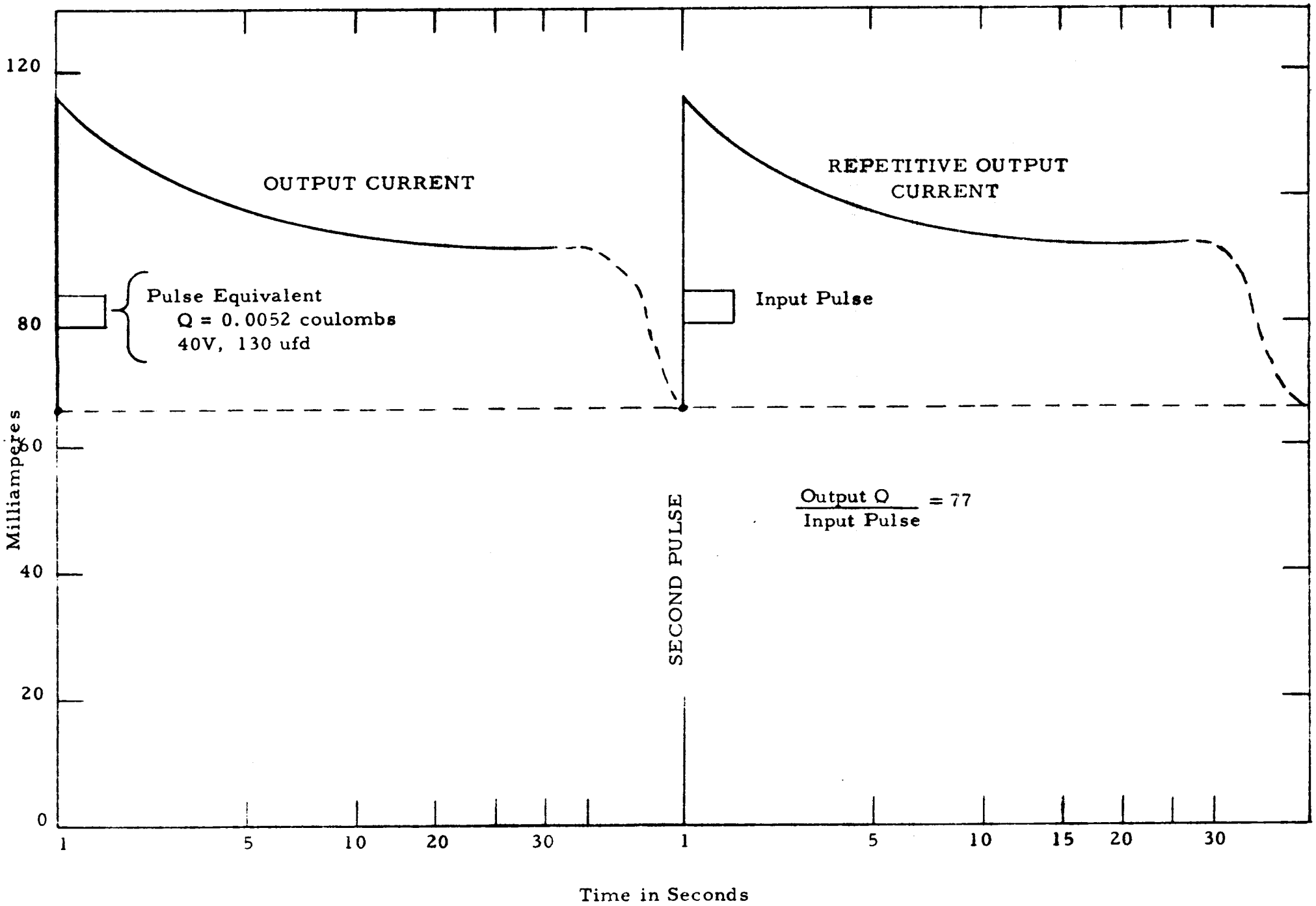
The last cell of Table III-5 raises an interesting point. No kinetic effect resulted from pulse catalysis with the aqueous sodium chloride electrolyte. It is implied that the adsorption of nitrate and/or perchlorate ions plays a substantial role in this kinetic improvement.

Figure III-5 shows cyclic operation of Cell A of Table III-5 . Improvement in kinetics resulting from pulse catalysis is graphically illustrated by the area of the pulse equivalent appended to the figure.

Alternating current is known to reduce polarization in plating operations, therefore, it is logical to assume from the data above that other, more practical cathodes may be improved by reactive loading.

Figure III-5

PULSE CATALYSIS CELL WITH CYCLIC OPERATION



ELECTROMOTIVE CELL TESTS IN PRACTICAL HARDWARE

It was felt desirable to conduct some of the cell testing in practical battery hardware. A number of integral activator-battery cases were obtained from a pilot production program so as to have finalized construction and practical performance standards.

The Mg/mDNB couple in liquid ammonia has a theoretical energy capability of 800 watt hours per pound of electrode reactants based on eight faradays per mol of mDNB and two faradays per mol of magnesium. In view of this, several tests designed to evaluate the possibility of utilizing the Mg/mDNB couple for construction of high energy batteries were performed. In addition, tests designed to study the potential usefulness of the Mg/S couple in liquid ammonia for construction of high energy batteries were conducted.

The results of the above-mentioned tests showed that the cathode reactions of these couples proceed with a relatively low electrochemical efficiency (10 to 30 per cent) in the comparatively short discharge times permitted by present ammonia battery structures. Minor modifications to the cathode mix composition did not significantly improve the performance of these cells.

Hence, it appears, from a comparatively small number of tests, that a qualitative improvement will be necessary in order to utilize mDNB or sulfur as high energy density cathodes in liquid ammonia.

MATERIALS COMPATIBILITY EVALUATION

In order to select suitable materials for use in cell construction, the chemical stability and corrosion resistance of ion exchange membranes, separator materials, and materials of construction (alloys, metals, polymers, resins, paper, and fibers) were determined in non-aqueous solvents and in selected environments which were composed of solvent, salt, and ligand. The selected environment represents the media in which these materials must exist during operation and storage. The severity of corrosion effects and decrease in chemical stability with time may be attributed to the synergistic action of the ligand (SO_2, NH_3, CO_2, etc.) and the ions resulting from the dissociation of the salt.

The performance of the specimens was determined by periodic inspection. Evaluation of the alloys and metals was based on the pitting, blistering, cracking, discoloration, crazing, and other changes in appearance that resulted from corrosion of the specimens. Objective evaluations of the ion exchange membranes and separator materials were based on change in appearance, dulling, swelling, discoloration, dissolution, and degrees of deterioration. The appearance of an ion exchange membrane does not necessarily indicate whether or not an adverse chemical effect on the resin has taken place; so the efficiency of an exchanger must be determined by performance tests in cells.

The results of the tests in pure solvents, without salts or ligands, are reported in Tables 1 and 2 of this section. The Identification of Ion-Exchangers, Separators, and Materials of Construction may be found at the end of this section.

In most cases, the materials were placed in a test tube, the solvent added, and the tube stoppered with glass wool and set aside for a sufficient period of time to yield the desired information. For volatile solvents, aluminum foil vapor barriers were placed over the mouths of the tubes.

Fig. VI-I of this section shows the equipment used for materials compatibility evaluations with fixed solvents. The work with solvents, such as liquid ammonia, which boil substantially below room temperature indicates that low temperature tests are inadequate. Many materials appear stable at low temperature and, subsequently, fail at room temperature where it is necessary to apply pressure to retain the liquid solvent, but yet provide for periodic examination. Techniques have been evolved for this work, and data are included for ammonia exposures. Essentially, the method consists of storing the materials for test inside the test tubes charged with the liquid solvent at low temperature. These tubes are sealed in stainless steel quick-coupler chambers

(Figure IV-2), pressurized to immobilize the solvent, and allowed to stand at room temperature. Examination is effected by refrigeration and venting of pressure. Re-exposure is then practical.

At the end of the test period, the ion exchange and separator materials were examined while in the solvents and after having been removed therefrom and dried.

A study of the test results in Table IV-1 indicates that the compatibility of the materials with p-fluorotoluene, Freon 114, aromatics, and a silicone oil was good to excellent. Most of the separators appeared compatible with ammonia except two ion exchange membranes. Cyclohexanone, propylene carbonate, and pyridine were hard on ion exchange materials; but SA 6404, a strong acid membrane, appeared to hold up in all solvents to which it was exposed. Cellulosic, polyalkane, and epoxy fiber papers gave generally good performance. Butylamine, nitromethane, cyclohexanone, butyrolactone, and n-methyl-pyrrolidone were increasingly severe.

With reference to Table IV-2, the materials which did not fail in any of the solvents in which they were tested are as follows: the Gelman ion-exchange membranes SB 6407, WA 6402, WA 6406; Whatman #42 filter paper; polypropylene (EM 476); R-2205 (cellulose); polyethylene; Epocel 10; IPC 1478; the Whatman ion-exchange membrane DE 20; and M 1406 (Nylon).

Those which failed in one solvent only are as follows: Gelman ion-exchangers WB 6403 and SA 6404; M 1216 (viscose); M 1231 (viscose); EM 478 (viscose); the Whatman ion-exchangers ET 20, AE 30, P 20, and CM 50; and the dynel fabrics EM 470, M 1410, and M 1450.

The solvents which did not exhibit destructive action on any of the materials tested are as follows: Freon 11, Freon 113, triallylamine, and petroleum ether.

In liquid ammonia, all of the Dynel fabrics shrank from 1/2" x 1-1/8" to 1/8" x 3/8". Viscose and Whatman filter paper (cellulose) were unaffected. However, the ion-exchange material in WB 6403 was partially removed from the Nylon; and Ultipor 9 seemed to have suffered some decomposition.

# # #

Considerable work has been done to determine the compatibility of ion-exchange membranes, separators, and materials of construction with solvent-atmosphere, and solvent-solute-atmosphere combinations. It is interesting to note that while many materials are compatible with many pure solvents, the addition of the atmosphere, and particularly the solute, makes many materials unsatisfactory. The conditions generated within the pressure chambers for the automatic

recording of electrolyte specific resistance and Tafel data combine the factors which may decompose or corrode materials of construction; thus, the pressure chambers were used to conveniently include samples for exposure. In order to accomplish this, the polypropylene cell holders were employed as containers for materials-testing by charging them with various solvent/solute combinations, after which samples of numerous materials of construction, ion exchange membranes, and separators were placed in the cells. The charged cells were then placed in the stainless steel chambers, and gas pressure was applied and maintained for the duration of the tests. At the conclusion of the test period, the pressure was released, and the samples were removed from the cells and examined for physical and chemical changes caused by the exposures.

Table IV-3 shows the combined effects of exposures to solutions of various salts in propylene carbonate in the presence of SO_2 at approximately 32 pounds per square inch gauge. Also, it was noted that the polypropylene cells swelled and became discolored; however, when they were cleaned and dried in a vacuum oven after use, both of these effects disappeared.

The same procedure was employed to investigate the effects of many other solvent-solute-ligand combinations on a large number of materials. A summary of the results is presented in Tables IV-4 and IV-5 of this section.

In Table IV-4 the following materials were visually satisfactory in all of the tests to which they were subjected: Whatman ion-exchange membranes DE-20 and P-20 (electrochemical effects unknown); Whatman No. 42 filter paper; M-1365 (cotton with Chandler binder); M-1406 (Nylon with Dynel binder); R-2205 (cellulose); polypropylene (EM-476, sheets and test cells); polyethylene; Aclar 33C (fluorohalocarbon resin); sterling silver; Teflon insulation; aluminum alloy (No. 3003 - H114); magnesium alloy (No. AZ31B0); and silicone rubber.

Those materials which were found to be visually satisfactory in all but one or two systems are as follows: Whatman ion-exchange membranes ET-20, AE-30, and CM-50 (with the possible exception of some chemical alteration of the resins); Viscose (M-1216 and M-1231); Devcon epoxy adhesive; Nylon; silver plating; and stainless steel (type 302).

The following materials were unsatisfactory in many cases: the Ionac ion-exchange membranes; EM-470 (Dynel); Nalco D-30 (vinyl); A-12 epoxy resin; tin plating; vinyl insulation; and copper.

The polypropylene cells have withstood all tests very well except for a yellow discoloration which developed in the liquid anion exchanger-ammonia and benzene-sulfur dioxide systems.

The nitrile rubber "O" rings (No. 488-70) that are used to seal the steel pressure chambers are satisfactory for use with ammonia and some other gases, but they were attacked by sulfur dioxide. The manufacturer recommended butyl rubber (No. 805-70) for use with the latter gas.

Numerous materials were tested in dimethyl sulfoxide solutions of $SnCl_2$ and $(CH_3)_4NI$ under an SO_2 atmosphere. The results are shown in Table IV-5.

Teflon, Flexite, polypropylene, and silicone rubber (RTV-11) withstood the exposures very well except for some discoloration of the polypropylene.

The system with $SnCl_2$ corroded Al and Mg severely and dissolved silver plated copper wire. The effects on stainless steel and sterling silver were relatively minor. Polyethylene and Nylon were unaffected except for a light yellow discoloration of the latter. The resin was removed from Membrane SA-6404; the papers ET-20 and P-29 were weakened; and XLMC-3235 was discolored.

The system with $(CH_3)_4NI$ had little effect on Al, Mg, Cu, and polypropylene. However, it dissolved stainless steel, sterling silver, and silver plate; caused polyethylene to curl and harden; and produced swelling, softening and discoloration of Nylon. It removed the resin from the Membrane XLMC 3235 and apparently dissolved Membranes SA-6404, ET-20, and P-20.

Secondary Observations

Secondary results from the conductivity tests show that in cell tests involving NH_3 at pressures from zero to one hundred and twenty pounds per square inch, the tin-plated copper wire would eventually corrode to such a great extent as to become powdered. The same was true for the solder connections which are sixty per cent tin, forty per cent lead. Apparently, ammonia will attack both tin and copper, and to such a degree as to powder both wires and solder containing these elements. The platinum wire was not affected.

As for the tin-plated copper wire, it was attacked by sulfur dioxide as it was by ammonia with much the same effects. Tin/lead solder was not employed, but instead, nickel-plated copper clips were used. After one test run, the nickel plating was completely gone, and the attack on the copper had already started. The platinum and the silver wires apparently were unaffected.

The Nylon and Teflon conductivity cells have apparently withstood the combined effects of various solvents, solutes, and three types of atmospheres (air, SO_2, and NH_3) without general damage.

Separator Materials Tests in Cells

Ten separator materials were tested for their suitability in Li/butyrolactone: $LiClO_4/CuCl_2$ flat -plate cells:

SA-6404 on Nylon
AE-30 anion exchanger
Whatman No. 541 filter paper
Whatman GF-A glass fiber filter sheet
Schleicher and Schuell glass fiber filter sheet No. 24
SM-91 polypropylene
Microporous rubber, ACE-SIL
No. 1698 Efficiency blotters
Polypropylene screen
Kodak 35 mm mounting frame (cardboard)

Experimental cells with each of the above materials were constructed and tested for discharge characteristics, but the test data were erratic, probably due to unrelated construction difficulties. Upon inspection of the discharged cells, several materials showed good strength and chemical inertness; of these, No. 1698 Efficiency blotting paper was used in a large number of subsequent cell tests because of its ready availability.

With the general improvement in cell performance and reproducibility of results brought about by modifications in cell construction, further separator studies appear to be in order.

FIGURE IV-1

MATERIALS COMPATIBILITY TEST EQUIPMENT

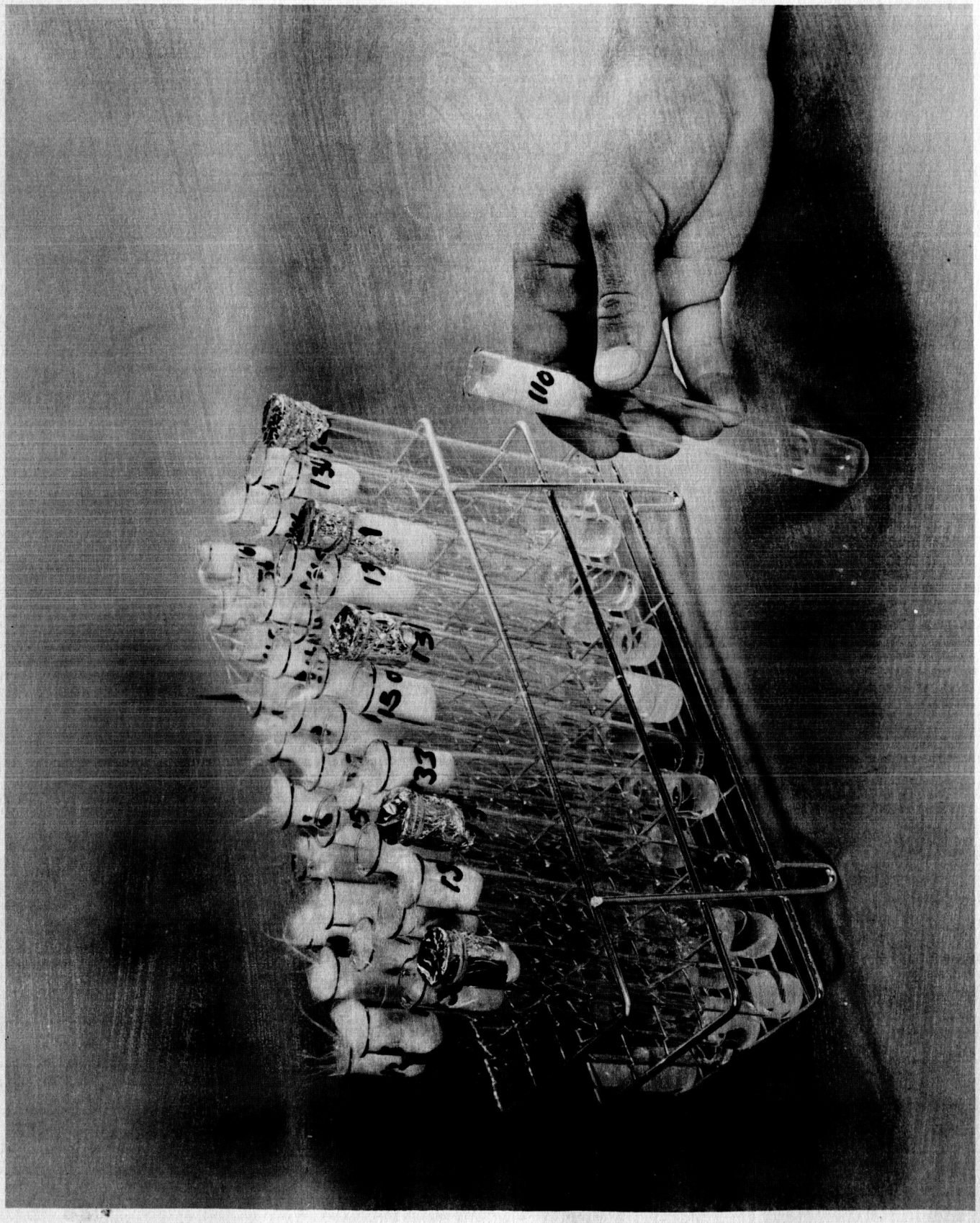


FIGURE IV-2

STAINLESS STEEL CHAMBER FOR MATERIALS COMPATIBILITY TESTS

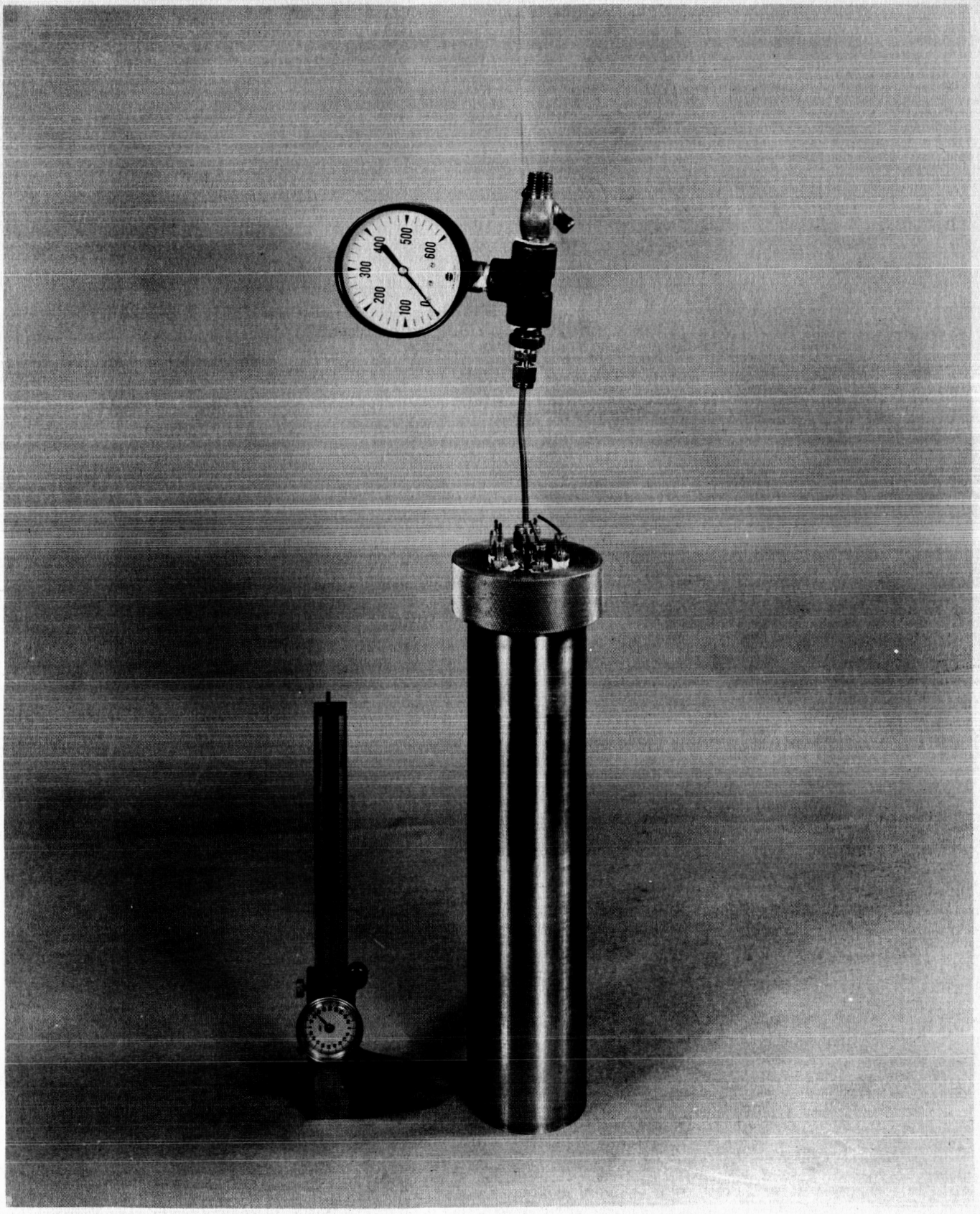


TABLE IV-1

COMPATIBILITY OF ION EXCHANGE MEMBRANES AND SEPARATOR MATERIALS IN SOLVENTS

Column No. (see Code & Comments)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Solvents			Butyrolactone	n-Methyl-2-Pyrrolidone	Liquid Ammonia	Propylene Carbonate	p-Fluorotoluene	Freon 114	Pyridine	Benzene	Toluene	Xylene	Butylamine	Nitromethane	Cyclohexanone	DC-200 Silicone Oil
Days Under Test			18	18	5	4	5	4	5	4	5	5	5	5	5	4
MATERIALS																
SB 6407	IE	n	R	R		R			R	E	E	G	E	R	R	
WA 6402	IE	n	R	R	G	R		G	R	E	E	E	E	R	R	
WB 6403	IE	n	R	R		R			R	E	E	E	E	R	R	
SA 6404	IE	n	G	G	G	G		G	G	E	E	E	E	G	G	
WA 6406	IE	v	R	R	G	R		G	R	E	E	E	E	R	R	
MC 3142	IE				R			G								
MA 3148	IE				R			G								
XLMC 3235	IE				G			G								
XLMA 3236	IE				G			G								
Whatman 42	S	l	E	E		E			E	E	E	E	E	E	E	
Whatman 50	S	l	E	E												
Textryl-C	S	d	G	G		G			G	E	E	E	Fb	E	G	E
Textryl-F	S	d	G	Fs		G			Fs	E	E	E	Fb	E	Fs	E
EM 470	S	a	D	D												
M 1401	S	a	D	D		I	E		D	G	E	E	E	D	D	E
M 1410	S	a	D	D												
M 1450	S	a	D	D												
M 1406	S	n	Fb	Fb												
EM 312	S	n	Fb	Fb		Fb	G		Fb	G	Fs	E	G	Fb	Fs	Fs
M 1216	S	v	Fm	Fb	G	G			Fb	G	G	E	Fb	Fs	Fs	E
M 1231	S	v	Fs	Fm		G			G	G	G	G	I	G	G	E
EM 478	S	v	Fm	Fm		G			G	G	E	E	Fb	E	E	E
M 1365	S	c	Fb	Fb	Sw	Fs	G		I	Fs	G	E	I	Sw	Fm	
EM 476	S	pp	E	E	G	G			G	E	E	G	G	G	E	E
R 2205	S	l			Sw	G	G		G	Fs	E	G	Sw	Sw	Sw	
(Bags)	S	pe			E	G			E	E	E	E	E	E	E	E
Ultipor 9	S	i				G			Fs	E	E	E	I	E	E	
Epocel 10	S	i				G			G	E	E	E	Fs	E	E	
IPC 1478	S	i				Fs			Fs	Fm	Fs	Fs	I	Fs	Sw	

CODE

Column 1

IE - Ion Exchanger
S - Separator

Column 2

n - Nylon
d - Dacron
v - Viscose
a - Dynel
c - Cotton
l - Cellulose
i - Impregnated Paper
pp - Polypropylene
pe - Polyethylene

Columns 3 to 16

E - Excellent
G - Good
D - Dissolved
Fs - Frayed or Disintegrated Slightly
Fm - Frayed or Disintegrated Moderately
Fb - Frayed or Disintegrated Badly
R - Part of All of Resin Removed
Sw - Swollen
I - Incompatible

COMMENTS

Column 3

SB 6407 - trace of yellow in solution
WB 6403 - yellow precipitate
Textryls - bright yellow solutions
EM 470 - slight yellow solution
M 1401 - bright yellow solution
M 1410 - bright yellow solution
M 1450 - bright yellow solution
EM 476 - slight yellow solution

Column 4

WB 6403 - slight yellow precipitate
M 1410 - trace of undissolved fibers

Column 5

M 1365 - not disintegrated
R 2205 - good

Column 6

M 1401 - Gelatinous and weak

Column 9

M 1365 - Gelled

Column 10

All good after one hour

Column 13

M 1231 - Soft pulp
M 1365 - Soft pulp
IPC 1478 - Soft pulp

Column 15

IPC 1478 - Probably good

TABLE NO. IV-2

Compatibility of Materials in Various Solvents

CODE:

IE = Ion Exchanger
S = Separator
n = Nylon
a = Dynel
l = Cellulose
i = Impregnated paper
pp = polypropylene
v = Viscose
c = Cotton

"C" = Compatible "I" = Incompatible "Q" = Questionable

SOLVENTS			Liquid Ammonia	Isopropylamine	Freon #11	Freon #113	Propylamine	Acetone	Ethyl Acetate	Triallylamine	N, N-Dimethyl-Formamide	Petroleum Ether
DAYS UNDER TEST:			5	5	4	6	5	4	4	4	4	4
SB 6407	IE	n	C	C	C	C	C					
WA 6402	IE	n		C	C	C	C					
WB 6403	IE	n	I	C	C	C	C					
SA 6404	IE	n		C	C	C	C	C	C	C	I	C
WA 6406	IE	v		C	C	C	C					
XLMC 3235	IE	-						I	I	C	I	C
XLMA 3236	IE	-						I	I	C	I	C
ET 20	IE	-	I					C	C	C	C	C
AE 30	IE	-	I					C	C	C	C	C
DE 20	IE	-	C					C	C	C	C	C
P 20	IE	-	I					C	C	C	C	C
CM 50	IE	-	I					C	C	C	C	C
Whatman 42	S	l	C	C	C	C	C	C	C	C	C	C
M 1401	S	a	I	C	C	C	C	I	C	C	I	C
EM 312	S	n	I	C	C	C	C	I	C	C	Q	C
M 1216	S	v		C	C	C	I					
M 1231	S	v	C	I	C	C	C	C	C	C	C	C
EM 478	S	v	C	C	C	C	I					
M 1365	S	c		I	C	C	I	C	C	C	Q	C
EM 476	S	pp		C	C	C	C	C	C	C	C	C
R 2205	S	l		C	C	C	C	C	C	C	C	C
Polyethylene	S	-		C	C	C	C	C	C	C	C	C
Ultipor 9	S	i	I	I	C	C	I					
Epocel 10	S	i	C	C	C	C	C					
IPC 1478	S	i	C	C	C	C	C					
EM 470	S	a	I									
M 1410	S	a	I									
M 1450	S	a	I									
M 1406	S	n	C									

TABLE IV-3

MATERIALS COMPATIBILITY TEST RESULTS
PROPYLENE CARBONATE, SO_2, AND VARIOUS SOLUTES

		Sulfur Dioxide Atmosphere	32 P.S.I.G. and Room Temperature				
Solute		None	None	$AlCl_3$	LiCl	LiF	KBr
Days Under Test		2	5	5	5	5	5
Material							
SA 6404	IE	-	Q	I	I	Q	Q
MC 3142	IE	-	Q	Q	Q	Q	Q
MA 3148	IE	-	Q	Q	Q	Q	Q
XLMC 3235	IE	-	Q	Q	Q	Q	Q
XLMA 3236	IE	-	Q	Q	Q	Q	Q
ET 20 Anion	IE	-	Q	C	C	Q	Q
AE 30 Anion	IE	-	Q	Q	-	-	-
DE 20 Anion	IE	-	Q	Q	-	-	-
P 20 Cation	IE	-	Q	C	C	Q	Q
CM 50 Cation	IE	-	Q	Q	-	-	-
Whatman 42	S	C	-	C	C	C	C
M 1216	S	C	-	C	C	C	C
M 1231	S	C	-	C	C	C	C
EM 478	S	C	-	-	-	-	-
M 1365	S	C	-	C	C	C	C
EM 476	S	C	-	-	-	-	-
Polypropylene Cell	M	-	C	C	C	C	C
R 2205	S	C	-	C	C	C	C
Polyethylene	SM	C	-	C	C	C	C
Ultipor 9	S	C	-	-	-	-	-
Epocel 10	S	C	-	-	-	-	-
IPC 1478	S	C	-	-	-	-	-
Nalco D 30	S	-	I	I	I	I	I
Aluminum	M	-	C	C	C	C	C
Stainless steel	M	-	C	-	-	-	-

Code: "C" = Compatible, "I" = Incompatible, "Q" = Questionable, "IE" = Ion Exchange Membrane, "S" = Separator Material, "M" = Material of Construction.

The use of "Q" to describe the results of most of the tests on ion exchange membranes indicates that the membranes appeared to be unaffected. However, the effects, if any, on the ion exchange resin cannot be determined with certainty by inspection. The efficiency of the resins as ion exchangers may be determined best by testing them in battery cells.

Most of the ion exchange membranes listed in Table V appeared to withstand the exposures very well. All of the separators and materials of construction which were checked in this series of tests were found to be satisfactory, except that Nalco D-30 was dissolved by propylene carbonate.

TABLE IV-4

MATERIALS COMPATIBILITY

Atmosphere	Ammonia Gas at Room											
Pressure	120 psig							120 psig			30 to	
Solvent	Liquid Anion Exchanger, "LA-1"							2-Ethanolpyridine				
Solute	None	$AlCl_3$	LiF	LiCl	NaI	KBr	$(CH_3)_4$-NCl	None	$AlCl_3$	LiF	LiF	LiCl
Duration, days	2	4	4	4	4	4	4	4	4	4	9	9
1 SA-6404												
2 MC-3142												
3 MA-3148												
4 XLMC-3235												
5 XLMA-3236												
6 ET-20												
7 AE-30												
8 DE-20												
9 P-20												
10 CM-50												
11 Whatman 42	C											
12 EM-470	I											
13 M-1216												
14 M-1231	C											
15 M-1365	C											
16 M-1406												
17 R-2205	C											
18 EM-476												
19 P.P. Sheet	C											
20 P.P. Cell	C	C	C	C	C	C	C	C	C	C	C	C
21 P.E.	C	C	C	C	C	C	C	C	C		C	C
22 Nalco D-30	I											
23 Aclar-33C												
24 A-12 Epoxy												
25 Devcon												
26 RTV-11												
27 Nylon Rod	C	C	C	Cd	C	Cd	C	C	C		C	C
28 Ag Tube	C											
29 Ag Plating	C	C	C	C	C	C	C	C	C	C		C
30 Teflon Insul.	C	C	C	C	C	C	C	C	C	C		C
31 Sn Plating	C	C	C	C	C	C	I	I	C	I		C
32 Vinyl Insul.	C	C	C	C	C	C	Ia	Ia	Ia	Ia		Ia
33 Copper									I	I		
34 Al Sheet	C	Ci	Ci	Ci	C	C	C	C	C		C	Ci
35 S.S. Sheet	C	C	C	C	C	C	C	C	C	C		C
36 Mg Alloy												

EVALUATION

Temperature						Sulfur Dioxide at Room Temperature							CO_2
90 psig			85 psig			32 psig							85 psig
			Pyridine			Benzene							P. C.
KBr	NaI	$(CH_3)_4$-NCl	None	$AlCl_3$	$(CH_3)_4$-NCl	None	$AlCl_3$	LiCl	NaI	KBr	$(CH_3)_4$-NCl	LiF	None
9	9	9	7	7	4	5	5	5	2	2	2	5	11
1			Cr	Ir	Q								Qr
2			Ir,j	Ir,j	Ir								
3			Ir,j	Ir,j	Ir								Qr
4			Ir	Ir	Ir								Qr
5			Ir	Ir	Ir								Qr
6			Q	Qr	Q								Q
7			Q	Qr	Q								Q
8			Q	Q	Q								Q
9			Q	Q	Q								Q
10			Q	Qr	Q								Q
11		C	C	C	C	C	C	Cd	Ch	C	C	C	C
12		C	C	Ij		I	I	Id	I	I	I	I	
13		C	C			C	C	Q	I	C	C	C	C
14		C	C	C	C	Ij	C	C	C	C	C	C	C
15		C	C				C	C	C	C	C	C	C
16							C	C	C	C	C	C	C
17		C	C	C	C	C							C
18				C		C	C	C	C	C	C	C	C
19													C
20	C	C	C	C	C	C	C	C	C	C	C	C	C
21	C	C	C	C		C	Cb	Cb	Cb	Cb	C	C	Cb
22					C	C	C	C	C	C	C	C	C
23					Ij	Ij	Id	Id	Ih	I	I	I	Ij
24				C	C	C							C
25				Ik	Ik								C
26						I							C
27	C	C	C	C	C	C	C	C	C	C	C	C	C
28							C	Cd	Ig	C	C	C	C
29	C	C	C	C	C	C	C	C	Ce	C	C	C	
30	C	C	C	C	C	C	C	C	I	C	I	C	C
31	C	C	C	C	C	C	C	C	C	C	C	C	C
32	Ia	Ia	Ia	Ik	Ik	Ik	C	I	I	C	I	I	C
33				I	I		Ia	Ia	Ia	Ia	Ia	Ia	Ia
34	C	C	C	Ci	Ci	Ci							C
35	C	C	C	C		C	C	C	C	C	Ci	Cc	Ci
36				Cl	Ci	Cl	C	C	C	Cf	C	C	C
													Ci

Code and Notes to Table IV-4

C = Compatible

I = Incompatible

Q = Questionable

P. C. = Propylene Carbonate

P. E. = Polyethylene

P. P. = Polypropylene

S. S. = Stainless Steel

The use of "Q" as applied to ion exchange membranes indicates that the physical appearance is relatively good. However, the chemical effect on the efficiency of the resins as ion exchangers may be determined best by testing them in battery cells.

a = The vinyl insulation shrank in length.

b = Light yellow color developed; color removed by cleaning and drying.

c = White film formed on aluminum sheet; some pitting took place.

d = Permanent light yellow color.

e = Dark gray surface film.

f = Surface etched.

g = Nylon turned black and became soft to a considerable depth.

h = Dark brown stain.

i = Gray coating, especially at edges, that can be scraped off.

j = Fabric dissolved or disintegrated.

k = Swelled and softened badly.

l = Trace of corrosion.

r = Part or all of resin removed.

TABLE IV-5

MATERIALS COMPATIBILITY EVALUATION

SOLVENT: **Dimethyl Sulfoxide**

ATMOSPHERE: Sulfur Dioxide at Vapor Pressure

SOLUTE:	$SnCl_2$	$(CH_3)_4NI$
DURATION, days:	8	8
MATERIALS:		
Al Sheet	Im	Cl
Mg Alloy	**Im**	**Ce**
Stainless Steel	Cl	In
Sterline Silver Tube	Ce	Iq
Silver Plate	In	In
Teflon Insulation	C	C
Copper Wire	In	C
Polyethylene	C	I
Flexite Tubing (PE)	C	C
EM 476 (PP)	C	C
Nylon Rod	Cd	Ik, d
RTV-11	C	C
SA-6404	Qr	*
XLMC-3235	Q	Ir
Whatman ET-20	Qo	*
Whatman P-20	Qo	*
Webril M-1365	Qo	*
PP Cells	Cd	Cd or p
PP Tubing	Cd	Cd

CODE

C = Compatible
I = Incompatible
Q = Questionable
PP = Polypropylene
PE = Polyethylene

NOTES

d = permanent light yellow color
e = dark gray surface film
k = swelled and softened badly
l = trace of corrosion
m = badly corroded
n = dissolved
o = fabric weakened
p = reddish-brown color
q = dissolved at center into 2 pcs.
r = part or all of resin removed

*Samples were dissolved, disintegrated, or lost.

Webril SM-91 was found to be compatible with N, N-Dimethylformamide.

BEST-TEST and CARTER'S rubber cements are compatible with Butyrolactone and are useful for cementing Whatman and Gelman ion-exchange membranes.

IDENTIFICATION OF ION-EXCHANGERS, SEPARATORS AND MATERIALS OF CONSTRUCTION

Gelman Instrument Company, Ion-Exchange Membranes, "Acropor":

SB-6407 on Nylon

WA-6402 on Nylon

WB-6403 on Nylon

SA-6404 on Nylon

WA-6406 on Viscose

Ionac Chemical Company, Ion-Exchange Membranes:

MC-3142 Cation Membrane

MA-3148 Anion Membrane

XLMC-3235 Cation Membrane

XLMA-3236 Anion Membrane

Rohm & Haas Company

LA-1 Liquid Ion-Exchanger - Anion - "Amberlite"

LA-2 Liquid Ion-Exchanger - Anion - "Amberlite"

Whatman Ion Exchange Membranes:

Manufactured by W. & R. Balston, Ltd., England

Anion Exchanger - Ecteola Cellulose	Paper ET 20
Anion Exchanger - Aminoethylcellulose	Paper AE 30
Anion Exchanger - Diethylaminoethylcellulose	Paper DE 20
Cation Exchanger - Cellulose Phosphate	Paper P 20
Cation Exchanger - Carboxymethylcellulose	Paper CM 50

American Machine and Foundry Company, "Amfion" Products:

C-60 Ion-Permeable Membrane, Strong Acid Type

C-103c Strong Acid Type

Arthur H. Thomas Company, Filter Paper:

Whatman No. 42

Whatman No. 50

Whatman No. 541

IDENTIFICATION OF ION-EXCHANGERS, SEPARATORS AND MATERIALS OF CONSTRUCTION

Continued

Webril Non-Woven Fabrics, Kendall Company, Walpole, Massachusetts

EM-470 Dynel

M-1401 Dynel

M-1410 Dynel

M-1450 Dynel

M-1406 Nylon - Dynel Binder

EM-312 Nylon - Dynel Binder

M-1216 Viscose - Vinyon Binder

M-1231 Viscose - Chandler Binder

EM-478 Viscose Gauze - Chandler Binder

M-1365 Cotton - Chandler Binder - Balance Acetate

EM-476 Polypropylene - 0.0027" thick

R-2801 Pure Cellulose

R-2901 Pure Cellulose

R-2401 Pure Cellulose

R-2205 Pure Cellulose

SM-91 Polypropylene - 0.005" thick

Polypropylene Sheet - 0.020" thick

Polyethylene Sheet from Bag Stock

Nalco Chemical Company:

D-30 Vinyl Type Dialysis Membrane

Allied Chemical Corporation, General Chemical Division, Film:

Aclar 33C, $\frac{1}{2}$ mil thickness (Fluorohalocarbon Resin)

Pall Corporation, Epoxy Resin Impregnated Paper:

Ultipor 9

Epocel - 3 micron

Epocel - 10 micron

Epocel - 30 micron

IDENTIFICATION OF ION-EXCHANGERS, SEPARATORS AND MATERIALS OF CONSTRUCTION

Continued

Knowlton Brothers, Paper:

IPC 1478 - Impregnated with Dibutoxyethylphthalate

Whitehead Metal Products Company, Inc.:

Alcoa Aluminum Alloy Sheet No. 3003-H114

Laminated Shim Company, Inc.:

Stainless Steel Sheet - Type 302 - 0.002" thick

Plastic and Rubber Products Company (Available from Beemer Engineering Co.):

"O" Rings - Compound No. 488-70 - Nitrile Rubber - Good for NH_3

"O" Rings - Compound No. 805-70 - Butyl Rubber - Good for SO_2

Belden Manufacturing Company:

No. 8530 Tin Plated Solid Copper Wire - Vinyl Insulation - MW-C-22-(1) U

L. Frank Markel & Sons:

C-20381 - Silver Plated Solid Copper Wire, 24 Gauge, Teflon Insulation

Flexite Shrinkdown PO tubing (Polyethylene) - Size 16

Armstrong Products Company:

A-12 Epoxy Resin Adhesive

Devcon Corporation:

Clear Epoxy Adhesive

A. R. Purdy Company, Inc.:

Magnesium Alloy No. AZ31BO
96% Mg + 3% Al + 1% Zn

Polymer Corporation of Pennsylvania

Nylon Rod

IDENTIFICATION OF ION-EXCHANGERS, SEPARATORS AND MATERIALS OF CONSTRUCTION

Continued

General Electric Company:

RTV-11 Silicone Rubber

T. B. Hagstoz and Sons:

Sterling Silver Tubing, 3/32" O.D. x 0.055" I. D.

The Carter's Ink Company:

Carter's Rubber Cement

Union Rubber and Asbestos Company:

Best-Test White Rubber Paper Cement

Arthur H. Thomas Company:

Whatman GF-A Glass Fiber Filter Sheet, 0.008" thick

Schleicher and Schuell Glass Fiber Filter Sheet No. 24, 0.040" thick

American Hard Rubber Company:

Microporous Rubber, ACE-SIL, 0.05" Veneer

No. 1698 Efficiency Blotters

Polypropylene Screen: Strand dia. ≐ .02"; screen openings ≐ .06"

Cardboard from Kodak Slide Frame

E. I. DuPont De Nemours & Company:

Textryl - Calendered - Dacron

Textryl - Fused - Dacron

Production has been discontinued.

BACKGROUND FOR ENERGY BALANCE

A comprehensive study of this task embraced a careful and recorded search of the literature and substantial deliberation by the research team assigned. A review of the facts indicates that Count Allessandro Volta invented his pile employing the zinc/copper couple and a dilute H_2SO_4 acid electrolyte. A century ago, Leclanché invented his cell which we know today as the flashlight battery; and today, after 164 years, substantially all batteries manufactured for sale are based upon the same solvent, water. Thus, one may presume that conventional battery design rules are based upon the properties of water.

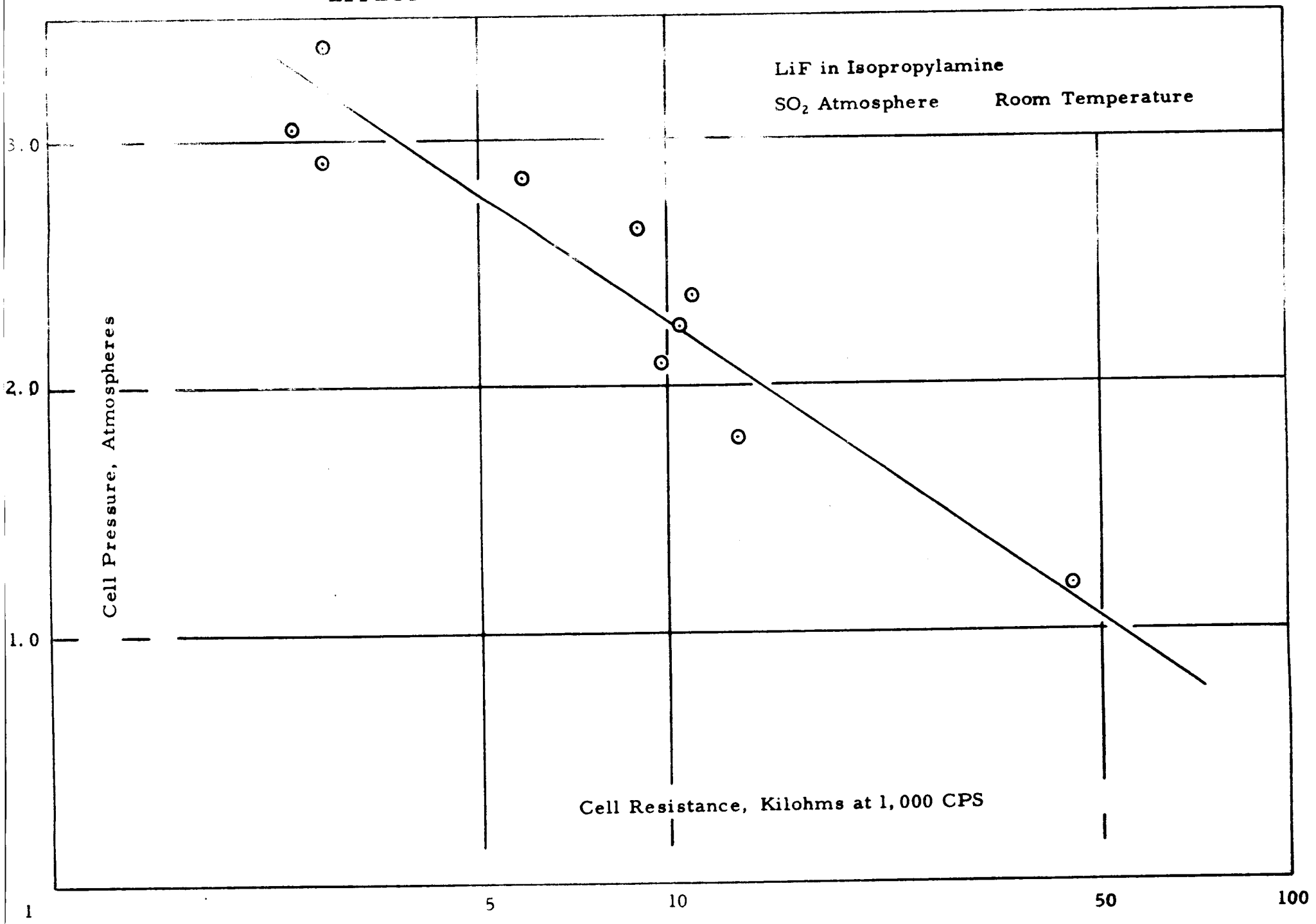
Numerous precepts, true, perhaps in water, have narrowed the thinking concerning batteries in a general sense. It is often concluded that a battery solvent must have a high dielectric constant because water has a dielectric constant of 80. Insoluble cathode materials have been generally sought for and employed.

More important than the dielectric constant, per se, are the coordination or solvation requirements of the solute ions. Thus, the ligand atmosphere concept was generated as a result of the subject project deliberations. It was realized that a one earth normal atmosphere or no atmosphere at all was being taken for granted. If this work were performed on a planet which contained ammonia in its atmosphere, it might have been conventional to have presumed an ammonia-containing atmosphere or none at all. Thus, we generalize and say that the atmosphere should be considered as a variable under the control of the designer. The introduction of this concept literally adds a third dimension to the total number of possibilities which may be considered in the design and construction of batteries. Obvious and significant variation is introduced by the ligand atmosphere pressure. This is demonstrated by Figure V-1, page V-2, where extensive variations in specific resistivity are demonstrated under the influence of changes in ligand atmosphere pressure.

The second-mentioned limiting restriction imposed by aqueous thinking was the requirement of insoluble cathode reactant. It is interesting to note that in a number of the non-aqueous solvents so far studied in this work, those materials which were truly insoluble were rather inert. Despite the difficulties thus imposed upon the anode, those cathode materials which show at least some solubility carry moderate currents, and those which are distinctly soluble will generally support substantial discharge rates.

Figure V-1

EFFECT OF LIGAND ATMOSPHERE ON SPECIFIC RESISTIVITY



ENGINEERING ENERGY BALANCE

The first law of thermodynamics has been used as a tool for evaluation of possible battery systems with considerable success. The first law may be expressed in a number of ways; for example, energy may neither be created nor destroyed in any process. The simple engineering energy balance of equation (1) results directly from the first law.

$$W = U - Q \tag{1}$$

W (the electrolyte figure of merit) is maximum useful work available from the battery; U is the total available energy; and Q represents the energy wasted through generation of heat by resistive and leakage processes. We have attacked the overall problem of the selection of battery electrolytes to be studied by means of the simple energy balance (1). Figure V-2, page V-4 shows how this reasoning has been applied to possible batteries and battery systems as the solvent, solute, and atmosphere are varied.

In a battery, the total available energy, U, may be defined in terms of electrode reactants available to produce energy. The conventional expression EF/M [where E is the combined potentials of the anode and cathode (fuel and oxidizer); F is Faraday's constant; and M is combined equivalent weight of the electrode reactants] was selected as a convenient form for the evaluation of U. The losses, Q, which can be directly attributed to the electrolyte are: (1) the obvious and conventional resistive loss I^2RT and (2) a less conventional, but nevertheless realistic, electrode local action loss in the form EiT, where E has been defined; [i] is the corrosion current; and T is time. Thus, equation (1) becomes:

$$W = \frac{EF}{M} - I^2RT - EiT \tag{2}$$

In equation (2) the term I may be replaced by the quantity F/MT giving equation (3):

$$W = \frac{EF}{M} - \frac{F^2}{M^2T} R - EiT \tag{3}$$

By calculus, W will be a maximum with respect to time when time is equal to the value shown in equation (4):

$$T = \frac{F}{M}\sqrt{\frac{R}{Ei}} \tag{4}$$

This may be conveniently demonstrated by the fact that when the corrosion and resistive losses are equal, their combined value will be a minimum. For example, in Figure V-3, page V-5 where W is shown as a general

ENERGY BALANCE

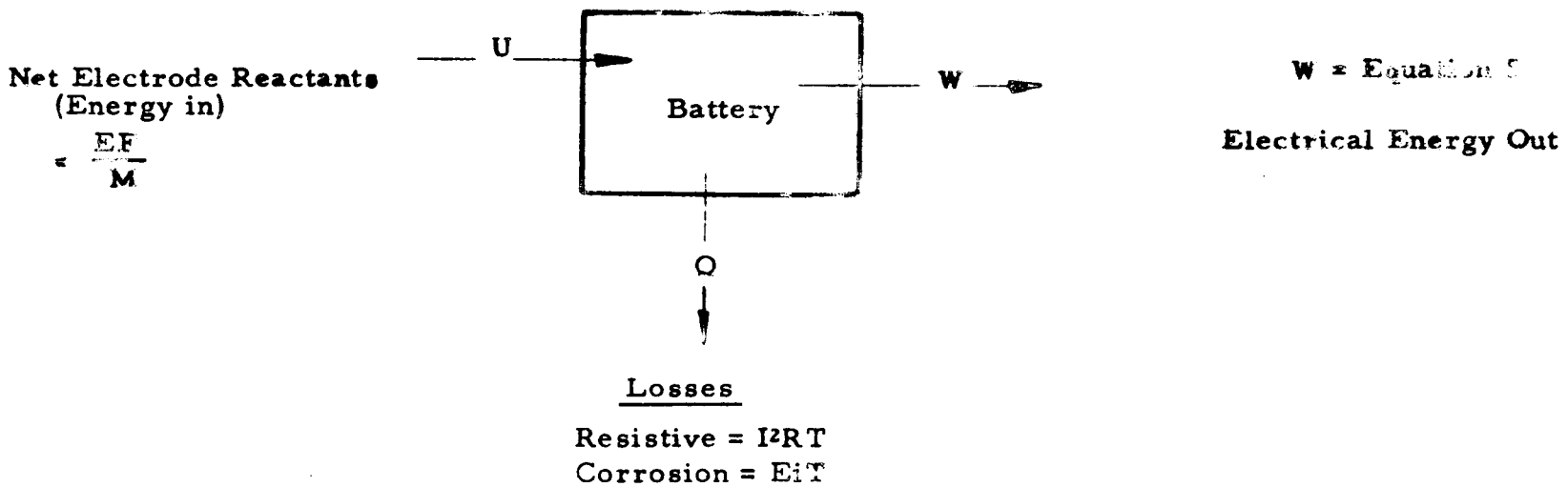
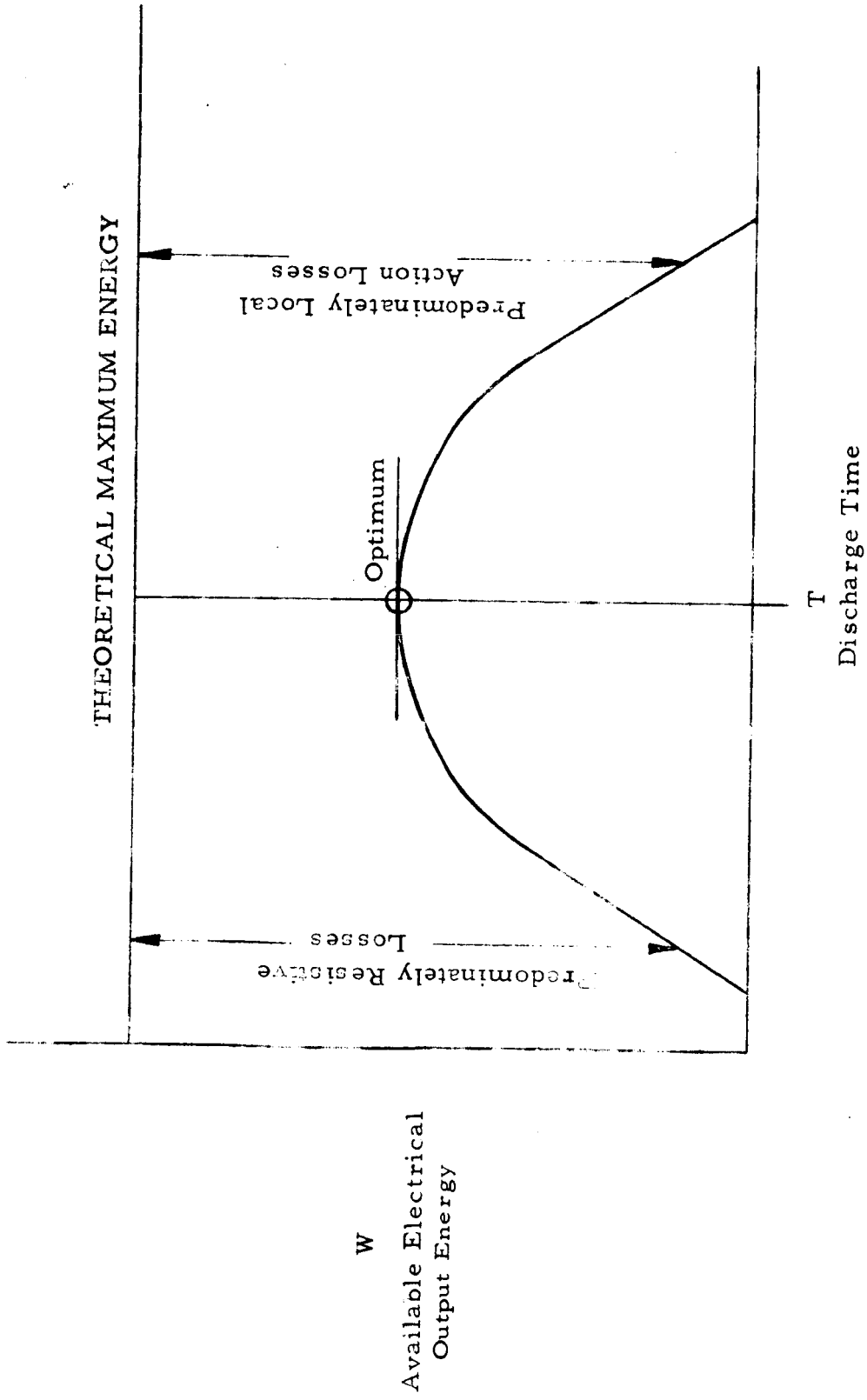


FIGURE V-2

Figure V-3


THEORETICAL MAXIMUM ENERGY
Predominately Local
Action Losses
Optimum
Predominately Resistive
Losses
W
Available Electrical
Output Energy
T
Discharge Time

function for T for essentially any battery system, when T is extremely small, the energy loss will be largely resistive; and when T is extremely large, the energy loss will be largely due to local action or wet stand. Thus, the optimum discharge time occurs when the losses in question are equal. Substituting the value for T from equation (4) into equation (3) gives a practical overall relationship expressed by equation (5):

$$W = \frac{F}{M}\left(E - \sqrt{2\ REi}\right) \qquad (5)$$

In order to apply equation (5) to the evaluation of specific battery electrolyte compositions, it is necessary to express all variables as functions of a single argument. The argument chosen for this work is E, the cell potential.

The value 12,180 ampere hours per pound equivalent weight was taken for F in order that the maximum figure of merit, W, for the electrolyte compositions would result in the proper units, watt hours per pound.

Since it is known that the voltage available from the net electrode reactants is dependent upon the position of the reactants in the atomic table, the term M, equivalent weight of the net electrode reactants, may be expressed as a function of E. Appendix B, page B-1, treats this matter in some detail and provides a mathematical statement of this fact as equation (6):

$$M = e^{(5.5 - 0.4E)} \qquad (6)$$

In equation (5), the quantity under the square root sign represents the combined losses attributable to the electrolyte.

Cell resistance, R, and local action current, i, depend upon the properties of each battery electrolyte under evaluation. The cell resistance is determined by the relationship:

$$R = \rho \frac{L}{A}$$

where ρ = specific resistance of the electrolyte

L = inter-electrode spacing

A = geometric electrode area

The specific resistance, ρ, for many electrolytes has been measured in this work and these are indexed in Appendix A.

The corrosion current, i, depends upon the cell potential and upon the geometric area:

$$i = JA$$

where J = the corrosion current density at both electrodes!
A = the geometric electrode area

J is a function of the cell potential and/or stress applied to the solvent. While the Tafel equation is frequently useful in expressing the dependence of J upon E, about one-third of the non-aqueous electrolyte compositions measured in this work conformed to a simple Tafel relationship. For these electrolytes, the modified Tafel constant and slope representing four measured points were tabulated (Table V-1, page V-8) under the heading C and D respectively. The computer code, N, was used to indicate the linearity of the Tafel data. When N = 0, the data points satisfied rank order correlation. Where the simple Tafel relationship did not adequately express the corrosion current density, actual measured value computations are tabulated with blanks in the spaces provided for C and D. Inclusion of the individual voltage-current density data would have required excessive effort and space.

Thus, in equation (5), all variables have been expressed as measured functions of E; and W may be solved for all values of E. We have place an upper limit of six volts upon E. Naturally, the maximum value of W (the figure of merit) for each electrolyte composition is reported.

Since our general theoretical battery consideration led to approximately 20 solvents x 12 solutes x 10 atmospheres, a substantial number of determinations was indicated. For this reason, as the program evolved, automatic instrumentation was developed and utilized for the mass measurement of specific resistance and corrosion current as a function of the applied voltage stress, E. The utilization of this equipment resulted in such volumes of raw data that manual calculation by human beings rapidly became a problem. For this reason, automatic data processing was instituted to calculate the machine-collected data ranging from 0 to 90 percent of the ligand vapor pressure at room temperature (limited to several hundred pounds per square inch).

Concerning the electrodes which were used to provide the specific resistance and local action current measurements, it is clear that for uniform measurements under widely varying conditions, the only practical choice was one or more noble metals. Platinum electrodes were utilized throughout. This choice introduces a conservative factor into all the measurements. For example, hydrogen evolution (a type of anode local action) is greatly enchanced on platinum electrodes. This highly conservative character of the search electrodes used has been deemed sufficient compensation for the incomplete

definition of the term T, time, applied above; the T used in the derivation should be strictly defined as the cell discharge time. However, in actual practice, at least some allowance must be made for wet stand time. Furthermore, at a meeting at Lewis Research Center[1] a theoretical figure of merit of 500 watt hours per pound was promulgated. This was justified on the basis that the zinc-aqueous KOH-silver peroxide battery has approached 100 watt hours per pound and has a theoretical maximum in the order of 250 watt hours per pound. This represents an overall efficiency of 40 percent of theoretical.

Those electrolyte systems whose measurements resulted in calculated figures of merit, W, watt hours per pound of net electrode reactants in excess of 500 have been summarized in Tables II-1 and II-2, pages II-4 through II-5. In Appendix A, an index of the print-out from the computer is presented. Our programmer informed us that the average computation time on the IBM 1620, per electrolyte composition point, was approximately 14 seconds. When it is realized that full manual calculation requires approximately two and one-half hours per composition, the use of the computer is highly justified.

The summary Table II-2 mentioned above indicated certain interesting trends. Ligand atmospheres analogous to the parent solvent are highly complementary. Thus, a sulfur dioxide atmosphere is of significant benefit to dimethyl sulfoxide as a solvent; a carbon dioxide atmosphere is of significant benefit to butyrolactone as a solvent; and an ammonia atmosphere is of significant benefit to N, N-dimethylformamide. While the general evaluation given in Tables II-1 and II-2 was only recently available, two potentially useful systems were determined by the partially complete work at an earlier date. Cell tests on some systems are described in the section entitled "Electromotive Cell Tests." A number of highly probable systems are now available for evaluation.

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[1] Technical Meeting at Lewis Research Center, September 18, 1963.

SPECIFIC RESISTANCE AND DECOMPOSITION POTENTIAL MEASUREMENTS

Under the previous heading "Engineering Energy Balance," a foundation was laid whereby the merits of a possible battery electrolyte may be evaluated in terms of specific resistance, corrosion current, and decomposition potential. There follows in this section a description of the implementation of this basis and the flow of the resulting mass of data from the recording instruments to punch cards, through a computer to punch cards, and finally to a machine print-out demonstrated by the sample in Table II-3, page II-7

The equipment consists of sealed pressure chambers into which a ligand atmosphere may be introduced. Glass-platinum measurement cells within these chambers are alternately connected to a 1,000-cycle voltage source used to provide specific resistance measurements and a dc voltage source for the measurement of nine corrosion current levels and a combination of both for the determination of a comparative ac polarized resistance (under a dc voltage stress). Peripheral equipment includes a strip chart recorder and related circuitry capable of measuring 144 data points per complete cycle.

Figure V-4, page V-10, outlines in broad diagram form the overall process of data collection, processing, and presentation.

The Specific Resistance and Decomposition Potential Cells and Related Equipment
Block A of Figure V-4, Page V-10

Specific resistance and decomposition potential measurements, Block A of Figure V-4, were conducted in cells of the type shown in Figure V-5, page V-12. As many as nine measurement cells were operated concurrently in the pressurized containers.

These cells were first charged with the solvent under consideration and a quantity of solute sufficient to result in a concentration of approximately one molar if solution were completed. The solvent was allowed to stand in contact with the solute until equilibrium readings were obtained at one atmosphere by the cell measuring system. Following this, the chambers containing the cells were purged with one of the ligands; and the ligand was gradually admitted to the chambers via a capillary tube. The measuring cycle was begun. The full vapor pressure of the ligand or a maximum of several hundred pounds per square inch was approached during a 16-hour period or longer. The cell measurements were conducted cyclically in accordance with the following explanation. A complete scan of all cells was accomplished in approximately 36 minutes and repeated until the termination of the experiment.

FLOW DIAGRAM OF SPECIFIC RESISTANCE AND DECOMPOSITION POTENTIAL DATA MEASUREMENT, RECORDING AND PROCESSING

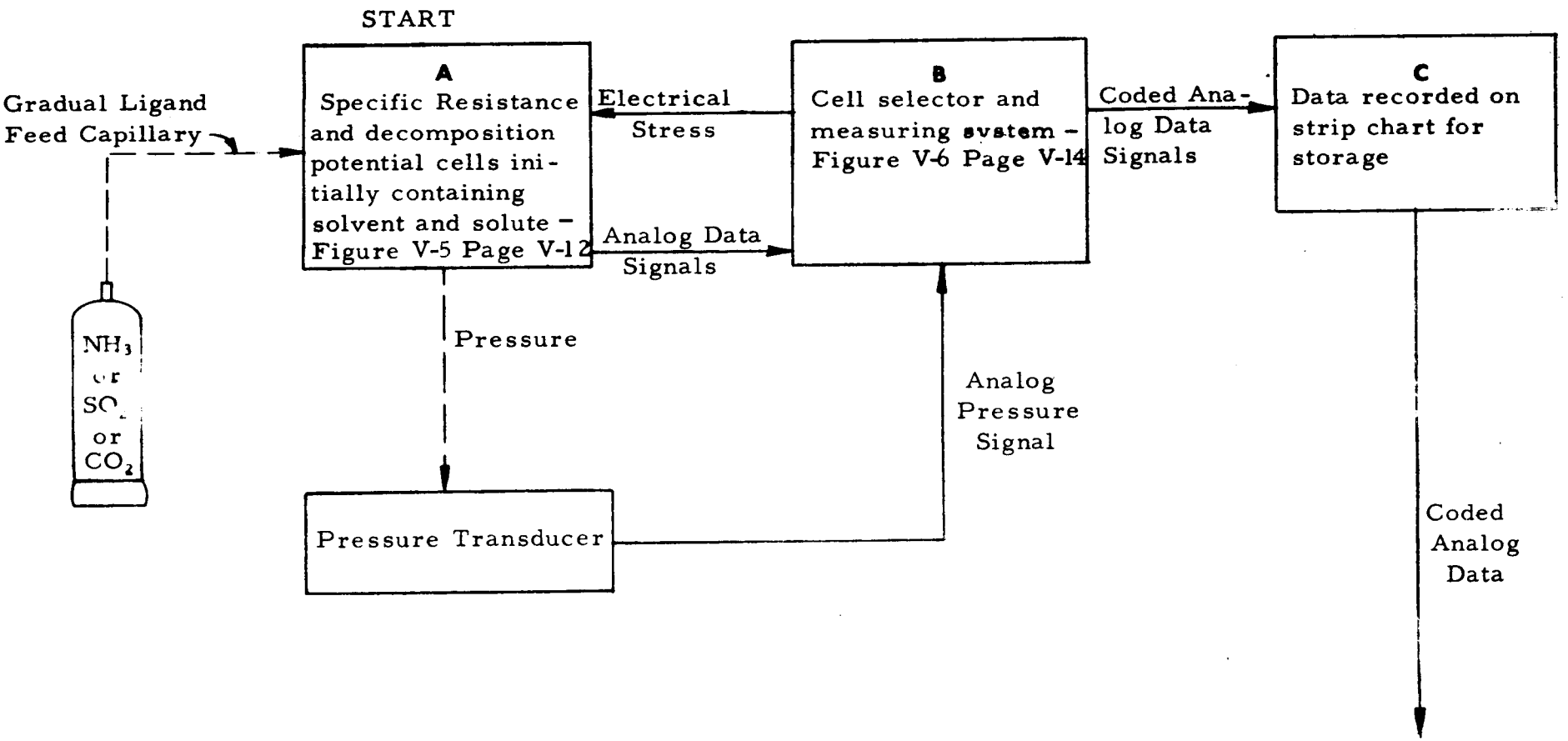


FIGURE V-4

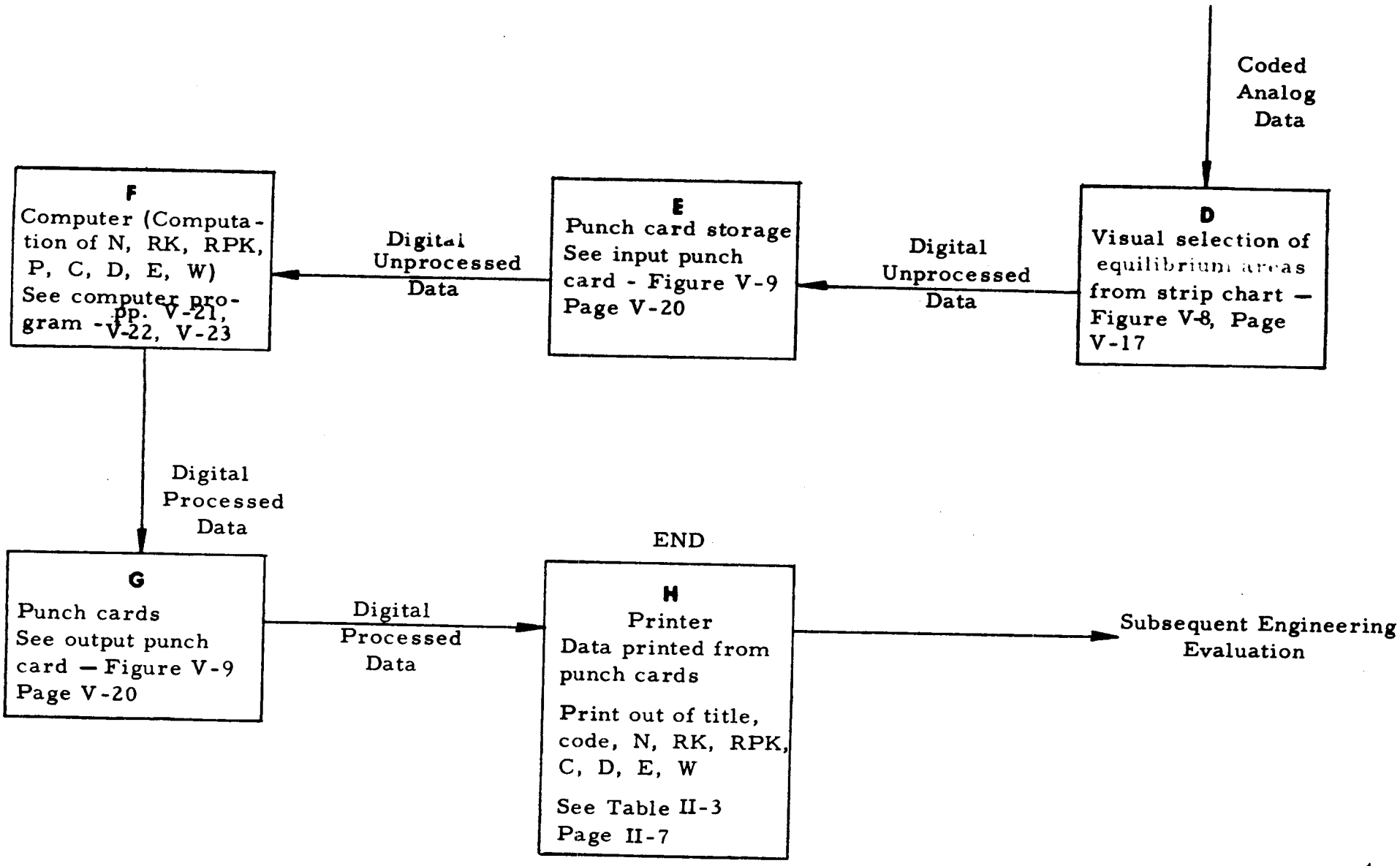
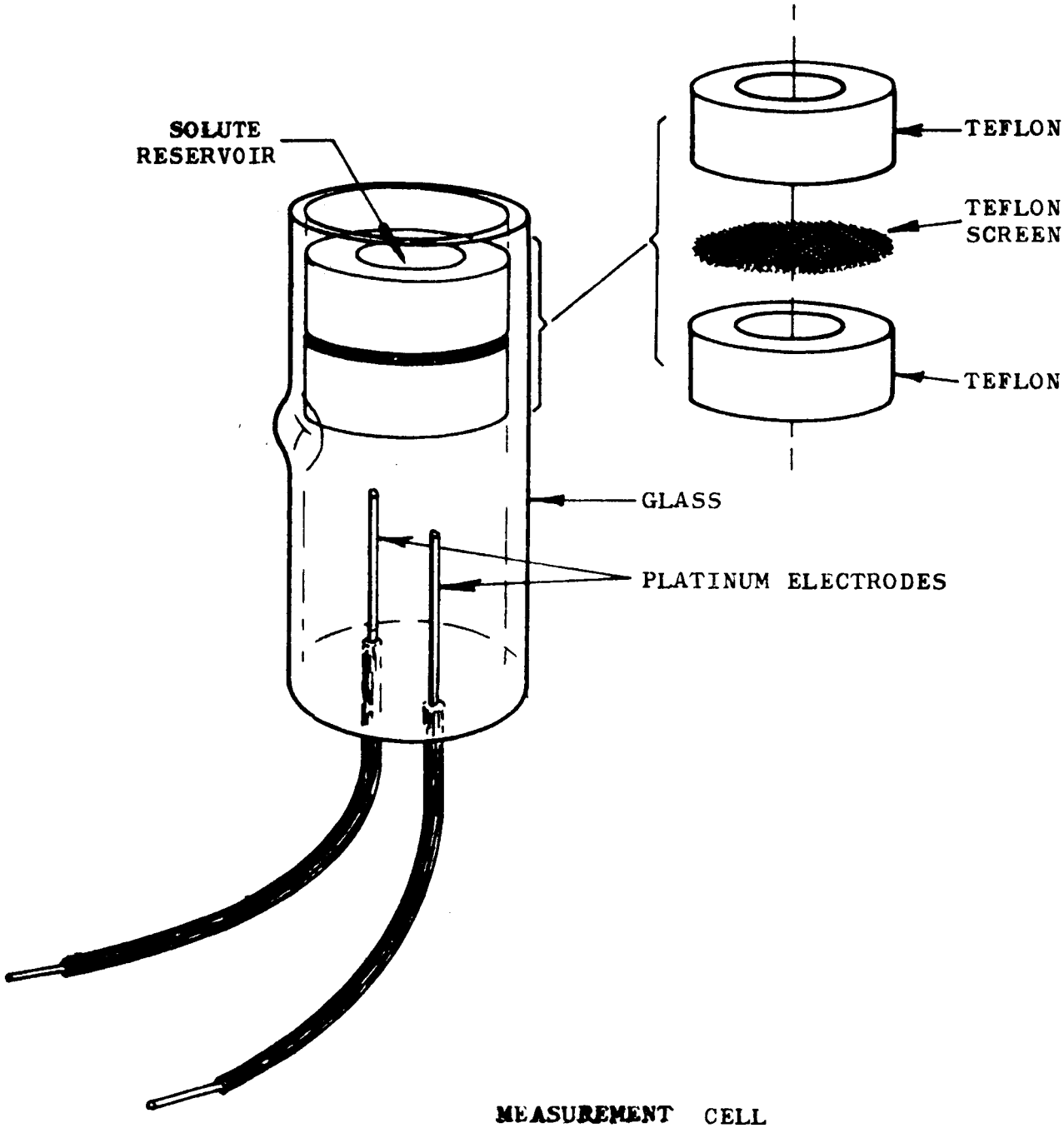


FIGURE V-4 Continued



MEASUREMENT CELL

FIGURE V-5

The Specific Resistance and Decomposition Potential Measuring System
Block B of Figure V-4, Page V-10

A symbolic diagram of the specific resistance and decomposition measuring circuitry is shown in Figure V-6, page V-14. The cell selector indexed from one cell to another and then began a new cycle after nine cells and three reference channels were scanned. The cell measuring sub-cycle is completed before the cell selector indexes to a new cell. Hence, 12 sub-cycles are made by the cell measuring switch each time one cycle is completed by the cell selector. Cell channels 10, 11, and 12 were allocated for reference purposes. Each measuring network generated one data point every 15 seconds of operation.

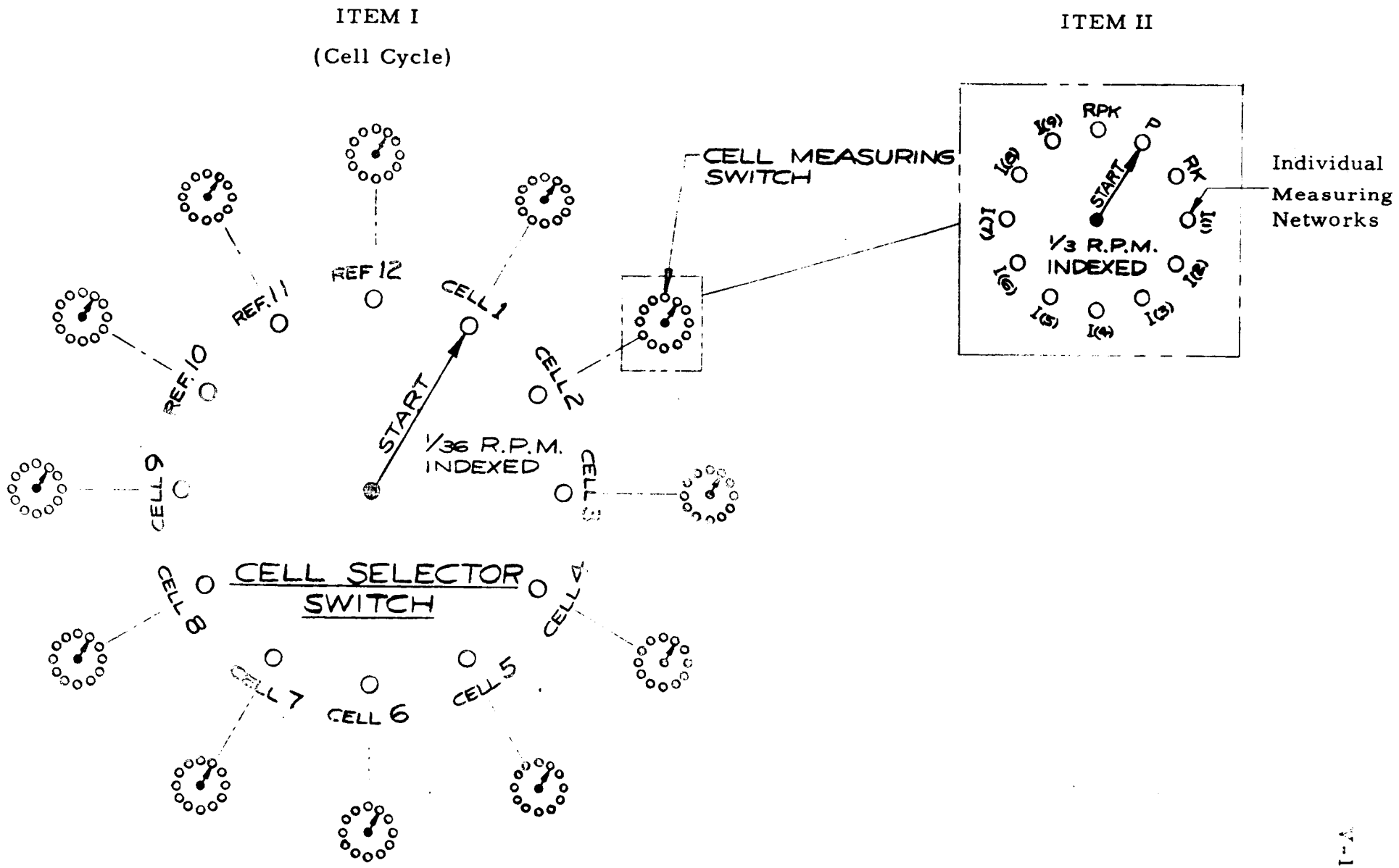
Item II of Figure V-6 helps to visulize the arrangement of the cell measuring networks. Each corrosion current measuring step of the decomposition potential relationship [I(1), I(2)...I(9)] constituted a cell in series with a voltage source, V, and a limiting resistance, R_M, (see Figure V-7, page V-15), which limited the corrosion current through the cell to an increasing maximum value. Table V-1, page V-16, details the functional steps of the cell measuring networks.

P is the pressure-measuring step, while RK and RPK are the electrolyte specific resistance and the comparable polarized resistance measurements. The measurements were recorded on charts as indicated by Block C of Figure V-4.

Selection of Specific Resistance and Decomposition Potential Measurements
Block D of Figure V-4, Page V-11

The measured data on the chart were examined, and representative measurement sub-cycles were selected for computer computation on the basis of frequent and stable values. The first area to be examined consisted of measurements made in an air atmosphere. An equilibrium cell selector cycle was isolated; and each cell measuring cycle therein was marked off and identified by a code number, see Figure V-8, page V-17. For example, the system acetonitrile/lithium fluoride/ammonia can be identified by the chemical system code 13104.01 defined on page V-18. The first digit, 1, represents a run with ammonia introduced as the ligand. The next two digits, 31, represent the code for acetonitrile. The next two digits, 04, represent the code for lithium fluoride. The last two digits to the right of the decimal point, 01, represent the first area from which the data was chosen. An .01 herein represented an air atmosphere. A number greater than 01 to the right of the decimal point represented equilibrium readings in a ligand atmosphere (air was removed by purging the system with the ligand at atmospheric pressure). These two

FIGURE V-6

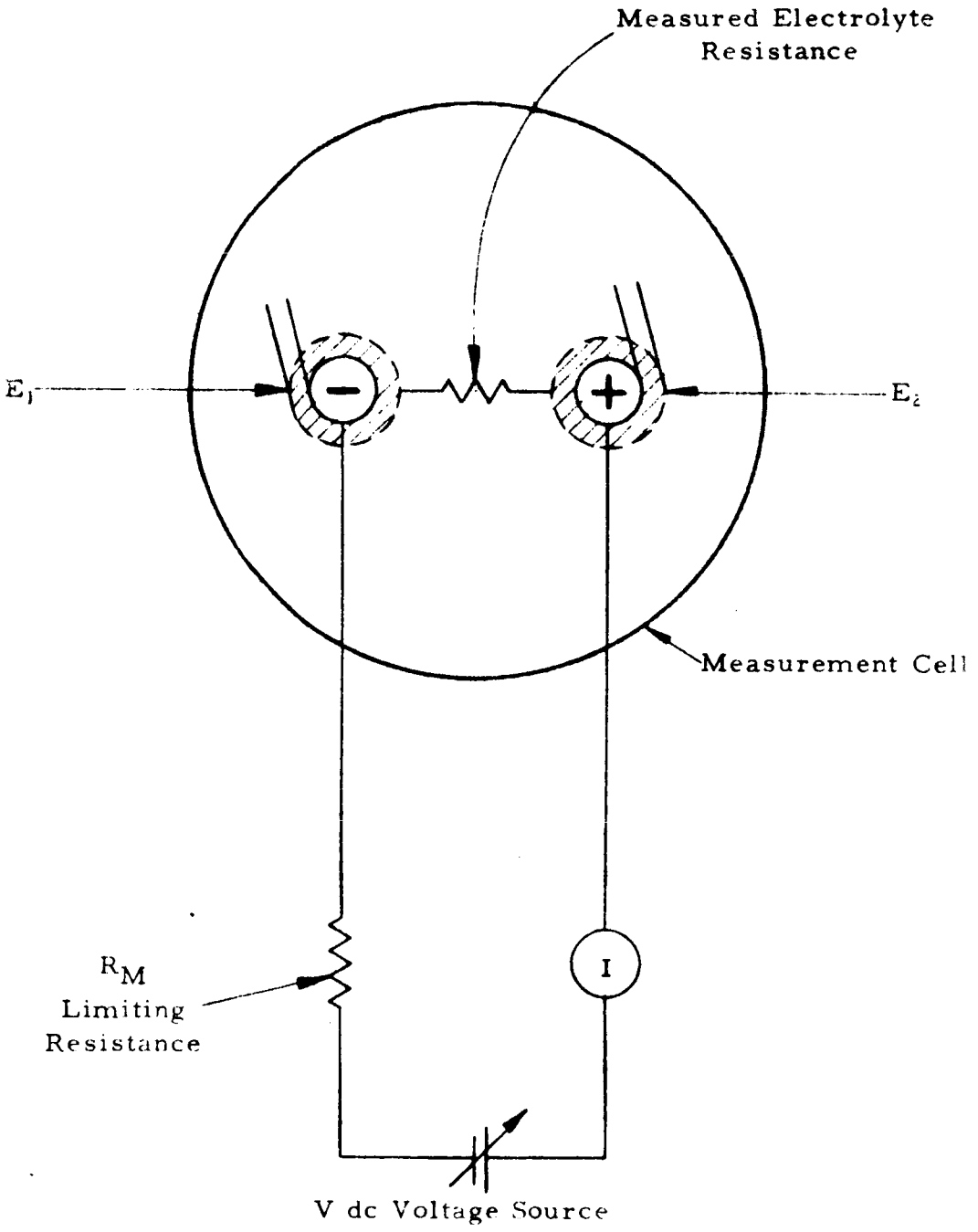


Symbolic diagram of specific resistance and decomposition potential measurements (expansion of Block B of Figure V-4, page V-10).

FIGURE V-7

PHYSICAL MODEL OF A CELL MEASURING NETWORK

See Item II, Figure V-6, page V-14 and Figure V-4, page V-10, Block B



Electrode Reaction Interface

E_1, E_2 - Interfacial Voltage

TABLE V-1

MEASURING SUB-CYCLE FOR A SINGLE CELL

MEASURING NETWORK	APPLIED VOLTAGE (volts dc) V	LIMITING RESISTOR (kilohms) R_M	RECORDER CURRENT RANGE (micro-amperes)
P	--	--	pressure
RK	--	--	ac specific resistance
I(1)	1	10	100
I(2)	2	20	100
I(3)	4	40	100
I(4)	6	60	100
I(5)	8	80	100
I(6)	10	100	100
I(7)	10	50	200
I(8)	10	20	500
I(9)	10	10	1000
RPK	10	10	polarized ac resistance

see Figure V-6 , page V-14 Item II

Specific Resistance-Decomposition Potential Recording Replotted for Clarity

Chemical System Acetonitrile/Lithium Fluoride/Ammonia Atmosphere

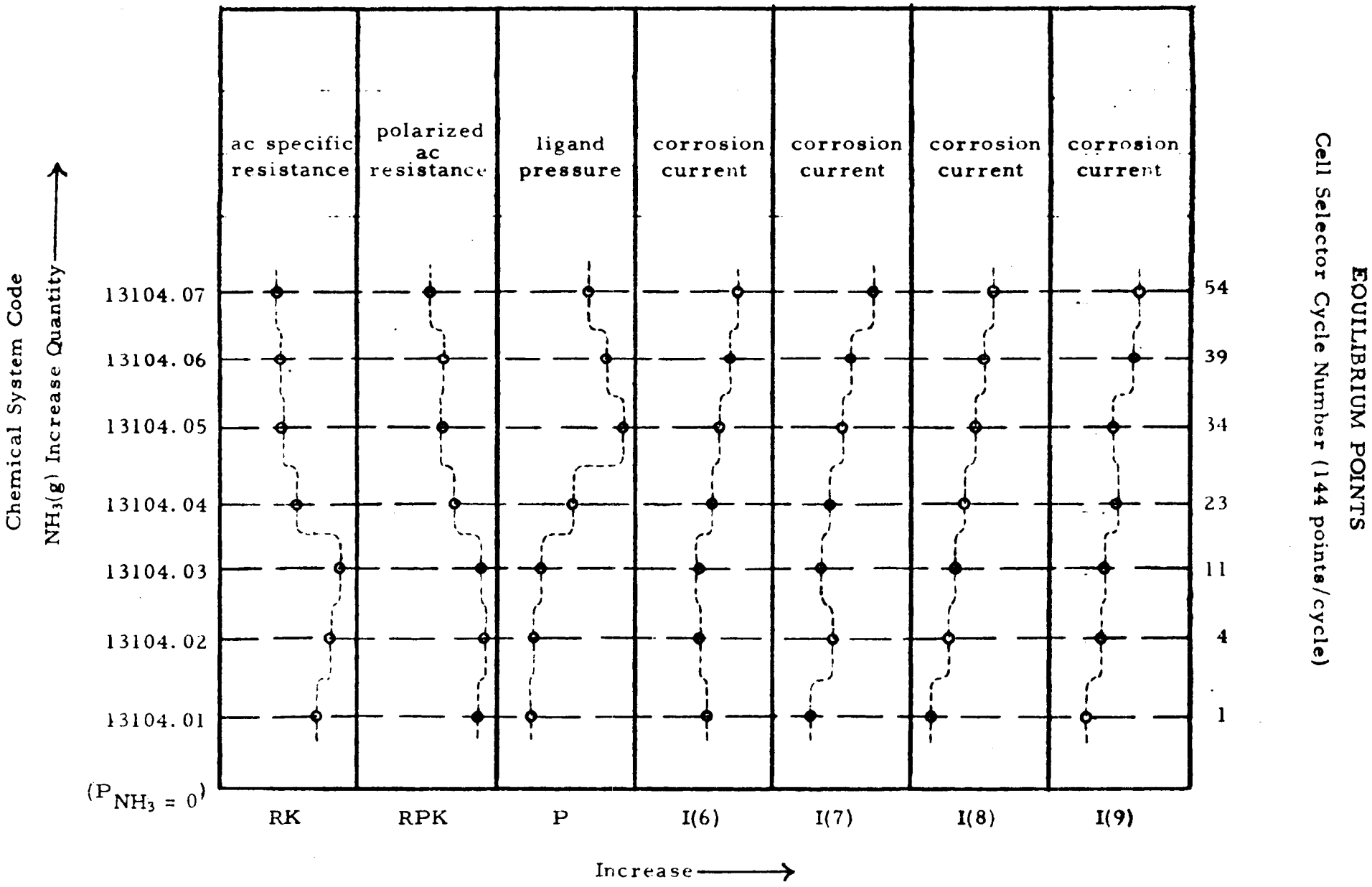


FIGURE V-8

SOLVENT-SOLUTE-ATMOSPHERE CODE

SOLVENT CODE

01	n-Butylamine	24	Hexylene Glycol
02	Ethyl Acetate	25	1-Fluoro-2, 4-Dintrobenzene
03	Propylene Carbonate	26	p-α-Dichlorotoluene
04	Acetone	27	2-Amino 3-Ethylpyridine
05	Benzene	31	Acetonitrile
06	Toluene	32	Dioxane
07	Pyridine	33	Ethylene Carbonate
08	Tetrahydrofuran	35	Para Chlorobenzotrifluoride
10	1, 1, 1-Trichloroethane	41	N, N-Dimethylformamide
11	iso-Propylamine	51	Formamide
12	Petroleum Ether	60	Dimethyl Sulfoxide
13	Butyrolactone	89	Amberlite LA-1-Freon 113 (50/50)
14	Methanol	90	Genesolv-D (Fluorotrichloroethane)
15	Fluorobenzene	91	Cyclohexanone
16	p-Fluorotoluene	95	Water
17	2-Ethanolpyridine	96	Ammonia
20	Nitromethane	97	Mercaptopropionic Acid
21	n-Propylamine	98	Amberlite LA-2
22	Phenyl Ether	99	Amberlite LA-1
23	N-Methyl-2-Pyrrolidone		

SOLUTE CODE

1.	AlF_3	8.	KCl	15.	$HONH_2 \cdot HCl$	22.	$SnCl_2$
2.	$AlCl_3$	9.	KSCN	16.	$(CH_3)_3N \cdot HCl$	23.	$(C_6H_5)_2CO$
3.	$Al_2(SO_4)_3$	10.	NaBr	17.	$MgCl_2$	24.	$C_6Cl_4O_2$
4.	LiF	11.	NaI	18.	$MgBr_2$	25.	$Mg(ClO_4)_2$
5.	LiCl	12.	NaCl	19.	KF	26.	$NaCO_2CCl_3$
6.	KBr	13.	$(CH_3)_4NCl$	20.	$MgSO_4$	27.	KCO_2CCl_3
7.	KI	14.	$(CH_3)_4NI$	21.	$AgNO_3$		

ATMOSPHERE CODE

0	Air	2	Sulfur Dioxide
1	Ammonia	3	Carbon Dioxide

digits can be interpreted to mean, in the order of their magnitude, the relative concentration of the ligand.

Figure V-8 also indicates how the large number of repeated measurements were characterized by a relatively small fraction of the total recorded points. Each chemical system code number represented another equilibrium cell measuring sub-cycle for a specific system, in this case acetonitrile/ lithium fluoride/ammonia. Each succeeding dashed grid line represents the same chemical system chosen at a different ligand pressure. Equilibrium measurement sub-cycles were selected by observing consistant and repeated recorded points of RK, RPK, P, and I(1) - I(9) for a given cell number. Corrosion current measurements I(6) - I(9) are plotted in this figure. These four corrosion current measurements were transferred to punch cards as representing the bulk of the pertinent decomposition data.

Inspection of this figure shows that RK and RPK increased with the application of the ligand and then decreased. The pressure increased and then dropped slightly due to excessive adsorption at the end of the run while the corrosion currents I(6) - I(9) increased gradually.

Computer Processing of Data
Blocks E, F, and G of Figure V-4, Page V-11

Measured data were transferred from selected areas on charts to punch cards (see input punch card, Figure V-9, page V-20). The digital unprocessed data points resulted from measurements of the corrosion currents I(6) - I(9), RK, RPK, and P.

The measured data from the input punch cards were then processed by a computer and converted to meaningful figures (see Computer Program No. 4, pages V-21, V-22, V-23). The maximum figure of merit, W, and the cell potential, E, were then calculated. The computer output consisted of additional punch cards (see output punch cards, Figure V-9, page V-20) on which were punched the following: the chemical system code; N, which indicated the curvature of the Tafel plot for that system; RK, the electrolyte specific resistance in kilohm - cm; RPK, the electrolyte polarized comparable resistance; P, the ligand pressure in pounds per square inch absolute when available; C and D (the modified Tafel constants); E, the cell potential; and W, the maximum figure of merit. The data were then tabulated from punch cards by means of a printer as indicated by the sample page of Table II-3, page II-7.

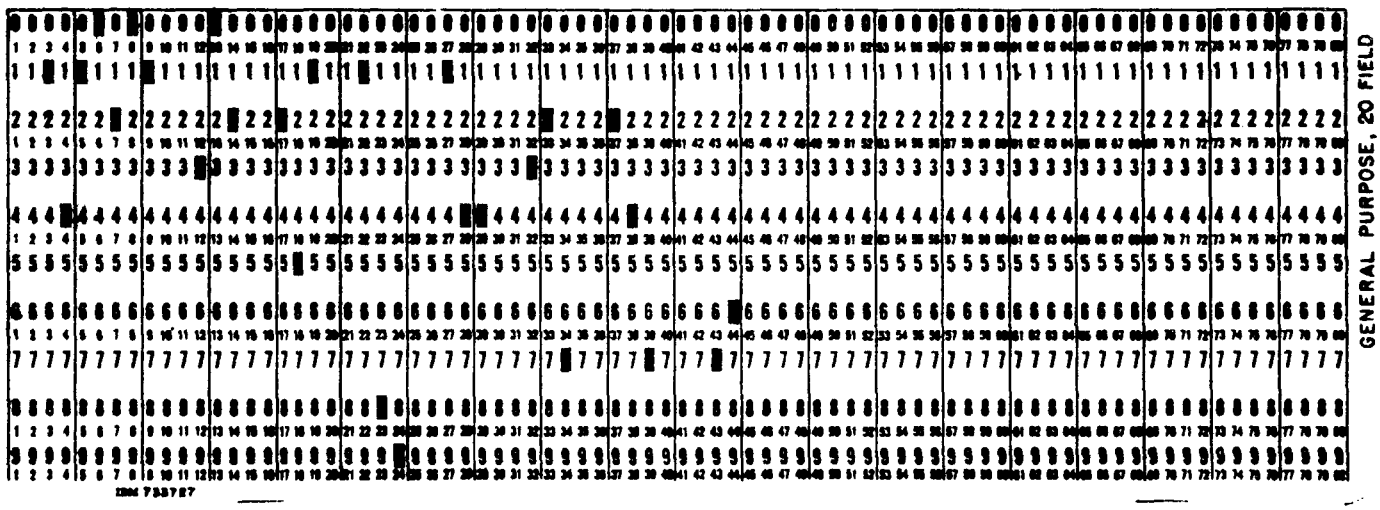
FIGURE V-9

Punch Cards for the Chemical System N, N-Dimethyl Formamide/Air/Aluminum Chloride

Input Punch Card (Unprocessed Data)

1410201 302 251 189 144 327 247 76

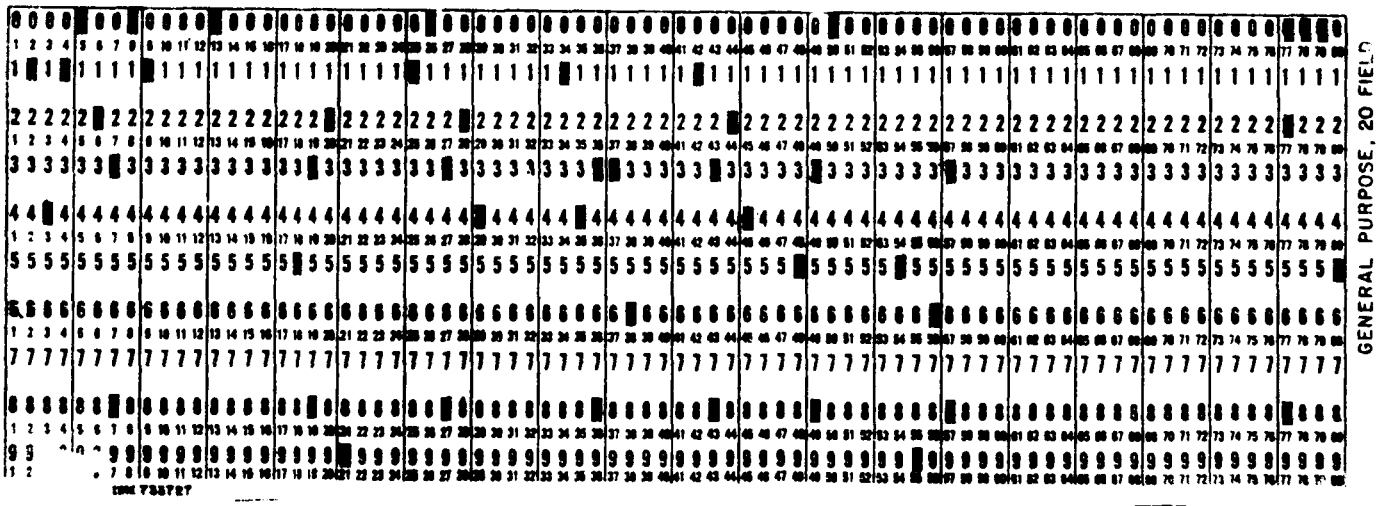
CODE I(6) I(7) I(8) I(9) RK RPK P



Output Punch Card, Processed Data

14102.01 0 5.29 10.24 14.36 1.24 5.0 596. W005

CODE N RK RPK P C D E W



See Table II-3, page II-7 and Figure V-4, page V-11, Blocks E and G.

```
C  LIVINGSTON ELECTRONIC CORP.  PROGRAM NO. 4
    1 READ 81
      PUNCH 81
      READ 82
      PUNCH 82
      PUNCH 83
      PUNCH 80
    2 READ 77, CODE, TFL6, TFL7, TFL8, TFL9,        S, PS
      IF (CODE) 3, 76, 3
    3 P= 0.97*(PS-130.0)
      N=0
      IF (RS - 60.0) 4, 4, 5
    4 RK= EXPF (3.94 - 0.026*RS)
      GO TO 8
    5 IF(RS - 410.0) 6,6,7
    6 RK = EXPF (2.87 - 0.0086*RS)
      GO TO 8
    7 RK = EXPF (7.48 - 0.0198*RS)
    8 R = 1000. * RK
      IF (RPS-60.0) 9, 9, 10
    9 RPK= EXPF (3.94 - 0.026*RPS)
      GO TO 13
   10 IF (RPS-410.0) 11, 11, 12
   11 RPK = EXPF ( 2.87 - 0.0086*RPS)
      GO TO 13
   12 RPK = EXPF (7.48 - 0.0198*RPS)
   13 RP = 1000. * RPK
      TFLC9 = 2.E - 6.*TFL9
      TFLC8 = 1.E - 6.*TFL8
      TFLC7 = 4.E - 7.*TFL7
      TFLC6 = 2.E - 7.*TFL6
      IF (TFLC9 - TFLC8) 16, 16, 14
   14 IF (TFLC8 - TFLC7) 17, 17, 15
   15 IF (TFLC7 - TFLC6) 18, 18, 20
   16 N = N + 400
      GO TO 14
   17 N = N + 200
      GO TO 15
   18 N = N + 100
      GO TO 20
   19 PUNCH 78, CODE, N, RK, RPK, P
      GO TO 2
   20 X9 = 10. - TFLC9*(R + 10000.)
      X8 = 10. - TFLC8*(R + 20000.)
      X7 = 10. - TFLC7*(R + 50000.)
      X6 = 10. - TFLC6*(R + 100000.)
      IF (X9 - X8) 23, 23, 21
   21 IF (X8 - X7) 24, 24, 22
   22 IF (X7 - X6) 25, 25, 26
   23 N = N + 40
      GO TO 21
   24 N= N + 20
      GO TO 22
   25 N = N + 10
```

```
      GO TO 26
   26 IF(N-0)27,61,27
   27 IF(N-60)28,44,28
   28 IF (N-70)29,44,29
   29 IF(N-400)30,44,30
   30 IF(N-600)31,44,31
   31 IF(N-700)32,44,32
   32 IF(N-300)33,44,33
   33 IF(N-40)34,44,34
   34 IF(N-30)35,44,35
   35 IF(N-20)36,44,36
   36 IF(N-10)37,44,37
   37 IF(N-770)38,44,38
   38 IF(N-100)39,44,39
   39 IF(N-200)40,44,40
   40 IF(N-710)41,44,41
   41 IF(N-720)42,44,42
   42 IF(N-730)43,44,43
   43 IF(N-740)45,44,45
   44 C = 1.0
      GO TO 46
   45 C = 2.0
   46 Y9=X9*1.22*EXPF(0.4*X9-5.5)*(1.-1.61*SQRTF(R/X9*TFLC9))
      W = Y9
      X = X9
      Y8=X8*1.22*EXPF(0.4*X8-5.5)*(1.-1.61*SQRTF(R/X8*TFLC8))
      IF(Y8-W) 55, 55, 48
   48 W = Y8
      X = X8
      Y7=X7*1.22*EXPF(0.4*X7-5.5)*(1.-1.61*SQRTF(R/X7*TFLC7))
      IF (Y7 - W) 55, 55, 51
   51 W = Y7
      Y6=X6*1.22*EXPF(0.4*X6-5.5)*(1.-1.61*SQRTF(R/X6*TFLC6))
      IF(Y6 - W) 55, 55, 54
   54 W= Y6
      X = X6
   55 IF (W-0.) 57, 57, 56
   56 IF (X-0.) 57, 57, 58
   57 W = 0.
      X = 0.
   58 IF (C - 1.) 59,60,59
   59 PUNCH 79, CODE, N, RK, RPK, P, X, W
      GO TO 2
   60 PUNCH 79, CODE, N, RK, RPK, P, X, W
      GO TO 61
   61 D = (X9 + X8 - X7 - X6)/LOG(TFLC9*TFLC8/(TFLC7*TFLC6))
      IF (D - 0.01) 62, 62, 63
   62 N = N + 1
      GO TO 19
   63 A = -D
      IF (A - .01) 62, 62, 64
   64 IF (D - 99.0) 65, 65, 66
   65 IF (A - 99.) 67, 67, 66
   66 N = N + 2
      GO TO 19
   67 C=.25*((X9+X8+X7+X6)-D*(4.63+LOG(TFLC9*TFLC8*TFLC7*TFLC6)))
      IF (C-999.0) 69, 69, 68
   68 N = N + 3
      GO TO 19
```

```
   69 B = -C
      IF (B-999.) 70, 70, 68
   70 X = 6.0
      W=3261.*(1.0-0.37*SQRTF(R)*EXPF((6.0-C)/(2.0*D)))
   72 X = X - 0.5
      Y = (49.6*X*EXP(0.4*X))*(1.0 - 0.9*SQRT(R/X)*EXP((X - C)/(2.*D)))
      IF (Y - W) 73, 73, 75
   73 X = X + 0.5
   74 PUNCH 79, CODE, N, RK, RPK, P, C, D, X, W
      GO TO 2
   75 W = Y
      IF (X - 0.5) 74, 74, 72
   76 PUNCH 83
      PUNCH 83
      GO TO 1
   77 FORMAT ( F9.2, F5.0, F5.0, F5.0, F5.0, F5.0, F5.0, F5.0)
   78 FORMAT (F9.2, I4, F6.2, F6.2, F6.1)
   79 FORMAT ( F9.2, I4, F6.2, F6.2, F6.1, F7.2, F7.2, F5.1, F7.0)
   80 FORMAT (43H    CODE     N    RK   RPK   P   C   D    X, 6X, 1HW)
   81 FORMAT (15X, 49H  FIRST TITLE CARD
   82 FORMAT (15X, 49H  SECOND TITLE CARD
   83 FORMAT(1H )
         END
```

The Computer Program
Block F of Figure V-4, Page V-11

The computer program, pages V-21, V-22, V-23, was formulated to apply the battery energy balance equation judiciously to the large volume of selected data. A chemical system code was provided to identify the system in question. An additional code, N, described the shape of the Tafel curve. This was especially valuable in that some insight may be given as to the electrochemical behavior of the system. RK, RPK, and P were discussed above, and C and D are derived in Appendix C.

Alternate ways of calculating E and W were provided for in the computer program. This was useful in that W could be evaluated with greater reliability. One method of computation which used the values of C and D (the modified Tafel constants) was based on a computer approximation of the Tafel line (see equation (7) below). This approximation was not always sensitive to solvent break-down; hence, excessive figures of W and E were censored see Figure V-10, page V-25. However, this method was most useful when N = 0 (indication of a linear Tafel plot) because W could be more accurately estimated since controlled increments of E were used in the computation.

The alternate method of computation employed the actual value of E (interfacial voltage in this case) and the corresponding current density, J, in order to evaluate W (see equation (8) below). The advantage of this method was that W determined at the observed voltage is more likely to be valid than by the first method of computation, since the first involves a questionable approximation of the Tafel line for non-linear plots.

$$W = EF\, e^{0.4E - 5.5} \left(1 - 0.9 \sqrt{\frac{\rho}{E}\, e^{\frac{E-C}{D}}} \right) \tag{7}$$

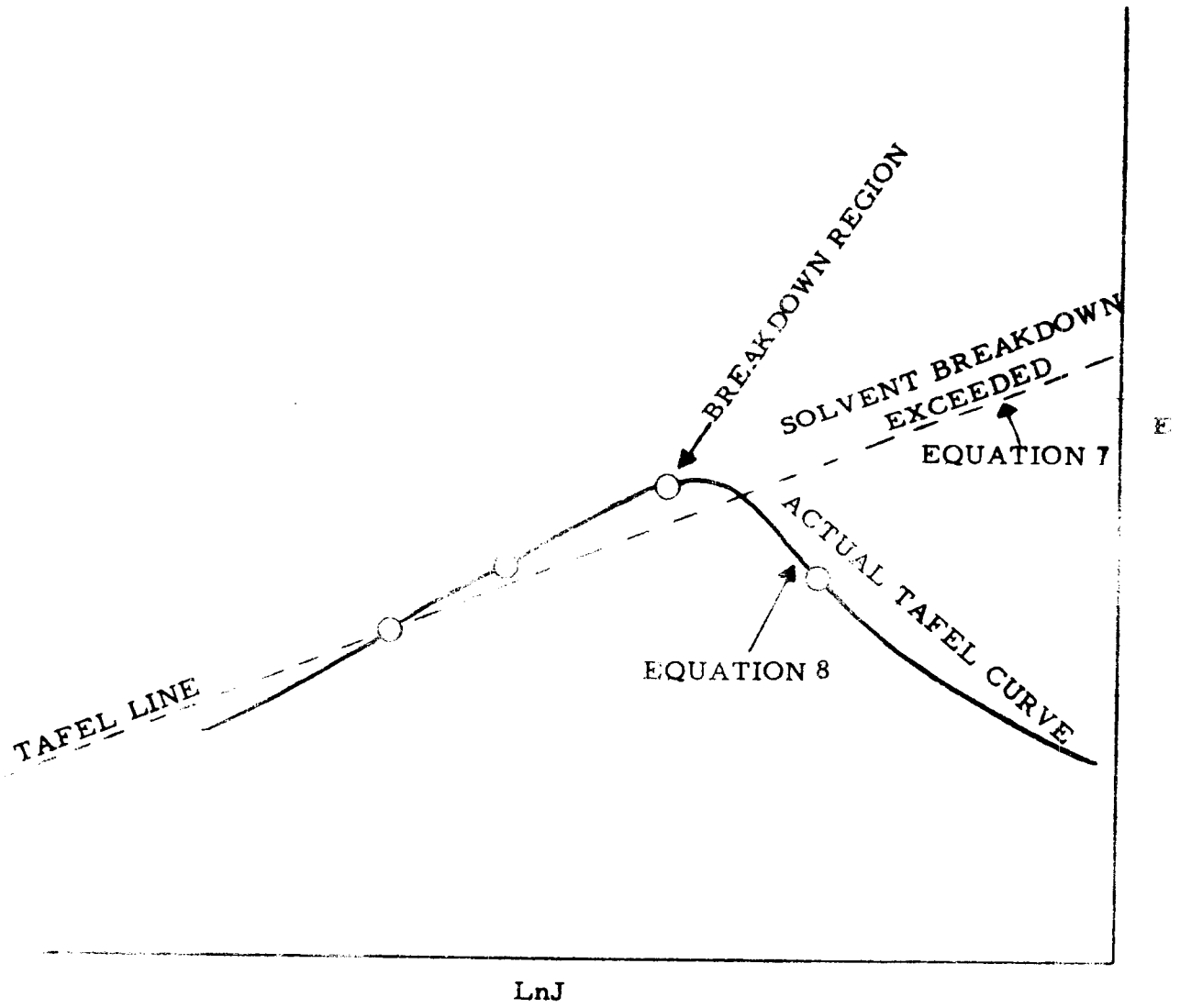
$$W = EF\, e^{0.4E - 5.5} \left(1 - 0.9 \sqrt{\frac{\rho J}{E}} \right) \tag{8}$$

The Computer Print-Out
Block H of Figure V-4, Page V-11

The computer output format was designed to present the computed numerical results in a form which allows for direct interpretation. In Table II-3, page II-7, the figure of merit, W, is listed in the right-hand column; and chemical systems providing values greater than 500 were summarized in Tables II-1 and II-2 starting on page II-4.

FIGURE V-10

Plot showing the application of the N code to the interpretation of the computer print-out.



See Table II-3, page II-7, Code No. 13102.10

Non-linear modified Tafel data often required two methods of computation due to the limited discretion that could be designed into the computer program. When this occurred, manual calculation was used to resolve the most correct interpretation of the W values.

VERIFICATION OF THE ENERGY BALANCE EQUATION (5) DERIVED FOR THE EVALUATION OF ELECTROLYTE SYSTEMS ON A FIGURE OF MERIT BASIS BY BATTERY PERFORMANCE

$$W = \frac{F}{M}\left(E - 0.9\sqrt{\rho EJ}\right) = e^{3.9 + 0.4E}\left(E - 0.9\sqrt{\rho EJ}\right)^{**}$$

Example I

The cell shown in Figure II-1, page II-3, will be used as the first example. E is first assigned a value of six volts. Rho and J are obtained from Figure V-11 on the following page.

$$W_6 = e^{3.9 + 2.4}\left(6 - 0.9\sqrt{99*6*6*10^{-3}}\right)$$

W_6 = 2, 320 watt hours per pound of net electrode reactants.

E is then decreased to 5.5 volts.

$$W_{5.5} = e^{3.9 + 2.2}\left(5.5 - 0.9\sqrt{99*5.5*4.7*10^{-4}}\right)$$

$$W_{5.5} = 2,220$$

The higher figure of 2, 320 watt hours per pound of net electrode reactants is taken as the figure of merit for the electrolyte $LiClO_4$ - butyrolactone.

**L set at 1/5 cm as a practical minimum.

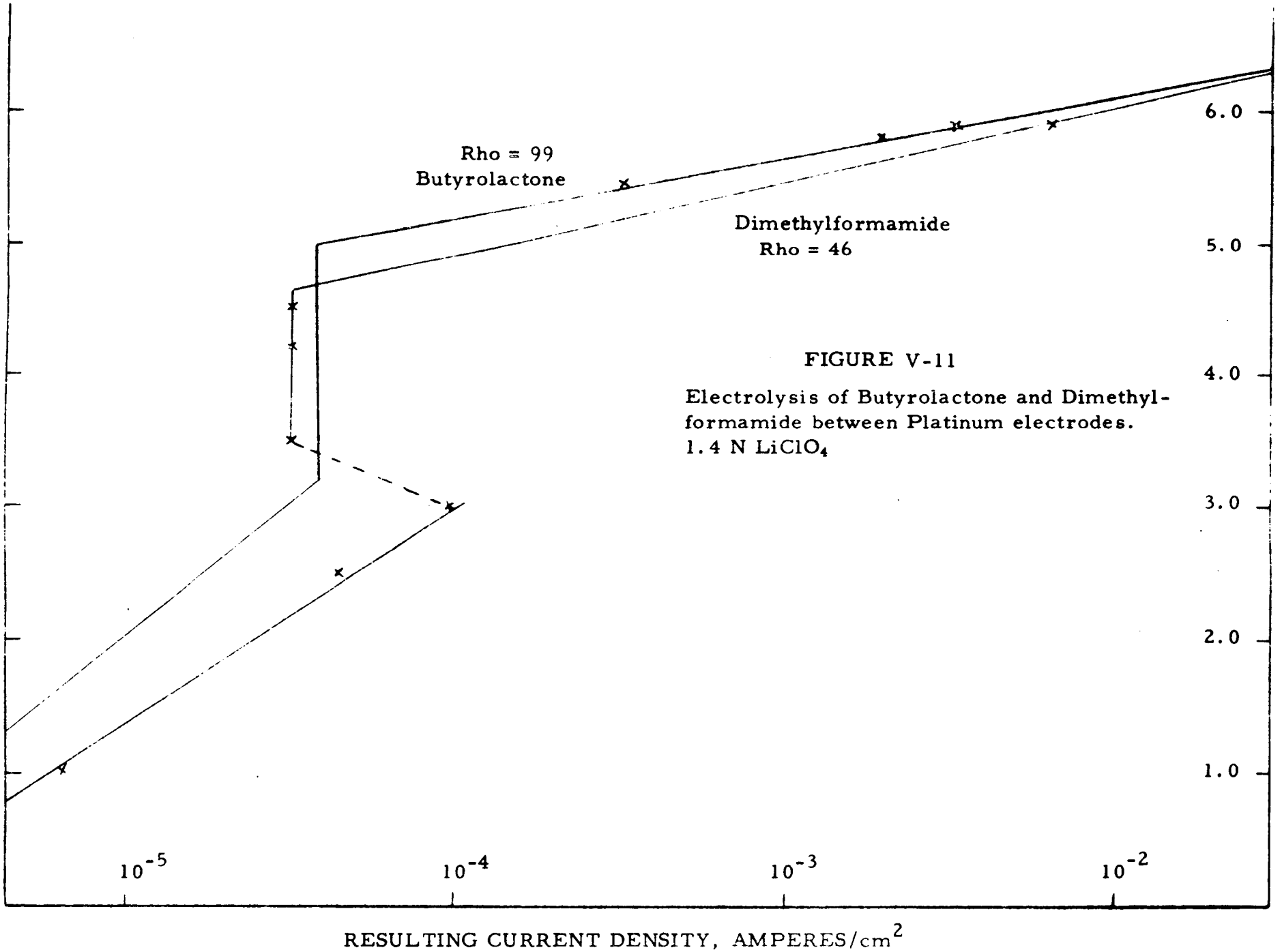
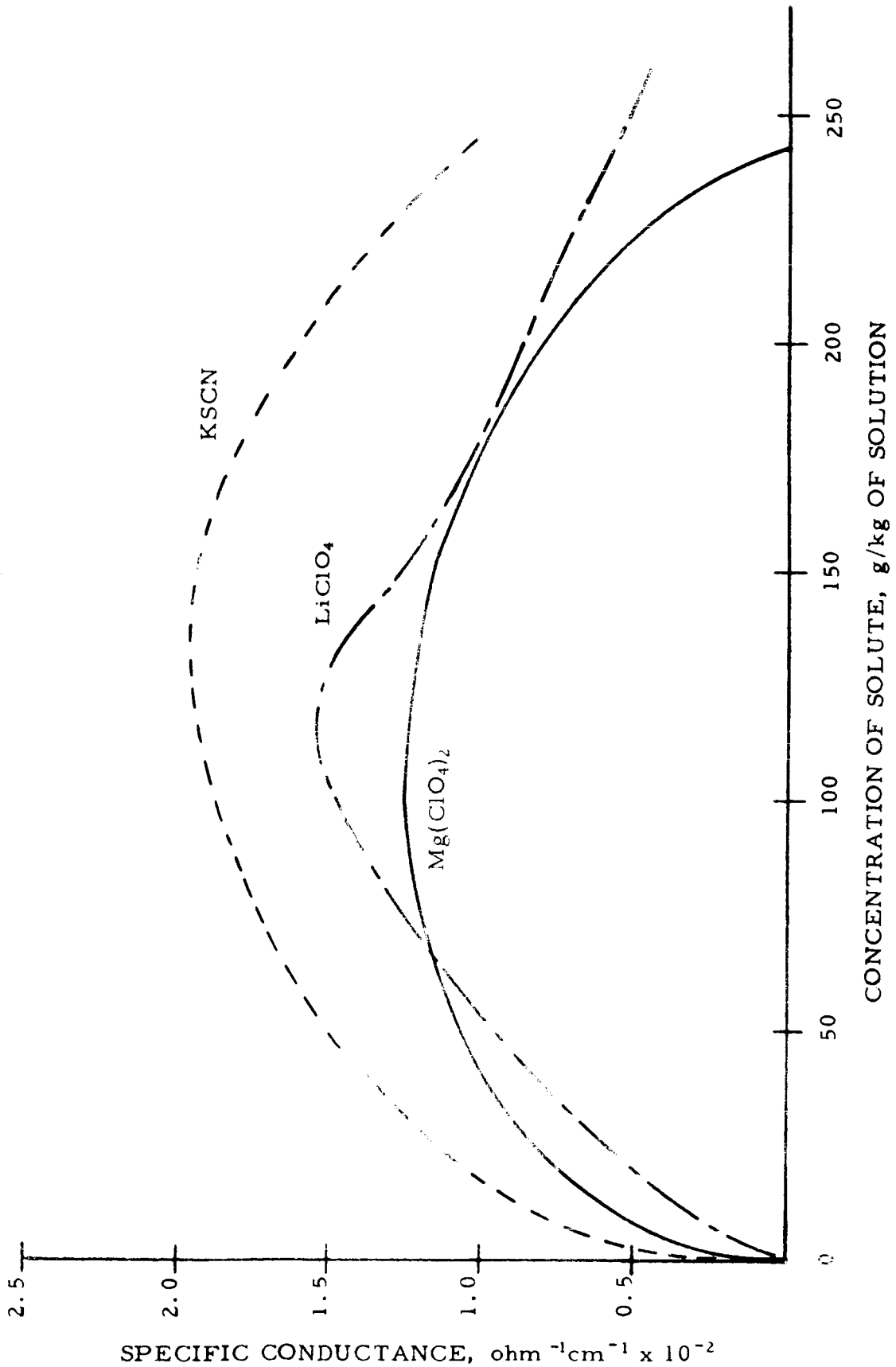


FIGURE V-11

Electrolysis of Butyrolactone and Dimethylformamide between Platinum electrodes.
1.4 N $LiClO_4$

FIGURE V-12

SPECIFIC CONDUCTANCE OF BUTYROLACTONE SOLUTIONS OF POTASSIUM THIOCYANATE, LITHIUM PERCHLORATE, AND MAGNESIUM PERCHLORATE AT ROOM TEMPERATURE



This figure is substantially greater than the minimum value of 500.

Cell #95 of Table III-1 and Figure II-1 , page II-3 , initially operated at 3.3 volts, not 6; hence, $W_{3.3}$ is used for comparison below:

$$W_{3.3} = e^{3.9 + 1.2} (3.3 - 0.9\sqrt{99*3.3*4*10^{-5}})$$

$$= e^{5.2} (3.3 - 0.9\sqrt{1.31*10^{-2}})$$

$$= 185(3.3 - 0.9*0.1)$$

$$= 185(3.20) = 593$$

Applying the packaging efficiency of 40 per cent

593*40% = 237 watt hours per pound

Since complete utilization of uncorroded cathode reactant is presumed by the energy balance:

237*85% achieved = 202 watt hours per pound

The maximum figure of W of 2,320 and its related cell potential of 6 volts implies the use of stronger electrodes for even greater energy density.

The achieved figure of 125 watt hours per pound represents 62 percent of the value of W at this voltage level. Further engineering of this cell structure may well provide 200 watt hours per pound.

Example II

For the second example, an aqueous cell not employing the auto-ionization constant will be used. Perry[2] gives an overvoltage and current density figures for H_2/Pt in aqueous H_2SO_4 and O_2/Pt in aqueous NaOH. From this, Tafel relationships for water may be calculated:

$$\eta_{H_2} = 0.68 + 0.22 \log J$$

$$\eta_{O_2} = 0.77 + 0.26 \log J$$

$$\eta_{H_2O} = \eta_{H_2} + \eta_{O_2} = 1.45 + 0.48 \log J$$

Converting to the natural base:

$$\eta_{H_2O} = 1.45 + 0.2 \ln J$$

Combining the decomposition potential of water:

$$E = \eta_{H_2O} + 1.2 = 2.65 + 0.2 \ln J$$

Converting to the exponential form:

$$J = \frac{E - 2.65}{0.2}$$

Using this value for J in the energy balance with ρ taken as unity:

$$W = e^{3.9 + 0.4E} (E - 0.9 \sqrt{\rho EJ})$$

gives the following results:

E	W	40% W
1.8	165	66
2.3	213	85
2.4	215	86
2.5	213	(suitable
2.6	181	for reserve
2.7	151	cells only)
3.0	Negative	

[2] J. H. Perry, Chemical Engineers Handbook, p. 2752.

The 40 per cent W figures compare reasonably well with the normally reported figures for aqueous batteries.

ION EXCHANGE MEMBRANE CELLS

In Example II of page V-31 an interesting improvement is obtained by further modifying the Tafel constant through the inclusion of the autoionization contribution:

$$E = \frac{RT}{NF} \ln 10^{-14} + 2.65 + 0.2 \ln J$$

$$= 0.84 + 2.65 + 0.2 \ln J$$

$$\doteq 3.5 + 0.2 \ln J$$

Whereby:

$$J = e^{\frac{E-3.5}{0.2}}$$

and W is increased from 284 to:

$$W_{3.2} = e^{3.9 + 1.3\left(3.2 - 0.9\sqrt{3.2}\ e^{\frac{3.2 - 3.5}{0.4}}\right)}$$ (ρ is taken as one ohm-cm for aqueous solutions)

$$= e^{5.2} * (2.4)$$

$$= 180 * (2.4) = 440 \text{ watt hours per pound}$$

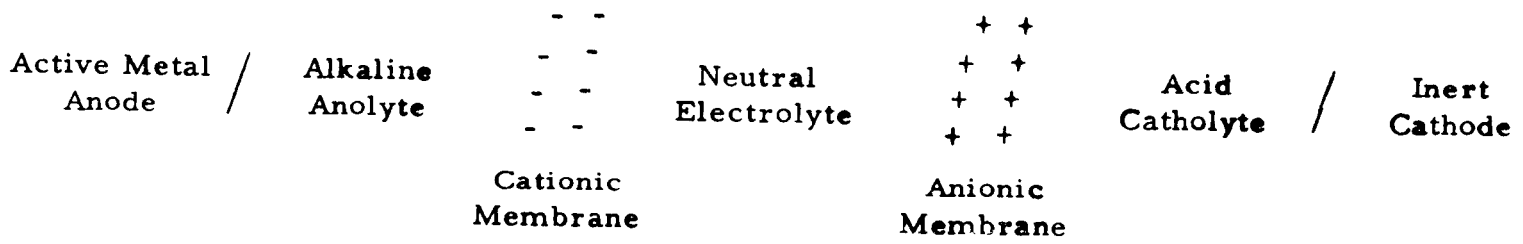
To obtain the indicated advantage of this increased figure of merit, it is required to maintain an alkaline anolyte and an acid catholyte to suppress the evolution of hydrogen and oxygen and consequent corrosion of the electrodes. This is theoretically possible by the use of ion-exchange membranes. Generally, two membranes would be required to retain hydroxyl ion concentration in the vicinity of the anode and hydrogen ions at the cathode.

Figure V-13, page V-34, shows a diagram of such a cell, which upon inspection, resembles a desalination cell in reverse. Table V-2 , page V-35, lists the structures of a number of such cells and the results obtained. Hybrid solvent cell voltages in the order of 3.6 volts were actually obtained. However, the cathode membranes used failed after varying periods of time, presumably due to acid oxidation.

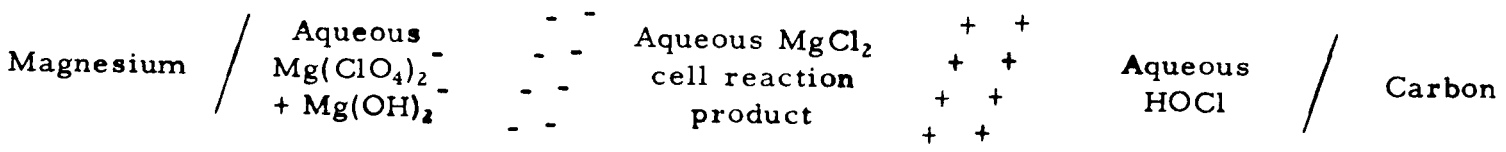
In the latter portion of the program, additional membranes were tested and, though it would appear that suitable membranes have been located, practical demonstration cells are yet to be built.

FIGURE V-13

ION EXCHANGE MEMBRANE CELL STRUCTURE



Example



Maximum voltage observed in the order of 2.8.

TABLE V-2

PILOT CELLS UTILIZING ION EXCHANGE MEMBRANES

Cell No.	Anode	Anolyte	Membrane	Catholyte	Cathode	o.c. Potential	Remarks
1	Mg/Li	Butyrolactone .25M KSCN	Gelman WB6403 Gelman WA6402	1M H_2SO_4**	$KMnO_4$/C	3.8	Anolyte-catholyte intermixing.
2	Mg/Li	Butyrolactone .25M KSCN	Permion 1010	1M H_2SO_4**	$KMnO_4$/C	4.2	Anolyte-catholyte intermixing.
3	Mg/Li	Butyrolactone .25M KSCN	Gelman WB6403	Butyrolactone $CuCl_2$*	$CuCl_2$/Cu	3.6	Anolyte-catholyte intermixing.
4	Mg/Li	Butyrolactone .25M KSCN	Permion 1010	Butyrolactone $CuCl_2$*	$CuCl_2$/Cu	3.7	No intermixing in 6 days; polarization 0.5v at 10^{-5} amp/cm^2.
5		Pt/Li-NH_3	Cationic glass	KCl**	AgCl/Ag	3.15	High cell resistance.
6		Pt/Li-NH_3	Gelman WA6402 Gelman WB6403	1M H_2SO_4**	$KMnO_4$/C	4.4	Catholyte permeation of membrane.
7		Pt/Li-NH_3	Gelman WA6402	4M H_2SO_4**	C	3.0	Catholyte permeation of membrane.
8		Pt/Li-NH_3	Gelman WA6402	4M H_2SO_4**	$KMnO_4$/C	4.1	Catholyte permeation of membrane.
9		Pt/Li-NH_3	Gelman WA6402	NH_3, KSCN*	S:C/Ag	2.5	Catholyte permeation of membrane
10		Pt/Li-NH_3	Gelman WA6402	NH_3, NH_4SCN*	S:C/Ag	2.5	Loss of potential after 25 hours.

*Saturated Solution

**Aqueous Solution

LITERATURE STUDIES

An example of the literature study conducted as part of the project deliberation is given on page V-37. This is a page taken from the cumulative abstract control index provided in the monthly and quarterly reports. Abstract control number 2006 represents a brief summary of a particular source. Page V-38 is a copy of the file card generated in that work for access by project members. Minor surveys upon miscellaneous subjects were also conducted and reported. The following has not been presented in previous reports and serves as an example of the miscellaneous studies.

A patent search upon recent developments in electrolytic capacitors was available through the courtesy of the parent company. Since this represents a technology distinctly related to the battery art, the material was studied primarily from the viewpoint of possible electrolyte combinations. A brief outline summary has been prepared and is presented on the following pages.

Log of Report Numbers

Card
Col.

4 5 6 Column 3 Code Entry 2

0 0 1 "Mechanism of Electrodeposition of Metals from Liquid Ammonia Systems" Electrochemical Society Journal, Vol. 110, No. 7, p. 723, Watt and Vaughn

0 0 2 "Mechanism of Electrodeposition of Cobalt from Liquid Ammonia Solutions of Spin-Paired Cobalt (3+) Complexes" Electrochemical Society Journal, Vol. 108, No. 4, p. 351, Watt & Vaughn

0 0 3 "Investigation of the Electrochemical Characteristics of Organic Compounds, VII-Organic Positive Iodine and Alphatic Azo Compounds" Electrochemical Society Journal, Vol. 108, No. 4, p. 303, Glickman and Morehouse

0 0 4 "Elucidation of Electrochemical Reactions and Systems" NAVWEPS Report 8135, NOLC, Tobias

0 0 5 "Polarization Capacitance Determinations of Surface Roughness" Electrochemical Society Journal, Vol. 109, No. 2, p. 168, Turpin and Testerman

0 0 6 "Electrochemical Battery Research" W.C.U.S., NOLC, Tech. Memo 44-8 Panzer, Spindler, Harris

0 0 7 "Analysis of a Theoretical Liquid Metal Cell for Energy Storage in Space" General Motors Eng. Journal, First Quarter 1963, Hietbrink and Karas

0 0 8 "The Reaction of Lithium with Water Vapor" Journal of Electrochemical Society, Vol. 110, No. 2, pp. 141-144, Feb. 1963, W.R. Irvine and J.A. Lund

0 0 9 "Electrochemistry in Pyridine I. Polarography and Macroscale Electrolysis of Inorganic Salts" J. Electrochemical Society, Vol. 110, No. 2, pp. 160-166, Feb. 1963

0 1 0 "Comparison of the Activation Energy for the Reorientation of Molecules with the Activation Energy of Viscous Flow" Optics and Spectroscopy, Vol. 6, No. 1, July 1960, pp. 47-48, M.F. Vuks

0 1 1 "Force Constants and Interaction Coefficient of Pyramidal Hydrides" Optics and Spectroscopy, Vol. 6, No. 1, pp. 18-20, G.I. Rybakova, D.S. Kovalchuk, V.P. Morozov

0 1 2 "The Crystal Structures of the Double Salt of Copper Pentammino-Perchlorate and Ammonium Perchlorate" Soviet Physics Crystallography, Vol. 5, No. 1, pp. 130-132, V.M. Gurevich, Rex, Zheludev

2006

Electrochemical Battery Research

Investigation of electrochemical cell systems in fused electrolytes of:

$Mg/LiCl-KCl-kaolin/V_2O_5-Ni$
$Mg/LiCl-KCl-kaolin/V_2O_5-B_2O_3-Ni$
$Mg/LiCl-KCl-kaolin/LiCl-KCl-V_2O_5/Ni$
$Mg/LiCl-KCl-kaolin/LiCl-KCl-CuO/Ni$

None of these cells displayed exceptional lifetime at high current density. Ohmic polarization and concentration polarization were probably a function of the low ohmic conductivity of the V_2O_5 cathode coating and the reduced amount of V_2O_5 available in the $V_2O_5-B_2O_3$ glass coating and lack of V_2O_5 in the catholyte respectively.

CuO does not appear to be a very promising cathode material. Ca, Mg, and 10% Li-Pb alloy anodes were used in these experiments. Li (10%)-PB (90%) gives an emf. only 0.2 volts less than that with calcium.

W. S. Harris, R. E. Panzer, & W. C. Spindler, U. S. Naval Ordnance Laboratory, Corona, California, Tech. Memo 44-8, December 1960.

2006

Card 2

$V_2O_5-B_2O_3$ and V_2O_5 glassodes or glass cathodes electrochemical efficiency was determined at 300 degrees C and 450 degrees C.

Liquid and vapor NH_3 activated cells were studied at -34 degrees C with 15, 20, 25 mole % NH_4SCN.

$Li/NH_4SCN-NH_3$/meta dinitrobenzene : Carbon
Trinitrobenzene was used as a cathode material in NH_3. Results indicated that it gives a higher potential than m-DNB and behaves in a similar manner.

A mathematical paper on the distribution of reaction in porous electrodes.

SELECTED PATENTS ON CAPACITORS

2,877,391 NH_3 l., methylamine, ethylamine

3,052,829 "Minimization of H_2 production" by use of selected cations in the electrolyte.
Water, organic solvents, N,N-dimethylacetamide

2,923,867 Many solutes and solvents are listed. Solvents: polyhydroxy alcohols such as ethylene glycol; lower alkyl phosphates such as triethylphosphate; mono and di lower alkyl substituted amides such as dimethylformamide; halogenated hydrocarbons such as 1,2-dichloroethane; partially fluorinated hydrocarbons; nitro alkanes such as nitromethane; and unsubstituted nitriles such as malono nitrile.

2,932,153 Solvents: ethylene glycol, propylene glycol, diethyleneglycol.

2,965,690 Solvents: propylene carbonate, gamma-valerolactone, butyrolactone, ethylene glycol.
Salts: benzyl triethyl ammonium chloride, phenyl dimethyl allyl ammonium iodide.

2,965,816 Solvents: dimethylformamide plus other amides.
Salts: listed.
Tested at -70°C.

2,977,514 gel electrolyte: LiCl + polyvinyl alcohol + boric acid.
Set gel with NH_3.

3,065,389 Solvents: propylene carbonate; bis(2-methoxyethyl)carbonate ($145/pound), pour point = -60°C., boiling point = 225°C.; bis(2-chloroethyl)carbonate ($8/100 grams), pour point = -60°C., boiling point = 218°C.; 10% ethylene carbonate + 90% propylene carbonate freezes at -55°C.

SELECTED PATENTS ON CAPACITORS Continued

3,082,360 Solvents: ethylene glycol with ammonium pentaborate + H_2O
H_2SO_4, 30%
Aqueous $PtCl_4$ + $PbAc^-$
Operable to -60°C.

3,098,182 Electrolyte: at least one aliphatic acid or anhydride and at least one heterocyclic compound having a nitrogen heterocyclic atom. See columns 3 and 4.

3,120,695 Electrolyte: at least one aliphatic acid or anhydride or arylhalide and at least one heterocyclic compound having a nitrogen heterocyclic atom.
Range: (-)60°C. to (+)150°C.

2,934,681 Range: (-)60°C. to (+)200°C.
Many electrolytes are listed, among them: Solvents: tertiary phosphate esters; trialkyl phosphites; neutral esters of phosphonic acids; neutral esters of phosphinos acids; aklyl esters of sulfinic, sulfonic, sulfuric, and vanadic acids. Salts: ammonium acetate, arsenate, nitrate, oxalate, and reaction products of List A with List B (column 4). Electrolytes: column 5.

2,934,682 Range: 125°C. to (-)60°C.
Electrolytes: comprising alkyl ammonium salts of alkyl esters of P-containing acids in non-aqueous solvents such as butanol, propylene glycol, diethylene glycol, triethylene glycol, 1,4-butane diol, ethylene glycol, and dimethylformamide.
Salts: examples - tris-(triethylammonium)-tri-methyl-tetraphosphate, bis-(triethylammonium)-monoethyl-orthophosphate, tri-ethylammonium diethylorthophosphate, tri-ethylammonium benzenephosphonate, hexanolammonium benzenephosphinate, tri-n-butylammonium di-n-octyl monoacid pyrophosphate.

SELECTED PATENTS ON CAPACITORS Continued

2,801,221 To improve low-temperature characteristics by adding certain free radicals to electrolyte (temperature not specified).
Example - stable free radicals: triarylmethyls, penta phenyl ethyl; aroxy radicals; triaryl hydrazyls; diaryl nitrogen oxides; nitrogen oxides; arylthiols; unstable free radicals (produced by oxidation or reduction): see column 2.
Solvents: dimethylformamide, triethylene glycol, butyronitrile.

2,830,237 Temperature range: +150°C. to (-)60°C.
Solvents: lower alkyl phosphates (as tri-n-butyl phosphate).
Salts: salt of a polynitro substituted phenol and a lower alkyl amine such as tri-n-butyl ammonium picrate.

2,872,629 Employ eutectic mixture of at least two lower alkyl amine salts in an organic plasticizer.
Solvents not required.
Many salts with melting points and plasticizers with boiling points listed.
Range: from eutectic point to about 250°C.

2,890,394 Ethylene glycol added to reduce operating temperature to -55°C.
Water soluble ammonium salt and soluble silicate added to prevent hydration of the Al_2O_3 film on the aluminum electrodes or other aluminum parts.
Examples: ammonium borate, sodium meta silicate.
"Remarkable improvement in... capacitance stability."
See column 5, lines 5 to 19.

2,941,946 "Method of Making an Electrolyte"
Claim 2: "A process... in which ethanol amine is mixed with ethylene glycol then trifluoroacetic acid → ethanol-ammonium trifluoroacetate in ethylene glycol." Adjust pH-8-9; add 0.25 to 2.5% water.
Gives good, reproducible properties.

SELECTED PATENTS ON CAPACITORS Continued

2,944,026 "Electrolytes"

Mixtures of adducts and solvent combinations may be used to extend operational range of capacitors.

Solutes: compounds of strong electron affinity and nudeophilic compounds.

Solvents: polyalchols, amides, nitriles.

See lists in patent.

2,945,164 "Electrolyte and Capacitor Utilizing the Same."

Solvents: unsubstituted simple nitriles - liquid from -60°C. to +130°C. See list.

Mixed solvents and co-solvents indicated.

Solutes: inorganic compounds, salts of organic acids, organic salts of strongly ionizing organic acids.

See lists.

2,965,187 "Electrolytes for... Capacitors."

Temperature range: -50°C. to 200°C.

Solvent: substituted amides of organic acids, other than formic.

Solutes: substituted ammonium pentaborates, boric acid, and salts of boric acid.

See examples.

3,003,089 "Non-Aqueous Electrolyte."

"Extremely Wide Temperature Range."

Solute: phenol amines (phenol may be replaced by halogen-substituted phenols or lower alkyl substituted phenols). List of useful amines given.

Solvents: Alkanols, alkyl phosphates, polyhydroxyl alcohols, ethylene glycol.

See examples.

STATISTICAL ANALYSIS OF PRIMARY BATTERY PERFORMANCE

Introduction

It is interesting to note that performance data of the conventional aqueous battery solutions follows a normal probability density function. This mathematical function is generally referred to as the bell shaped curve.

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \qquad \exp - \frac{(x-u)^2}{2\sigma^2}$$

where: x = random variable
u = overall mean
σ^2 = variance

This phenomenon enables probability estimates to be made regarding the generation of 200 watt hours per pound capability using conventional aqueous battery systems.

Background

Table I presents the historical data on primary battery systems collected to date. The data was extracted from "Selected Papers on New Techniques for Energy Conversion", Sumner, Levine; Dover Publications, 1961, page 361.

TABLE I

CONVENTIONAL AQUEOUS BATTERY PERFORMANCE

Rank	Type Battery	Chemical Notation	Watt Minutes Per Gram Of Cell
1	Alkaline Zinc-Manganese Dioxide (Crown)	Alk Zn/MnO_2	2.6
2	Leclanche	Zn/MnO_2	4.0
3	Magnesium-Manganese Dioxide	Mg/MnO_2	5.8

Rank	Type Battery	Chemical Notation	Watt Minutes Per Gram Of Cell
4	Magnesium-Bismuth Trioxide	Mg/Bi_2O_3	6.2
5	Zinc-Mercuric Oxide (RM)	Zn/HgO	7.0
6	Magnesium-Organic	Mg/Org	8.5

Analysis of Rank-Order Correlation

Normal-probability paper enables the average and the variance to be calculated graphically. It has been shown by many (a good reference is Introduction to Statistical Analysis, pages 55-57, second edition (1957), Dixon & Massey, McGraw-Hill) that if one plots the cumulative distribution and observes a straight line fit, then a normal distribution can be assumed. This proven assumption generates valid probability statements.

Figure 1 presents the data shown below.

Rank	Cumulative Probability	Watt Minutes Per Gram	Type of Cell
1	1/7 = 14 2/7%	2.6	Alk Zn/MnO_2
2	2/7 = 28 4/7%	4.0	Zn/MnO_2
3	3/7 = 42 6/7%	5.8	Mg/MnO_2
4	4/7 = 56 1/7%	6.2	Mg/Bi_2O_3
5	5/7 = 71 3/7%	7.0	Zn/HgO
6	6/7 = 85 5/7%	8.5	Mg/Org

Estimation of the Probability of 200 watt hours per pound

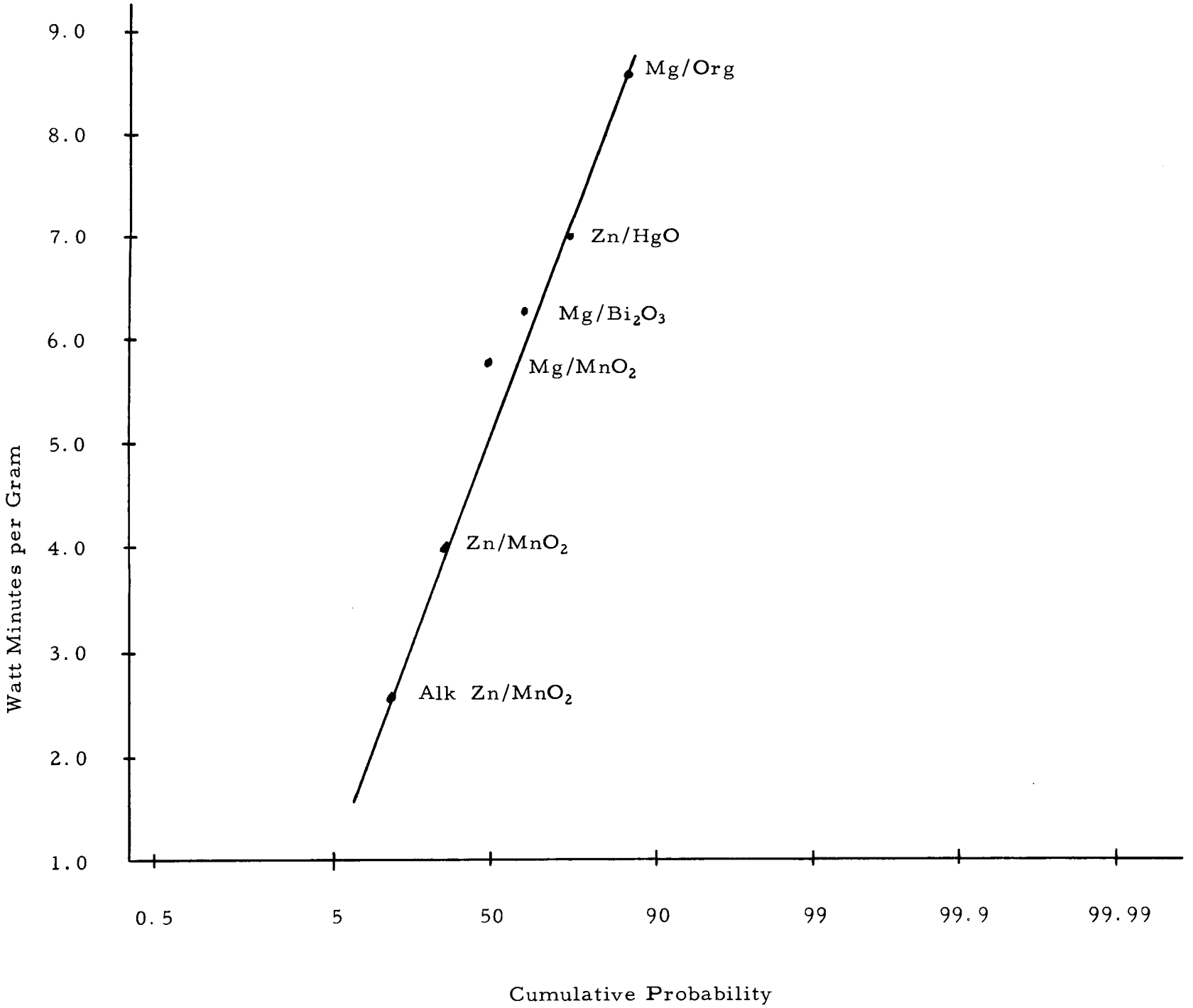
Figure 1 allows estimation of the mean or average value by reading the 50% point which is approximately 5.7 watt minutes per gram. An estimate of the Standard Deviation could be made with the knowledge that 34% of the

area from the average equals one standard deviation. Thus, reading the ordinate on Figure 1 at 84%, we get 8.4. Subtracting the average 5.7, the standard deviation is 2.7.

The requirements of 200 watt hour per pound equates to 26.43 watt minute per gram. This capability is calculated to be 7.68 probability ordinates away from the average [26.43 = 5.7 + 7.68 (2.7)].

Thus, from a Table of Probability Ordinate, we find that 7.68 equates to a chance of less than one in 1,000,000,000, or one in one billion.

CUMULATIVE PROBABILITY VERSUS WATT-MINUTES/GRAM



INDEX OF SPECIFIC RESISTANCE, DECOMPOSITION

Atmosphere Code: 0 = air; 1 = ammonia; 2 = sulfur dioxide, 3 = carbon dioxide

NOTE: The first entry refers to the atmosphere code number, the second indicates the print-out page number.

	SALTS	None	$AlCl_3$	AlF_3	$Al_2(SO_4)_3$	$(CH_3)_4NCl$
	SOLVENTS:					
1	Acetonitrile	1- 9	1- 9	1- 9	1-11	1-14
2	Acetonitrile	1-13	1-10		1-12	
3	Acetonitrile		1-11			
4	Amberlite LA-1	1-16	1-16	1-16	1-17	1-19
5	Amberlite LA-1					
6	50/50 LA-1 + Freon 113		3-20	3 20	3-20	
7	Amberlite LA-2	3- *	3- *	3- *	3- *	
8	Benzene	2- *	2- *	2- *		2- *
9	Butyrolactone	3-22		3-22	3-22	3-26
10	Butyrolactone	1-68	3-22			1-69
11	Butyrolactone					
12	Butyrolactone		3-25			
13	Butyrolactone		3-26			
14	Butyrolactone		1-69			
15	Cyclohexanone		1-74			
16	N, N-Dimethylformamide	1-40	1-40	1-40	1-41	1-50
17	N, N-Dimethylformamide	1-44	0-43	0-43	0-43	
18	N, N-Dimethylformamide		1-46	1-44	1-46	
19	N, N-Dimethylformamide			1-45		
20	Dimethyl Sulfoxide		2-27	2-27	2-27	2 29
21	2-Ethanolpyridine		1-63	1-63		1-65
22	Genesolv D	1-66				1-66
23	Methanol	0-73				
24	N-Methyl-2-Pyrrolidone	3-34	3-35	3-34	3-35	3-38
25	N-Methyl-2-Pyrrolidone	1-70	1-71	3- *	3- *	0-71
26	N-Methyl-2-Pyrrolidone		3- *			
27	N-Methyl-2-Pyrrolidone					

NOTE: For copies of complete print-out or specific systems, address Mr. William A. Robertson, MS 86-1, National Aeronautics Space Administration, Lewis Research Center, 21000 Brookpark Road Cleveland, Ohio 44135

VOLTAGE MEASUREMENTS AND COMPUTATIONS

*Specific resistance too great to produce a high value of "W."

NOTE: All tests were started with air atmosphere, so "0" is shown only when no other atmosphere was applied.

	$(CH_3)_4NI$	KBr	KI	KSCN	LiCl	LiF	$MgSO_4$	NaBr	NaI
1		1-15	1- *		1-12	1-14	1- *		
2		1-15			1-13	[illegible]			
3									
4		1- *	1-18		1-18	1-17		1- *	1- *
5					[illegible]	[illegible]			
6		3-21			3-21	3-20			
7					3- *	3- *			
8		2- *	2- *		2- *	2- *			2- *
9		3-24	3-24	3-24	3-23	3-23	1-69		3-24
10		1-69	3-25	3-25	1-68				3-25
11			3-26	3-26					
12									
13									
14									
15					1-74				
16		1-44	1-42		1-42	1-41	1-49	1-49	1-49
17		[illegible]	1-50		1-43	1-42			
18		1-49			1-48	1-47			
19									
20	2-30			2-28	2-28	2-27		2-28	2-29
21		1-65			1-64	1-64			
22	1- *	1-66				1-66			
23		0-73			0-73				
24	3-39	3-36	3-37	3-37	3-36	3-35	1-71		
25		3-38			1-70				
26		0-71							
27		0- *							

INDEX OF SPECIFIC RESISTANCE, DECOMPOSITION

Atmosphere Code: 0 = air; 1 = ammonia; 2 = sulfur dioxide; 3 = carbon dioxide.

NOTE: The first entry refers to the atmosphere code number; the second indicates the print-out page number.

	SALTS	None	$AlCl_3$	AlF_3	$Al_2(SO_4)_3$	$(CH_3)_4NCl$
	SOLVENTS:					
28	Petroleum Ether	1-73	2-79			2-74
29	Petroleum Ether	2-78				
30	iso-Propylamine		2-75			2-33
31	iso-Propylamine					
32	n-Propylamine	1-68				1-68
33	Propylene Carbonate	3-51	3-51	3-51	3-51	3-54
34	Propylene Carbonate	3-55	1-72		3-55	3-55
35	Propylene Carbonate	1-71	2-77			2-78
36	Propylene Carbonate	2-76				2-76
37	Pyridine	1-56	1-56			1-57
38	Pyridine	1-59	0-62			1-61
39	Pyridine	0-62				1-62
40	Pyridine	1-69				1-70
41	Tetrahydrofuran		2- *			
42	Toluene	1-72	1-72	2- *		1-73
43	Toluene		2- *			2- *
44	Water		2- *			

VOLTAGE MEASUREMENTS AND COMPUTATIONS

*Specific resistance too great to produce a high value of "W."

NOTE: All tests were started with air atmosphere, so "0" is shown only when no other atmosphere was applied.

	$(CH_3)_4NI$	KBr	KI	KSCN	LiCl	LiF	$MgSO_4$	NaBr	NaI
28		2-79	2-74		1-73				
29					2-78	2-78			
30		2-33			2- *	2-75			2-33
31									
32		1-68			1-68				
33		3-52	2-76	3-52	3-52	3-51	1-72	3-53	3-53
34		3-55			1-71	2-76			2-78
35		2-77			2-77				
36									
37	1-58	1-57			1-57	1-56			
38		0-61			1-59	1-60			
39		1-70			1-61	1-61			
40					1-70				
41					2- *	2- *			
42		1-72			1-72				
43		2- *			2- *	2- *			
44					2- *	2- *			

INDEX OF SPECIFIC RESISTANCE, DECOMPOSITION VOLTAGE MEASUREMENTS AND COMPUTATIONS

*Specific Resistivity too great to produce a high value of "W."

NOTE: All tests were started with an air atmosphere; so "air" is shown only when no other atmosphere was applied.

SOLVENTS	SALTS	ATMOSPHERE	PRINT-OUT PAGE NO.
Acetone	LiCl	Air	75
Dimethyl Sulfoxide	$(CH_3)_3N \cdot HCl$	SO_2	31
Dimethyl Sulfoxide	$NH_2OH \cdot HCl$	SO_2	30
Dimethyl Sulfoxide	$SnCl_2$	SO_2	31
Dimethyl Sulfoxide	CCl_3COONa	SO_2	32
Dimethyl Sulfoxide	CCl_3COOK	SO_2	32
Dimethyl Sulfoxide	NaCl	SO_2	29
Genesolv-D	$MgBr_2$	Air	*
Genesolv-D	$NH_2OH \cdot HCl$	NH_3	66
Hexylene Glycol	No Salt	Air	74
Hexylene Glycol	LiCl	Air	74
N-Methyl-2-Pyrrolidone	$NH_2OH \cdot HCl$	CO_2	*
Propylene Carbonate	$MgBr_2$	CO_2	54
Propylene Carbonate	NaCl	CO_2	54
Pyridine	$(CH_3)_3N \cdot HCl$	NH_3	58
Pyridine	$C_6Cl_4O_2$	NH_3	58

APPENDIX B

DETERMINATION OF EQUIVALENT WEIGHT VERSUS CELL POTENTIAL RELATIONSHIP

In order to apply the first law of thermodynamics to a wide range of anode and cathode combinations, a method was needed to express the electrode equivalent weight, M, as a function of the electrode potential. This was accomplished by first plotting the log of the equivalent weight of various anode materials against their corresponding aqueous oxidation potentials and the log of the equivalent weights of various cathode materials against their corresponding aqueous reduction potentials. (See Figure B-1 on page B-2)

The known generalization that "high potential with low possible equivalent weight and low potential with large equivalent weight" may be approximated by the lower two dashed lines. The top dashed line resulted from the combination of the two lower lines and the modification of the abscissa. As a consequence the anode and cathode are restricted to equal stress. The upper ordinate scale then represents the logarithm of the combined equivalent weights of the electrode reactants. Hence, the anode and the cathode potentials are given equal stress in the Energy Balance Equation.

The combined electrode equivalent weights can now be generalized as a function of cell voltage. The slope of the upper curve is

$$\frac{\text{Ln } 250 - \text{Ln } 22}{6} = -0.4$$

while the intercept of the ordinate in Ln 250 = 5.5. The standard equation for a straight line was used to express the combined equivalent weight (M) of the electrode reactants as a function of the cell voltage, (E). Hence:

$$\text{Ln } M = 5.5 - 0.4E \qquad (1)$$

$$M = e\,(5.5 - 0.4E) \qquad (2)$$

The expression in equation (2) is used in the energy balance equation. Tables B-1 and B-2 on pages B-3 and B-4 show the various anode and cathode reactions for the electrode materials plotted.

SEMI-LOG PLOT OF ELECTRODE EQUIVALENT WEIGHT VERSUS AQUEOUS POTENTIAL

FIGURE B-1

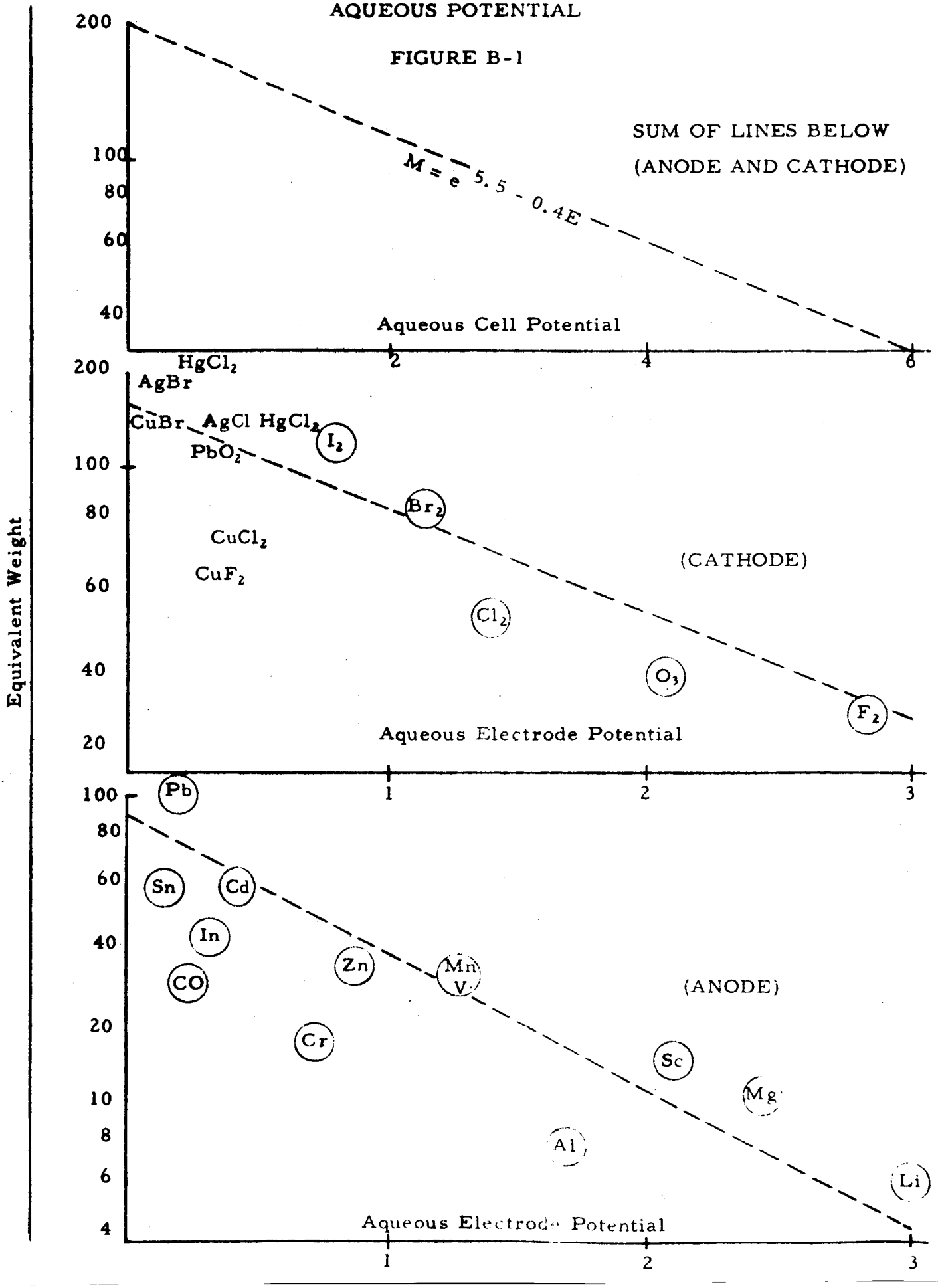


TABLE B-1

TABULATION OF
STANDARD AQUEOUS OXIDATION POTENTIALS
AND EQUIVALENT WEIGHTS*

	Potential	Equivalent Weight
$Al = Al^{+++} + 3\bar{e}$	+1.7	9.0
$Cd = Cd^{++} + 2\bar{e}$	+0.4	56.2
$Co = Co^{++} + 2\bar{e}$	+0.3	29.5
$Cr = Cr^{+++} + 3\bar{e}$	+0.7	17.3
$In = In^{+++} + 3\bar{e}$	+0.3	38.3
$Li = Li^{+} + \bar{e}$	+3.0	7.0
$Mg = Mg^{++} + 2\bar{e}$	+2.4	12.2
$Mn = Mn^{++} + 2\bar{e}$	+1.2	27.5
$Pb = Pb^{++} + 2\bar{e}$	+0.1	103.6
$Sc = Sc^{+++} + 3\bar{e}$	+2.1	15.0
$Sn = Sn^{++} + 2\bar{e}$	+0.1	59.4
$V = V^{++} + 2\bar{e}$	+1.2	25.5
$Zn = Zn^{++} + 2\bar{e}$	+0.8	32.7

TABLE B-2

TABULATION OF STANDARD AQUEOUS REDUCTION POTENTIALS AND EQUIVALENT WEIGHTS*

		Potential	Equivalent Weight
$AgBr + \bar{e}$	$= Ag + Br^-$	+0.1	187.8
$AgCl + \bar{e}$	$= Ag + Cl^-$	+0.2	143.4
$Br_2 + 2\bar{e}$	$= 2Br^-$	+1.1	79.9
$Cl_2 + 2\bar{e}$	$= 2Cl^-$	+1.4	35.5
$CuBr + \bar{e}$	$= Cu + Br^-$	+0.03	143.5
$CuCl_2 + 2\bar{e}$	$= Cu + 2Cl^-$	+0.4	67.2
$CuF_2 + 2\bar{e}$	$= Cu + 2F^-$	+0.4	50.8
$F_2 + 2\bar{e}$	$= 2F^-$	+2.9	19.0
$Hg_2Cl_2 + 2\bar{e}$	$= 2Hg + 2Cl^-$	+0.3	236.0
$HgCl_2 + 2\bar{e}$	$= Hg + 2Cl^-$	+0.4	135.8
$I_2 + 2\bar{e}$	$= 2I^-$	+0.5	126.9
$O_3 + 2H^+ + 2\bar{e}$	$= O_2 + H_2O$	+2.1	25.0
$PbO_2 + H_2O + 2\bar{e}$	$= PbO + 2OH^-$	+0.2	128.1

*W. M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solutions (1959)

APPENDIX C

MODIFIED TAFEL EQUATION

This appendix illustrates one path whereby the Tafel equation[1]

$$\eta = a + b \log i \tag{1}$$

may be modified to generalize the corrosion current of batteries which may be constructed using a wide variety of solvents. The terms of this equation (1) normally are restricted to one electrode and do not include the initial reaction standard potential nor the effects of concentrations upon reaction potential:

η = overvoltage (volts)

a = the Tafel constant (volts)

b = the Tafel slope (volts)

Battery local action may be characterized by a single equation of the same form when the terms are conveniently chosen. This equation may then be rearranged to yield a theoretical value for battery local action current density as an explicit function of battery potential in terms of conveniently measured parameters of the solvent-atmosphere combination:

$$J = e^{(E-C)/D} \tag{2}$$

Starting with a generalized solvent autoionization reaction (3) applicable to most solvents:

$$AB = A^{+} + B^{-} \tag{3}$$

The voltages required to decompose the solvent AB by the physical model of Figure V-7 on page V-15, using a neutral solute of high decomposition potential, is given by equations (4) and (5)[2,3]. Equation (4) treats battery anode local action and (5) battery cathode local action.

$$E_1 = E_1^{\circ} - \frac{rt}{NF} \ln \frac{[A^{+}]}{[AB]} + \eta_1 \tag{4}$$

$$E_2 = E_2^{\circ} + \frac{rt}{NF} \ln \frac{[B^{-}]}{[AB]} - \eta_2 \tag{5}$$

Subtracting E_2 from E_1 gives the cell potential[4], E:

$$E = E_1 - E_2 \tag{6}$$

DEFINITION OF TERMS

E_1 = The potential of the anode in a battery and consequently the driving force behind local action or decomposition of the solvent at this electrode.

E_2 = The potential of the cathode in a battery and the driving force of cathode local action.

E = $E_1 + E_2$ or the cell potential.

J = The corrosion current density to distinguish this from the previously assigned I, stoichiometric current. (See page V-3.)

r = The universal gas constant chosen to distinguish this from the previous R, cell resistance. (See page V-3.)

t = Absolute temperature chosen to distinguish this from the previously assigned T, discharge time. (See page V-3.)

F = Faraday's constant.

$[AB]$ = 1, the hypothetical one molar standard state. An example is cited in footnote 4, page C-3.

$[A^+]$ = The activity of the cationic autoionization product.

$[B^-]$ = The activity of the anionic autoionization constant. .

$[A^+][B^-]/[AB]$ = Autoionization equilibrium constant.

η_1 & η_2 = Overvoltage, (1) anodic, (2) cathodic, local action driving force-natural log base.

c = $E_1^\circ - E_2^\circ - \frac{rt}{NF} \ln \frac{[A^+][B^-]}{[AB]}$

a_1 & a_2 = Tafel constants in the original connotation - natural log base.

b_1 & b_2 = Tafel slopes in the original connotation - natural log base.

C = $c + (a_1 + a_2)$, Modified Tafel constant.

D = $(b_1 + b_2)$, Modified Tafel slope.

e = Base of natural logarithms.

Substituting the values for E_1 and E_2 in (6) gives:

$$E = E_1^\circ - E_2^\circ - \frac{rt}{NF} \ln \frac{[A^+][B^-]}{[AB]} + \eta_1 + \eta_2 \qquad (7)$$

Since the first three terms are constants they are combined into the single contant, c:

$$E = c + \eta_1 + \eta_2 \qquad (8)$$

Expanding η_1 and η_2 by the Tafel equation and regrouping gives:

$$E = c + (a_1 + a_2) + (b_1 + b_2) \ln J \qquad (9)$$

Combining the constants of (9) gives:

$$E = C + D \ln J \qquad (10)$$

Solving equation (10) for J, the corrosion current density, gives equation (2):

$$J = e^{(E-C)/D} \qquad (2)$$

The parameters C and D may be conveniently evaluated in the majority of cases from a simple voltage (E) - current density (J), or modified Tafel plot, as shown by the Figure C-1 on page C-4.

[1] "Electrochemistry," Edmund C. Potter, Cleaver-Hume Press Ltd., London, Page 128 (1956).

[2] "Interpreting Liquid Ammonia Chemistry with Thermodynamics," William L. Jolly, J. Chem. Ed., 33, 10, Page 513, (1956).

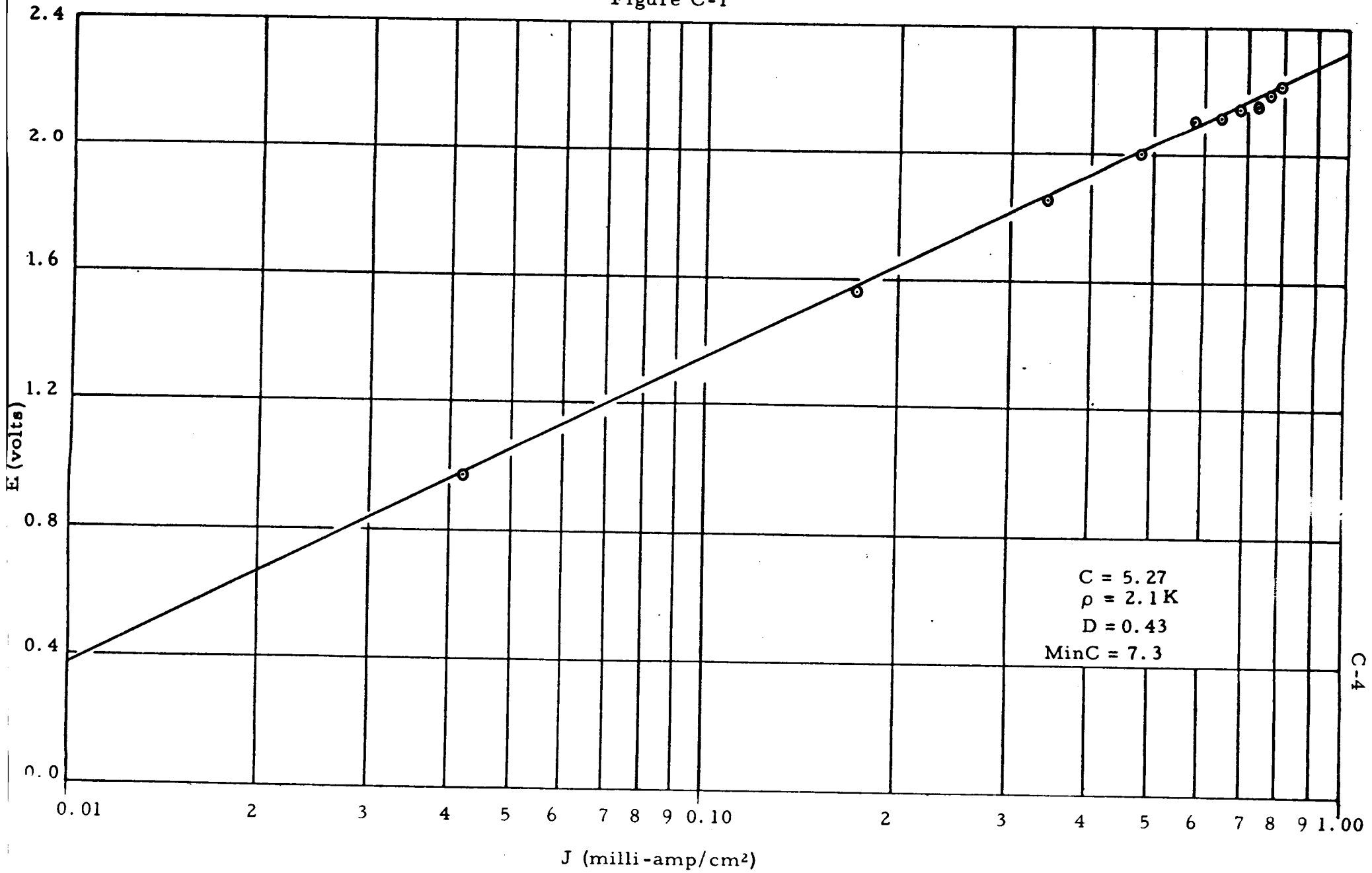
[3] "Standard Electrode Potential and Decomposition Voltage of Solutions in Liquid Ammonia," V. Pleskov, Acta Phys Chim 20, Page 583, (1945).

[4] E. C. Potter, ibid., Page 152.

MODIFIED TAFEL PLOT

ISOPROPYLAMINE + LiCl + SO_2 at 21.5 psia

Figure C-1



MANUAL TRACE CALCULATION OF W

SYSTEM N, N-DIMETHYL FORMAMIDE/AIR/ALUMINUM CHLORIDE (14102.01)

(Slide Rule Computation)

Data From Input Punch Card

I(6)	I(7)	I(8)	I(9)	RK	RPK	P	input punch card
TFL6	TFL7	TFL8	TFL9	RS	RPS	PS	computer program
302	251	189	144	327	247	76	digital values

Calculation of Specific Resistance and Polarized Resistance

Note: This example was run under a different resistance measuring network than Program #4.

$$RK = 10*(\frac{500-RS}{RS}) = 10*(\frac{500-327}{327}) = 5.29$$

$$RPK = 10*(\frac{500-RPS}{RPS}) = 10*(\frac{500-247}{247}) = 10.24$$

Calculation of Corrosion Current From I(6), I(7), I(8), and I(9)

(Follows statement #13 of Program #4)

$$I(6) = TFLC6 = 2*10^{-7}*TFL6 = 2*10^{-7}*302 = 6.04*10^{-5}$$

$$I(7) = TFLC7 = 4*10^{-7}*TFL7 = 4*10^{-7}*251 = 1.00*10^{-4}$$

$$I(8) = TFLC8 = 1*10^{-6}*TFL8 = 1*10^{-6}*189 = 1.89*10^{-4}$$

$$I(9) = TFLC9 = 2*10^{-6}*TFL9 = 2*10^{-6}*144 = 2.88*10^{-4}$$

Calculation of Interfacial Voltage

(Statement #20 of Program #4)

$$X6 = 10. - TFLC6*(R + 100,000.) = 10. - 6.04*10^{-5}(105,290) = 3.64$$

$$X7 = 10. - TFLC7*(R + 50,000.) = 10. - 1.00*10^{-4}(55,290) = 4.47$$

$$X8 = 10. - TFLC8*(R + 20,000.) = 10. - 1.89*10^{-4}(25,290) = 5.22$$

$$X9 = 10. - TFLC9*(R + 10,000.) = 10. - 2.88*10^{-4}(15,290) = 5.60$$

Calculation of D, The Tafel Slope

(Statement #61 of Program #4)

$$D = (X(9) + X(8) - X(7) - X(6)/Ln(TFLC9*TFLC8/(TFLC7*TFLC6))$$

$$= (5.22 + 5.60 - 4.47 - 3.64)/Ln\,(2.88*10^{-4}*1.89*10^{-4}/1.00*10^{-4}*6.04*10^{-5})$$

$$= 2.71/\ln(9.07) = 2.71/2.20 = 1.24$$

Calculation of C, The Tafel Intercept

(Statement #67 of Program #4)

$$C = .25*((X9 + X8 + X7 + X6) - D*(4.36 + Ln\,(TFLC9*TFLC8*TFLC7*TFLC6)))$$

$$= .25*((5.60 + 5.22 + 4.47 + 3.64) - 1.23*(4.63 + Ln(2.88*10^{-4}*1.89*10^{-4}*10^{-4}*6.04*10^{-5})))$$

$$= .25*(18.93 - 1.23*(4.63 + Ln\,32.9*10^{-17}))$$

$$= .25(18.93 - 1.23*(4.63 + 3.49 - 17*2.30)) = 14.3$$

Calculation of the Maximum Figure of Merit, W

(Follows Statement #72 of Program #4)

$$W_{5.0} = 49.6*X*e^{(0.4*X)}*(1.0 - 0.9\sqrt{\frac{R}{X}}*e^{(\frac{X-C}{2D})})$$

Calculation of the Maximum Figure of Merit, W Continued

$$W_{5.0} = 49.6*5.0*e^{(0.4*5.0)}*(1.0 - 0.9\sqrt{\frac{5290}{5.0}}*e^{\left(\frac{5.0 - 14.3}{2.48}\right)})$$

$$= 49.6*5.0*7.35*(1.0 - 0.9*32.6*.023)$$

$$= 49.6*5.0*7.35*.326 = 596 \text{ (maximum)}$$

$$W = 596$$

NOTE: $W_{4.5}$ and $W_{5.5} < W_{5.0}$

APPENDIX E

IDENTIFICATION OF SALTS

Salts		Lot No.	Cat. No.
Ag_2O	Phillips & Jacobs, Inc.	-	-
Ag_2O_2	Prepared in Livingston Laboratory	-	-
Al_2O_3	Fisher Scientific Co., Adsorption 80-200 mesh	731883	A-540
Al_2O_3	Fisher Scientific Co., certified anhydrous	W-141	A-591
$AlCl_3$	Fisher Scientific Co., anhydrous certified reagent	723393	A-575
AlF_3	Olin Mathieson Chemical Corp., Anhydrous Grade	0659088	-
$Al_2(SO_4)_3$	J. T. Baker Chemical Co., U. S. P.	20439	-
B_2O_3	Fisher Scientific Co., Boric Acid, fused	732643	A-76
x CaO	Fisher Scientific Co., certified, lump	731956	C-116
x CaO	Fisher Scientific Co., certified	733520	C-117
C Cl_3CO_2Na	Special product of Corson	-	-
C Cl_3CO_2K	Special product of Corson	-	-
$C_6Cl_4O_2$	Eastman Organic Chemicals* Practical	-	P-603
$(CH_3)_4NCl$	Eastman Organic Chemicals*	-	3592
$(CH_3)_4NI$	Eastman Organic Chemicals*	-	2434
$(CH_3)_3N{\cdot}HCl$	Eastman Organic Chemicals*	-	265
CoF_3	Matheson, Coleman and Bell**, Anhydrous	7822	CX-1835
$\pm CuBr_2$	J. T. Baker Chemical Co., Analytical Reagent	28099	1780
$CuCl_2$	Baker & Adamson, Anhydrous Reagent	W-340	1637
$CuCl_2$	Fisher Scientific Co., Certified Anhydrous	W-183	C-456
CuF_2	A. D. MacKay, Inc., Anhydrous, C.P., 96-100%	-	-
CuO	Fisher Scientific Co., Certified Anhydrous	723401	C-472
CuS	Matheson, Coleman and Bell**, Anhydrous Reagent	CB-351	CX-2210
$\pm Fe_2O_3$	Fisher Scientific Co., Certified Anhydrous	732232	I-116
$\pm GeO_2$	K. & K. Laboratories, Inc., 99.98%	46890	-
$HgSO_4$	Mallinckrodt Chem. Works, Analytical Reagent	-	1430
$\pm I_2O_5$	K. & K. Laboratories, Inc.	42156	-
KBr	Fisher Scientific Co., Certified Reagent	720110	P 205

IDENTIFICATION OF SALTS Continued

Salts		Lot No.	Cat. No.
±$KC_2H_3O_2$	Matheson, Coleman and Bell**	CB 589	PX-1330
±$KF \cdot 2H_2O$	J. T. Baker Chemical Co., Analyzed Reagent	25010	3122
KI	J. T. Baker Chemical Co., U. S. P.	25291	3168
KSCN	Fisher Scientific Co., Certified Reagent, A. C. S.	730253	P-317
LiCl	Fisher Scientific Co., Certified Reagent	724595	L-121
$LiClO_4$	Foote Mineral Co., Anhydrous	-	-
$LiClO_4 \cdot 3H_2O$	Foote Mineral Co. (dehydrated by Corson Lab)	-	-
LiF	J. T. Baker Chemical Co., Analyzed Reagent	23101	2380
±LiI	Mallinckrodt Chemical Works	G71R-1	1056
±Li_2O_2	Foote Mineral Co.	171-59	-
±$LiBO_2 \cdot 2H_2O$	Foote Mineral Co.	0325	-
$MgBr_2 \cdot 6H_2O$	Matheson, Coleman and Bell Reagent**	3041442	MX 30
$Mg(ClO_4)_2$	Fisher Scientific Co., Anhydrous Reagent	121462 112563	7-573
$Mg(ClO_4)_2$	A. H. Thomas Co., "Dehydrite"	-	-
±MnF_3	Harshaw Chemical Co., Anhydrous	3	-
±$MgF_2 \cdot XH_2O$	Matheson, Coleman & Bell** approx. 85% MgF_2	CB-874	MX-50
$MgSO_4 \cdot 7H_2O$	J. T. Baker Chemical Co., Analyzed Reagent	-	2500
MnO_2	Fisher Scientific Co., Certified	733328	M-108
NaBr	J. T. Baker Chemical Co., Analyzed Reagent	25289	3588
NaCl	Merck & Co., Inc., Reagent, A. C. S.	60452	7407
NaI	Merck & Co., Inc., U. S. P.	61163	5080
$NH_2OH \cdot HCl$	Eastman Organic Chemicals* 95-98% Practical	-	P 340
NiF_2	Varlacoid Chemical Co., Anhydrous	3210M	-
$NiF_2 \cdot 4H_2O$	General Chemical Div.***, Technical	V-208	2024
Ni_2O_3	Fisher Scientific Co., Certified	761542	N-66
$NaBO_3 \cdot 4H_2O$	Fisher Scientific Co., Certified	V249J	S-359
±RbI	Fisher Scientific Co., Purified	701358	R-318

IDENTIFICATION OF SALTS Continued

Salt		Lot No.	Cat. No.
S	Merck & Co., Inc., U.S.P. Precipitated	50108	6449
$SnCl_2 \cdot 2H_2O$	J. T. Baker Chemical Co.	22280	3980
SnO_2	General Chemical Div., Anhydrous***	V-255	2332
SnO_2	Fisher Scientific Co., Certified	-	T-148
±$Sn(SO_4)_2$	City Chemical Corporation, Purified	VA679	-
V_2O_5	Fisher Scientific Co., Certified Anhydrous	733214	V-7

*Eastman Organic Chemicals, Dept., Distillation Products Industries, Division of Eastman Kodak Company

**Division of The Matheson Co., Inc.

***Division of Allied Chemical Co.

±Experiments have been planned with these materials, but have not yet been carried out.

x Solvent drying agent.

IDENTIFICATION OF SOLVENTS

Solvents		Lot No.	Cat. No.
Acetone	Fisher Scientific Co., 99 Mol % Pure, Certified	734354	A-20
Acetone	Fisher Scientific Co., Spectranalyzed, Certified	732565	A-19
Acetone	Matheson, Coleman & Bell**, Spectroquality	-	AX-115
Acetone	Fisher Scientific Co.	732563	A-18
Acetone	J. T. Baker Chemical Co., Analyzed Reagent, 99.5% Pure	22932	9006
Acetonitrile	Matheson, Coleman & Bell**, Practical Grade	P-2726	AX150
Amberlite LA-1	Rohm & Haas Company	6981	-
Amberlite LA-2	Rohm & Haas Company	5605	2870207
Benzene	Fisher Scientific Co., Certified, 99 Mol % Pure	732469	B-414
+ Benzophenone	Fisher Scientific Co., Certified	732246	B-270
±Bis(2-Chloroethyl)Carbonate	Eastman Organic Chemicals*	-	901
° n-Butylamine	Fisher Scientific Co., Certified, 99.5%	722837	B-415
Butyrolactone	Antara Chemicals Div., General Aniline & Film Corporation	11-72707	R-773
Butyrolactone	Eastman Organic Chemicals*	-	6922
° p-Chloro benzotrifluoride	Hooker Chemical Corporation	-	63-1533
Cyclohexanone ("Nadone")	National Aniline Div., Allied Chemical Corp.	3438	-
° p-α-Dichlorotoluene	Eastman Organic Chemicals*, Practical	-	P-1103
Dimethyl Sulfoxide	Crown Zellerbach Corporation	T-128	-
N, N-Dimethylformamide	Matheson, Coleman & Bell**	5974	DX 1730
N, N-Dimethylformamide	Matheson, Coleman & Bell**, Spectroquality	SG 5974	DX 1725
2-Ethanolpyridine	Reilly Tar & Chemical Co., 95% Minimum Purity	-	-
° Ethyl Acetate	Merck & Co., Inc., 90% Ethyl Acetate, U.S.P. VIII	62672	0561

IDENTIFICATION OF SOLVENTS Continued

Solvents		Lot No.	Cat. No.
Ethylene Carbonate	Matheson, Coleman & Bell**	-	EX-500
1-Fluoro-2,4-dinitrobenzene	Eastman Organic Chemicals*	-	6587
p-Fluorotoluene	Eastman Organic Chemicals*	-	2969
Freon 11	The Matheson Co., Inc., 99.9% Minimum purity	-	-
Freon 113	The Matheson Co., Inc., 99.0% Minimum purity	-	-
Freon 114	The Matheson Co., Inc., 95.0% Minimum purity	-	-
Genesolv-D	General Chemical Division***, Electronic Grade	K-909006	-
Hexylene Glycol	Union Carbide Chemicals Co.	S 262660	-
Mercaptopropionic Acid	Evans Chemetics, Inc., 100% Assay	643-397	-
Methanol	Merck & Co., Inc., Reagent Methyl Alcohol, Anhydrous, A. C. S.	61763	7168
N-Methyl-2-Pyrrolidone	Antara Chemicals Div., General Aniline & Film Corp.	-	-
Nitromethane	Matheson, Coleman & Bell**, Practical	P-1240	NX 615
Nitromethane	Matheson, Coleman & Bell**, Spectroquality	SG 1240	NX 613
Petroleum Ether	J. T. Baker Chemical Co., Analyzed Reagent (20 - 40° C.)	25825	9272
Phenyl Ether	Fisher Scientific Co., Certified	725063	D-89
iso-Propylamine	Matheson, Coleman & Bell**	5470	PX 1845
n-Propylamine	Eastman Organic Chemicals*	-	1216
Propylene Carbonate	Eastman Organic Chemicals*, Practical Grade	-	P-7050
Pyridine	Fisher Scientific Co., Certified Reagent, A. C. S.	732238	P-368
Silicone Oil, DC-200	Dow Corning Corporation	-	-
Tetrahydrofuran	Matheson, Coleman & Bell**	5962	TX-280

IDENTIFICATION OF SOLVENTS Continued

Solvents		Lot No.	Cat. No.
Toluene	Fisher Scientific Co., Certified Reagent, A. C. S.	733991	T-324
° Triallylamine	Shell Chemical Company	-	-
° Trichlorobenzene	Eastman Organic Chemicals*	-	1801
° Trichlorobenzene	Matheson, Coleman & Bell**	9193	TX 1067
° (1, 1, 1) Trichloroethane	Fisher Scientific Co., purified, inhibited	783937	T-398
± Xylene	J. T. Baker Chemical Co., Analyzed Reagent, A. C. S.	22458	9490

*Eastman Organic Chemicals, Dept., Distillation Products Industries, Div. of Eastman Kodak Co.

**Division of The Matheson Company, Inc.

***Division of Allied Chemical Company

±Experiments have been planned with these materials, but have not yet been carried out.

+Used unsuccessfully as a chelating agent.

Used only in materials compatibility tests.

° These solvents were tested manually during the First Quarter, but conductive solutions were not obtained.