

NASA CR-54782
MRB5010Q1

Quarterly Report No. 1

RESEARCH AND DEVELOPMENT OF THE
DRY TAPE BATTERY CONCEPT

9 June to 8 September 1965

FACILITY FORM 602

N 66-12169	
(ACCESSION NUMBER)	(THRU)
51	1
(PAGES)	(CODE)
	03
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

GPO PRICE	\$	_____
CFSTI PRICE(S)	\$	_____
Hard copy (HC)		3.00
Microfiche (MF)		.50

by

ff 653 July 65

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prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-7624

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SUMMARY

A new tape couple, based on the Mg/AlCl₃,HCl/trichlorotriazinetrione (Monsanto ACL-85[®]) system, has been developed. This cell discharges at 2.6 volts at 0.2A/in.² and 2.2 volts at 0.8 A/in.². Cathode coulombic efficiencies range from 60-80%, with individual test results as high as 87%. The discharge curve is flat and current density has little effect on cathode efficiency. This tape couple can tolerate current drains in excess of 1A/in.², but cell voltage falls below 2.0 volts.

The cathode tape configuration is identical to that developed in our previous program (NAS3-4168) except that less inert material is required with ACL-85 compared with previous (potassium periodate, picric acid) cathode materials. Present cathodes operate satisfactorily with up to 75 wt-% active material. Maximum active material content in previous systems was 60 wt-%.

Energy output from the Mg/ACL-85 system is substantially higher than any other system studied to date. Accurate electrolyte requirement data have not yet been determined but, on a dry basis, delivered energy densities over 300 watt-hour/pound of complete tape cell, excluding electrolyte, have been obtained.

A satisfactory method was developed for preparing ACL-85 tape cathodes from a trichloroethylene slurry. Vacuum pretreatment of the acetylene black conductor is required to prevent hydrolytic decomposition of the active chlorine material during tape processing and storage.

The best nonaqueous electrolytes for lithium were found to be potassium hexafluorophosphate and lithium perchlorate in methyl formate. Anode half cell voltages of -2.1 to -2.3 volts vs. NCE could be maintained for extended periods at 0.5 amp/in.². Results for magnesium in nonaqueous electrolytes were erratic due primarily to sensitivity to anode surface preparation.

Vapor phase chromatographic techniques for water analysis are being developed. It appears that concentrations as low as 10 ppm can be determined routinely for most electrolyte systems.

New electroanalytical test equipment has been designed and built for both static and dynamic tests. Fast switching pulse current equipment is now available to record the trace of electrode performance during the first ten milliseconds of discharge. In addition, IR-free voltage measurements can be made at currents up to three amperes. A new dynamic test station was built that is capable of automatic data recording, tape speed control, and electrolyte input. The unit can run unattended for 24 hours.

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I. INTRODUCTION

A. BACKGROUND

This work is a continuation of research performed under Contracts NAS3-2777 and NAS3-4168. During the initial program (NAS3-2777) the feasibility of the Dry Tape Concept was demonstrated using a divalent silver oxide-coated, porous polypropylene tape that was drawn between two current collectors. One current collector was a zinc block that also served as the anode. The cathode current collector was a thin silver plate. Electrolyte was supplied by a second tape prewetted with electrolyte and stored separately ("dual tape system"). The system was activated by bringing the two tapes together just prior to their entry into the current collector zone.

The tapes were driven by a spring-wound motor, contained in a separate housing. Within this housing was an output metering and load section. Four such drive housings, together with 20 tape decks, were supplied to NASA for demonstration. In continuous operation, silver peroxide utilizations of over 90% were obtained at current densities of 1 amp/in.².

In the follow-on program (NAS3-4168), the "dual tape system" using the established battery couple, $A_2O/KOH/Zn$, was replaced by a single tape configuration using a thin foil magnesium anode and cathode coatings containing nonconducting, higher energy organic (dinitrobenzene, picric acid, trichloro-triazinetriene) and inorganic (potassium meta-periodate) depolarizers. Efficient, high drain rate discharge of these cathode materials was achieved through use of the "thin plate tape electrode" configuration. The single tape configuration was optimized for the system, $Mg/2MA1Cl_3;0.5M HCl/KIO_4$. Up to 80% KIO_4 utilization was achieved with a cell voltage of 2.2 volts at a current density of 0.5 amp/in.² while in a moving configuration. In addition, to tape electrode configuration development, methods of electrolyte incapsulation and tape activation were devised. Also, techniques for supplying multiple cell voltage, parasitic drive and continuous coated tape manufacture were developed.

B. CONTRACT OBJECTIVES

Specific objectives of this program are to:

1. Develop a high energy tape couple that will deliver 200 watt-hours per pound in a practical configuration.
2. Incorporate this couple in a tape configuration that will exhibit prescribed flexibility and abrasion resistance during operation.

The major objective is to improve substantially the energy density output of the dry tape system. Despite good electrode efficiencies, the best delivered energy densities obtained with organic nitro compound or periodate cathode systems were under 100 watt-hours per pound. This was primarily due to high electrolyte consumption and a high cathode inert weight requirement.

In the present work, only couples with extremely high potential energy densities are being considered. Couples with theoretical energy densities greater than 750 watt-hours per pound are to be incorporated into the tape electrode configurations developed in previous programs.

C. FIRST QUARTER OBJECTIVES

Objectives for this quarter were to:

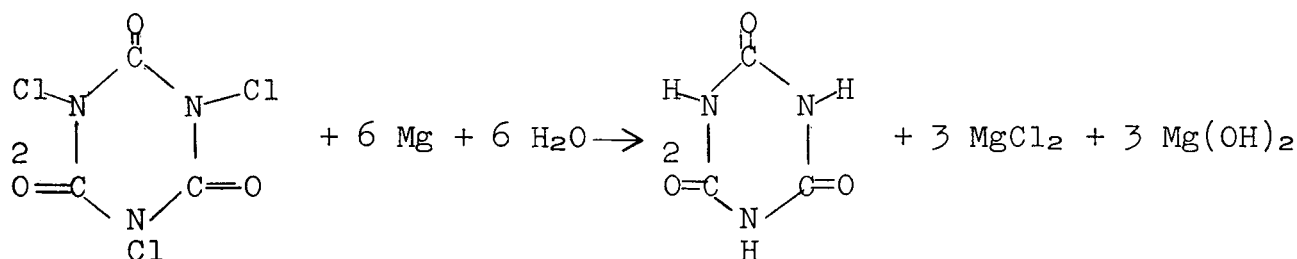
1. Develop and evaluate a new aqueous system, based on the magnesium/2,4,6-trichlorotriazinetrione (Monsanto AC1-85) couple.
2. Screen discharge characteristics of lithium and magnesium in selected organic solvent-electrolyte combinations.
 - a. Build improved half-cell testing stations.
 - b. Purify and analyze solvents and electrolyte salts.
 - c. Determine the effect of purity on conductivity.
 - d. Determine polarization and efficiency characteristics of lithium and magnesium in selected electrolyte systems.
3. Initiate study of stability and solubility of cathode materials in selected organic solvents.
4. Design, build, and test an improved dynamic test station.

II. TASK I. HIGH ENERGY COUPLE RESEARCH

A. CATHODE RESEARCH AND DEVELOPMENT

1. 2,4,6-Trichlorotriazinetrione in Aqueous Electrolyte

The theoretical energy density of the magnesium-2,4,6-trichlorotriazinetrione couple is estimated to be 785 watt-hours per pound of reactant, assuming the following reaction:



Previous work in this laboratory showed that this material would exhibit flat, efficient discharge in aqueous electrolyte. Preliminary work in the previous tape program (NAS3-4168) indicated that a trichlorotriazinetrione tape cathode could tolerate higher drain rates with less inert weight than the organic nitro compound and periodate based tapes.

The development program during this period was designed to optimize energy output at the highest current drains possible. Tape cell evaluations were performed using the simple static test described in our previous program. A complete tabulation of results is shown in Table A-1.

a. Tape Cathode Preparation

To avoid possible activity loss due to hydrolysis prior to discharge a method for cathode tape preparation was developed by which the cathode mix is cast or extruded onto the tape from a trichloroethylene slurry and dried under vacuum at 60-70°C. The acetylene black, active cathode material (Monsanto ACL-85) and reinforcing fibers (carbon or dynel) are dry-blended by stirring. The acetylene black and carbon fibers are prefluffed in a Waring Blendor prior to use. The polyvinyl formal binder is added as a trichloroethylene solution (0.005 g PVF/ml solution). The resulting slurry is thoroughly mixed by mechanical stirring and hand cast onto the separator tape, using a doctor blade technique. The same slurry may be used for continuous tape manufacture by the extrusion process developed in the previous contract. Hand-cast tapes are vacuum-dried for one hour at 60-70°C.

This technique initially was tested using the potassium periodate cathode formulation developed in our prior program (NAS3-

4168). Discharge results summarized in Table 1 show somewhat improved output and reproducibility compared with similar periodate tapes made from aqueous slurries and then air dried.

Table 1

DISCHARGE CHARACTERISTICS OF POTASSIUM PERIODATE CATHODE
TAPES PREPARED FROM TRICHLOROETHYLENE SLURRIES
AND VACUUM DRIED

54 wt-% KIO_4 , 40.5 wt-% acetylene black, (50% compressed) 2.75 wt-% polyvinyl formal, 2.75 wt-% carbon fibers, 3.5 mil dynel tape.

primary magnesium foil anode - 2M $AlCl_3$ ·0.5M HCl electrolyte

	<u>Operating Cell Voltage, volts</u>	<u>Cathode Efficiency, %</u>	<u>Current Density, amp/in.²</u>
Summary of eight tests	2.14 ± 0.07	70 ± 7%	0.5

This procedure works well for ACL-85. However, it was found that a vacuum drying pretreatment (12 hours, 200°C) of the acetylene black is required to prevent substantial cathode activity loss during processing and storage. The reasons for this are presented in the following section.

b. Stability of Trichlorotriazinetrione Tape Cathode

The stability of ACL-85 tape cathode was monitored by both discharge-efficiency tests and active chlorine chemical analysis. The analytical method for determining the active chlorine content of tape cathodes consists of an iodometric titration with sodium thiosulfate to a starch endpoint. The detailed analysis is described in Table A-2.

Tapes prepared with "as received" acetylene black showed substantial activity loss during processing and on subsequent standings. It appears that water, adsorbed on Shawinigan acetylene black, is the cause of activity loss of 2,4,6-trichlorotriazinetrione (Monsanto Company ACL-85). Although ACL-85 is fairly stable to moisture in the air, the acetylene black appears to catalyze hydrolysis by adsorbed water. Vacuum drying of the acetylene black eliminated significant activity loss that previously occurred during tape processing. In addition, tapes prepared with dried acetylene black, retained this stability on standing in air at least up to seven days. Activity loss data are reported in Table 2.

Table 2.

THE EFFECT OF ACETYLENE BLACK PRETREATMENT ON ACL-85[®] STABILITY

<u>Material and Condition</u>	<u>Measured Active Chlorine Content, %</u>	
	<u>As Received</u>	<u>Dried Acetylene</u>
	<u>Acetylene Black</u>	<u>Black</u>
ACL-85, as received, theoretical	91.54	
ACL-85, as received, analyzed	90.1 ± 0.1	
Tape (50% ACL-85), freshly prepared	77.1 ± 0.4	85.4 ± 1.3
Tape (50% ACL-85), 24 hours in air	71.0 ± 1.0	84.0 ± 0.9
Tape (50% ACL-85), 96 hours in air	64.3 ± 2.6	82.5 ± 1.1
Tape (50% ACL-85), 168 hours in air	61.2 ± 1.8	83.3 ± 0.4

There appears to be 3-5% activity loss on processing, and a slight loss appears to occur with time during air storage, but measured losses are almost within experimental error.

c. Discharge of ACL-85 Tape Cathodes in Aqueous Electrolyte

Polarization and efficiency measurements were carried out in magnesium chloride, magnesium perchlorate, and aluminum chloride-hydrochloric acid electrolyte with primary magnesium as the anode electrode. Cathode formulations varied from 50 to 80 wt-% ACL-85. Acetylene black, polyvinyl formal binder and dynel fiber comprised the remainder.

As a general rule, polarization was less severe in the aluminum chloride-hydrochloric acid electrolyte. Figure 1 is a typical illustration. There was little difference in polarization characteristics between the 50 wt-% and 75 wt-% active material concentration, as shown in Figure 2.

The effect of electrolyte on the shape of the discharge curve is significant. In neutral magnesium chloride or magnesium perchlorate, the voltage drops steadily. In strong acid electrolyte, a fairly constant voltage is maintained until the cell is nearly depleted. This behavior is illustrated in Figure 3. The initial emf difference is primarily a pH effect. However, the steady voltage drop during discharge is due solely to cathode polarization according to half cell measurements. The use of mixed salt electrolyte eliminates this deterioration. Figure 4 shows the effect of adding aluminum chloride to magnesium chloride and magnesium perchlorate. The initial potential dip occurring in some cases is due to the finite time required to break down the oxide layer on the anode surface.

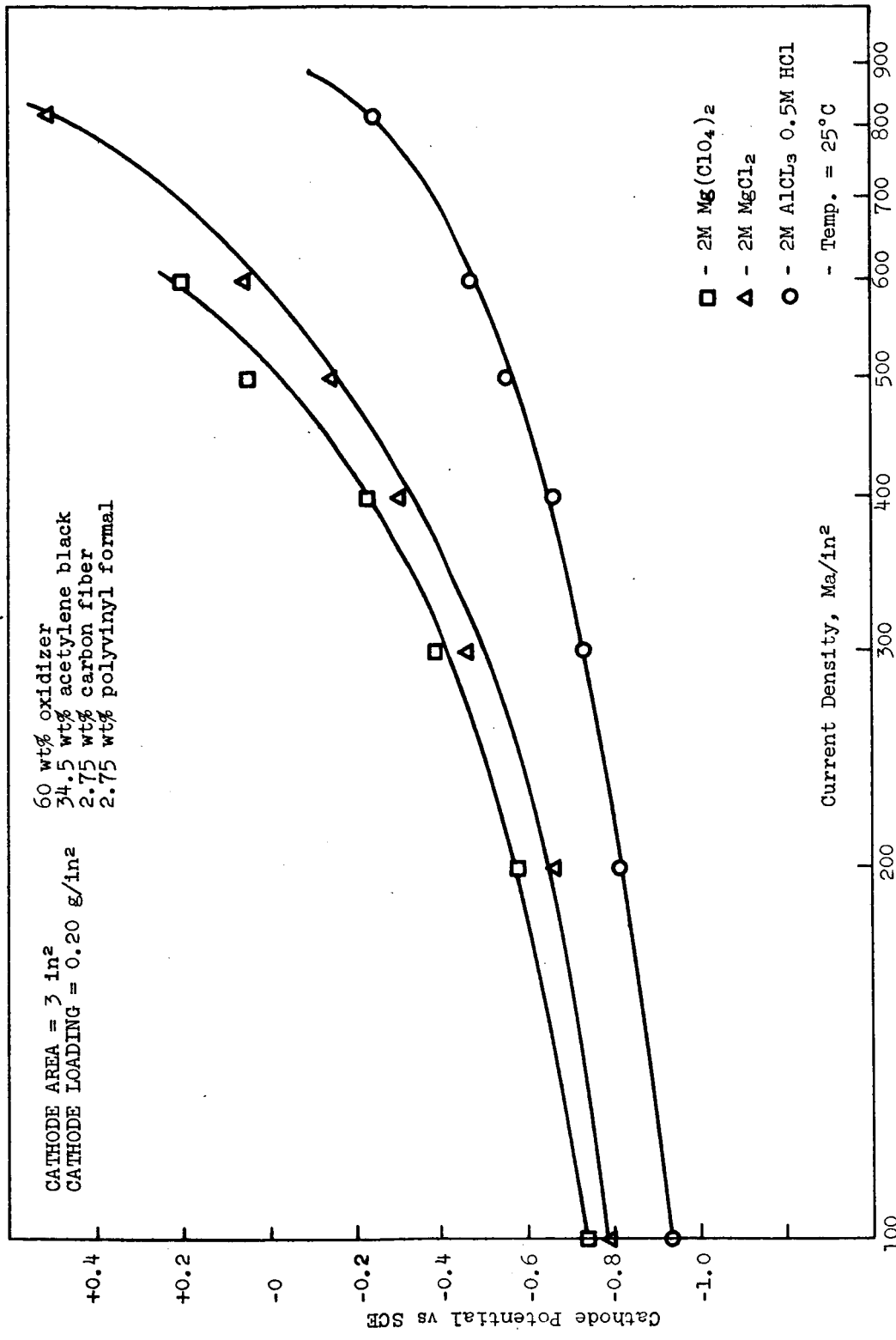


Figure 1. Effect of Electrolyte on Polarization of 2,4,6-Trichloro-Triazine-Triene Cathodes

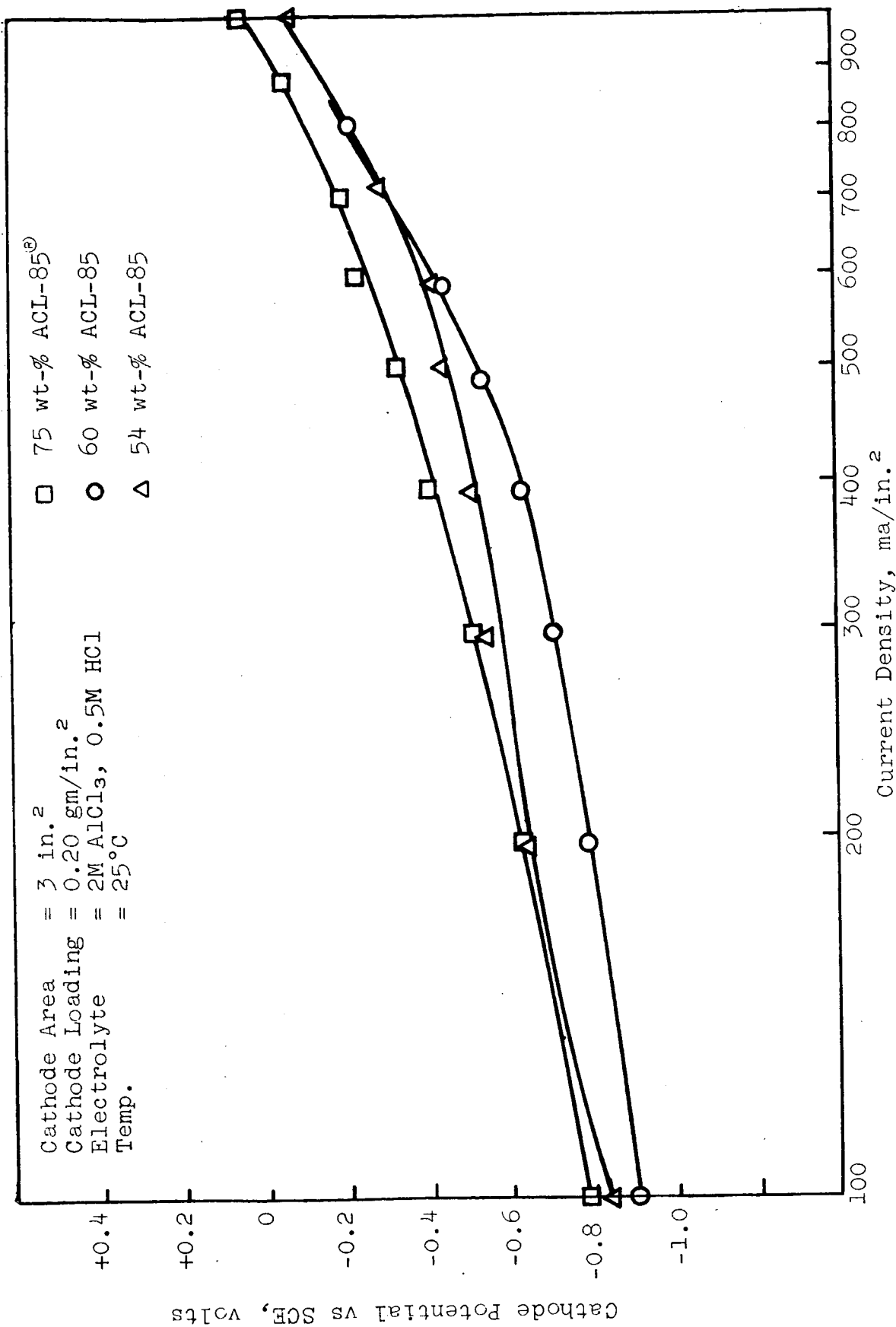


Figure 2. Effect of Active Material Concentration in Cathode Mix on Polarization.

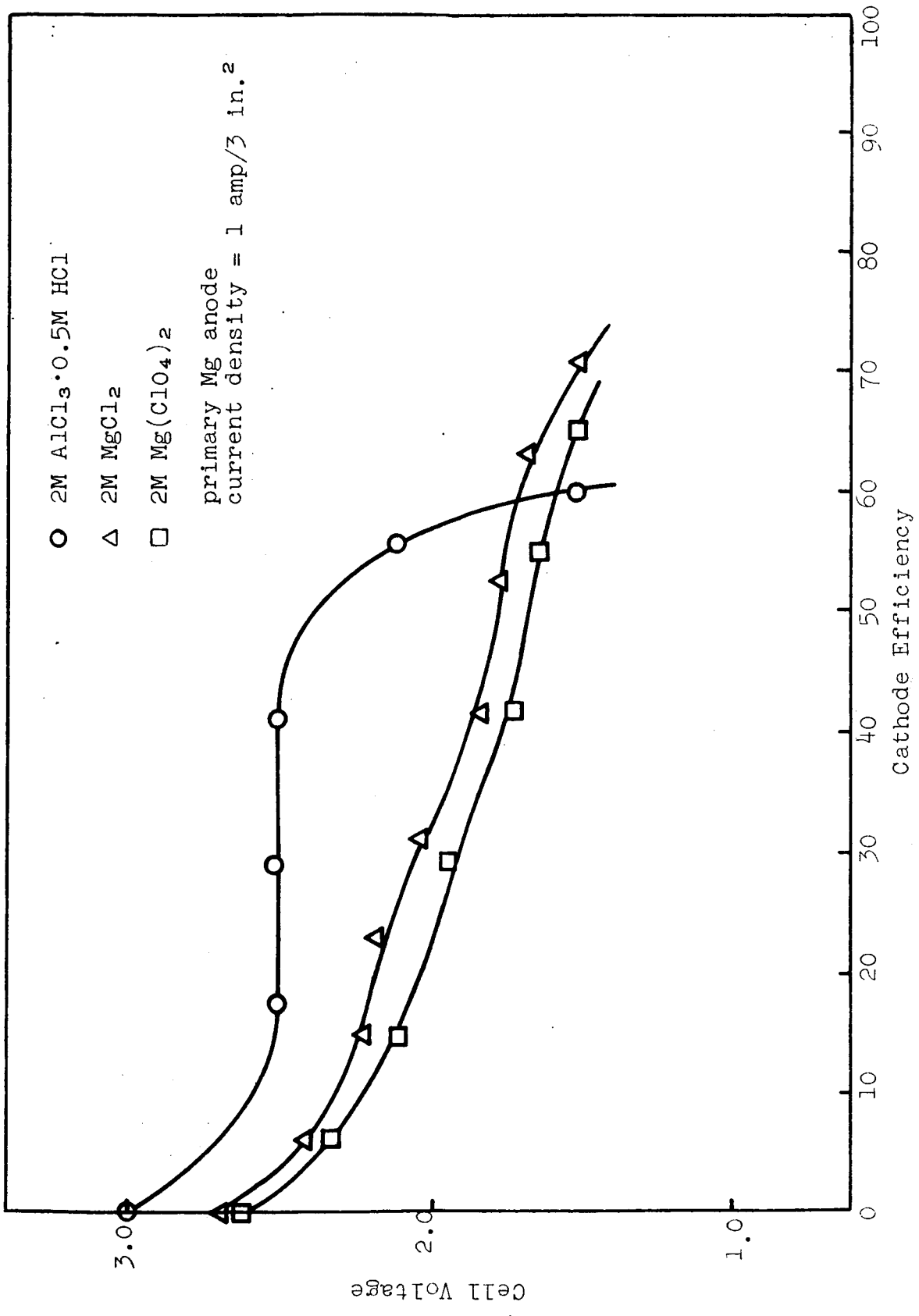


Figure 3. Discharge Characteristics of Mg-Trichloro-Triazine-Trione Tape Cell in Various Electrolytes.

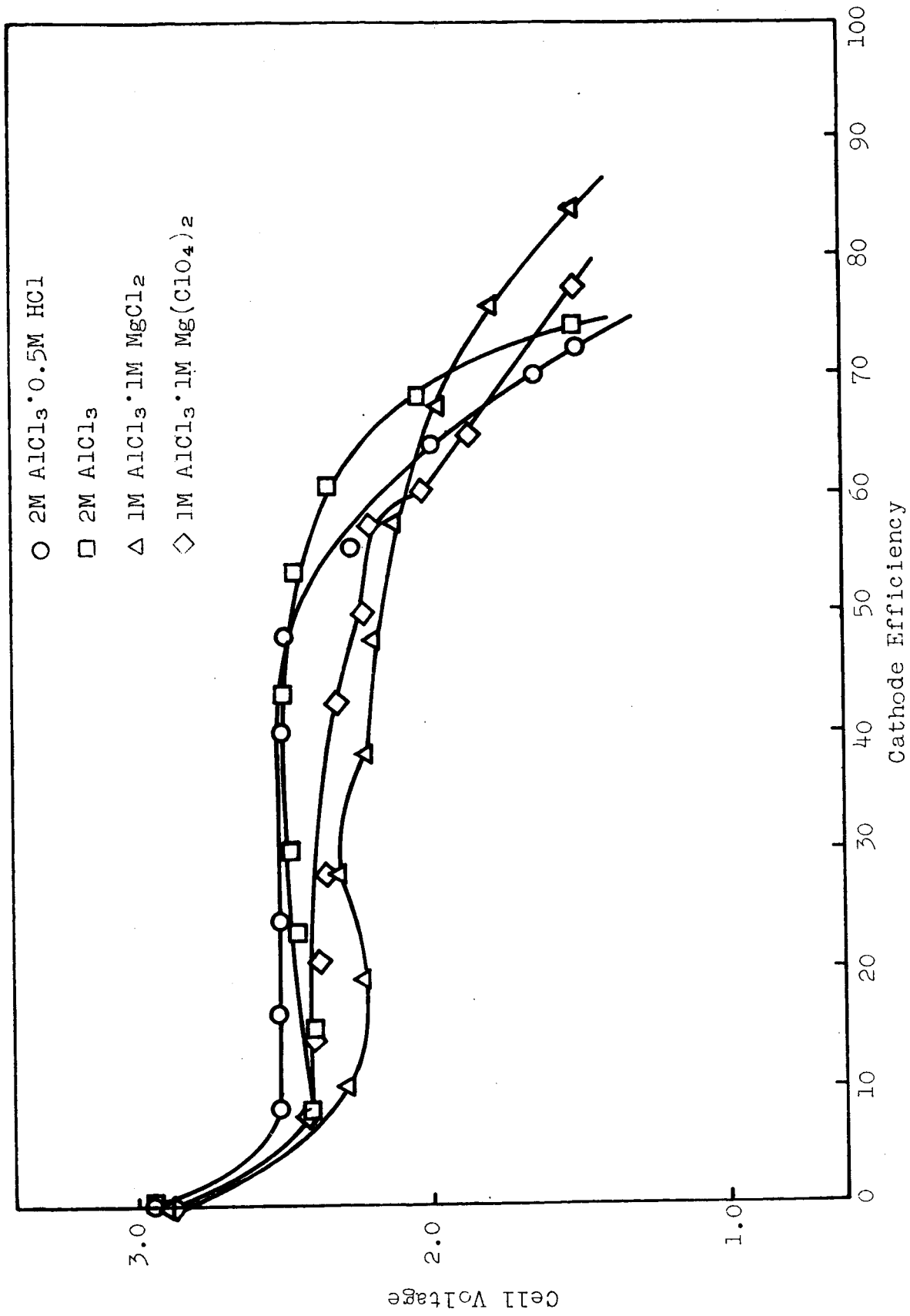


Figure 4. Discharge Characteristics of Mg-Trichlorotriazinetrione Tape Cells In Mixed Electrolyte.

Morehouse and Glicksman (ref. 1) previously observed this phenomenon and ascribed it to poor cathode stability in neutral electrolyte. However, the results here show no significant capacity loss in neutral electrolyte. Rather, the gradual emf deterioration seems to indicate polarization caused by accumulation of some reaction product. The nature of this behavior is not known at present, and is the subject of current study.

To date, the best cathode coulombic efficiencies (70-80%) have been obtained with 65-70 wt-% ACL-85 cathode tapes. Discharge voltages vs primary magnesium range from 2.65 v at 0.170 amp/in.² to 2.20 v at 0.800 amp/in.². There is no effect on efficiency over this current density range. Some typical static cell discharge data are shown in Table 3, and are illustrated in Figure 5. All efficiency data are based on actual active chlorine content, as determined by analysis.

Accurate power density data for tape cells require precise electrolyte consumption data, which are available only from dynamic testing. In static tests, energy densities of approximately 300 watt-hours/lb of dry cell (excluding electrolyte weight) are obtained. A typical example is shown in Table 4. The delivered energy density per unit cell weight will be considerably lower when accurate electrolyte requirement data are included. These figures are useful, however, in evaluating changes in formulations and discharge conditions while still in the static cell test phase. Dynamic testing of promising ACL-85 tape cells will be initiated early in the second quarter.

2. 2,4,6-Trichlorotriazinetrione in Nonaqueous Electrolyte

Independent work in this laboratory indicated that ACL-85 was a promising cathode material for nonaqueous systems. A Li/1M LiClO₄, butyrolactone/ACL-85 cell in a tape configuration discharged at 3.1 volts under a current density of 0.07 amp/in.². During this quarter, some preliminary compatibility tests were performed prior to full-scale cell testing, which will be carried out during the second quarter.

a. Solubility of ACL-85 in Organic Solvents

Simple screening tests based on visual observation were performed to check stability of ACL-85 in several potential organic electrolyte solvents. In addition, solubilities at 25°C were determined.

Table 3

TYPICAL DISCHARGE DATA FOR
Mg/AlCl₃, HCl/ACL-85[®] SYSTEMS

Cell Area = 3 in. x 1 in., Electrolyte = 2M AlCl₃ 0.5M HCl

<u>Cell No.</u>	<u>ACL-85, wt-%</u>	<u>Current, I, amps</u>	<u>Average Voltage, volts</u>	<u>Cathode Coulombic Efficiency, % (1.5 volt cutoff)</u>
78673-8	65	0.5	2.65	71
78673-6	65	1.0	2.48	76
78673-1	65	1.0	2.50	75
78673-10	65	1.5	2.45	83
78673-2	65	1.5	2.38	77
78673-9	65	2.0	2.40	82
78673-3	65	2.0	2.31	84
78673-7	65	2.5	2.20	76
78677-2	70	1.0	2.50	79
78677-7	70	1.5	2.40	80
78677-6	70	1.5	2.40	80
78677-9	70	2.0	2.30	79
78677-3	70	2.0	2.25	80
78677-4	70	2.5	2.20	79
78677-1	70	3.0	1.90	68

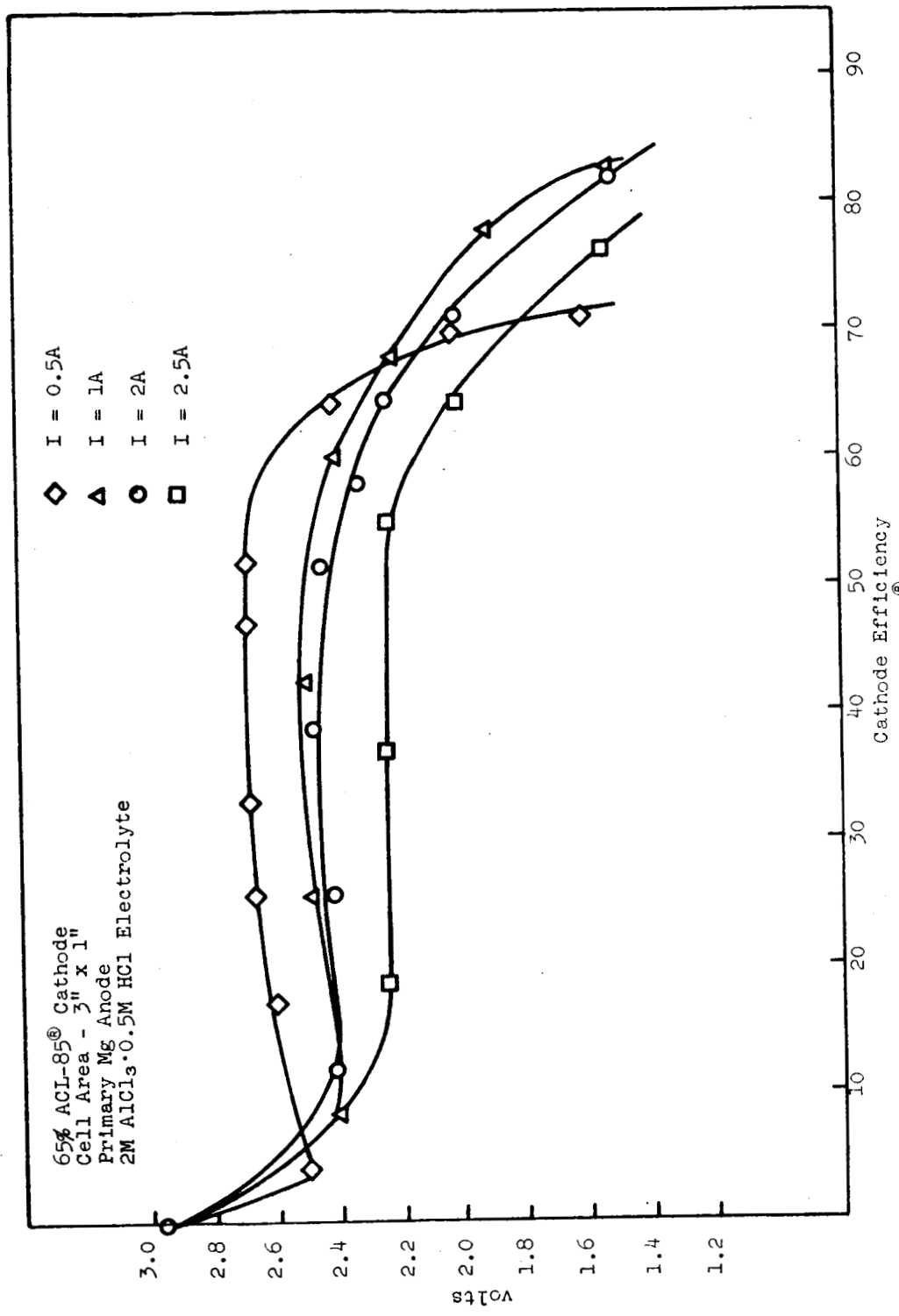


Figure 5. Discharge Characteristics of ACL-85[®] Tape Cells at Various Current Densities.

Table 4

ENERGY DENSITY CALCULATION FROM STATIC CELL DISCHARGE DATA

Cell No. 78677-6

Cathode Formulation: 70 wt-% ACL-85[®]
 24.5 wt-% Shawinigan Acetylene Black
 2.75 wt-% 1/8 in. Dynel Fiber
 Separator 2.75 wt-% Polyvinyl formal binder
 .035 in. Dynel
 Anode: 5-mil perforated primary Magnesium

Cell Weight:	Cathode Coat	0.9324 g
	Separator	0.0883 g
	Magnesium	<u>0.1201 g</u>
		1.1408 g

Electrolyte 2M AlCl₃ 0.5M HCl
 Current Density 0.5 amp/in.²
 Current = 1.5 amp (cell area = 3 in.²)
 OCV = -2.92 v (cathode = 1.02 vs S.C.E.)
 Average Operating Voltage = 2.40 v

$$\text{Power Density} = \frac{2.40 \text{ v} \times 1.5 \text{ a} \times 12.2 \text{ min} \times 454 \text{ g/lb}}{1.1408 \text{ g} \times 60 \text{ min/hr}}$$

= 292 watt hours/lb dry cell (excluding electrolyte)

Table 5.

SOLUBILITY AND OBSERVABLE STABILITY OF ACL-85
IN VARIOUS ORGANIC SOLVENTS

<u>Solvent</u>	<u>Observed Reaction</u>	<u>Solubility g/100 cc at 25°C</u>
Methanol	none	21.4
Acetone	none	10.1
Butyrolactone	none	18.2
Acetonitrile	none	11.2
Dimethyl formamide	none	46.2
Methyl formate	none	2.4

3. Plans for Second Quarter (Cathode Research and Development)

The energy density output by the aqueous Mg/ACL-85 system will be optimized and the complete tape system will be evaluated under dynamic conditions.

The performance of active chlorine compounds in nonaqueous electrolyte will be investigated and full cell tape configuration studies using a lithium foil anode will be started.

B. ANODE RESEARCH AND DEVELOPMENT

1. Lithium in Nonaqueous Electrolyte

Work during this quarter was devoted primarily to setting up suitable electrochemical test apparatus, materials purification and analysis, and screening of selected lithium-electrolyte systems.

a. Half Cell Test Apparatus for Nonaqueous Systems

In past work with aqueous systems, no attempt was made to identify quantitatively the separate components that contributed to polarization. In dealing with nonaqueous systems, IR polarization becomes important. The electrical apparatus for half cell and full cell static testing was designed to give as much quantitative information as possible about the various polarization effects.

Electrodes are evaluated initially using a free electrolyte half cell test. Constant current is used and an oscilloscope trace shows IR polarization and, in some cases, isolates concentra-

tion polarization and passivation effects. The test cell and associated circuitry are described completely in Section IV. Using this system, IR can be determined within 1 millisecond of application of current. A platinum counter electrode is employed to eliminate interfering cathode effects. In addition, the test cell is designed to measure gassing rate. Two typical oscilloscope traces are shown in Figure 6.

Nonaqueous systems in a tape configuration are evaluated using the conventional sandwich cell static test unit. To give an indication of IR polarization, interruptor-type bridges have been modified for battery work. These circuits are described in Section IV. The cell itself is constructed from polypropylene for stability in nonaqueous solvents. Working counter electrodes are silver chloride, platinum screen or in some cases ACL-85 cathode tapes. The silver chloride cathode was prepared by anodizing a discharged silver oxide electrode (Yardney Electric Silcad[®] YS10) in hydrochloric acid. This cathode operates satisfactorily but suffers from fragility.

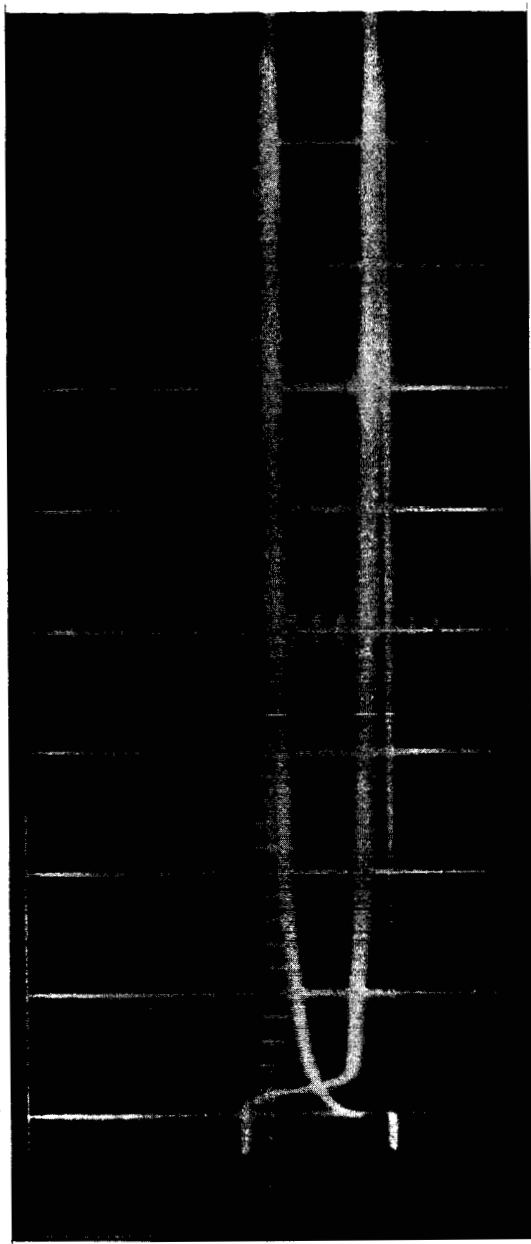
b. Materials

The electrolyte systems were selected on the basis of previous NASA-sponsored nonaqueous battery system research. All solvents were dried over Linde 4A Molecular Sieves. Methanol was predried over Linde 5A Molecular Sieves. The solvents were separated by vacuum distillation. Salts, except for morpholinium hexafluorophosphate, were vacuum-dried at 150°C for a minimum of 24 hours. Hygroscopic salts such as perchlorates required drying times up to 72 hours. Morpholinium hexafluorophosphate was dried in a vacuum dessicator over phosphorus pentoxide to avoid decomposition at elevated temperatures.

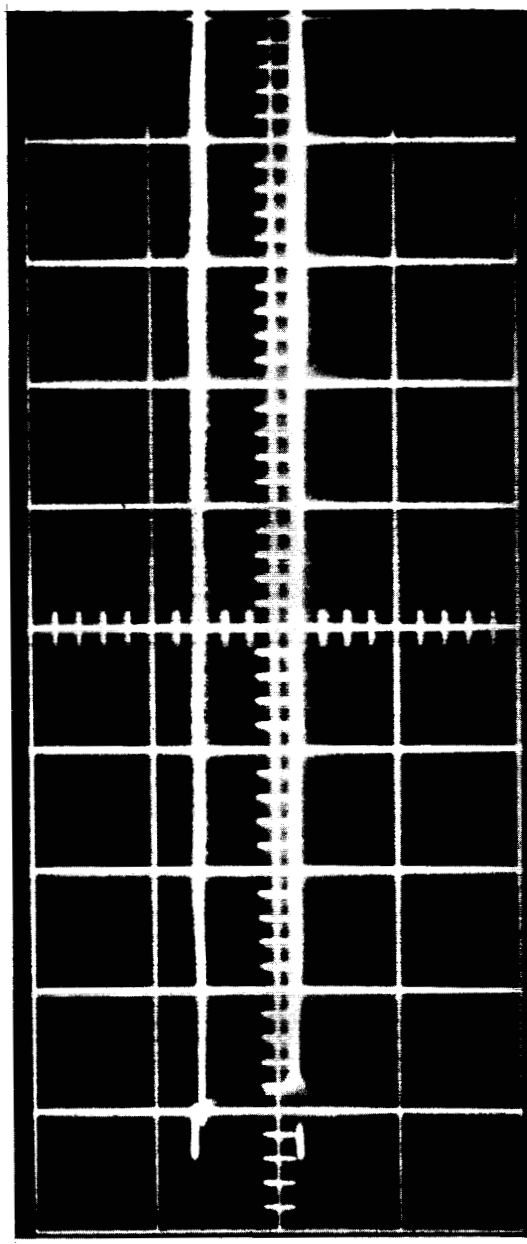
Dried materials transfer and electrochemical measurements were carried out in a Kewaunee Scientific Equipment (2C380) drybox under an argon atmosphere. Phosphorus pentoxide drying agent is used to trap any water vapor.

Water analyses reported here were performed using a Karl Fisher amperometric titration with a Beckman KF-3 Aquameter. A vapor phase chromatographic technique is being developed that promises to be more reproducible. Details of this method are reported in Section IV. Water concentrations below 0.5 mg H₂O/ml of solution, as measured by the Karl Fisher method, are questionable because of the high concentration reagents used. All water analyses are listed in Tables 6 and 7.

Conductivities were measured using an Industrial Instruments Conductivity Bridge Model RC16B2. The conductivity cell (Beckman) used has a cell constant of 0.1. Conducting data are also listed in Tables 6 and 7.



(a) Magnesium



(b) Lithium

Figure 6. Oscilloscope Traces of Lithium and Magnesium in γ -Butyrolactone (1M KPF_6) Electrolyte.

Table 6
FREE ELECTROLYTE CELL DISCHARGE DATA FOR LITHIUM IN NON-AQUEOUS ELECTROLYTE

Electrolyte System	K $\times 10^{-2} \Omega^{-1} \text{cm}^{-1}$	H ₂ O mg/ml	Gassing		Voltage at amp/in. ² (volts vs NCE)							IR, V/in. ²	CD amp/in. ²	Notes			
			w/o I	w I	0	.025	.05	.01	.02	.03	.04				.05		
1. KPF ₆ ≈ 0.2M AN	1.8	1.5	y	y	3.0	2.7	2.3	1.9	0.9						1.1	0.1	White precipitate near surface. Gelatinous precipitate forms IR → 6V "
2. LiClO ₄ 1M DMF	1.86	2.5	n	n	3.2	2.6	2.2	2.0	1.2								
3. Li Cl 1M DMF	0.86	1.6	n	n	3.25	2.95	2.75	2.35	1.2								
6. LiClO ₄ 1M γ-BL	1.14	1.1	n	n	3.1	2.8	2.65	2.25	1.55						0.8	0.1	
9. LiClO ₄ 1M MF	1.22	3.5	n	n	3.0	2.95	2.90	2.75	2.55	2.40	2.25	2.15	0.5	0.2			
4. KSGN 1M DMF	2.4	0.38	y	y	3.25	2.95	2.9	2.8	2.55	2.3	2.0	0.3	0.3	0.3	0.3	0.3	Yellow gelatinous ppt.
5. MPF ₆ 1M DMF	2.65	0.56	n	n	3.2	3.15	3.1	3.05	2.95	2.8	2.3				0.32	0.3	
7. KSCN 1M γ-BL	0.96	0.64	n	n	3.25	3.1	3.0	2.8	2.55	≈2					0.64	0.2	
10. KSCN ≈ 0.5M MF	0.16	0.41		y	3.25	2.85	2.6	2.25	1.33	0.3					1.2	0.2	
11. KPF ₆ 1M MF	0.20	0.67	n	n	3.25	2.95	2.9	2.8	2.75	2.7	2.6	2.3	0.2	0.2	0.2	0.2	
8. KPF ₆ 1M γ-BL	0.81	0.55	n	n	2.85	2.55	2.45	2.3	2.1	1.95	1.2				0.4	0.2	

Table 7.

FREE ELECTROLYTE CELL DISCHARGE DATA FOR MAGNESIUM IN NONAQUEOUS ELECTROLYTE

Electrolyte System	$\chi \cdot 10^{-2} \text{V}^{-1} \text{cm}^{-1}$	H_2O mg/ml	Gassing	Voltage at amp/in. ² (volts vs NCE)			IR, v	CD, amp/in. ²	Notes				
				0	0.05	0.1				0.2	0.4	0.5	
1 KPF ₆ /0.2M AN	1.8	1.5	No	1.4	0.95	0.80	0.45	0.85	0.05	Improves in use; turns black			
2 LiCl 1M DMF	0.86	1.6	No	2.2	1.60	1.25	0.45	0.5	0.10	" " " " "			
3 Mg(ClO ₄) ₂ 1M MeOH	2.6	8	*	2.0	1.65	1.5	1.32	0.98		" " " " "			
3 LiCl 1M DMF	0.86	1.6	No	2.0	1.8	1.6	1.2			" " " " "			
7 LiClO ₄ 1M γ-BL	1.14	1.1	No	1.05	0.25					Grey precipitate			
10 LiClO ₄ 1M MF	1.22	2.2	No	1.38	1.13	1.05	0.91	0.25		Ppt.			
4 LiCl 1M DMF	0.86	1.1	No	1.95	1.82	1.64	1.56			Pat'd etch soln.			
5 KSCN 1M DMF	2.4	0.38	Yes	1.4	1.1					Black surface			
6 MPF ₆ 1M DMF	2.65	0.56	No	0.75	0.80	0.75	0.68			Black surface spots			
8 KSCN 1M γ-BL	0.96	0.64	No	2.00	1.46	1.26	0.48			Immediate After Use			
15 KSCN 1M MeOH	3.7	1.7	Yes	1.62	1.5	1.5	1.3	1.1	0.8	0.6	0.5	0.4	0.2
14 LiClO ₄ 1M MeOH	3.1	2.1		2.10	2.02	1.98	1.89	1.73	1.60	1.44	1.30	0.45	0.3
11 KSCN 1M MF	0.16	0.41		1.77	0.90	0.56						0.7	0.025
12 KPF ₆ 1M MF	0.20	0.67	No	1.16	0.40								
9 KPF ₆ 3M γ-BL	0.81	0.55	No	0.95	0.56	0.50	0.30						
16 LiCl 1M MeOH	1.8	2.6	Yes	2.05	1.98	1.92	1.80	1.59	1.40	1.22	1.08	0.6	0.3

* No gassing at open circuit--0.5 ml/min/in.² (moderate) with current drain.

All solutions were saturated with electrolyte or made one molar when possible. First quarter work with lithium was restricted to free electrolyte testing. A clean lithium surface was cut from a block (Fisher Scientific Co.) and used without further treatment.

c. Discharge of Lithium in Nonaqueous Electrolytes

The results of the free electrolyte half cell tests are shown in Table 6.

The lithium/acetonitrile (AN) system showed considerable gassing although the water content was relatively low. Formation of a white precipitate and poor performance in the presence of KPF_6 electrolyte eliminated this solvent for further work during this quarter.

With N,N-dimethylformamide (DMF), lithium voltages improved. However, a gelatinous precipitate formed on the anode and caused significant IR drop as the discharge progressed. Morpholinium hexafluorophosphate (MPF_6) was the best of the solutes tested.

In γ -butyrolactone (γ -BL), the effect of solute (LiClO_4 , KSCN , KPF_6) was inconclusive.

Methyl formate with KPF_6 or LiClO_4 gave the best results with lithium. Lithium performance was somewhat better with KPF_6 despite the lower electrolyte conductance. The polarization curves are illustrated in Figure 7. Satisfactory voltages were maintained at current densities up to 0.5 amp/in.^2 .

The Li/LiClO_4 1M in methyl formate showed some gassing at open circuit. The open circuit potential was -3.0 v vs NCE. At high currents there was some boiling of the solvent, but true gassing at the lithium did not appear to increase. The IR measurement at 0.2 amp/in.^2 showed a perfect square wave oscilloscope trace at 10 msec/cm . The IR of 0.5 v added to the operating voltage of 2.55 shows that all the polarization is due to IR. The current was maintained at 0.2 amp/in.^2 for over 2 hours, with the operating voltage changing randomly between 2.55 and 2.65 v .

With KPF_6 in the Li/methyl formate systems, potentials were higher and gassing was not observed. However, the lithium surface turned grey. No long-term test has been made with this system.

It is apparent that KSCN decomposes too rapidly to be useful as a solute in any electrolyte system with lithium.

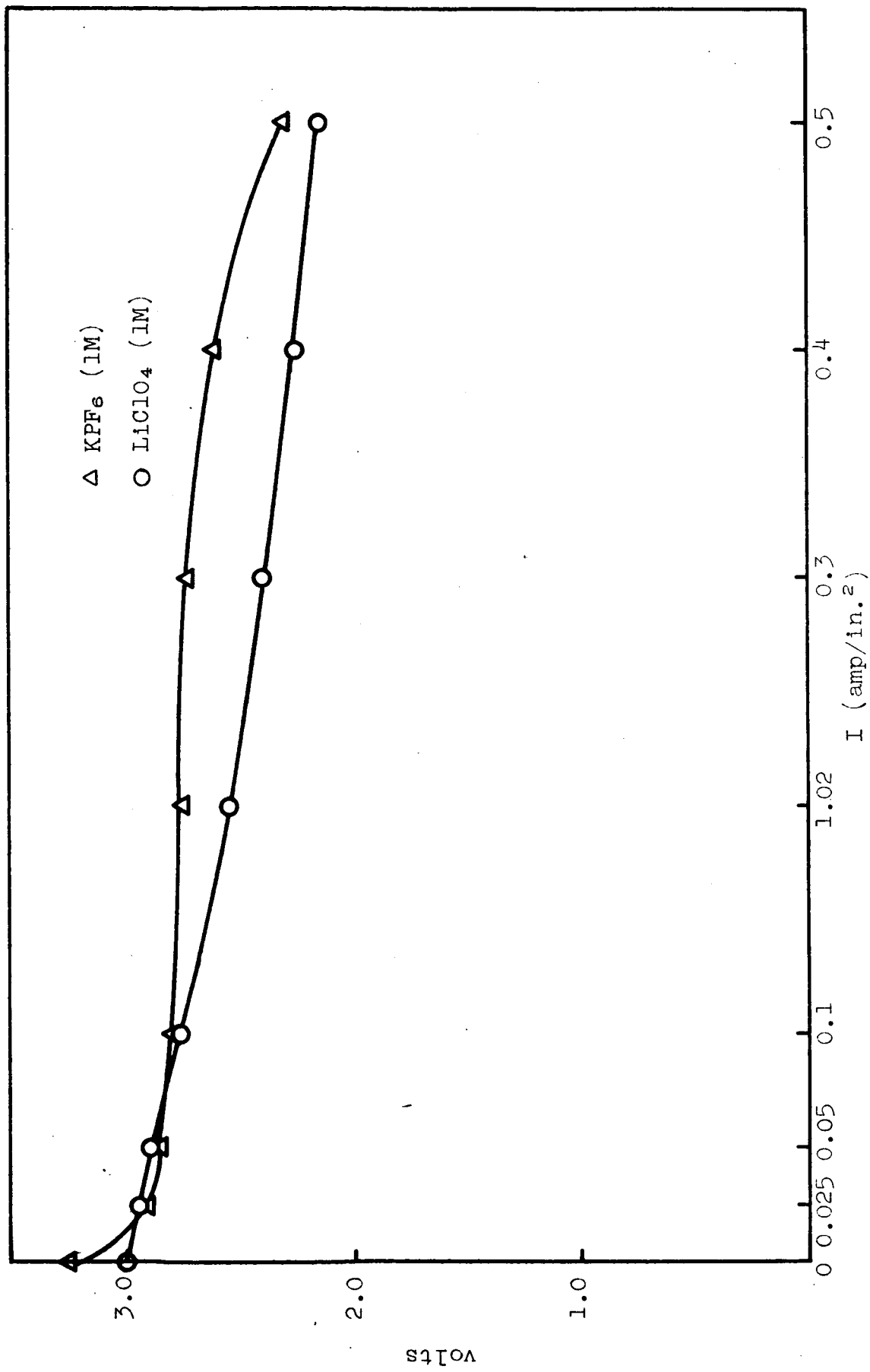


Figure 7. Polarization Curves of Lithium in Methyl Formate

It must be emphasized that these results are from initial screening and are of relative value only. The Luggin capillary was adjusted from ≈ 4 mm to ≈ 0.5 mm after the following systems were tested: AN (KPF_6), DMF($LiClO_4$), DMF ($LiCl$), γ -BL ($LiClO_4$).

In general, the oscilloscope traces using lithium anodes showed IR-type polarization only (<1 millisecond to attain final voltage). A typical trace is shown in Figure 6.

2. Magnesium in Nonaqueous Electrolyte

Magnesium in neutral aqueous electrolyte was studied using the free electrolyte cell and tape configuration cell for comparison. The anode material was primary magnesium foil (10 mil) from Dow. The various surface treatments are described individually below.

The OCV of -1.70 v vs NCE for $Mg/Mg(ClO_4)_2$ aqueous system in the free electrolyte cell test is in agreement with previous static cell data. However, the operating voltage at 0.5 amp/in.² was -1.12 v. An oscilloscope trace showed an IR component of 0.4 v. This operating voltage was less than that of a tape cell and we can, in retrospect, attribute this to lack of cleaning and to lack of chloride ion in solution. Thus, the magnesium may remain somewhat passive. The gassing rate increased under load, and was 1.4 ml/min/in.² at 0.5 amp/in.². The time for complete discharge at this rate was 62 minutes, giving a coulombic efficiency of 86%.

In the tape configuration static test, the silver chloride counter electrode was used.

A capacity of 20 minutes at 0.5 amp/in.² was obtained for the AgCl electrode (from the Yardney Silcad[®] AgO plate) in aqueous $Mg(ClO_4)_2$ electrolyte versus expanded magnesium. An anode potential of -1.70 v vs NCE was obtained at 0.5 amp/in.² drain. This potential includes an IR of 0.15 v as determined by the interrupter circuit (Fig. 11). Using a solid magnesium anode, no appreciable current could be drawn, due apparently to gas blocking. With the same system, but with a gassing platinum screen cathode, much electrolyte had to be added during the test. However, 32 minutes at 0.5 amp/in.² was obtained for a solid magnesium anode at an operating potential of -1.5 v vs NCE. This test appears to substantiate the gas blockage theory and also the earlier result that chloride ion improves the magnesium discharge, probably by breaking down the passive magnesium oxide surface film. The magnesium for these anodes was cleaned with detergent or KOH and then chemically polished with 0.1M HCl.

Discharge data for magnesium in nonaqueous electrolyte are difficult to interpret because of sensitivity to surface cleaning methods. In many cases a high open circuit would be

obtained but no appreciable current could be drawn. Electrodes often improved with time under load, or they improved if a higher current was passed initially.

Of the cleaning methods, 3% HCl in DMF was better than 1% HCl in H₂O, which in turn was better than light polishing with emery paper. However, the best method is based on a patented cleaning solution. This solution was used for the free electrolyte cell results in Table 7 except for the AN (KPF₆) and MeOH[Mg(ClO₄)₂] systems.

The etching solution used was:

23 vol-% dioxane
60 vol-% isopropyl alcohol
10 vol-% HNO₃ (70% HNO₃ in H₂O)
5 vol-% HCl (38% HCl in H₂O)
2 vol-% acetic acid.

The solution was used in the drybox and the magnesium was wiped clean of the etching solution before assembling the cell.

Although the oscilloscope pictures using lithium anodes showed IR-type polarizations only (<1 millisecond to attain final voltage), magnesium anodes showed varied and complicated polarization behavior. The best IR measurement was the initial break from the on-to-off cycle. The off-to-on cycle often showed a larger initial polarization, which may be the IR of the semi-passive film on the magnesium. There have been instances in which the trace showed a maximum polarization and then improvement of potential for an off-to-on cycle. Also there have been maxima in the potential of the on-to-off cycle.

Some limited data are available for tape configuration static tests with magnesium in methanol. A Mg/Mg(ClO₄)₂ 1M in MeOH system was tested with a gassing platinum cathode and AgCl cathode. The methanol water content was 17 mg/ml and an aqueous HCl etch was used for the magnesium. The data are given in Table 8.

The high water content of the electrolyte and unsatisfactory surface treatment are reflected in the poor anode voltage and high polarization under current drain.

Table 8.

CURRENT VOLTAGE DATA FOR THE Mg/Mg(ClO₄)₂ METHANOL SYSTEM

<u>I, amp.</u>	<u>Pt Cathode</u>		<u>AgCl Cathode</u>	
	<u>E (v vs NCE)</u>	<u>IR* (v)</u>	<u>E (v vs NCE)</u>	<u>IR (v)</u>
0	-1.48		-1.45	
0.025	-1.47	0.11	-1.34	0.12
0.05	-1.46	0.17	-1.26	0.16
0.1	-1.45	0.23	-1.24	0.32
0.2	-1.43	0.29	-1.13	0.41
0.3	-1.39	0.35	-0.90	0.55
0.4	-1.35	0.39	-0.90	0.68
0.5	-1.20	0.56		

* IR-Anode to calomel on anode side of separator. Obtained with interrupter circuit.

3. Plans for Second Quarter (Anode Research and Development)

The screening of selected lithium and magnesium systems will continue, using the free electrolyte test cell. In addition, this technique will be used to isolate and define problems that may be encountered in full cell tests.

The effect of lithium purity and system water content will be determined.

Development of a lithium anode in a tape configuration will be undertaken. A specific effort will be made to produce a high surface area electrode.

Full cell tests starting with the ACL-85 cathode as counter electrode will be initiated.

III. TASK II - TAPE CELL EVALUATION

A. TAPE CELL PREPARATION

The continuous cathode tape manufacturing machine was serviced and refitted with improved press drying rolls and take-up reels. Production of continuous lengths of ACL-85 tapes will begin early in the second quarter.

B. DYNAMIC TESTING

No dynamic testing was performed in the first quarter. A new test unit was designed and constructed. Complete details are given in Section IV. Dynamic testing of the aqueous Mg/ACL-85 system will begin early in the second quarter.

IV. SUPPORTING RESEARCH

A. TEST EQUIPMENT DESIGN AND IMPROVEMENT

1. Free Electrolyte Half Cell Unit

A special current pulsing switch device has been constructed and is being used with an oscilloscope to measure electrode characteristics during the first few milliseconds of discharge. The switch consists of a mercury-wetted relay that closes the cell current circuit and generates a trigger output to start the oscilloscope sweep. When the cell current is driven by a properly loaded constant current supply, the oscilloscope display represents the electrode performance at the selected current density for the period of time from open circuit through the first 10 milliseconds of discharge. Figure 8 illustrates the electrical diagram for the system. The test cell itself is shown in Figure 9.

2. Limited Electrolyte Full Cell Static Test Unit

Pulse current equipment has been built and used which is a modification of the Kordesch-Marko bridge and the Allis-Chalmers bridge. The modification used biases the pulse transistor in such a way as to keep it in the cut-off state when high voltage cells (3.0-4.5 volts) are being tested. These modified bridges are capable of measuring the IR-free electrode performance from open circuit to 3-amp discharge current. The Kordesch-Marko bridge records an IR-free voltage reading while the Allis Chalmers bridge records the V_{IR} contribution directly. The circuitry involved is illustrated in Figures 10 and 11.

3. Dynamic Test Station

The new dynamic test station for dry tape batteries has been completed (see Figure 12). The tester is capable of tape speeds of 0.002 to 1.0 in./min. The speed is continuously variable and accurately maintained by a Zero-Max drive system.

An automatic voltage-current recording system has been incorporated to make 24-hour operation possible. The electrolyte feed for the test station is provided by a Milton-Roy controlled volume pump. The electrolyte storage tanks provided have capacity for 24 hours of testing on tape batteries before refilling is required.

Calibration of the drive system and electrolyte feed system has been completed. Evaluation of the aqueous Mg/ACL-85 tape system will begin early in the second quarter. Compared with the earlier test apparatus, the new dynamic test station has the advantages of long-term unattended operation and more accurate speed and electrolyte feed control.

- V - Tektronix 545-A oscilloscope type L plug in (fast rise calibrated preamp. 1 meg impedance).
- P.S. - Harrison Laboratories Model 6200A power supply.
- S - Potter and Bromfield Mercury wetted contact relay JMI 121M. Toggle switch and 90 v dc used to activate relay and trigger CRD.
- MA - Weston Model 911 milliammeter.
- C - Platinum auxiliary electrode (cathode).
- R - Reference electrode.
- A - Test electrode (anode).

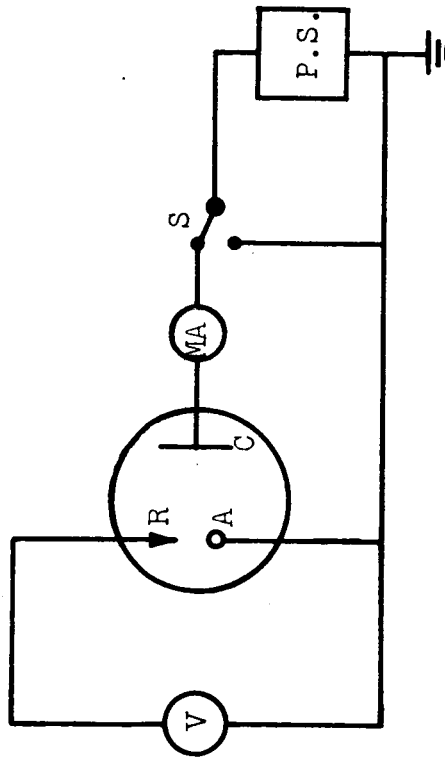


Figure 8. Circuitry for Free Electrolyte Half Cell Test

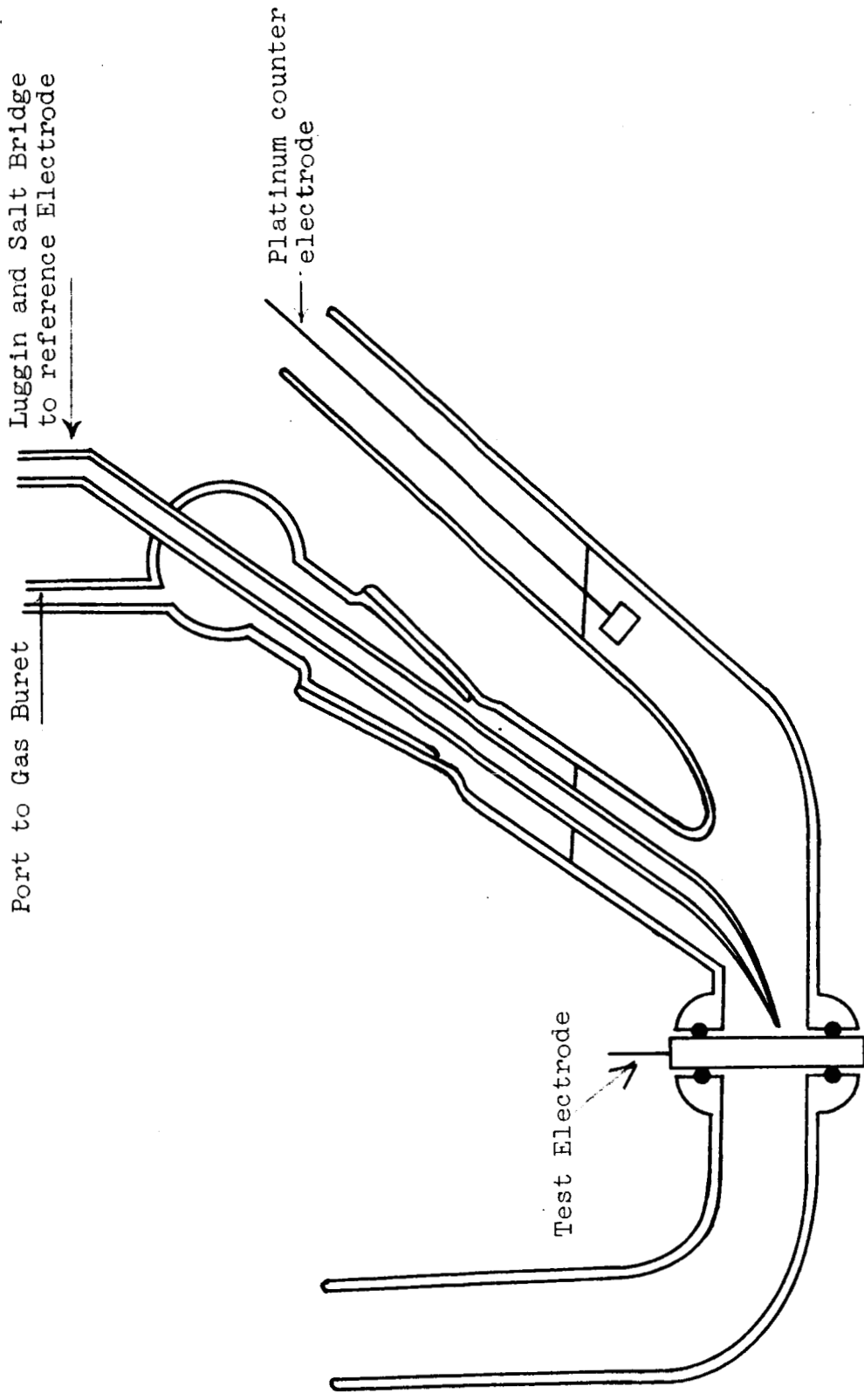


Figure 9. Free Electrolyte Test Cell.

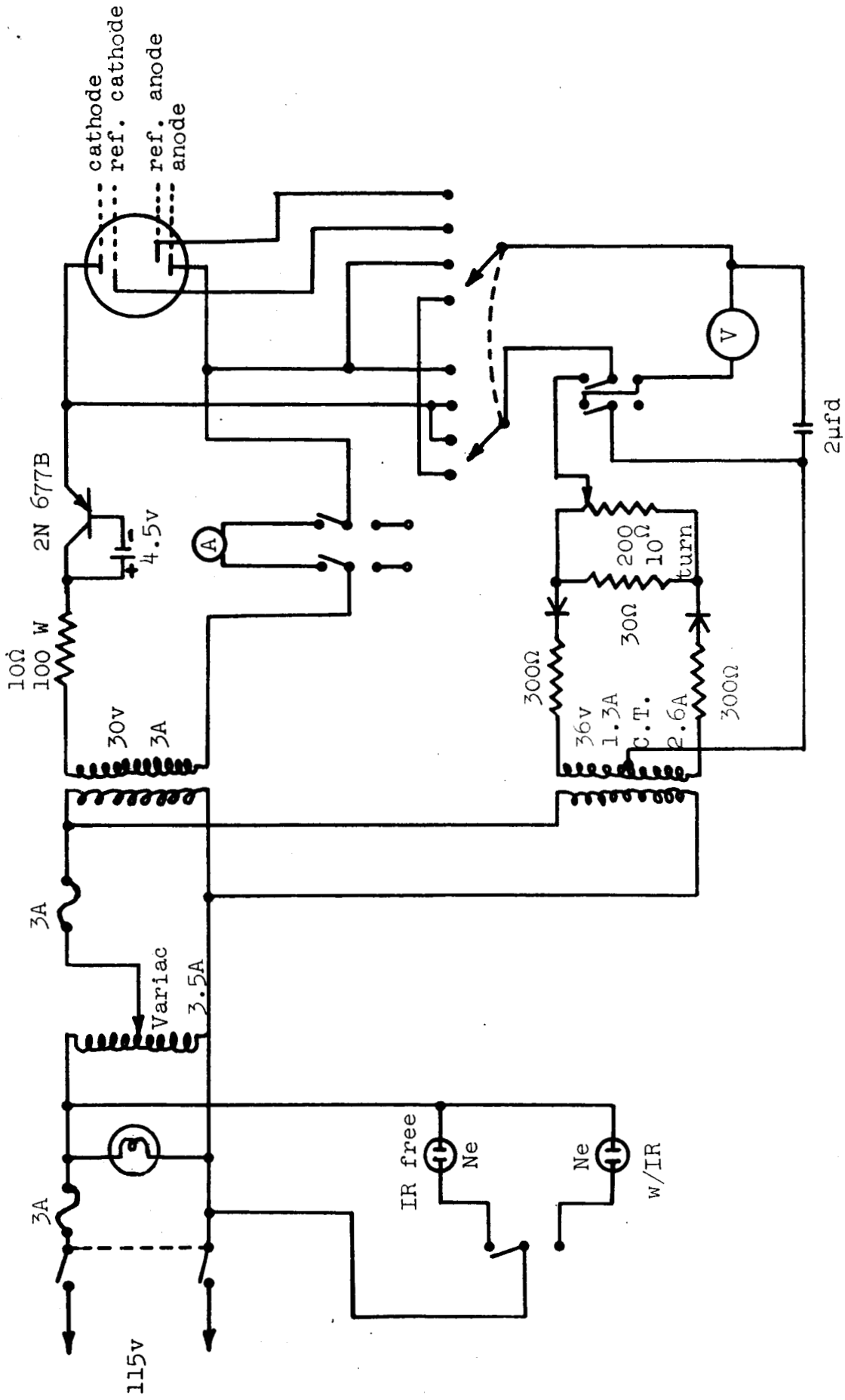


Figure 10. Kordes-Marko Type Interrupter Circuit Diagram

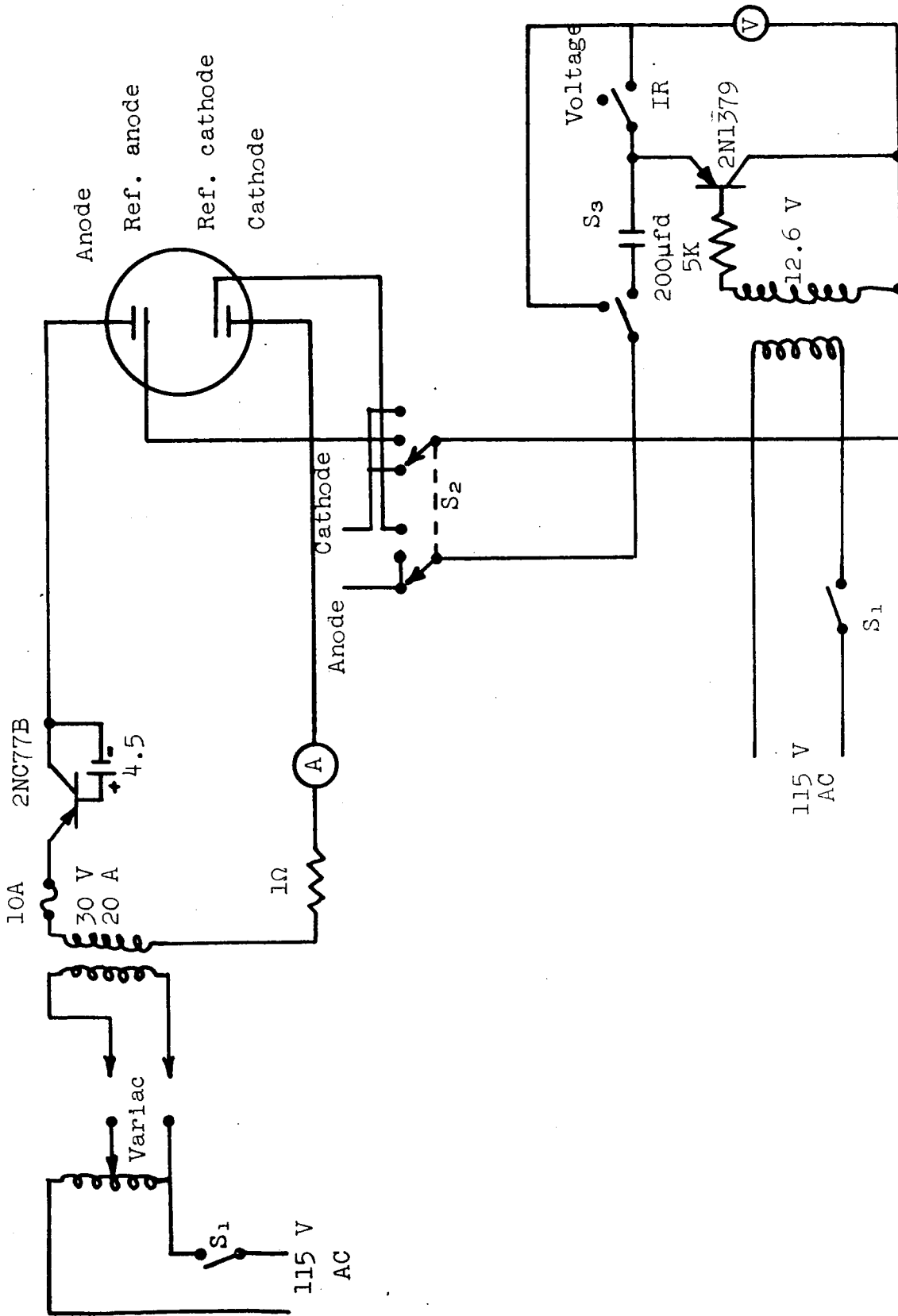


Figure 11. Allis-Chalmers Type Interrupter Circuit Design

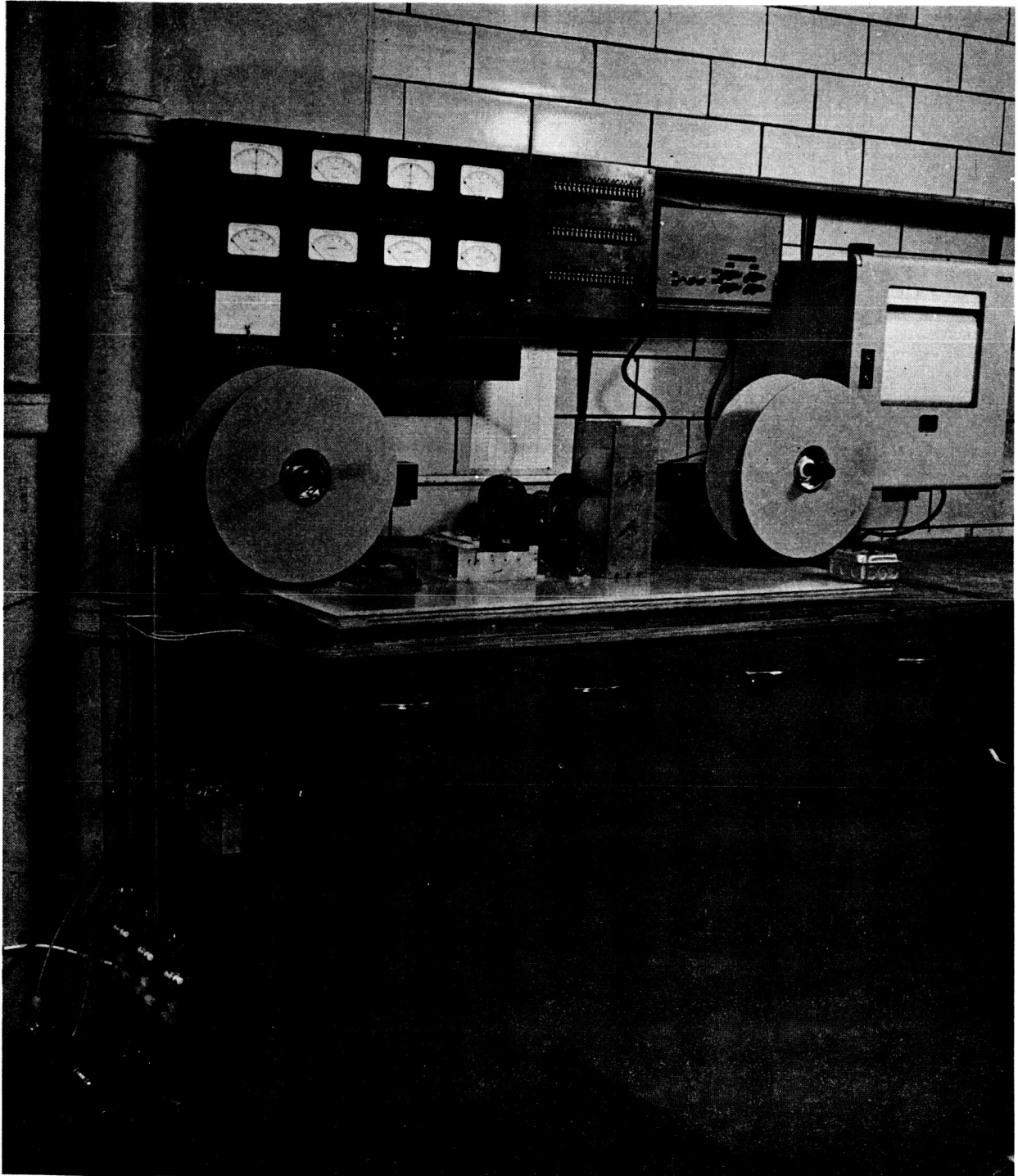


Figure 12. Dynamic Test Unit--Drive, Recorder, and Electrolyte Supply.

4. Improved Water Analysis Techniques

The automatic Karl-Fisher titration currently being used for water analysis has reliability limitations, particularly at very low water concentrations. Several other faster and more reproducible techniques are being investigated with the goal of improving sensitivity. Two techniques examined during this report period were the use of nuclear magnetic resonance and vapor phase chromatography. Nmr was discarded early as a useful technique because its sensitivity limit was approximately 0.1% (too high for our purposes). In addition, its use is restricted to solvents that do not have -OH or N-H bonds.

Two vapor phase chromatographic procedures were investigated: (a) gas-solid chromatography and (b) gas-liquid chromatography.

a. Gas-Solid Chromatography

Vapor phase chromatograms of water show the phenomenon of tailing, as evidenced by nonsymmetric chromatographic peaks. The high polarity of water accounts for this tailing. The quantitative measurement of chromatographic peak areas is thus subject to tailing-dependent error and the accuracy, and precision of analyses are affected. The possible application of gas-solid chromatography to minimize this error was investigated.

Columns were prepared from Fluoropaks, a perfluorocarbon chromatographic column support (Wilkins Scientific Instruments, Inc.). The column dimensions were 6 ft x 1/4 in. The He carrier gas flow rate was 77 cc/min, and column temperature was constant at 30°C. Injection temperature was 290°C, and the temperature of the hot wire detector was 320°C. Under these operating conditions, a useful separation of water from dimethylformamide does occur and water analyses were possible. Further investigations, however, showed two limitations of this gas-solid chromatographic procedure. First, the procedure was found to be not universal but limited to high boiling solvents (low boiling solvents elute with the water peak and interfere in analyses). Second, gases (e.g., O₂, N₂) dissolved in the solvent elute just before water and may give interference, particularly at low water concentrations. In view of these limitations and of the desirability of a universally applicable method, the use of gas-solid chromatography was discarded.

b. Gas-Liquid Chromatography

The following column was prepared and investigated for water analysis: 8% Carbowax 20M (Carbide and Carbon Chemicals Co.) on a perfluorocarbon coated diatomaceous earth, Gas-Pack F, 60-80 mesh, (Chemical Research Services, Inc.). Column dimensions were 7 ft x 1/4 in. in 304 stainless steel. Column operating temperature was constant at 100°C and He carrier gas flow rate was

86 cc/min. The instrument was the Perkin-Elmer Vapor Fractometer Model 154. Ten microliters of sample were routinely injected to maximize sensitivity. A typical chromatogram of 0.8% water in dimethylformamide is shown in Figure 13. Retention times are in parentheses for air (0.5 min), unidentified peak, perhaps dimethylamine (1.1 min), water (3.9 min), and dimethylformamide (17.2 min). A series of standards of water in dimethylformamide was prepared and water peak area calibration data were obtained using the method of standard addition.

Peak area measurements are reproducible to ± 0.05 in.² at 0.1% water concentration. This corresponds in this procedure to a precision of $\pm 0.01\%$ water at 0.1% water concentration. Some of the preliminary calibration data are shown in Table 9.

The procedure is now being extended to lower water concentrations. The data thus far obtained indicate a limit of detection of 0.001% or 10 ppm water, with an accuracy of $\pm 10\%$ of the water concentration.

Preliminary studies of additional solvents have begun. Vapor phase chromatograms of these solvents are shown in Figures 14 (methanol), 15 (methyl formate), 16 (ethyl formate), 17 (γ -butyrolactone), and 18 (acetonitrile). The retention times show that this method of water analysis is applicable to these solvents with one limitation. The tailing of acetonitrile, Figure 18, was shown to limit water analysis in acetonitrile to water concentrations above the 1% level. Water in the other five solvents will be detectable at the 0.001% concentration level.

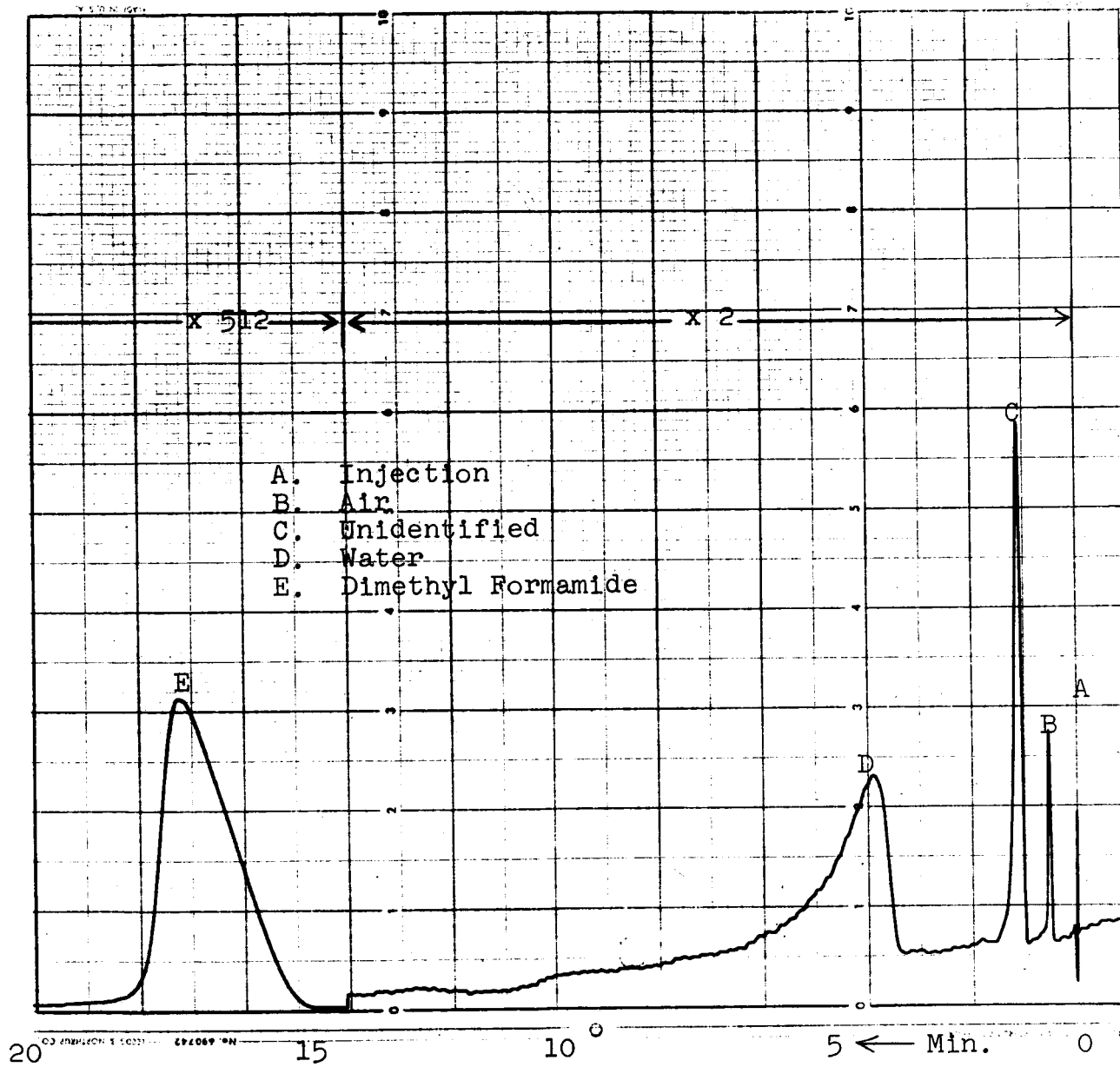


Figure 13. Dimethyl Formamide Vapor Phase Chromatogram.

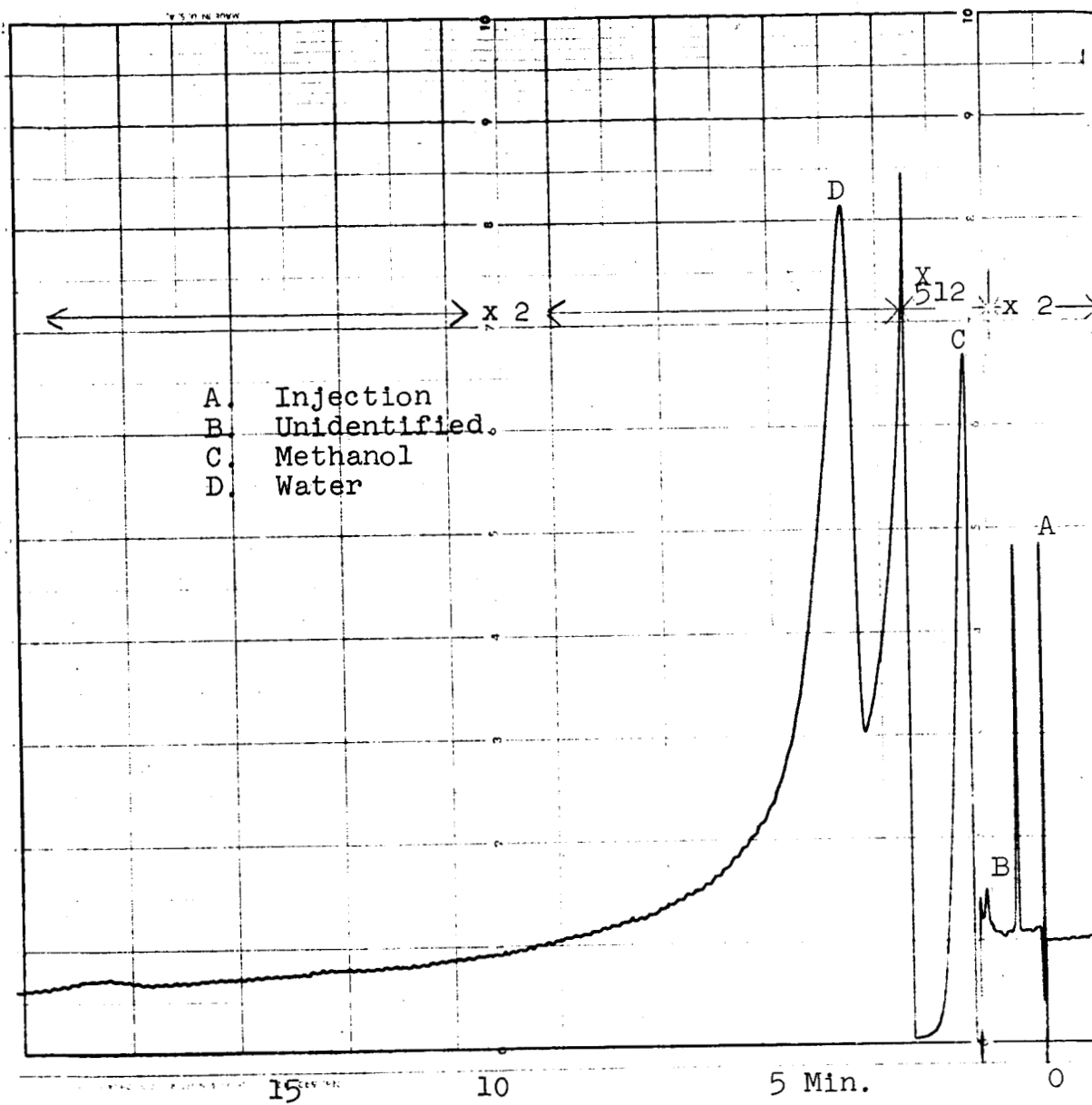


Figure 14. Methanol Chromatogram.

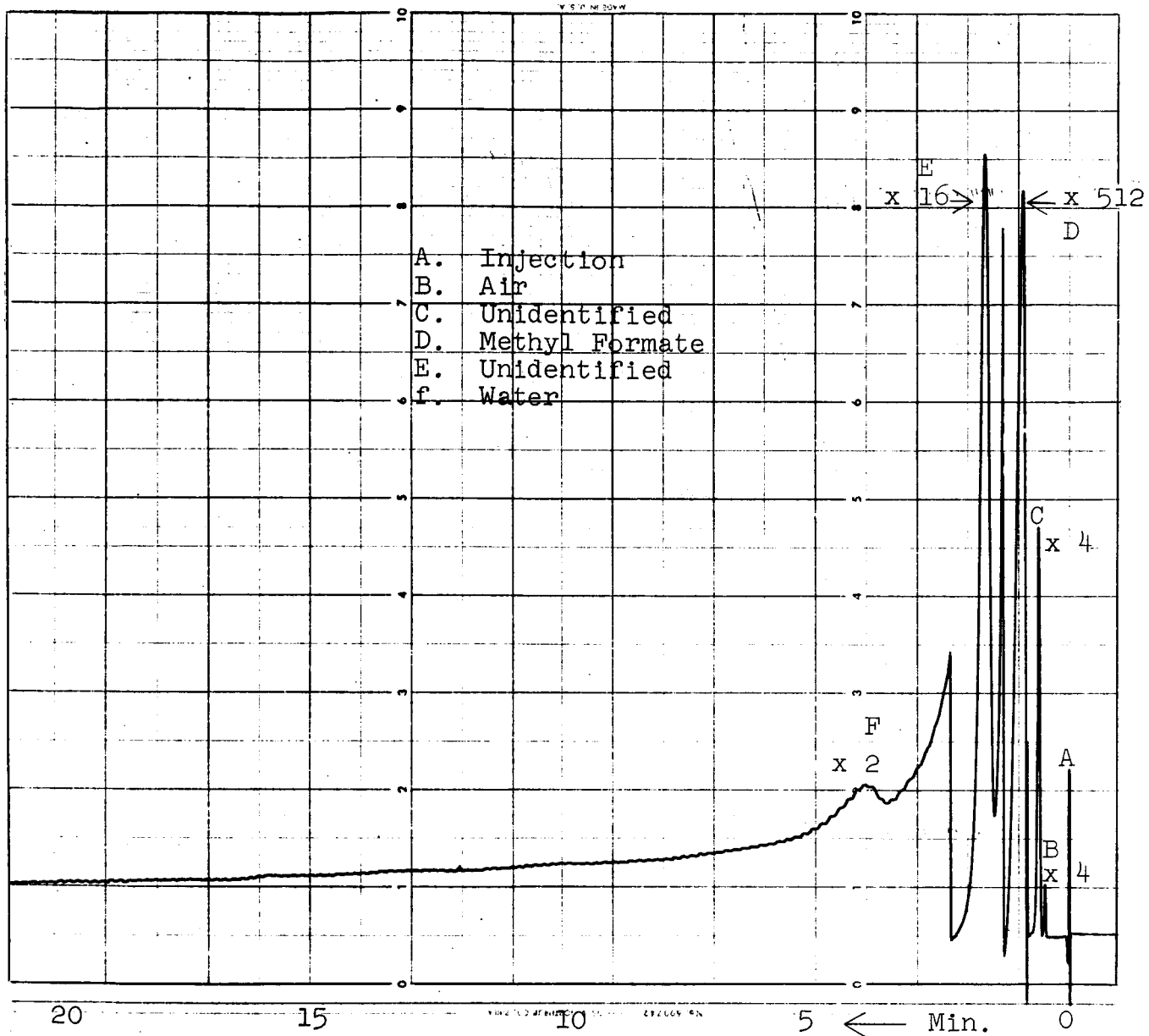


Figure 15. Methyl Formate Chromatogram

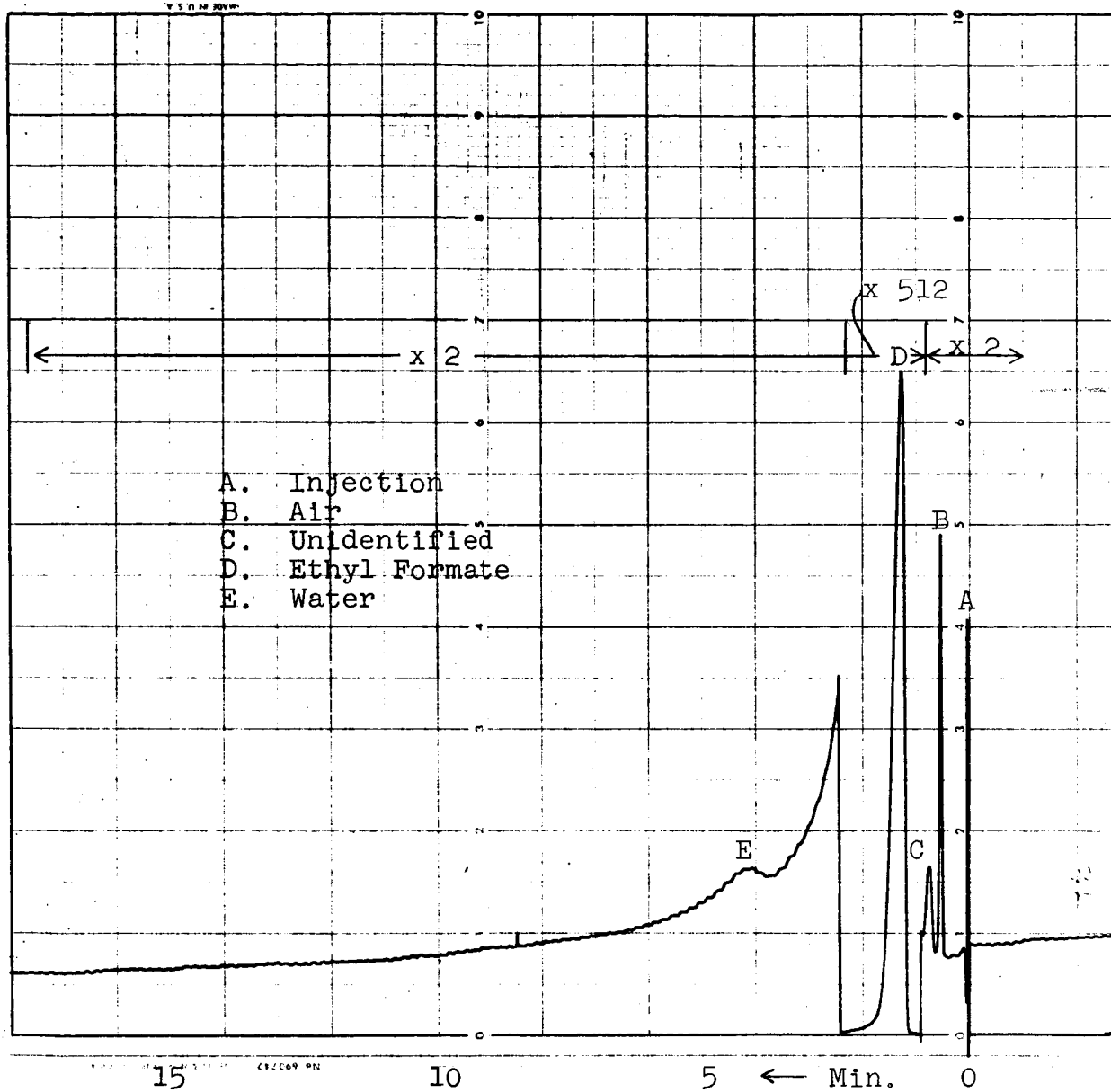


Figure 16. Ethyl Formate Chromatogram.

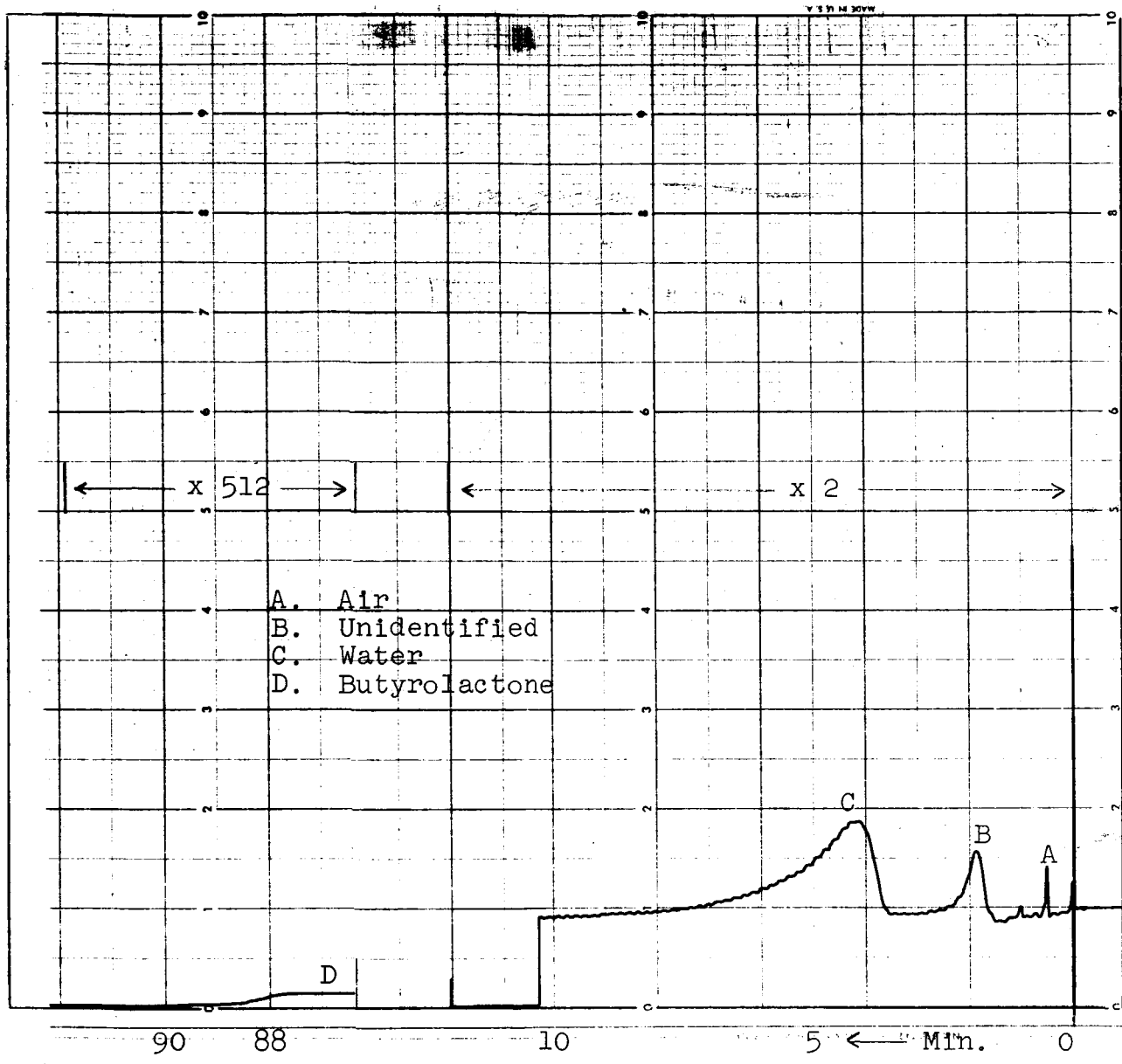


Figure 17. γ -Butyrolactone Chromatogram.

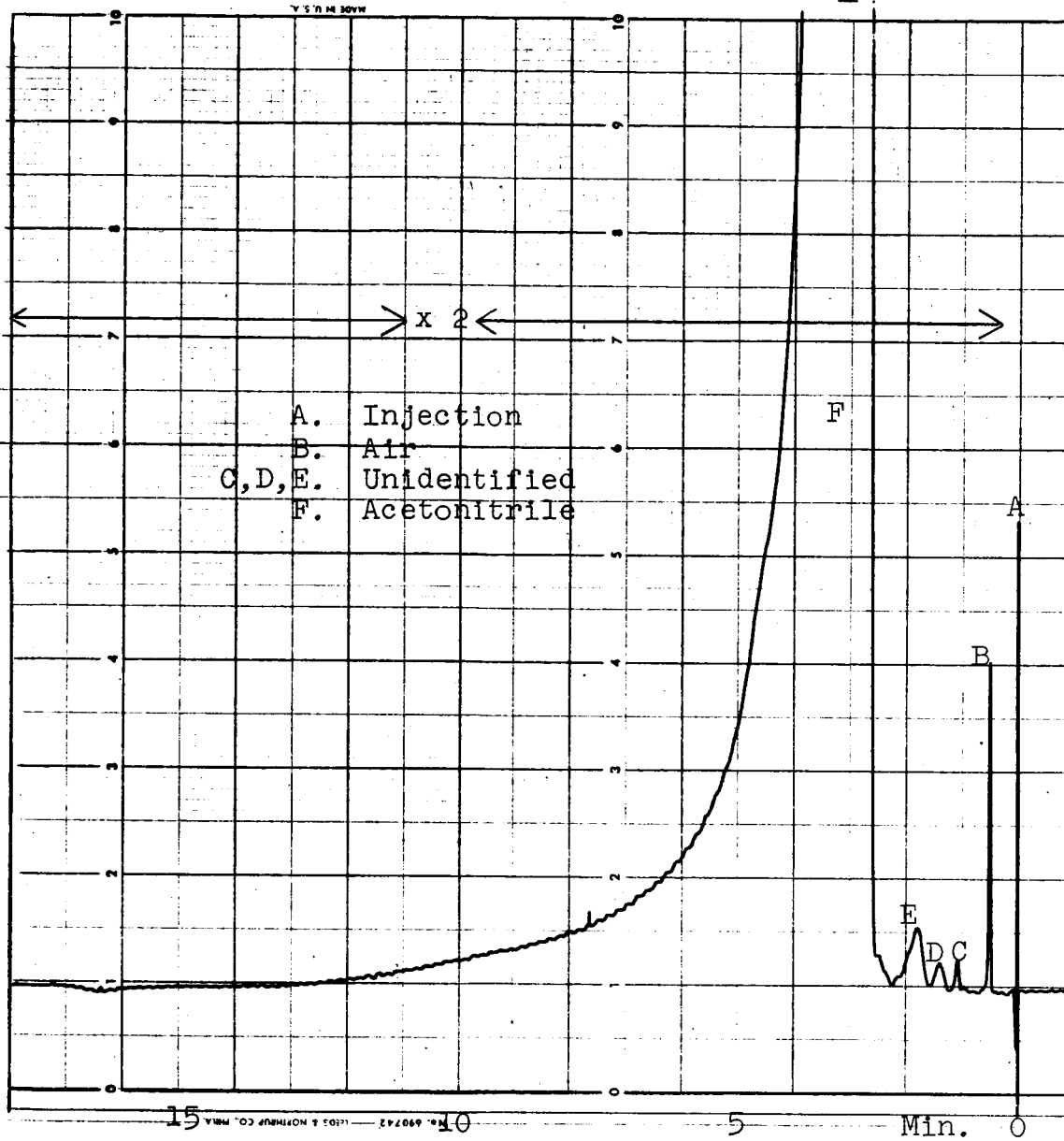


Figure 18. Acetonitrile Chromatogram

Table 9.

PRELIMINARY CALIBRATION DATA FOR VAPOR PHASE
CHROMATOGRAPHIC DETERMINATION OF WATER

<u>Peak Area,</u> <u>in.²</u>	<u>Water</u> <u>Concentration,</u> <u>%</u>	<u>in.², %</u>
0.398 ± 0.045	0.109	3.65
0.582 ± 0.026	0.129	4.51
2.043 ± 0.020	0.579	<u>3.52</u>
	Mean	3.86 ± 0.40

Table 10.

SOLVENT RETENTION TIMES

<u>Solvent</u>	<u>Retention Time,</u> <u>Min.</u>
Methyl Formate	0.9
Ethyl Formate	1.2
Methanol	1.4
Acetonitrile	3.0
Water	3.9
Dimethylformamide	17.2
γ-Butyrolactone	87.0

V. REFERENCES

1. C. K. Morehouse and R. Glicksman, J. Electrochem. Soc., 104, No. 8, 467 (1957).

Table A-1

STATIC CELL DISCHARGE DATA FOR TRI-N-CHLOROTRIAZINETRIONE TAPE CATHODES

Cathode Composition: Trichlorotriazinetrione (Monsanto AC1-85[®])
 Acetylene black (Shawinigan)-unless specifically otherwise noted
 Polyvinyl formal binder (2.75 wt. %)
 1/8" dynel fiber (2.75 wt. %)

Tape Cell Area = 3 inches x 1 inch

Anode = primary magnesium foil (Dow)

Separator = 4 Mil Dynel (unless specifically noted)

Run No.	Wt. % Active Material	Theoretical Capacity Amp-Min/in. ²	Electrolyte	Current Density Amp/in. ²	Cathode Efficiency %	Operating Voltage, V	Remarks
78602-6	50	8.9	2MAlCl ₃ ·1MHCL	0.1	37	2.15	
78602-7	50	6.4	"	0.2	35	1.99	
78602-8	50	10.8	"	0.3	18	1.90	
78604-4	60	9.5	"	0.08	50	2.15	Steady cathode v drop
78618-4	54	3.0	2MMgCl ₂	0.5	34	1.85	
78618-4	54	2.9	2MAlCl ₃	0.5	35	2.10	
78618-3	54	3.2	2MMg(ClO ₄) ₂	0.5	24	1.75	Steady cathode v drop
78618-11	54	4.8	"	0.5	39	1.70	"
78620-7	54	3.1	"	0.5	37	1.85	"
78620-9	54	3.0	"	0.1	39	2.00	
78624-1	54	2.6	2MMgCl ₂	0.5	28	1.70	20% A-625 " Graphite
78624-2	54	3.1	2MMg(ClO ₄) ₂	0.5	26	1.72	"
78624-3	54	1.9	2MAlCl ₃	0.1	33	2.08	"
78624-4	54	3.7	2MMgCl ₂	0.33	18	1.72	"
78623-8	54	3.0	2MMg(ClO ₄) ₂	0.33	55	1.95	Steady cathode emf drop
78623-9	54	2.9	2MMgCl ₂	0.33	53	1.90	"
78623-10	54	4.0	2MMg(ClO ₄) ₂	0.33	60	1.95	"
78623-11	54	4.0	2MAlCl ₃	0.33	48	1.80	"
78623-12	54	3.0	2MMgCl ₂	0.33	50	2.45	Flat discharge curve
78624-5	54	3.3	2MMgCl ₂	0.33	47	1.80	Tape pressed at 1000 psi
78624-6	54	4.1	2MMg(ClO ₄) ₂	0.33	32	1.90	"
78627-3	60	3.7	2MMgCl ₂	0.33	40	1.75	
78627-1	60	2.5	2MMg(ClO ₄) ₂	0.33	34	1.70	
78627-2	60	4.3	2MAlCl ₃	0.33	34	2.50	Flat discharge curve
78627-4	60	3.7	2MMgCl ₂	0.33	30	1.80	
78627-5	60	4.3	2MMg(ClO ₄) ₂	0.33	38	1.70	
78627-12	60	4.3	2MAlCl ₃	0.33	53	2.45	Flat discharge curve
78629-1	60	3.9	2MMgCl ₂	0.33	50	1.80	
78629-2	70	4.3	2MMgCl ₂	0.33	46	1.86	Tape pressed at 1000 psi

Table A-1 (Cont'd)

Run No.	Wt. % Active Material	Theoretical Capacity Amp-Min./in. ²	Electrolyte	Current Density Amp./in. ²	Cathode Efficiency %	Operating Voltage, V	O.C.V. vs. Mg
78629-3	70	5.3	2MMg(ClO ₄) ₂	0.33	34	1.80	2.62
78629-5	70	4.2	2MAlCl ₃	0.33	40	2.40	2.90
78629-9	70	4.5	2MMgCl ₂	0.33	35	1.85	2.62
78631-1	80	4.2	2MAlCl ₃	0.5	31	1.52	2.89
78631-3	80	4.5	2MMg(ClO ₄) ₂	0.5	11	1.70	2.68
78631-6	80	5.3	2MAlCl ₃	0.33	30	2.00	2.89
78631-7	80	4.7	2MAlCl ₃	0.175	35	1.90	2.90
78631-10	80	5.3	2MMg(ClO ₄) ₂	0.175	32	2.10	2.60
78634-7	70	4.5	2MMgCl ₂	0.167	51	1.86	2.63
78634-8	70	4.7	2MMg(ClO ₄) ₂	0.167	35	1.85	2.60
78634-9	70	5.4	2MAlCl ₃	0.167	39	2.90	2.90
78633-12	60	4.0	2MMgCl ₂	0.167	46	1.80	2.62
78641-5	75	4.8	2MAlCl ₃ ·0.5MHCl	0.40	21	2.30	2.92
78651-5	70	3.4	"	0.33	57	2.03	2.99
78651-11	70	3.8	"	0.33	65	2.05	2.93
78651-7	70	5.0	"	0.33	61	2.15	2.90
78651-9	70	5.3	"	0.33	59	2.15	2.92
78656-6	70	2.9	"	0.33	65	2.10	2.92
78656-8	70	4.2	"	0.33	62	2.00	2.91
78656-9	70	4.5	"	0.33	56	2.10	2.91
78656-10	70	3.1	"	0.33	39	1.80	2.93
78656-14	70	4.5	"	0.33	36	1.80	2.97
78659-3	60	4.5	"	0.33	80	2.30	2.95
78659-4	60	5.3	"	0.33	79	2.24	2.95
78659-5	60	5.1	"	0.33	79	2.20	2.95
78661-3	70	4.0	"	0.33	58	2.20	2.96
78661-2	70	3.6	"	0.33	54	2.05	2.95
78661-5	70	3.3	"	0.33	57	2.05	2.95
78663-9	75	4.1	"	0.33	47	2.20	2.92
78663-10	60	3.7	"	0.33	69	2.25	2.97
78665-6	60	3.7	"	0.33	66	2.22	2.92
78665-7	60	3.7	"	0.50	66	2.18	2.92
78665-4	60	4.7	"	0.50	70	2.10	2.94
78665-5	60	4.2	"	0.50	59	2.00	2.92
78667-9	65	4.3	"	0.33	70	2.15	2.93
78667-2	65	4.6	"	0.33	73	2.10	2.92
78667-7	65	4.4	"	0.50	66	1.90	2.90
78667-9	65	4.7	"	0.50	67	2.00	2.92
78667-3	65	4.6	"	0.33	70	2.20	2.96
78667-5	65	5.3	"	0.50	73	2.10	2.93
78670-10	50	5.7	"	0.50	67	2.45	2.93
78670-5	50	2.4	"	0.20	67	2.18	2.95
78670-3	50	3.2	"	0.33	66	2.18	2.95

First vac. dried SAB

Tape stored 24 hrs. in air

" " " " " "

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Tested fresh

Tested after 24 hours

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Tested fresh

Tested after 24 hours

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Tested fresh

Tested after 72 hours

Tested fresh

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Tested after 24 hours

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Tested after 24 hours

Tested fresh

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Tested after 24 hours

Tested fresh

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Tested after 24 hours

Tested fresh

Table A-1 (Continued)

Run No.	Wt. % Active Material	Theoretical Capacity Amp-Min/in. ²	Electrolyte	Current Density Amp/in. ²	Cathode Efficiency %	Operating Voltage, V	O.C.V. vs. Mg	Remarks
78670-7	50	4.4	"	0.50	53	2.00	2.92	A.C. Bridge
78670-9	50	4.8	"	0.50	56	2.00	2.92	"
78670-4	50	3.3	"	0.50	65	2.10	2.95	"
78670-8	50	3.9	"	0.33	71	2.35	2.92	"
78673-8	65	3.9	"	0.17	72	2.65	2.91	"
78673-6	65	4.0	"	0.33	75	2.45	2.92	"
78673-10	65	5.8	"	0.50	80	2.45	2.92	"
78673-9	65	5.2	"	0.67	78	2.40	2.97	"
78673-7	65	4.5	"	0.84	75	2.20	2.92	"
78673-2	65	3.7	"	0.50	77	2.30	2.94	"
78673-3	65	4.8	"	0.67	77	2.25	2.92	"
78673-1	65	3.1	"	0.33	70	2.50	2.47	"
78677-1	70	3.2	"	0.5	79	2.40	2.98	"
78677-5	70	7.6	"	0.5	80	2.15	2.92	"
78677-9	70	4.5	"	0.67	79	2.30	2.92	"
78677-3	70	4.2	"	0.67	80	2.25	2.96	"
78677-2	70	3.5	"	0.33	79	1.90	2.93	"
78677-1	70	3.8	"	1.00	68	2.50	2.95	"
78677-4	70	3.7	"	0.84	79	2.20	2.94	"
78677-8	70	3.2	"	0.33	79	1.70	2.69	Steady cathode emf drop
78677-10	70	2.6	2MMgCl ₂	0.17	61	1.80	2.71	"
78678-6	75	7.0	2MAICl ₃ ·0.5MHCl	0.67	62	2.20	2.93	"
78678-1	75	4.5	"	0.50	69	2.30	2.91	"
78678-5	75	5.6	"	0.84	67	1.80	2.95	"
78678-10	75	6.5	"	1.00	54	2.40	2.93	"
78678-2	75	4.4	"	0.33	72	1.75	2.94	"
78678-3	75	5.3	2MMgCl ₂	0.50	25	1.75	2.71	Steady cathode emf drop
78678-4	75	4.7	2MMgCl ₂	0.33	44	1.80	2.70	"
78678-9	75	5.7	2MMgCl ₂	0.40	45	1.80	2.70	"
78683-7	65	4.6	2MMgCl ₂	0.40	28	1.80	2.72	"
78685-5	65	4.2	2MMg(ClO ₄) ₂	0.40	29	1.70	2.66	"
78685-10	65	4.4	2MAICl ₃ ·0.5MHCl	0.40	64	2.40	2.96	Steady cathode emf drop
78685-3	65	5.3	2MAICl ₃	0.40	72	2.40	2.95	"
78685-4	65	5.3	1MAICl ₃ ·1MMgCl ₂	0.40	87	2.20	2.91	"
78685-1	65	5.3	1MAICl ₃ ·1MMgCl ₂	0.50	82	2.15	2.93	"
78685-8	65	3.4	2MMg(ClO ₄) ₂	0.33	45	1.70	2.71	"
78685-2	65	5.7	1MAICl ₃ ·1MMg(ClO ₄) ₂	0.40	73	1.90	2.91	"
78688-6	65	5.2	1.3MMg(ClO ₄) ₂ ·0.7MAICl ₃	0.50	41	1.90	2.85	"
78688-2	65	3.9	1.3MMgCl ₂ ·0.7MAICl ₃	0.50	37	1.90	2.90	"
78688-5	65	5.7	2MAICl ₃	0.50	54	2.10	2.92	"
78688-4	65	6.0	2MAICl ₃	0.67	70	2.30	2.95	Steady cathode emf drop
78688-1	65	3.8	1.3MMg(ClO ₄) ₂ ·0.7MAICl ₃	0.67	56	2.00	2.87	"
78688-7	65	4.7	1.3MMgCl ₂ ·0.7MAICl ₃	0.67	77	2.00	2.92	"

Table A-1(Continued)

Run No.	Wt. % Active Material	Theoretical Capacity Amp-Min/in. ²	Electrolyte	Current Density ² Amp/in. ²	Cathode Efficiency %	Operating Voltage, V	O.C.V. vs. Mg	Remarks
78688-3	65	7.7	2MAlCl ₃ ·0.5MHCl	0.67	76	2.45	2.93	
78690-6	65	7.4	2MAlCl ₃	0.67	69	2.20	2.93	Steady cathode emf " drop
78690-5	65	7.5	1.5MMg(ClO ₄) ₂ ·0.7MAlCl ₃	0.67	50	2.00	2.90	"
78690-4	65	8.2	1.5MMgCl ₂ ·0.7MAlCl ₃	0.67	70	1.95	2.95	"
78690-3	65	10.0	2MAlCl ₃ ·0.5MHCl	0.67	67	2.35	2.95	"
78690-1	65	5.5	"	0.67	57	2.30	2.92	"
78690-8	65	9.1	2MAlCl ₃ ·0.2MHCl	0.67	43	2.30	2.91	"
78690-12	65	9.6	2MAlCl ₃ ·0.1MHCl	0.67	77	2.35	2.93	"
78690-7	65	6.6	2MAlCl ₃ ·0.5MHCl	0.50	54	2.40	2.92	"
78690-9	65	10.0	2MAlCl ₃ ·0.1MHCl	0.50	68	2.35	2.92	Stored five days in air
78690-10	65	9.2	2MAlCl ₃ ·0.25MHCl	0.50	84	2.35	2.92	"
78693-9	65	9.2	2MAlCl ₃ ·0.1MHCl	0.50	57	2.30	2.91	"
78693-10	65	9.2	2MAlCl ₃ "	0.50	69	2.35	2.95	"
78693-4	65	8.8	2MAlCl ₃ ·0.25MHCl	0.50	63	2.35	2.95	"
78693-8	65	8.0	2MAlCl ₃ "	0.50	63	2.30	2.91	"
78693-1	65	8.4	2MAlCl ₃ ·0.5MHCl	0.50	53	2.40	2.93	"
78693-12	65	8.0	2MAlCl ₃ "	0.50	47	2.40	2.94	"
78693-11	65	8.0	2MAlCl ₃ ·0.1MHCl	0.67	45	2.00	2.92	Stored three days in air
78694-6	70	9.1	2MAlCl ₃	0.50	58	2.20	2.92	"
78694-2	70	9.1	2MAlCl ₃	0.50	69	2.30	2.92	"
78694-11	70	9.7	2MAlCl ₃ ·0.2MHCl	0.50	61	2.25	2.92	"
78694-12	70	11.1	2MAlCl ₃ "	0.50	62	2.20	2.92	"
78694-8	70	8.3	2MAlCl ₃ ·0.25MHCl	0.50	59	2.25	2.95	"
78694-7	70	8.7	M	0.50	60	2.30	2.91	"
78694-2	70	6.4	2MAlCl ₃ ·0.1MHCl	0.50	66	2.20	2.94	"
78694-1	70	9.1	2MAlCl ₃ "	0.50	69	2.25	2.92	"
78694-5	70	9.2	2MAlCl ₃ ·0.5MHCl	0.50	65	2.30	2.92	"
78694-10	70	11.0	2MAlCl ₃ "	0.67	49	2.30	2.92	"
78694-3	70	11.2	2MAlCl ₃ ·0.25MHCl	0.67	49	2.15	2.92	"
78694-4	70	10.0	2MAlCl ₃ ·0.11MHCl	0.67	55	2.15	2.92	"
78694-4	70	10.0	2MAlCl ₃ ·0.11MHCl	0.67	57	2.15	2.92	"

Table A-2.

ANALYTICAL METHOD FOR THE DETERMINATION OF AVAILABLE CHLORINE

The determination of available chlorine in formulated products containing chlorinated cyanuric acid is performed by means of an iodometric titration with sodium thiosulfate to a starch end-point.

The method given below is recommended.

1. Reagents and Equipment

0.1N standard sodium thiosulfate solution

3% potassium iodide solution

1:1 sulfuric acid

Starch indicator solution

50-ml burette

500-ml Erlenmeyer flask

250-ml graduate cylinder

25-ml graduate cylinder

Magnetic stirrer

Teflon-covered stirring bar

Distilled water wash-bottle

Glassine weighing paper

Analytical balance

2. Procedure

Using the analytical balance, weigh onto a glassine weighing paper the calculated amount of sample for an approximate 40-ml sodium thiosulfate titration. Transfer the sample to a 500-ml Erlenmeyer flask containing 250 ml of 3% potassium iodide solution. Rinse the weighing paper and the walls of the flask with distilled water. Add a stirring bar covered with DuPont's "Teflon" to the flask and place it on a magnetic stirrer. Continue to stir until solution has been effected (usually 3-5 minutes). Add approximately 50 g of crushed ice, and then add 25 ml of 1:1 sulfuric acid. (Caution: when the formulation contains a carbonate, the acid should be added with extra care in order to avoid an excessive rate of CO₂ evolution.) Titrate with 0.1N standard sodium thiosulfate to a light yellow color while continuing to stir the contents of the flask. Add starch indicator solution to give a deep purple color, and continue to titrate slowly until the color just disappears. Record the volume of sodium thiosulfate solution used, and calculate the available chlorine level according to the following formula:

$$\% \text{ Available Chlorine} = \frac{\text{ml thiosulfate} \times N \text{ thiosulfate} \times 0.03546 \times 100}{\text{wt sample ACL-85}^{\circ}}$$