ANL/OEPM-80-13

LH. 2689
ANL/OEPM-80-13

MASTER

236
6-1-81
RH740
①

**ANNUAL REPORT FOR 1980 ON
RESEARCH, DEVELOPMENT, AND DEMONSTRATION
OF NICKEL-ZINC BATTERIES FOR
ELECTRIC VEHICLE PROPULSION**

Contract No. 31-109-38-4248

by

Energy Research Corporation

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Operated for the U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) among the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona	The University of Kansas	The Ohio State University
Carnegie-Mellon University	Kansas State University	Ohio University
Case Western Reserve University	Loyola University of Chicago	The Pennsylvania State University
The University of Chicago	Marquette University	Purdue University
University of Cincinnati	The University of Michigan	Saint Louis University
Illinois Institute of Technology	Michigan State University	Southern Illinois University
University of Illinois	University of Minnesota	The University of Texas at Austin
Indiana University	University of Missouri	Washington University
The University of Iowa	Northwestern University	Wayne State University
Iowa State University	University of Notre Dame	The University of Wisconsin-Madison

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government or any agency thereof, nor any of their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A12
Microfiche copy: A01

Distribution Category:
Energy Storage—Electrochemical--
Near-Term Batteries (UC-94ca)

ANL/OEPM-80-13

Annual Report for 1980 on
RESEARCH, DEVELOPMENT, AND DEMONSTRATION
OF NICKEL-ZINC BATTERIES FOR
ELECTRIC VEHICLE PROPULSION

Prepared for
The Office for Electrochemical Project Management
Argonne National Laboratory
Under Contract No. 31-109-38-4248

by
Energy Research Corporation
Danbury, Connecticut

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

March 1981

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ENERGY RESEARCH CORPORATION

THIRD ANNUAL NON-PROPRIETARY REPORT 1980

CONTRACT NO. 31-109-38-4248

Prepared For:

ARGONNE NATIONAL LABORATORY

9700 South Cass Avenue

Argonne, Illinois 60439

Attention: Dr. N.P. Yao

Submitted By:

Energy Research Corporation

Stanley Januszkiewicz

Hari Vaidyanathan

Mark Dodin

Tony Leo

Approved By:

Allen Charkey

Program Manager

Date:

January 30, 1981

TABLE OF CONTENTSPage No.

SECTION I	
EXECUTIVE SUMMARY -----	1
SECTION II	
NICKEL ELECTRODE DEVELOPMENT FOR NICKEL-ZINC CELLS-(TASK I) ----	5
1.0 <u>INTRODUCTION</u> -----	6
2.0 <u>TECHNICAL DISCUSSION</u> -----	8
2.1 ERC 1.5% COBALT-NICKEL HYDRATE -----	8
2.2 GRAPHITE ADDITION DURING HYDRATE PREPARATION -----	12
2.3 STANDARD VS CELLOPHANE WRAP -----	16
2.4 SODIUM HYDROXIDE ADDITION -----	18
2.5 COMMERCIAL NI HYDRATE I: EFFECT OF PARTICLE SIZE -----	20
2.6 COMMERCIAL NI HYDRATE I: PREFORMED PLATES -----	20
2.7 COMMERCIAL NI HYDRATE I (MAY 1980) -----	22
2.8 COMMERCIAL NICKEL HYDRATES II -----	24
2.9 COMMERCIAL NICKEL HYDRATES III -----	26
2.10 COMMERCIAL NICKEL HYDRATE IV -----	28
2.11 NICKEL-ZINC VS NICKEL-CADMIUM PERFORMANCE -----	28
2.12 TEFLONIZED GRAPHITE -----	31
2.13 ERC NICKEL HYDRATE VARIATIONS -----	32
2.14 ELECTROLYTE ADDITIVES -----	34
3.0 <u>CONCLUSIONS</u> -----	37
4.0 <u>FUTURE WORK</u> -----	39

TABLE OF CONTENTSPage No.

SECTION III

ZINC ELECTRODE DEVELOPMENT FOR NI-ZN CELLS - (TASK II)----- 40

1.0 INTRODUCTION ----- 412.0 TECHNICAL DISCUSSION ----- 42

2.1 BASIC ELECTROCHEMICAL STUDY ----- 42

2.1.1 Experimental ----- 422.1.2 Dependence of Kinetics on OH⁻ Concentration ----- 432.1.3 Electrode Polarization, Tafel Slope and Exchange Current- 532.1.4 Physical Significance of the Polarization Results ----- 563.0 CONCLUSIONS ----- 57

SECTION IV

SEPARATOR DEVELOPMENT FOR NICKEL-ZINC CELLS - (TASK III) ----- 73

1.0 INTRODUCTION ----- 742.0 TECHNICAL DISCUSSION ----- 762.1 IMPROVED COMPOSITION AND PRODUCTION TECHNOLOGY FOR CROSS-
LINKED PVA SEPARATOR FILMS ----- 762.1.1 Various Compositions for Improved Crosslinked PVA
Separator ----- 772.1.2 Zinc Penetration Test ----- 862.1.3 The Permeability Mechanism Through PVA Films ----- 912.1.4 Failure Mode Observation of Cells Containing PVA Based
Separator Films ----- 100

2.2 IMPROVED COMPOSITION FOR POLYMER-BLEND SEPARATOR FILMS -- 101

2.2.1 Evaluation of Polymer-Blend as a Separator Material ----- 1022.2.2 Testing of Cells Containing One Layer of Polymer-Blend
Separator Films ----- 110

2.3 DESIGN AND TEST RESULTS OF THE IMPROVED SEPARATOR SYSTEM- 119

TABLE OF CONTENTS

	<u>Page No.</u>
2.3.1 <u>Small Cell Testing of Various Separator Systems</u> -----	119
2.3.2 <u>Testing Different Separator Systems in Full Size, Single Electrode Cells</u> -----	138
3.0 <u>CONCLUSIONS</u> -----	152
3.1 PVA-BASED SEPARATOR MATERIALS -----	152
3.2 POLYMER-BLEND SEPARATOR MATERIALS -----	155
3.3 DESIGN AND TEST RESULTS OF THE IMPROVED SEPARATOR SYSTEM-----	155
4.0 <u>FUTURE WORK</u> -----	156
SECTION V	
DEVELOPMENT OF SEALED NICKEL-ZINC CELLS - (TASK IV) -----	158
1.0 <u>INTRODUCTION</u> -----	159
2.0 <u>TECHNICAL DISCUSSION</u> -----	160
2.1 EXPERIMENTAL SEPARATOR AND ABSORBER DESIGNS -----	161
2.2 CELLS WITH Ag-HgO RECOMBINATION ELECTRODE PARTITIONS -----	166
3.0 <u>CONCLUSIONS AND FUTURE WORK</u> -----	182
SECTION VI	
SYSTEM ENGINEERING (TASK V) -----	183
1.0 <u>INTRODUCTION</u> -----	184
2.0 <u>TECHNICAL DISCUSSION</u> -----	185
2.1 TESTING OF 20 AMPERE-HOUR CELLS -----	185
2.1.1 <u>Zinc Electrode Tests</u> -----	185
2.1.2 <u>Investigation of Alternate Electrolytes</u> -----	188
2.2 FULL-SIZE, SINGLE ELECTRODE TESTS -----	190
2.2.1 <u>Evaluation of Zinc Electrode Designs</u> -----	192

TABLE OF CONTENTS

Page No.

2.2.2	<u>Evaluation of Separator System Design</u>	-----	197
2.3	<u>250 AH CELL TESTS</u>	-----	202
2.3.1	<u>Cell Test with PVA Separator and Bi₂O₃ Zinc Electrode Additive</u>	-----	202
2.3.2	<u>Cell Tests with Advanced Separator and Electrode Designs</u>	-----	206
2.3.3	<u>Simulated Vehicle Use Test</u>	-----	211
3.0	<u>CONCLUSIONS</u>	-----	220
4.0	<u>FUTURE WORK</u>	-----	222

LIST OF FIGURES

<u>Figure No.</u>	<u>Page No.</u>
SECTION II	
NICKEL ELECTRODE DEVELOPMENT FOR NICKEL-ZINC CELLS - (TASK I)	
I.1 Effect of Cycling 250 Ah Single Plate Ni-Zn Cell -----	29
SECTION III	
ZINC ELECTRODE DEVELOPMENT FOR NI-ZN CELLS - (TASK II)	
II.1 Electrochemical Cell for Cycling and Polarization Experiments -----	44
II.2 The Dependence of Zinc Potential on OH^- Concentration at Open Circuit -----	45
II.3 Dependence of Reaction Rate on pH at a Constant Overvoltage of 15 mV from E_{OCV} Before Cycling -----	47
II.4 Dependence of Reaction Rate on pH at a Constant Overvoltage of 15 mV from E_{OCV} After Cycling -----	49
II.5 Dependence of Reaction Rate on pH at a Constant Overvoltage of 20 mV from E_{OCV} Before Cycling -----	50
II.6 Dependence of Reaction Rate on pH at a Constant Overvoltage of 20 mV from E_{OCV} After Cycling -----	51
SECTION IV	
SEPARATOR DEVELOPMENT FOR NICKEL-ZINC CELLS - (TASK III)	
III.1 Zinc Penetration Test Cell -----	90
III.2 Effect of Exposure Time in KOH on the Electrical Resistance of PVA Films -----	96
III.3 Electrical Resistance vs OH^- Diffusion for (2N) Polymer-Blend -----	109
III.4 Pore Size Distribution of Polymer-Blend Film -----	111
III.5 Dependence of Cell Capacity and End-Of-Discharge Voltage on Number of Cycles -----	118
III.6 Dependence of Cell Capacity and End-Of-Discharge Voltage on Number of Cycles, Cells 6 and 8 -----	133

LIST OF FIGURES

<u>Figure No.</u>	<u>Page No.</u>
III.7 Dependence of Cell Capacity and End-Of-Discharge Voltage on Number of Cycles, Cells 9 and 10 -----	134
III.8 Dependence of Cell Capacity and End-Of-Discharge Voltage on Number of Cycles, Cell 9 -----	135
III.9 Dependence of Cell Capacity on Number of Cycles -----	142
III.10 Dependence of Cell Capacity on Number of Cycles -----	143
III.11 Dependence of Cell Capacity on Number of Cycles -----	150
III.12 Dependence of Cell Capacity on Number of Cycles -----	151
III.13 Dependence of Cell Capacity on Number of Cycles -----	153
III.14 Dependence of Cell Capacity on Number of Cycles -----	154

SECTION V

DEVELOPMENT OF SEALED NICKEL-ZINC CELLS - (TASK IV)

IV.1 Pressure and Voltage on a 4A Charge for Cells S-1-1, S-1-2 and S-2 -----	164
IV.2 Ni-Zn Cell with Recombination Electrode Partition -----	167
IV.3 Pressure and Recombination Current on 4A Charge for Cell 2R-5 -----	168
IV.4 Charge Efficiency on Charge for Cell 2R-5 (Based on O ₂ Recombination Current) -----	169
IV.5 Open Circuit Oxygen Recombination for Cell 2R-5 -----	171
IV.6 Relationship Between Recombination Rate and Oxygen Pressure During Open Circuit Recombination, Cell 2R-5 -	172
IV.7 Performance of Cell 2R7 on Cycle #7 -----	178
IV.8 Performance of Cell 2R8 on Cycle #7 -----	179
IV.9 Cell 2R7 Recombination Rate vs O ₂ Pressure -----	180

LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
SECTION VI		
SYSTEM ENGINEERING - (TASK V)		
V.1	Cycle Performance of Cells with Bi_2O_3 Additive -----	187
V.2	Cycling Heat-Treated ZnO -----	189
V.3	Standard Ni-Zn Design in Different Test Cell Constructions all on Constant Current Cycle -----	193
V.4	Cycle Data for Cell SE-12 -----	198
V.5	Cycle Data for Cells with PbO/CdO Additive -----	199
V.6	Cycle Test Results of Cells with PVA Separator and Bi_2O_3 Zinc Additive -----	204
V.7	Ni-Zn Cycle Test with Various Charge Procedures PVA Separator and Bi_2O_3 Additive -----	207
V.8	Cycle Performance of Cells with Pellon and Asbestos Absorber -----	208
V.9	250 Ah Cycle Data -----	210
V.10	250 Ah Cell Cycle Test Data -----	212
V.11	Cell 151-1 Voltage and Temperature Data for Cycle 59 --	213
V.12	Cell 157 Long Cell Voltage and Temperature Data for Cycle 55 -----	214
V.13	Four Current Steps to Provide a Simplified Approximation to the J227AD/DOE-GE-Chrysler Vehicle (with regenerative braking) -----	217
V.14	Weekly Variable Depth Test Sequence -----	218
V.15	Simulated EV Use Testing of Cell 162 -----	219
V.16	Variable Depth Life Test -----	221

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
SECTION II		
NICKEL ELECTRODE DEVELOPMENT FOR NICKEL-ZINC CELLS - (TASK I)		
I.1	1.5% Cobalt-Nickel Hydrate 20 Ah Ni-Cd Cells -----	9
I.2	1.5% Cobalt-Nickel Hydrate Treated Graphites, 20 Ah Ni-Cd Cells -----	11
I.3	5% Cobalt-Nickel Hydrate with Treated Graphite -----	13
I.4	Effect of Added Graphite on 5% Cobalt-Nickel Hydrate --	15
I.5	Standard vs Cellophane Wrap, ERC 10% Co-Ni(OH) ₂ ; 20 Ah Ni-Cd Cells -----	17
I.6	5% Sodium Hydroxide, 5% Cobalt-Nickel Hydrate, 20 Ah Ni-Cd Cells -----	19
I.7	Commercial Hydrate I Coarse and Fine Hydrate, 20 Ah Ni-Cd Cells -----	21
I.8	Commercial Ni Hydrate I Preformed Plates, 20 Ah Ni-Cd Cells -----	23
I.9	Commercial Ni Hydrate I, May 1980, 20 Ah Ni-Cd Cells --	23
I.10	Commercial Nickel Hydrates II, 100% Ni(OH) ₂ ; 20 Ah Ni-Cd Cells -----	25
I.11	Other Nickel Hydrates, 20 Ah Ni-Cd Cells -----	27
I.12	Nickel-Zinc vs Nickel-Cadmium, ERC 1.5% Cobalt-Nickel, 250 Ah Single Plate Cell -----	30
I.13	ERC 1.5% Cobalt-Nickel Variations, 250 Ah Single Plate Ni-Zn Cells -----	35
I.14	Electrolyte Additives, Commercial Ni Hydrate I, 250 Ah Single Plate Ni-Zn Cells -----	35
SECTION III		
ZINC ELECTRODE DEVELOPMENT FOR NI-ZN CELLS - (TASK II)		
A.1	Electrode P-IIB -----	60
A.2	Electrode P-IIC -----	61

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
A.3	Electrode P-IID -----	62
A.4	Electrode P-IIE -----	63
A.5	Electrode P-IIIA -----	64
A.6	Electrode P-IVA -----	65
A.7	Electrode P-VA -----	66
A.8	Comparison of Polarization Data Before Cycling -----	67
A.9	Comparison of Polarization Data After Initial Cycling-----	68
A.10	Comparison of Polarization Data After 32 Cycles -----	69
A.11	Comparison of Polarization Data After 43 Cycles -----	70
A.12	Comparison of Polarization Data After 57 Cycles -----	71
A.13	Comparison of Polarization Data After 69 Cycles -----	72

SECTION IV

SEPARATOR DEVELOPMENT FOR NICKEL-ZINC CELLS - (TASK III)

III.1	Characteristics of Various PVA Films -----	78
III.2	Testing of Various PVA Films -----	79
III.3	Tensile Strength and Deflection of Various PVA Films -	80
III.4	Test Results for Small Cells -----	82&83
III.5	Electrical Resistance of PVA-Based Films -----	84
III.6	Tensile Hanging Test for PVA-Based Films -----	85
III.7	Electrical Resistance of PVA Films Crosslinked with Glutaraldehyde and P-Phenylenediamine -----	87
III.8	Tensile Hanging Test for PVA Films Crosslinked with Glutaraldehyde and P-Phenylenediamine -----	87
III.9	Time of Zinc Penetration for PVA-Based Separator Films -----	89
III.10	Concentration of Residual Solvent and Electrical Resistance of PVA Films -----	93

LIST OF TABLES

<u>Table No.</u>	<u>Page No.</u>
III.11 Variation in Electrical Resistance of PVA Films Containing Different Quantities of Residual Solvent ---	95
III.12 Constants of Equation (3) for PVA-Based Systems -----	98
III.13 Electrical Resistance of Nylon-Based Films During Extended Exposure Time in KOH -----	103
III.14 Tensile Strength of Polymer-Blend Films -----	104
III.15 Comparison of Zinc Penetration Time for Polymer-Blend Separator Films -----	105
III.16 Electrolyte Diffusion Rate Measurements -----	107
III.17 Results of Testing Different Polymer-Blend Films -----	108
III.18 Cumulative Pore Size Distribution of Polymer-Blend Film -----	112
III.19 Quantity of Residual Solvent in Polymer-Blend Films ---	113
III.20 Influence of Separator Design on the Zinc Electrode and on Cycle Life of the Cell -----	115
III.21 Comparison of K-307 and Polymer-Blend Separators -----	117
III.22 Time of Zinc Penetration for Improved Separator System-	121
III.23 Effect of Separator Configuration on Cycle Life and Failure Mode -----	122
III.24 Test Results for Cells with Various Separator Systems -	124&125
III.25 Zn Penetration Time for ERC-Developed and Commercially Available Separator Systems -----	128
III.26 Effect of Other Separator Configurations on Cycle Life and Failure Mode of the Cells -----	130&131
III.27 Cycle Life of the Cells Containing Immobilizers for Liquid Layer in Separator System -----	137
III.28 Cycle Life of Full Size Single Electrode Cells -----	140
III.29 Cycle Life of the Full Size Cells Containing Liquid Layer in the Separator System -----	144&145

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
III.30	Test Results of the Full Size Cells Containing Different Separator Systems -----	147
SECTION V		
DEVELOPMENT OF SEALED NICKEL-ZINC CELLS - (TASK IV)		
IV.1	Cycle Test Results of Cells with Coated Celgard Film -----	163
IV.2	Performance Data for Sealed Cells -----	163
IV.3	Formation Data for Cells with Recombination Electrodes-	175
IV.4	Cycle Performance of Sealed Cells with Recombination Electrodes -----	177
SECTION VI		
SYSTEM ENGINEERING - (TASK V)		
V.1	Evaluation of Zinc Electrode Additives in 20 Ah Ni-Zn Cells -----	186
V.2	Alternate Electrolyte Mixes in 20 Ah Ni-Zn Cells -----	191
V.3	Cycling of Cells with PVA Separator and Zinc Additive Variations -----	194
V.4	Cycle Test Data for Cells with Celgard K-306 Separator and Zinc Additive Variations -----	196
V.5	Cycle Data for Cells with Bi ₂ O ₃ Zinc Additive and Various Separator Systems -----	201
V.6	Cycle Performance of Cells with ERC and Commercial Ni(OH) ₂ Positive Active Material -----	205
V.7	Annual Electric Vehicle Trip Distribution for 75th Percentile Operator -----	216

SECTION I
EXECUTIVE SUMMARY

ENERGY RESEARCH CORPORATION

- NICKEL ELECTRODE - Nickel electrodes containing active material prepared by the ERC process with 1.5% Co(OH)_2 have yielded over 500 cycles in 100% DOD testing in 20 Ah size nickel-cadmium cells. In cycling Ni-Zn cells, zinc compounds in the positive plate considerably reduced the cycle life. Commercial sources for Ni(OH)_2 are being pursued.
- ZINC ELECTRODE - The major function of various additives to the zinc electrode have been identified and have resulted in improved cycle life, reduced shape change and dendritic shorting. A combination of additives is now used in the zinc electrode which improves the mechanical strength with regard to resistance to the swelling of the positive electrode, improves water and electrolyte retention, reduces Zn solubility, and reduces dendritic forms of zinc. Electrodes prepared with these additives exhibit lower anodic and cathodic polarization and have shown cycle lives in excess of 200 at 100% DOD in 20 Ah size cells. Results obtained from polarization data of single electrodes are being used to formulate a new theory for zinc shape change. Simply stated, the lower the anodic shift of the open circuit voltage and overvoltage during polarization the lower the degree of shape change.
- SEPARATOR - The use of cross-linked PVA separator increases the failure of cells by shape change and decreases the incidence of zinc shorting. The use of ERC type composite separators results in a substantial reduction in shape change but poor zinc dendrite stopping ability. Reproducible

results were obtained in the range of 300 to 400 cycles in 3 Ah size cells.

Multi-component separator systems of dissimilar materials yield longer cycle life compared to simple multi-layer systems comprised of similar materials.

- SEALED CELLS - The potential benefits of sealed cells construction which include zero maintenance and reduced shorting have not been realized in Ni-Zn cells. The predominant failure mechanism in cells is redistribution of electrolyte which results in drying out of the electrodes during cycling. This phenomenon is accelerated by the limited electrolyte quantity required by the sealed cell configuration. The longest lived cells to date have only yielded 30 cycles. Due to budgetary constraints efforts in this area will be discontinued in FY 1981.
- SYSTEM ENGINEERING - A test regime has been established for 250 Ah cells which simulates a pattern of vehicle use based on trip distributions of 100 miles and under. The initial data obtained from cells which gave only 30 cycles on constant current 80% DOD cycling showed that almost 13,000 miles could be obtained before the equivalent range dropped to 60 miles. Improved 250 Ah cells with 25 wh/lb energy density have been cycled at the C/3 rate to 80% DOD yielding 150 cycles, and are presently being tested on the simulated vehicle regime. Large size single positive electrode tests have yielded over 250 100% DOD cycles at the C/2 rate with improved designs.

ENERGY RESEARCH CORPORATION

These results have been achieved without reconditioning and with periodic water addition the only maintenance procedure employed.

SECTION II
NICKEL ELECTRODE DEVELOPMENT
FOR NICKEL-ZINC CELLS - (TASK I)

1.0 INTRODUCTION

During the past 12 months, work has been in progress to optimize nickel hydrate preparation and the structure of the roll bonded positive electrode. The preparation of nickel hydrate has been directed at using the least amount of cobalt and reducing the number of process steps. The technical investigation has centered on:

- Non-cobalt additives
- Coprecipitated cobalt-nickel hydrate
- Addition of cobalt to nickel hydrate
- Addition of graphite during hydrate preparation
- Treatment of graphite and other graphite sources
- Hydrate preparation using NaOH
- Commercial sources of nickel hydrate

The nickel hydrates were made into positive electrodes using the plastic bonded electrode structure. These electrodes were evaluated in 20 Ah size nickel-cadmium cells to determine voltage characteristics and active material utilization. Following initial screening, the cells were life cycle tested using a two-hour 100% depth of discharge and a six-hour 110% charge input to determine capacity maintenance for various positive electrode types.

Tests conducted using 20 Ah nickel-cadmium cells showed that it was possible to make a hydrate with 1.5% cobalt which met the objectives of this program. The emphasis was changed to reproduce these same results in the nickel-zinc system where the solubility of zinc and dendritic growth influence the behavior of the nickel electrode.

The test vehicle used was the 250 Ah size, single plate nickel-zinc cell consisting of one positive and two negative plates with a nominal capacity of 20 Ah. Initially, commercial PVA was used as the membrane barrier; later, based upon the experience of others, the separator was changed to Celgard K-306, a porous polypropylene film coated with cellulose acetate.

The cycling tests were performed using two different cyclers, one which discharged to 1.20V and the other to 0.80V. In the latter case, the capacity to 1.20V was recorded on the monitored cycles.

The initial tests were directed at determining the assembly or test conditions required to obtain full positive plate capacity in the nickel-zinc cell without positive formation. This approach was only partially successful so it was augmented by hydrate preparation adjustments to improve the electrode structure and electrolyte additions to decrease the effect of soluble zinc products on the positive plate.

2.0 TECHNICAL DISCUSSION

2.1 ERC 1.5% COBALT-NICKEL HYDRATE

At ERC, the preparation of nickel hydrate has been directed at the use of the least amount of cobalt and the fewest process steps. Commercial I hydrate containing 1.5% cobalt has been used in much of our work because of its availability. For a direct comparison, 1.5% cobalt-nickel hydrates were prepared using the ERC WD procedure. These hydrates utilized surface concentrated cobalt as well as coprecipitates with 33 and 45% excess caustic. In conjunction with these hydrates several graphites were also tested using the 45% excess caustic hydrate. These include treated Asbury 7102, (our normal graphite). The aim of the treatment was to make the graphite both wettable and to pre-age it so that it might be more stable to additional oxidation. Two other commercial graphites which were tested using the same hydrate were Lonza KS-44 and Dixon Air Spun 200-08. The former has properties similar to Asbury 7102; the latter represents graphite pulverized with an air jet mill whose particle distribution has a narrower range. These particles have a 10 μ m average. Except as noted, 20 Ah nickel-cadmium test cells were made using standard procedures. Data for these cells including 503 standard charge-discharge cycles are given in Table I.1.

The formation capacities of these cells were lower than expected, yielding a utilization of 75^o of theoretical. The cyclic capacities however were very stable during the test. The addition of cobalt to neutral nickel hydrate to form

Table I.1

1.5% COBALT-NICKEL HYDRATE
20 Ah Ni-Cd CELLS

	External Cobalt	33% Excess	45% Excess	Treated Asbury 7102	Lonza KS-44	Dixon 200-08
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT					
Cycle 4 at 10 Amps	1.158-18.5/18.7	1.162-19.1/19.4	1.160-18.5/18.8	1.167-19.6/19.8	1.166-18.9/19.2	1.166-19.2/19.3
	AUTOMATIC CYCLING					
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT					
Cycle 1	1.148/0.926	1.152/1.093	1.151/1.060	1.157/1.091	1.158/1.066	1.154/1.086
Cycle 13	1.160/0.684	1.166/0.921	1.162/0.670	1.173/1.042	1.172/0.774	1.172/20.0
Cycle 28	1.157/0.674	1.162/0.886	1.161/0.692	1.174/1.100	1.172/0.774	1.174/0.831
Cycle 55	1.149/0.728	1.167/0.854	1.160/0.648	1.180/1.092	1.172/0.813	1.166/19.8
Cycle 76	1.140/19.2	1.166/0.604	1.146/19.2	1.184/1.070	1.170/0.648	1.152/19.0
Cycle 108	1.122/19.3	1.143/19.3	1.128/19.2	1.178/0.887	1.166/0.638	1.139/18.7
Cycle 159	1.108/19.5	1.137/19.5	1.114/19.2	1.170/0.778	1.164/0.605	1.117/18.2
Cycle 195	1.111/19.5	1.138/19.8	1.112/19.8	1.172/0.644	1.164/0.564	1.110/17.8
Cycle 252	1.104/19.8	1.136/0.598	1.108/19.7	1.170/0.637	1.160/0.560	1.102/17.7
Cycle 299	1.104/0.601	1.144/0.600	1.114/19.8	1.170/0.740	1.166/0.549	1.117/17.7
Cycle 356	1.116/0.548	1.148/0.560	1.108/19.7	1.168/0.755	1.164/0.591	1.117/17.3
Cycle 404	1.113/19.8	1.150/0.568	1.084/18.8	1.164/20.0	1.165/0.537	1.093/16.3
Cycle 431	1.110/19.5	1.148/0.557	1.080/18.7	1.161/19.3	1.158/19.8	
Cycle 452	1.098/19.5	1.144/0.548	1.048/18.2	1.158/19.0	1.152/19.5	
Cycle 473	1.101/19.3	1.136/0.510	1.046/17.2	1.153/19.0	1.130/19.3	
Cycle 503	1.102/19.3	1.152/0.463	1.077/17.5	1.148/18.7	1.121/17.8	

Note: All results are the average of two cells.

externally concentrated cobalt does not appear to be beneficial. The 33% excess caustic hydrate cells are better than those with 45% and would appear near optimum for the WD procedure. The treatment of graphite was beneficial with an improvement in the cell discharge voltage and capacity. The treatment of the graphite also decreased cell swelling by about 25% compared to cells with untreated graphite. The cells fabricated with Lonza graphite were better than those with Asbury graphite and comparable to those with the treated graphite. The cells with Dixon graphite were poorer than both other groups.

A test was made to compare treated Asbury 7102 and Lonza KS-44 graphites. Both of the treated graphites were used to make electrodes with the same 1.5% cobalt-nickel hydrate using 33% excess caustic. The 20 Ah nickel-cadmium test cells utilized standard procedures. The data for these cells including 454 charge-discharge cycles are given in Table I.2.

These new cells showed a utilization of 90% of theoretical in comparison to the previous 75%. It is believed that part of this better utilization is due to normal cell variation in addition to the treated graphite. The cyclic capacities of cells with either treated Asbury 7102 or Lonza KS-44 were stable and equivalent through 400 cycles, after which the cell capacities started to drop off due to the development of soft shorts.

Present data indicate that the use of treated graphite leads to a 5% improvement in cell capacity due to better utilization. In addition, the discharge curve has a sharper knee and the gradual increase in cell capacity between 1.00V and 0.70V with cycling at the two hour rate is delayed by 150 cycles.

Table I.2
1.5% COBALT-NICKEL HYDRATE
TREATED GRAPHITES
20 Ah Ni-Cd CELLS

	Treated Asbury 7102	Treated Lonza KS-44		Treated Asbury 7102 Plate Tabs
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (AH) TO 1.00/0.70 VOLT			
Cycle 3 at 10 AMPS	1.158-22.7/22.9	1.156-22.5/22.6		1.188-20.6/23.3
	AUTOMATIC CYCLING			
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY		TO 0.70 VOLT	
Cycle 1	1.162/1.114	1.160/1.110	Cycle 1	1.193/1.144
Cycle 13	1.173/1.072	1.170/1.068	Cycle 10	1.200/1.110
Cycle 25	1.168/0.990	1.164/0.998	Cycle 22	1.202/1.068
Cycle 55	1.182/1.042	1.176/1.040	Cycle 54	1.203/0.782
Cycle 67	1.180/1.043	1.174/1.036	Cycle 75	1.203/0.922
Cycle 85	1.180/1.028	1.172/1.025	Cycle 105	1.189/18.7
Cycle 103	1.178/1.042	1.170/1.036	Cycle 129	1.172/18.0
Cycle 151	1.182/1.008	1.178/1.008	Cycle 150	1.166/17.8
Cycle 202	1.184/0.976	1.179/0.978	Cycle 201	1.158/17.0
Cycle 256	1.181/0.890	1.180/0.904	Cycle 255	1.153/16.8
Cycle 298	1.180/0.870	1.182/0.911	Cycle 297	1.152/16.8
Cycle 349	1.181/0.755	1.183/0.792	Cycle 348	1.134/15.4
Cycle 379	1.176/19.3	1.178/19.8	Cycle 378	1.112/14.3
Cycle 403	1.172/17.8	1.174/18.8	Cycle 399	1.050/13.1
Cycle 424	1.160/15.8	1.172/18.2	Cycle 429	1.082/13.2
Cycle 454	1.146/14.3	1.156/15.8	Cycle 450	1.018/12.2

Note: All results are the average of two cells.

Another set of 20 Ah nickel-cadmium cells was made using the same 1.5% cobalt-nickel hydrate and treated Asbury graphite. In this case, nickel strip tabs were substituted for the usual wires so that the post connection could be spot welded for better electrical contact. The data for these cells including 450 standard charge-discharge cycles are also given in Table I.2.

The expected improvement in the discharge voltage was obtained as shown by the voltage at one hour. The initial hydrate utilization to 1.0V was 80% and to 0.70V it exceeded 90%.

2.2 GRAPHITE ADDITION DURING HYDRATE PREPARATION

Experiments were conducted to improve electrode performance by incorporating a portion of the conducting graphite during 5% cobalt-nickel hydrate preparation. If the graphite could be used more effectively, it would be possible to use less and thereby commit a larger portion of the electrode volume to the active hydrate. In the first experiments, either 10 or 15% treated Asbury graphite was added to the precipitation caustic based on the expected yield of graphite plus hydrate by the WD procedure. A portion of the 10% graphite hydrate was treated as a WDW hydrate to reduce the sulfate content from 1.06 to 0.60%. The addition of cobalt was also varied from a coprecipitate to addition in sequence after the nickel was precipitated as well as being added after the graphite nickel hydrate had been washed to neutral. Positive plates were made by adding additional treated graphite to yield a total of 25%. Otherwise, the finished 20 Ah cells were made according to standard procedures. The data for these cells as well as 302 standard charge-discharge cycles are given in Table I.3.

Table I.3

5% COBALT-NICKEL HYDRATE WITH TREATED GRAPHITE

PREPARATION VARIABLE	10% Graphite Coprecipitate	10% Graphite Rewashed	15% Graphite Coprecipitate	10% Graphite Co after Ni	10% Graphite Co when neutral
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT				
Cycle 4 at 10 Amps.	1.167-23.2/23.5	1.166-22.8/23.1	1.168-23.2/23.6	1.174-25.5/25.7	1.166-24.1/24.2
AUTOMATIC CYCLING					
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT				
Cycle 1	1.168/1.120	1.166/1.116	1.168/1.118	1.174/1.129	1.164/1.112
Cycle 16	1.176/1.082	1.173/1.078	1.170/1.075	1.176/1.072	1.166/1.060
Cycle 31	1.176/1.034	1.174/1.036	1.172/1.019	1.180/1.030	1.168/0.880
Cycle 58	1.188/1.044	1.176/1.034	1.181/1.026	1.186/1.036	1.170/0.802
Cycle 73	1.192/1.052	1.178/1.038	1.186/1.030	1.190/1.042	1.174/0.833
Cycle 97	1.185/1.041	1.171/1.034	1.184/1.021	1.187/1.030	1.166/19.8
Cycle 122	1.186/1.003	1.178/1.003	1.182/0.963	1.187/0.996	1.162/0.652
Cycle 143	1.187/0.988	1.176/1.000	1.184/0.966	1.187/0.982	1.164/0.644
Cycle 164	1.186/0.944	1.166/0.943	1.174/0.870	1.184/0.924	1.154/0.519
Cycle 179	1.186/0.946	1.173/0.968	1.180/0.916	1.188/0.940	1.164/0.684
Cycle 197	1.186/0.944	1.173/0.960	1.178/0.900	1.187/0.938	1.166/0.830
Cycle 227	1.188/0.927	1.174/0.932	1.178/0.854	1.190/0.912	1.169/0.748
Cycle 248	1.186/0.915	1.174/0.922	1.173/0.822	1.187/0.896	1.166/0.757
Cycle 269	1.182/0.878	1.166/0.879	1.163/19.3	1.184/0.841	1.157/19.3
Cycle 290	1.179/0.823	1.161/0.802	1.156/18.0	1.180/0.751	1.148/17.8
Cycle 302	1.176/19.7	1.172/0.793	1.150/17.0	1.179/19.2	1.135/15.2

Note: All results are the average of two cells.

The addition of 15% rather than 10% graphite during hydrate preparation does not improve electrode conductivity or cyclic capacity maintenance. The additional washes to decrease the sulfate content below 1% do lead to improved capacity maintenance during extended cycling. The sequential addition of cobalt after nickel results in initial improved utilization of the hydrate. With cycling, this initial advantage changes to favor coprecipitation of nickel and cobalt. The addition of the cobalt to the nickel hydrate after washing to neutral does not appear to be a viable approach.

Another series of cell tests was conducted with 5% cobalt-nickel hydrate to further define the relationship of graphite addition during hydrate versus electrode preparation. For these tests, treated Asbury graphite was used to make 5% and 10% graphite/nickel hydrates as well as in electrode preparation. The cobalt was added as a coprecipitate as well as sequentially to the nickel hydrate precipitation to confirm previous results. The total graphite was varied between 30%, 25% and 20% to determine the minimum requirement for satisfactory cycling. The desired electrode loadings were obtained experimentally by comparing the bulk density (Scott volumeter) of the standard (30% graphite) to the other variations. A listing of the cell formulations made as well as the formation and cyclic capacities is given in Table I.4.

The cells were given eight formation cycles to develop stable capacities prior to cycling. They were then given 151 standard charge-discharge cycles. The sequential addition of cobalt showed better initial utilization of the hydrate than

Table I.4

EFFECT OF ADDED GRAPHITE ON 5% COBALT-NICKEL HYDRATE

GRAPHITE ADDITION

Hydrate, %	0	0	0	10	10	5	5
Electrode, %	30	30	25	15	15	20	15
COBALT ADDITION	Coprecipitate	Sequential	Coprecipitate	Coprecipitate	Sequential	Coprecipitate	Coprecipitate
THEO. CAP., (Ahr)	24.7	24.7	29.1	29.1	29.1	29.1	33.9
FORMATION CYCLES	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT						
Cycle 2 AT 10 AMPS.	1.143-19.0/19.2	1.152-22.8/23.0	1.156-23.4/23.6	1.156-23.6/23.8	1.161-25.3/25.6	1.156-21.9/22.1	1.162-25.6/25.
Cycle 4 At 10 AMPS.	1.148-20.7/21.0	1.156-23.5/23.8	1.165-24.3/24.6	1.164-24.4/24.7	1.166-25.5/25.8	1.159-23.2/23.4	1.171-26.4/26.
Cycle 6 At 10 AMPS.	1.150-21.0/21.8	1.157-23.2/23.7	1.168-24.3/24.4	1.166-24.3/24.6	1.166-24.8/25.2	1.160-23.5/23.8	1.174-26.1/26.
Cycle 8 AT 10 AMPS.	1.147-20.5/21.6	1.156-22.2/22.8	1.166-23.3/23.5	1.164-23.2/23.6	1.164-23.5/23.8	1.160-22.9/23.2	1.169-24.8/25.

AUTOMATIC CYCLING

CELL VOLTAGE AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT

Cycle 1	1.148/1.084	1.154/1.095	1.164/1.109	1.163/1.105	1.161/1.104	1.158/1.100	1.168/1.112
Cycle 7	1.152/1.031	1.150/0.848	1.156/1.033	1.154/1.014	1.154/1.002	1.150/1.018	1.152/1.026
Cycle 25	1.146/1.005	1.130/0.255	1.156/1.026	1.156/1.009	1.142/0.996	1.141/1.000	1.155/1.030
Cycle 37	1.146/1.008	1.128/19.7	1.172/1.037	1.166/1.020	1.140/0.826	1.141/0.882	1.166/1.029
Cycle 49	1.141/1.046	1.130/0.632	1.174/1.050	1.170/1.046	1.132/0.874	1.134/1.016	1.168/1.046
Cycle 70	1.128/0.843	1.112/19.0	1.163/1.028	1.162/0.990	1.118/19.8	1.114/0.802	1.162/1.013
Cycle 79	1.128/0.822	1.106/19.0	1.160/1.006	1.158/0.776	1.109/19.5	1.110/0.620	1.160/0.994
Cycle 104	1.123/0.730	1.097/18.8	1.164/0.644	1.172/0.660	1.106/19.2	1.119/20.0	1.160/0.876
Cycle 113	1.120/19.8	1.096/18.0	1.161/0.656	1.170/0.661	1.108/18.5	1.114/19.5	1.151/0.804
Cycle 125	1.124/19.8	1.093/17.5	1.162/0.650	1.168/0.652	1.103/17.8	1.112/18.8	1.144/19.7
Cycle 139	1.114/19.7	1.088/17.8	1.152/0.628	1.164/0.666	1.100/18.2	1.098/18.8	1.124/19.2
Cycle 151	1.107/19.7	1.080/17.8	1.144/0.616	1.161/0.669	1.092/17.8	1.088/19.3	1.104/18.8

Note: All results are the average of two cells.

the coprecipitate. This better utilization was not maintained during cycling in agreement with previous results. Decreasing the graphite content from 30 to 25% leads to an increase in cell capacity even though the utilization is decreased. Much of this increased capacity was maintained during cycling. The benefit of adding a portion of the graphite during precipitation has still not been confirmed. The scatter of the results, with a 10% addition being better and a 5% poorer, will require a re-evaluation of this technique. This work on the addition of graphite during hydrate preparation was terminated to concentrate on the study of the nickel hydrate performance in nickel-zinc cells.

2.3 STANDARD VS CELLOPHANE WRAP

In 20 Ah Ni-Cd test cells, the separator system consists of a 7 mil Pellon bag on both the positive and negative plates. With this system, one of the modes of failure is the penetration of cadmium through the separator and the development of soft shorts. A possible solution to this problem is the use of a membrane barrier. Identical electrodes were made into test cells having two layers of 5 mil Pellon on the positive plate and a U-wrap with 3 mil cellophane on the negative plate. Four 20 Ah Ni-Cd test cells were made with 10% cobalt-nickel hydrate using each separator configuration. The data for these cells together with 405 standard charge-discharge cycles are given in Table I.5.

Up to 350 cycles, the cells without cellophane were superior in voltage and cyclic capacity maintenance. After this point, these cells began to develop soft shorts that led to a

Table I.5

STANDARD VS. CELLOPHANE WRAP
ERC 10% Co-Ni(OH)₂; 20 AH Ni-Cd CELLS

	STANDARD WRAP		CELLOPHANE WRAP	
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT			
Cycle 4 AT 10 Amps.	1.146-19.4/20.2	1.145-19.3/20.2	1.140-19.8/20.5	1.142-19.8/21.0
	AUTOMATIC CYCLING			
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT			
Cycle 1	1.149/1.063	1.148/1.061	1.142/1.063	1.143/1.068
Cycle 25	1.175/1.066	1.174/1.063	1.165/1.054	1.168/1.054
Cycle 59	1.178/1.042	1.176/1.038	1.175/1.032	1.176/1.030
Cycle 83	1.176/1.040	1.176/1.044	1.165/1.001	1.162/0.968
Cycle 113	1.150/0.845	1.158/1.000	1.127/19.0	1.116/18.3
Cycle 134	1.151/0.824	1.150/0.992	1.132/19.7	1.127/19.3
Cycle 156	1.154/0.846	1.150/0.991	1.136/19.8	1.128/19.3
Cycle 177	1.159/0.850	1.160/1.001	1.134/19.8	1.132/19.3
Cycle 198	1.172/0.898	1.169/1.000	1.134/19.8	1.128/19.3
Cycle 249	1.178/0.702	1.172/0.943	1.128/19.0	1.124/18.7
Cycle 303	1.167/0.874	1.175/0.897	1.120/19.2	1.109/18.7
Cycle 324	1.172/0.800	1.175/0.862	1.128/19.3	1.112/18.3
Cycle 351	1.172/0.743	1.164/19.2	1.132/19.2	1.104/17.8
Cycle 379	1.166/17.0	1.137/14.0	1.120/17.7	1.090/16.3
Cycle 393	1.154/14.3	1.138/12.8	1.111/16.8	1.076/15.3
Cycle 405	1.148/14.2	1.133/12.8	1.100/16.2	1.062/14.7

Note: All results are the average of two cells.

more rapid decrease in capacity. Although the development of soft shorts in this case was earlier than expected, it is evident that a membrane barrier will aid in preventing them.

2.4 SODIUM HYDROXIDE ADDITION

In the nickel-cadmium pocket plate industry, sodium hydroxide is primarily used for hydrate preparation instead of KOH to achieve cost effectiveness. In addition, residual sodium ions in the nickel hydroxide lattice are reported to act similar to lithium in promoting cyclic capacity maintenance. Coprecipitated 5% cobalt-nickel hydrate was prepared using 50% sodium hydroxide by the WD procedure. In addition, several tests were conducted using a partial graphite addition during hydrate preparation. In one experiment, a 10% graphite-hydrate was made by adding graphite to the caustic. In a second experiment, the graphite was first wet with 10% of the cobalt-nickel solution before adding the caustic. After this step, the remainder of the cobalt-nickel solution was added to make a 10% graphite-hydrate. All of these hydrates were made into 20 Ah nickel-cadmium test cells by adding the appropriate amount of treated graphite to the positive plates so that all active material contained 30% graphite. The data for these cells including 352 standard charge-discharge cycles are given in Table I.6.

The formation data show that the cells with graphite/nickel hydrate had a large capacity increment between 1.00 and 0.70V. In addition, the voltage level of these cells was suppressed during cycling. The cells with conventional sodium hydroxide coprecipitated hydrate did perform satisfactorily

TABLE I.6

5% SODIUM HYDROXIDE
5% COBALT-NICKEL HYDRATE
20 Ah Ni-Cd CELLS

	Coprecipitate Ni + Co	Graphite to KOH	Ni to Graphite, then KOH
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT		
Cycle 5 AT 10 Amps	1.148-20.2/20.8	1.138-20.8/24.4	1.145-20.7/22.8

AUTOMATIC CYCLING

CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT		
Cycle 1	1.146/1.102	1.132/1.095	1.134/1.095
Cycle 25	1.156/1.036	1.128/1.035	1.131/1.032
Cycle 55	1.172/0.890	1.122/18.8	1.113/18.7
Cycle 76	1.176/0.776	1.120/18.2	1.114/17.3
Cycle 96	1.176/0.746	1.109/17.8	1.108/17.2
Cycle 127	1.176/0.684	1.102/16.8	1.088/16.3
Cycle 150	1.178/0.682	1.120/19.3	1.108/19.7
Cycle 183	1.172/19.2	1.118/18.7	1.104/18.7
Cycle 204	1.176/0.710		
Cycle 222	1.174/0.708		
Cycle 256	1.169/0.695		
Cycle 277	1.164/19.7		
Cycle 298	1.151/19.8		
Cycle 321	1.153/17.2		
Cycle 343	1.128/15.7		
Cycle 352	1.113/15.3		

Note: All results are the average of two cells.

and it should be possible to substitute sodium hydroxide for potassium hydroxide for cost effectiveness.

2.5 COMMERCIAL NI HYDRATE I: EFFECT OF PARTICLE SIZE

Previous experiments on the effect of nickel hydrate particle size were conducted by classifying ERC 10% cobalt-nickel hydrate into four fractions. These tests showed that the more coarse fractions produced cells having the best cycling characteristics. To determine whether the same was true for the commercial hydrate I, a 50 pound portion was classified into two equal fractions. Coulter Counter measurements showed an initial particle size of 16.2 μm that was divided into a coarse fraction of 24 and a finer fraction of 9.6 μm . These fractions were made into 20 Ah Ni-Cd cells using both regular and treated Asbury graphites. The cycle data for these cells are given in Table I.7.

The formation cycles showed a small improvement with the coarse hydrate. In both instances there was an additional improvement with treated graphite. None of the cells exhibited the desired cyclic stability. The scatter of the results makes meaningful interpretation difficult, but it does appear that there was no effect due to particle size and the cells with regular graphite held up better during cycling.

2.6 COMMERCIAL NI HYDRATE I: PREFORMED PLATES

Five 20 Ah nickel-cadmium cells were made using preformed (April 1979) commercial Ni hydrate I to determine their behavior on cycling. The formation utilization of the cells was less than 75% of theoretical and the cells did not cycle well.

Table I.7
COMMERCIAL HYDRATE I COARSE AND FINE HYDRATE
20 Ah Ni-Cd CELLS

	Coarse		Fine	
	Regular Graphite	Treated Graphite	Regular Graphite	Treated Graphite
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT			
Cycle 4 AT 10 Amps	1.155-22.4/22.8	1.158-23.3/24.0	1.156-22.1/22.4	1.154-22.5/23.3
AUTOMATIC CYCLING				
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT			
Cycle 1	1.162/1.112	1.164/1.118	1.160/1.112	1.160/1.113
Cycle 19	1.175/1.070	1.177/1.010	1.176/0.892	1.176/1.068
Cycle 31	1.171/1.049	1.164/19.5	1.163/20.0	1.173/0.994
Cycle 52	1.162/0.814	1.164/0.702	1.152/19.2	1.157/0.576
Cycle 70	1.146/0.695	1.153/20.0	1.148/19.2	1.140/19.5
Cycle 103	1.118/19.4	1.136/19.5	1.140/19.2	1.126/19.0
Cycle 124	1.118/19.2	1.142/19.5	1.147/19.3	1.130/19.0
Cycle 157	1.120/19.3	1.147/19.7	1.146/19.3	1.135/19.3
Cycle 178	1.122/20.0	1.150/0.538	1.147/0.661	1.141/19.8
Cycle 199	1.117/0.668	1.138/18.3 *	1.148/0.686	1.141/0.552
Cycle 235	1.120/19.8	1.143/18.5	1.150/0.714	1.148/0.558
Cycle 250	1.133/19.7 *	1.150/18.7	1.156/0.672	1.150/19.7
Cycle 268 †	1.134/0.719	1.150/18.2	1.157/0.721	1.148/20.0
Cycle 280	1.130/19.7	1.141/17.0	1.153/19.8	1.140/18.2
Cycle 301	1.127/19.8	1.131/16.3	1.152/19.7	1.135/16.7
Cycle 310	1.130/19.8	1.127/15.8	1.153/19.7	1.128/16.3

* Results are the average of two cells except those

† Cycler shut down for power changeover prior to this cycle.

ENERGY RESEARCH CORPORATION

This test was repeated to determine a possible reason for the behavior. The data for five new cells including 183 standard charge-discharge cycles are given in Table I.8. In addition, the average data of the previous cells are presented for ready comparison. The new formation data are better, having a utilization of 80%. The cyclic capacities have not been stable and these cells also fail to duplicate old unformed cells, some of which gave over 400 cycles before falling below 20 Ah.

2.7 COMMERCIAL NI HYDRATE I (MAY 1980)

A new supply of commercial Ni hydrate I (May 1980) was received. Their new specification calls for 0.6% rather than 1.5% cobalt. An agreement was made to supply ERC with 1.5% cobalt hydrate; the new 0.6% cobalt hydrate would be pretested prior to extensive use at ERC. The 20 Ah Ni-Cd test cells were fabricated with nickel hydrates containing 0.6 and 1.5% cobalt as well as ERC washed $\text{Ni}(\text{OH})_2$ containing 1.5% cobalt. The rewashing of the hydrate removes traces of free alkali and decreases the sulfate content from 1.5 to under 1%. The data for these cells are given in Table I.9.

The formation results for these cells are normal with 0.6% cobalt hydrate having the expected higher discharge voltage. The small difference in cyclic capacity maintenance favors the use of 1.5% cobalt. The washing of the hydrate improves the discharge voltage, but its effect on cell capacity to 0.70V appears marginal. A comparison to the cyclic performance of previous unformed cells shows that the new cells are generally poorer. The results indicate that commercial Ni hydrate I con-

Table I.8
COMMERCIAL NI HYDRATE I PREFORMED PLATES
20 Ah NI-CD CELLS

	No. 1	No. 2	No. 3	No. 4	No. 5	Previous Cells (Av.5)
FORMATION CYCLES	VOLTAGE AT 1 HOUR - CAPACITY TO 1.00/0.70 VOLT					
Cycle 2 AT 10 Amps	1.143-19.3/20.8	1.143-20.2/21.7	1.142-20.0/21.5	1.139-20.0/20.5	1.143-20.0/20.7	1.150-16.9/17.7
Cycle 4 At 10 Amps	1.139-19.3/20.8	1.140-20.2/21.7	1.139-20.2/21.7	1.136-20.2/21.0	1.140-20.3/21.5	1.163-17.9/18.4
AUTOMATIC CYCLING						
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT					
Cycle 1	1.142/1.101	1.140/1.101	1.128/1.098	1.135/1.098	1.139/1.100	Cycle 1 1.165/19.4
Cycle 7	1.150/19.7	1.143/19.7	1.142/19.7	1.140/19.8	1.145/20.0	Cycle 4 1.165/18.8
Cycle 16	1.142/19.5	1.135/19.3	1.135/19.3	1.133/19.5	1.136/19.5	Cycle 19 1.134/18.2
Cycle 25	1.134/19.7	1.131/19.0	1.131/18.8	1.129/19.0	1.131/19.2	Cycle 25 1.122/18.0
Cycle 34	1.132/20.0	1.127/19.3	1.126/19.5	1.125/19.7	1.128/19.8	Cycle 31 1.113/18.0
Cycle 46	1.124/19.5	1.123/18.5	1.122/18.2	1.120/18.5	1.126/18.3	Cycle 40 1.114/18.5
Cycle 55	1.121/0.990	1.120/19.5	1.119/19.3	1.113/19.3	1.121/19.5	Cycle 47 1.106/18.0
Cycle 76	1.123/19.0	1.123/18.0	1.124/17.8	1.120/17.7	1.121/18.5	
Cycle 96	1.121/18.5	1.119/17.2	1.122/17.5	1.112/17.2	-/-	
Cycle 118	1.118/17.8	1.109/15.7	1.122/16.5	1.104/15.7	1.116/17.2	
Cycle 127	1.112/17.5	1.100/14.8	1.114/16.5	1.097/14.8	1.121/16.7	
Cycle 135	1.108/18.0	1.097/15.0	1.110/17.3	1.097/15.2	1.117/16.5	
Cycle 150	1.110/18.3	1.098/14.8	1.115/16.8	1.092/15.2	1.115/16.8	
Cycle 162	1.103/17.5	1.084/14.2	1.102/16.0	1.073/15.0	1.107/16.3	
Cycle 171	1.112/17.5	1.095/13.8	1.111/15.5	1.086/15.0	1.109/16.0	
Cycle 183	1.104/17.8	1.091/14.0	1.103/16.3	1.072/15.5	1.104/16.3	

Note: Previous data are the average of five NIFE test cells.

Table I.9
COMMERCIAL NI HYDRATE I, MAY 1980
20 AH NI-CD CELLS

	0.6% Cobalt	1.5% Cobalt	1.5% Cobalt-Washed
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT		
Cycle 4 AT 10 AMPS.	1.166-21.2/21.3	1.160-21.2/21.4	1.160-20.0/20.2
AUTOMATIC CYCLING			
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT		
Cycle 1	1.168/1.116	1.162/1.108	1.164/1.066
Cycle 7	1.174/0.933	1.167/0.940	1.170/19.7
Cycle 16	1.175/1.074	1.168/0.915	1.174/0.768
Cycle 25	1.174/1.036	1.162/19.5	1.173/19.8
Cycle 37	1.172/0.922	1.152/20.0	1.172/19.7
Cycle 49	1.165/0.626	1.136/18.7	1.164/18.7
Cycle 58	1.160/0.638	1.132/19.2	1.160/19.2
Cycle 79	1.143/19.2	1.116/19.3	1.136/18.0
Cycle 91	1.135/18.7	1.110/19.0	1.120/17.2
Cycle 103	1.134/18.8	1.114/19.2	1.122/18.2
Cycle 121	1.130/18.7	1.108/19.0	1.120/18.2
Cycle 142	1.122/18.8	1.102/19.3	1.122/18.8
Cycle 154	1.119/18.2	1.098/18.8	1.128/19.0
Cycle 163 *	1.125/18.5	1.108/19.3	1.144/19.8
Cycle 172	1.127/18.7	1.116/19.3	1.147/20.0
Cycle 181	1.123/18.7	1.113/19.3	1.144/19.8

* Cycler shut down prior to this discharge due to power supply.

taining 0.6% cobalt can be used for our work with only a minimal performance change.

2.8 COMMERCIAL NICKEL HYDRATES II

A cooperative effort has been made with various producers of nickel compounds to develop alternate sources of nickel hydrate. Two commercial samples of nickel hydrate II made from nickel chloride were received and the samples were designated A8078 and A8080, the latter being a portion of the former subjected to an additional WD cycle to decrease the chloride content from 0.09 to 0.02%. Sample A8078 was very coarse and extensive grinding was required to screen material through 500 μm openings to make a suitable layer. A8080 required only minimal grinding to pass through a 1100 μm opening screen. In both cases, approximately 60% of the final material would not pass through a 200 mesh (75 μm) screen.

Twenty Ah Ni-Cd test cells were made with these hydrates using standard procedures. The cells were subjected to 252 standard charge-discharge cycles as given in Table I.10. The hydrate utilization was 70% of theoretical and improvement will require adjustment of the hydrate or electrode preparation. The cyclic capacity was stable after the initial decrease in capacity.

Nickel chloride received from commercial source II was converted into the hydroxide at ERC using the WD procedure. No difficulties were experienced in its preparation and the

Table I.10

COMMERCIAL NICKEL HYDRATES II
100% Ni(OH)₂; 20 Ah Ni-Cd CELLS

	A8078	A8080	ERC Chloride	Borate
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT			
Cycle 4 AT 10 AMPS.	1.140-17.9/18.1	1.138-18.3/18.3	1.145-19.2/19.5	1.132-18.7/22.7
AUTOMATIC CYCLING				
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT			
Cycle 1	1.136/19.8	1.138/0.936	Cycle 1 1.144/1.088	Cycle 1 1.128/0.989
Cycle 25	1.152/19.7	1.138/19.3	Cycle 10 1.158/1.021	Cycle 10 1.111/18.2
Cycle 59	1.130/18.8	1.115/18.0	Cycle 19 1.152/0.994	Cycle 19 1.094/18.0
Cycle 71	1.124/18.3	1.106/17.7	Cycle 31 1.132/19.0	Cycle 31 1.077/19.2
Cycle 92	1.125/17.5	1.104/15.7	Cycle 49 1.140/0.316	Cycle 49 1.102/17.0
Cycle 113	1.096/16.3	1.064/15.7	Cycle 79 1.150/0.674	Cycle 58 1.105/16.2
Cycle 134	1.120/17.2	1.077/14.8	Cycle 100 1.158/0.546	Cycle 79 1.081/18.3
Cycle 156	1.131/17.5	1.074/15.2	Cycle 120 1.157/0.553	Cycle 91 1.082/16.3
Cycle 165	1.130/17.7	1.088/14.0	Cycle 151 1.144/0.376	Cycle 100 1.057/13.5
Cycle 177	1.135/17.7	1.092/14.7	Cycle 171 1.099/0.496	Cycle 111 1.047/12.7
Cycle 198	1.132/18.2	1.095/14.8	Cycle 204 1.052/0.353	Cycle 120 1.071/13.2
Cycle 207	1.128/17.8	1.104/14.0	Cycle 225 0.862/19.8	Cycle 142 1.045/12.2
Cycle 219	1.122/17.8	1.121/15.2	Cycle 255 0.883/18.5	
Cycle 228	1.127/17.5	1.121/16.2	Cycle 276 1.013/17.5	
Cycle 240	1.126/17.5	1.114/15.3	Cycle 297 0.975/14.8	
Cycle 252	1.126/17.2	1.114/15.5	Cycle 308 0.592/14.5	

final hydrate contained 1.8% chloride. The 20 Ah Ni-Cd test cells were made using standard procedure. The data for 308 standard charge-discharge cycles are given in Table 1.10. The best cell gave over 200 cycles before the capacity went below 20 Ah, which is the best performance of a non-additive Ni-Cd cell produced under this program. The manufacturer's analysis listed only 4 ppm of cobalt in the initial salt, thereby eliminating cobalt as the reason for the improved cycling.

Commercial Ni hydrate II also supplied a nickel hydrate prepared from nickel borate. The data for this 20 Ah Ni-Cd test cell are presented in Table 1.10. In this case, there was a gradual loss of cyclic capacity.

2.9 COMMERCIAL NICKEL HYDRATES III

A third company supplied two samples of nickel hydrate for evaluation. One was trivalent nickel oxide to which they added 25% graphite. In making the electrodes, 30% Asbury graphite was added to the former for conductivity while to the latter only the binder was added. The assembly of the 20 Ah Ni-Cd cells was according to standard procedures. The data for these cells including 181 standard charge-discharge cycles are given in Table I.11.

The formation cycles showed a depressed discharge voltage level in comparison to the usual non-cobalt containing cells. In particular, the hydrate containing graphite cells did not have a sharp knee in the discharge curve as evidenced by a large capacity difference between the 1.00 and 0.70V endpoints.

Table I.11
OTHER NICKEL HYDRATES
20 AH NI-CD CELLS

Commercial Ni Hydrate III			Commercial Ni Hydrate IV
Oxidized Nickel		Oxidized Nickel w/graphite	ERC WD 5% Cobalt
THEORETICAL CAP., AH	26.0	30.6	24.7
FORMATION CYCLE	VOLTAGE AT 1 HOUR - CAPACITY (Ah) TO 1.00/0.70 VOLT		
Cycle 2 AT 10 AMPS	1.136-18.5/21.2	1.101-16.2/23.1	1.144-19.5/19.9
Cycle 4 AT 10 AMPS	1.140-19.9/22.8	1.136-20.4/23.5	1.148-19.8/20.3
AUTOMATIC CYCLING			
CELL VOLTAGE	AT 1 HOUR/2 HOURS OR CAPACITY (Ah) TO 0.70 VOLT		
Cycle 1	1.138/19.8	1.134/1.006	Cycle 1 1.150/1.083
Cycle 7	1.145/0.896	1.119/0.828	Cycle 19 1.170/1.054
Cycle 16	1.142/0.854	1.109/0.817	Cycle 49 1.156/1.060
Cycle 25	1.134/19.7	1.097/0.757	Cycle 79 1.167/1.049
Cycle 49	1.112/18.7	1.074/20.0	Cycle 100 1.183/1.024
Cycle 70	1.100/18.3	1.046/19.3	Cycle 151 1.182/1.016
Cycle 91	1.103/18.8	1.016/20.0	Cycle 154* 1.192/0.955
Cycle 103	1.107/19.2	1.020/19.8	Cycle 181 1.192/0.974
Cycle 112	1.104/18.8	1.000/19.7	Cycle 205 1.194/0.969
Cycle 121	1.104/19.3	0.984/19.8	Cycle 226 1.192/0.931
Cycle 133	1.097/18.8	0.966/19.7	Cycle 247 1.182/0.943
Cycle 142	1.105/19.5	† 1.022/0.672	Cycle 277 1.176/0.853
Cycle 154	1.100/19.3	1.022/20.0	Cycle 299 1.184/0.806
Cycle 163	1.101/19.3	1.024/19.3	Cycle 309 1.178/0.886
Cycle 172	1.102/19.2	1.023/19.3	Cycle 327 1.186/0.888
Cycle 181	1.098/19.0	1.001/19.3	Cycle 348 1.184/0.862

Note: All results are the average of two cells.

*Cracked cases repaired. Cells not cycled for 21 days.

†One cracked case repaired.

During automatic cycling, the depressed voltage has continued. The utilization of the active material and cyclic capacity stability have been marginal.

2.10 COMMERCIAL NICKEL HYDRATE IV

A fourth company supplied a 5% cobalt-nickel hydrate made according to the ERC WD procedure. This hydrate required the normal grinding to make 20 Ah Ni-Cd test cells by standard procedures. These cells have had 348 standard charge-discharge cycles and the data are given in Table I.11. The cells have shown good cyclic capacity stability.

2.11 NICKEL-ZINC VS NICKEL-CADMIUM PERFORMANCE

In an attempt to determine the effect of the microporous barrier on the mass transport of the electrolyte, the same hydrate was used to make nickel-zinc and nickel-cadmium cells. Identical ERC 1.5% cobalt-nickel hydrate plates were fabricated into a nickel-zinc cell with PVA, nickel-cadmium cell with PVA and nickel-cadmium cell without PVA. For consistency, these cells were cycled to 0.80V cut-off noting the 1.20V endpoint for the nickel-zinc and 1.0V for the nickel-cadmium cells. The data for these cells are given in Table I.12.

The nickel-zinc cell initially had a small increase in capacity with cycling before the capacity decreased. Figure I.1 shows the effect of cycling on the development of a second plateau in the nickel-zinc cell leading to a decrease in cell capacity. Theories proposed for this behavior include blocking of the positive plate pores by zinc oxide and electrode delamination

FIGURE I.1

EFFECT OF CYCLING 250 AH SINGLE PLATE NI-ZN CELL

Table I.12

NICKEL-ZINC VS. NICKEL-CADMIUM

ERC 1.5% COBALT-NICKEL

250 AH SINGLE PLATE CELL

	Nickel-Zinc with PVA	Nickel-Cadmium with PVA	Nickel-Cadmium no PVA
FORMATION	CAPACITY (Ah) TO 1.20 OR 1.00/0.80 VOLT		
10 AMP. DISCHARGE	14.0/14.8	14.8/15.3	15.0/15.3
	AUTOMATIC CYCLING		
	CAPACITY (Ah) TO 1.20 OR 1.00/0.80 VOLT		
Cycle 1	15.3/17.2	16.5/17.2	16.0/16.7
Cycle 25	11.2/15.5	17.0/10.2	17.5/18.3
Cycle 52	5.0/12.7	18.8/19.3	18.3/19.2
Cycle 99	2.3/8.8	18.8/19.3	18.5/19.2
Cycle 114	2.7/7.8	18.8/19.5	18.5/19.2
Cycle 153	Nickel-Cadmium with PVA	18.8/19.7	18.3/19.5
Cycle 201		18.3/19.7	17.7/19.5
Cycle 222		18.0/19.5	17.3/19.5
	*12.2/16.8		
Cycle 240	11.3/17.2	17.8/19.5	16.7/19.2
Cycle 252	11.2/17.7	17.8/20.0	16.0/19.3
Cycle 273	11.3/17.5	17.8/19.8	15.0/19.0
Cycle 306	-/15.7	16.0/19.5	11.2/18.7
Cycle 324	7.2/14.3	15.8/19.2	11.3/18.2
Cycle 355	5.3/11.0	14.8/19.7	9.8/16.7
Cycle 373	4.5/7.7	12.8/18.2	9.3/14.5
Cycle 400	4.5/7.7	12.5/18.3	9.2/13.2

* This cycle is cycle 7 as a nickel-cadmium cell after 114 cycles as a nickel-zinc cell.

causing an increase in IR between collector and active material.

The cycling was discontinued at 114 cycles and the positive plate was washed free of alkali, re-pressed and used to build a new nickel-cadmium cell with PVA. The plate recovered much of its initial capacity although it was not equivalent to the other cells. With cycling, this rebuilt cell showed the effect of its previous history. The cell developed a very high end-of-charge voltage exceeding 2.15 V and had an initial discharge voltage that exceeded 1.80 V for several minutes. This indicates that some zinc left in the positive plate had plated onto the negative plate.

Both nickel-cadmium cells had essentially stable capacities for 250 cycles. This would imply that the mass transport of the electrolyte is not materially affected by the microporous barrier. The subsequent decrease in capacity is believed due to electrode deterioration. No long-term effect of zinc or zinc oxide contamination of the positive was evident.

2.12 TEFLONIZED GRAPHITE

In an attempt to eliminate the second discharge plateau and improve capacity, cells were made with pre-Teflonized graphite. A diluted dispersion of Teflon 3170 was mixed with Asbury graphite until the Teflon was absorbed and formed agglomerates. These were filtered and dried at 50°C. Teflon-graphite concentrations of 1 and 2% were made into electrodes using commercial Ni hydrate I, and 1% Teflon binder. For comparison, electrodes were also made with 1, 2 and 3% Teflon binder with Asbury graphite. These were formed into 250 Ah single plate nickel-zinc cells with PVA microporous barriers.

The cells were given 50 standard charge-discharge cycles to essentially 60% of their nominal capacity. At this point, the effect of increased Teflon content was minimal in improving cell capacity and eliminating the second discharge plateau.

Another experiment was conducted using a modification of this pre-Teflonized graphite. In an experiment which was similar to the previous one, a diluted dispersion of Teflon 3170 was mixed with Lanza graphite until the Teflon particles were absorbed, forming agglomerates. These were filtered and dried at 50°C. The mass was then heated at 300°C for 90 minutes so that the final product was in powder form. Teflon-graphite concentrations of 0, 0.25 and 0.50% were made into electrodes using commercial Ni hydrate I and 2% Teflon binder. These electrodes were made into 250 Ah single plate nickel-zinc cells using Celgard K-307 microporous barriers.

The cells were given a number of deep discharge cycles after the initial cycling failed to develop full capacities. Inputs of as much as 400% made only a small improvement in the cell capacities, achieving only 60% utilization. At the end of 80 cycles, the effect of pre-Teflonization of the graphite to decrease the second plateau was minimal. It appears that the elimination of the second discharge plateau will require a different approach.

2.13 ERC NICKEL HYDRATE VARIATIONS

Several different nickel hydrates that showed improved results in nickel-cadmium cells were made into nickel-zinc cells to determine whether there was a difference in the charge efficiency of the positive plate. These included 1.5 and 5% coprecipitated cobalt-nickel, 5% cobalt after nickel and 5% coprecipitated

cobalt-nickel hydrate made using sodium hydroxide. These hydrates were made into 250 Ah single plate cells using standard procedures with PVA microporous barriers.

The cells were tested using the standard charge-discharge cycle and all were below 60% of nominal capacity after 40 cycles. These variations produced only nominal changes in the cell behavior. Additional cobalt aids in developing the positive plate capacity and the addition of cobalt after nickel hydroxide is precipitated imparts additional charge efficiency although the cyclic capacity loss is greater than with coprecipitated hydrate. This is similar to results with nickel-cadmium cells. Precipitation with sodium hydroxide does not appear to produce any improvement, but its use could be justified on an economic basis.

In an experiment to improve the utilization of the ERC 1.5% cobalt-nickel hydrate, several variations were made in its preparation. Previous tests had shown that if cobalt was added after the nickel precipitation, rather than as a coprecipitate, the positive plate obtained its maximum capacity in a fewer number of cycles. This was offset by the fact that the coprecipitated hydrate had a more stable cyclic capacity. In an experiment to combine both advantages, a portion of the cobalt was coprecipitated and a portion was added later. In addition, a test was made on the effect of adding cadmium after a coprecipitate of cobalt and nickel.

The hydrates were made into electrodes using standard procedures. The 250 Ah cells made using Celgard K-307 microporous barriers and 1% lead oxide + 2% cadmium oxide as the zinc

additive. All of the variations and test data are given in Table I.13.

The cycling data show that adding 1% cobalt after a coprecipitate of 0.5% cobalt-nickel will result in a hydrate that achieves an improved capacity with fewer cycles and is more stable during cycling. Additional variations are being tried to densify the nickel hydrate to improve electrode structure and capacity for nickel-zinc cells before incorporating this improvement in our standard procedure.

2.14 ELECTROLYTE ADDITIVES

In another approach to improve the capacity of the positive plate, electrolyte additives are being tried to decrease the interaction of the soluble zinc products and nickel hydrate. In this experiment, unformed cells were filled with standard electrolyte containing 5% barium hydroxide or 5% potassium fluoride. Although not all of the barium compound appeared to dissolve, the quantity which did dissolve should react with the zincate ion to form an insoluble species. In the case of potassium fluoride, it was expected that the formation of the relatively insoluble zinc fluoride would occur. For comparison, cells with preformed and unformed plates were tested with standard electrolyte. The data for these cells as well as 136 standard charge-discharge cycles are given in Table I.14.

The formation data show that the addition of barium and fluoride serves to increase the cell capacity between 1.20 and 0.80 V. During automatic cycling to 1.20V, these additions had an adverse effect upon the development of cell capacity.

Table I.13
ERC 1.5% COBALT-NICKEL VARIATIONS
250 Ah SINGLE PLATE NI-ZN CELLS

Coprecipitate, Co	1.5%	1.0%	0.5%	1.0%
Additional, Co or Cd	-	0.5%	1.0%	0.5% Cd
FORMATION	CAPACITY (Ah) TO 1.20/0.80 VOLT			
10 AMP. DISCHARGE	11.2/11.7	11.0/11.5	11.5/12.3	10.7/11.8
AUTOMATIC CYCLING				
CAPACITY (Ah) TO 1.20 VOLT				
Cycle 1	9.8	9.8	11.2	9.8
Cycle 5	10.9	11.7	13.4	11.0
Cycle 10	12.2	13.0	14.3	11.9
Cycle 15	14.0	14.7	16.2	13.7
Cycle 20	15.4	16.2	17.1	15.0
Cycle 25	15.5	16.2	16.8	15.1
Cycle 37	15.8	16.2	16.7	15.2
Cycle 49	15.5	15.8	16.2	14.5
Cycle 61	15.8	16.0	16.2	14.7
Cycle 70	15.7	15.3	15.7	14.3
Cycle 80	15.3	14.7	15.3	13.8
Cycle 89	15.2	14.5	15.0	13.5
Cycle 101	14.5	14.2	14.8	13.2
Cycle 110	13.8	13.7	14.5	12.7
Cycle 119	12.8	13.2	14.0	12.2
Cycle 131	11.2	12.3	13.0	11.2
Cycle 143	10.2	11.7	12.5	10.5
Cycle 152	9.6	11.0	11.5	9.5

Table I.14
ELECTROLYTE ADDITIVES
COMMERCIAL NI HYDRATE I
250 Ah SINGLE PLATE NI-ZN CELLS

TEST VARIABLES	Unformed	Unformed 5% Ba(OH) ₂	Unformed 5% KF	Preformed
FORMATION	CAPACITY (Ah) TO 1.20/0.80 VOLT			
10 AMP. DISCHARGE	11.7/13.3	11.2/18.7	10.0/18.0	10.7/11.7
AUTOMATIC CYCLING				
CAPACITY (Ah) TO 1.20 VOLT				
Cycle 1	12.5	11.0	10.0	11.2
Cycle 4	12.3	11.0	10.3	12.2
Cycle 13	15.2	13.5	14.3	16.8
Cycle 19	16.7	15.0	15.3	17.8
Cycle 25	17.7	15.8	15.2	17.8
Cycle 34	17.7	15.8	14.7	17.5
Cycle 40	17.0	15.3	14.2	17.0
Cycle 46	16.7	14.8	13.3	16.8
Cycle 55	16.3	13.7	11.8	16.0
Cycle 67	15.8	12.2	10.2	14.8
Cycle 76	15.7	11.3	9.2	14.7
Cycle 88	15.2	10.5	7.8	13.8
Cycle 97	15.0	10.2	7.3	13.3
Cycle 103	14.0	9.8	7.0	13.2
Cycle 109	14.7	9.7	6.7	12.8
Cycle 121	14.3	9.3	5.8	12.2
Cycle 127	13.8	8.8	5.3	11.5
Cycle 136	13.2	8.2	4.8	10.8

ENERGY RESEARCH CORPORATION

The preformed plate showed only a slight advantage over the unformed plate in developing its maximum capacity. The unformed plate however had better cyclic capacity maintenance. Other compounds having an affinity for the zincate ion will be tried to determine their effect upon improving positive plate capacity with cycling.

3.0 CONCLUSIONS

Cells with 1.5% cobalt-nickel hydrate prepared by the WD procedure gave stable cyclic capacity for over 500 cycles.

The use of treated Asbury graphite improved the discharge voltage and cell capacity of nickel-cadmium cells. Substitution of Lonza graphite for Asbury graphite produced cells that are almost equivalent to those with treated Asbury graphite.

The benefit of adding a portion of the conducting graphite during precipitation was not resolved. This technique used by some manufacturers of pocket plate nickel hydrate will require further investigation.

The sequential addition of cobalt after nickel, rather than as a coprecipitate, improves the initial charge acceptance of the nickel hydrate. However, coprecipitated cobalt-nickel hydrate has better cyclic capacity stability.

Preparation of the hydrate with sodium hydroxide does not appear to improve its cyclic capacity stability, but its use could be economically justified.

The use of a microporous membrane barrier to prevent cadmium soft shorts is not required for 20 Ah nickel-cadmium cells up to 300 cycles although some cells have given 700 cycles prior to any indication of soft shorts. Commercial Ni hydrate I, classified into two different particle sizes, did not show any significant effect due to particle size.

Commercial nickel hydrate I, made into plates that were preformed prior to final assembly in 20 Ah nickel-cadmium cells

did not cycle satisfactorily.

Commercial nickel hydrate I received during May 1980 produces cells having cyclic capacity stability equivalent to some previous tests. Reduction in the cobalt content from 15. to 0.6%, leads to a small loss of cyclic capacity stability.

Commercial nickel hydrate II, made from nickel chloride gave marginally acceptable performance. Nickel hydrate made from their nickel chloride at ERC was incorporated in a cell which gave over 200 cycles before falling below 20 Ah.

Experiments with commercial trivalent nickel hydrate III produced cells with acceptable performance and will require additional investigation.

A cell with commercial cobalt-nickel hydrate IV using the ERC procedure has satisfactory cyclic capacity stability.

Nickel-zinc cells develop a second plateau in the discharge curve with cycling that leads to a decrease in cell capacity. Nickel-cadmium cells made with the same microporous barrier do not show this phenomena. Zinc compounds deposited in the positive plate were shown to be responsible for this behavior.

The pre-Teflonization of graphite to improve electrode integrity and decrease possible delamination had little effect on decreasing the formation of the second plateau.

Variation in the preparation of 1.5% cobalt-nickel hydrate to add a portion of the cobalt as a coprecipitate and sequentially leads to a small improvement in the charge acceptance of the positive active material.

Additions to the electrolyte to decrease the influence of soluble zinc species on the nickel hydrate will require a systematic evaluation of known insoluble zinc compounds.

4.0 FUTURE WORK

The testing of nickel hydrates in nickel-cadmium cells will be performed primarily to verify results obtained in nickel-zinc cells. The aim will be to improve the utilization of the nickel electrode (Ah/g) through improved charge acceptance and utilization.

Variations will be made in the hydrate preparation procedure to modify hydrate morphology. This will lead to an improved electrode structure to obtain optimum utilization of the active material in nickel-zinc cells.

Electrolyte additions to decrease the influence of soluble zinc species on the nickel electrode will be investigated further.

SECTION III
ZINC ELECTRODE DEVELOPMENT
FOR NI-ZN CELLS - TASK II

1.0 INTRODUCTION

The performance related problems of the Ni-Zn cell (such as gas evolution during charge, decline in capacity with cycling, abrupt failure, inability to operate in the sealed condition and drying out of the electrode plates) are directly traceable to the zinc electrode.¹ Some of these problems are attributed to shape change, dendritic deposition and passivation at the zinc electrode.² Therefore, the objective of this task is to find cost-effective solutions to these problems and develop a zinc electrode which is capable of 300 cycles in a large Ni-Zn battery.

The experimental work is divided into electrode technology and basic electrochemical study of the reversible Zn electrode. The technical approach to electrode technology is based on polymer bonded ZnO containing a suitable combination of substrate and additives.³ As substrate, a thin copper foil (thickness = 0.002 in.) has been selected based on previous results.

The objective of the basic study is to rationalize shape change and passivation. A steady state polarization study, has been initiated in order to elucidate the kinetics of zinc dissolution and deposition, particularly the sequence of partial reactions, dependence of reaction rate on temperature, OH^- and zincate concentrations and repetitive cycling. An electrochemical cell consisting of a segmented zinc electrode, nickel-oxy hydroxide counter electrode and Hg/HgO reference electrode is used for this study.

2.0 TECHNICAL DISCUSSION

2.1 BASIC ELECTROCHEMICAL STUDY

The kinetics of Zn dissolution and deposition is being investigated using a galvanostatic polarization procedure. Although the study examines the sequence of partial reactions, reaction order terms, and rate-determining steps, the primary objective is to explain the changes in the polarization characteristics of zinc with cycling and relate these changes to shape change and passivation.

2.1.1 Experimental

The polarization and cycling experiments were performed with a specially designed cell consisting of one positive and one negative electrode and arranged in a Plexiglas housing. A separator system consisting of a layer of Pellon and three layers of PVA was used as electrical insulation between the electrodes. The positive electrode (the counter electrode during polarization) is the standard ERC roll-bonded NiOOH pasted to a nickel exmet collector. The negative electrode (working electrode during polarization) is the usual ERC roll bonded ZnO electrode with some variations. Silver foil with nine spot-welded tabs distributed over the surface of the electrode is used as the substrate for the Zn electrode. These tabs are used to monitor overvoltages during polarization of different Zn electrode areas.

For normal cell cycling (charge and discharge) the three strands of silver wire which are welded to the substrate at one corner are used. The roll bonded ZnO is pasted to the side opposite the voltage monitoring tabs. The region opposite each voltage monitoring tab forms a particular section at the electrode. Thus there are nine distinct sections at the Zn electrode for comparison of polarization characteristics. The entire assembly is oriented in the horizontal position during all experiments. The top side of the Plexiglas case has orifices which coincide with the tab locations. A Hg/HgO reference electrode is inserted through the orifices for potential measurement. The cell is filled with KOH of appropriate concentration. Figure II.1 illustrates the cell.

A PAR potentiostat/galvanostat, Model 371, is used as a galvanostat to polarize the working electrode. For cycling purposes an automatic cycler with a six-hour charge and two-hour discharge regime is used.

2.1.2 Dependence of Kinetics on OH^- Concentration

A zinc electrode prepared from 98% ZnO and 2% TFE was used for this study. The variations of potential with current under steady state conditions during reduction and oxidation of this electrode was studied in four different concentrations of KOH. The procedure consisted of first determining the open circuit voltage (OCV) as a function of pH. Then the electrode was polarized to a certain overvoltage in both cathodic and anodic directions. The variations of OCV with KOH concentration are given in Figure II.2. Note that the data correspond to a fresh electrode before any cycling,

CROSS SECTIONAL VIEW

CELL SKETCH

TOP VIEW

FIGURE II.1: ELECTROCHEMICAL CELL FOR CYCLING AND POLARIZATION EXPERIMENTS.

FIGURE II.2: THE DEPENDENCE OF ZINC POTENTIAL ON OH^- CONCENTRATION AT OPEN CIRCUIT

and the entire relationship is for one of the nine sections of the electrode (the one closest to the edge). The data for the other section studied (the one at the center) was in agreement with the edge section.

The relationship between E_{ocv} and pH was linear with a slope of 0.137. The intercept is -1.215V. This behavior has been reported previously. It is believed that the potential is Nernstian.⁵

If it is assumed that the equilibrium

exists at open circuit, the expression for the equilibrium constant is

$$K = \frac{[\text{OH}^-]^4}{[\text{Zn(OH)}_4^{-2}]} \quad (2)$$

substituting molarity for activity and neglecting liquid junction, the Nernst equation can be written as

$$E = E^o + \frac{2.303RT}{2F} \log \frac{[\text{OH}^-]^4}{[\text{Zn(OH)}_4^{-2}]} \quad (3)$$

The expression predicts a slope of 118 mV for the plot of potential versus OH^- concentration. The experimental value of 137 mV compares well with that predicted by the equation.

Figure II.3 shows the relationship between $\log i$ versus pH at an overvoltage of 15 mV from E_{ocv} , for the deposition reaction. The experimental points in the curve correspond to both electrode sections studied. The relationship is linear with a slope of 0.76. The result indicates that the rate of deposition

FIGURE II.3: DEPENDENCE OF REACTION RATE ON pH AT A CONSTANT OVERVOLTAGE OF 15 mV FROM E_{OCV} BEFORE CYCLING.

increases with an increase in pH (i.e., $\log (\text{OH})^- + 14$). This is an unexpected result since the reduction of zincate yields OH^- as a product.⁶

The effect of cycling on the $\log i$ vs pH relationship was also determined. The Zn electrode was cycled as in a normal operating battery against a $\text{Ni}(\text{OH})_2$ electrode. After several cycles (11-14) the pH dependency was determined. Figure II.4 shows the pH dependency obtained after cycling. Here again, the rate of deposition increases with pH but the rate of increase is diminished, as is evident from the slope of the curve. This observation suggests that as the electrode is cycled, the reaction mechanism changes.

The electrode was cycled further and the pH dependency was determined. The experimental results showed a great scatter with poor reproducibility. However, the overall effect of cycling was a tendency toward lower dependence of the reaction rate on pH.

The dependence of the kinetics on the OH^- concentration during anodic polarization was also determined. Figure II.5 shows the pH dependency for the dissolution reaction for a fresh electrode before cycling. The relationship is linear with a slope of 0.76.

The electrode was cycled as in a battery and the pH dependency was determined again. The value for $\partial (\log i) / \partial \text{pH}$ decreased after 14 cycles. Figure II.6 shows the effect of cycling on the reaction order with respect to OH^- concentration. With further cycling, the value for $\partial (\log i) / \partial \text{pH}$ decreases and it becomes an almost insignificant value.

The anomalous dependency of the cathodic reaction on OH^- concentration, may be explained by assuming a change in the sequence of partial reactions with cycling. In the beginning, the following sequence

FIGURE II.4 DEPENDENCE OF REACTION RATE ON pH AT A CONSTANT OVERVOLTAGE
OF 15 mV FROM E_{OCV} AFTER CYCLING.

FIGURE II.5: DEPENDENCE OF REACTION RATE ON pH AT A CONSTANT OVERVOLTAGE
 OF 20 mV FROM E_{OCV} BEFORE CYCLING

FIGURE II.6: DEPENDENCE OF REACTION RATE ON pH AT A CONSTANT OVERVOLTAGE OF 20 mV FROM E_{OCV} AFTER CYCLING.

of partial reactions occur.

Equation 7 is assumed to be the rate determining step (RDS). Equations 8 and 9 are included only to indicate the probable path through which metallic Zn is produced. A kinetic expression for the rate of reduction can be formulated based on this RDS, which would explain the initial dependence of the rate on OH^- concentration.

This sequence of partial reactions, including the RDS, changes with cycling. The importance of conversion of ZnO to Zn(OH)_4^{-2} as a condition for reduction diminishes. In addition, the dominant active species on the electrode is no longer the ZnO which was initially present. Instead a "compact ZnO" variously described as Type II film dominates the surface (which is believed to be produced during anodic polarization).^{7,8} The "compact ZnO" differs structurally from the normal ZnO with lower solubility in KOH. On cathodic polarization the species is reduced to Zn as symbolized in the following equation:

Thus zincate formation is less important in the kinetics of a cycled electrode. The reduction reaction may be composed of a new set of partial reactions.

The changes observed on the reaction order term with cycling during anodic polarization may also be explained by assuming a change in the mechanism of reaction. At the beginning the reaction goes through a zincate path to form ZnO. The reaction can be formulated as follows:

The zincate so produced generates ZnO by a decomposition-precipitation reaction

which is independent of the anodic polarization reaction.

Upon cycling, the reaction rate depends less on the OH^- concentration. The mechanism changes to:

Where ZnO is the "compact ZnO" described in Reference 7. Equation 13 predicts a lower dependency on OH^- concentration.

Experiments are in progress to substantiate the observations about reaction mechanisms during cathodic and anodic processes.

2.1.3 Electrode Polarization, Tafel Slope and Exchange Current

To obtain diagnostic criteria on the reaction mechanism, parameters such as steady-state, open circuit potential, Tafel slope and exchange current were determined for the following types of zinc electrodes and electrolyte concentrations:

ZINC ELECTRODE	P-II				P-III	P-IV	P-V
	B	C	D	E	A	A	A
Studied in Solution of: % KOH	38	20	6	11	35	35	35
% LiOH	1	1	1	1			
Electrode Composition, %	98 ZnO 2 TFE				93 ZnO 5 CdO 2 TFE	85 ZnO 13 Mixed Oxides 2 TFE	89 ZnO 7 CdO 1 Fe ₂ O ₃ 3 TFE

As mentioned earlier, the location of the electrode area (or section) studied was one of the variables in the experiments. The experimental results are given in Appendix A. The scatter in the experimental results for Tafel slope, polarization at a particular current-density, etc., is normal, considering the nature of the experiment and interaction of parameters. Despite this, the data show a definite trend which can be used advantageously in providing some theoretical explanations. The Appendix contains information for important sections of the electrode, i.e., Section 3 which corresponds to the edge and Section 5 which corresponds to the center.

The OCV showed a shift to the anodic direction when the value for the edge section was compared to that of the center section. The magnitude of this shift is a function of the electrode type and it increases in this order: P-IIB > P-IIIA > P-IVA > P-VA (i.e., the potential distribution was more uniform for P-VA which contains CdO + Fe₂O₃ as additives, and P-IVA, which contains a mixed oxide type additive). Upon Cycling, the magnitude of the shift which is not linear with the ordinal number of cycles increases. Again, the magnitude of the

ENERGY RESEARCH CORPORATION

shift with cycling is greater for P-IIB than for P-IVA.

The overvoltage of the Zn during cathodic and anodic polarization at a current density of 4 and 12 mA/cm², respectively, was studied as a function of the same variables. A cathodic current density of 4 mA/cm² corresponds to the normal charging current density in an operating battery and the anodic current density of 12 mA/cm² corresponds to the normal discharge current density. Again, the overvoltage for the edge section was found to be greater than that for the center section in all instances, i.e., the edge sections are more polarized than the center sections. Further comparison of the electrode types shows the ability to polarize increases in the order; P-IIB > P-IIIA > P-IVA.

The exchange current density, i_0 , which is a direct measure of the reversibility of the reaction (important in rechargeable batteries) was examined as a function of electrode type and cycling. The i_0 was generally greater for P-IVA than for P-IIB. The i_0 decreased for P-IIIA with cycling which was not the case for P-IVA and P-VA.

The Tafel slope generally falls in the range of 30 to 60 mV/decade of current. There are exceptions which may be attributed to shorting, interference from trapped H₂ and O₂, or passivation. When an experiment was thought to be free of any of the above problems, the Tafel slope was 35 to 45 mV/decade. Due to the scatter in the experimental data, it is difficult to form conclusions about the dependence of Tafel slope on cycling.

2.1.4 Physical Significance of the Polarization Results

The trends shown by the data on open circuit potential and overvoltage (polarization) may be related to the deactivation of the electrode by shape change. As stated in Section 2.1.2, the OCV may be considered Nernstian and it provides a direct indication of OH^- concentration. Since the OCV shows an anodic shift when comparing the OCV of the center to the OCV of the edges, it may be concluded that the concentration of OH^- is higher at the edges than at the center. Thus a pH gradient is established on the Zn electrode. The higher concentration of OH^- contributes to increased dissolution of ZnO at the edges. Since the anodic shift increases with cycling, greater difference in OH^- concentration exist and a greater amount of ZnO can be dissolved from the edges with progressive cycling.

The overvoltage during polarization is higher at the edges than at the center. The magnitude of the difference is such that during cathodic polarization, H_2 evolution begins earlier at the edges. This is equivalent to saying that the amount of Zn deposited is less at the edges than at the center. The overvoltage (or degree of polarization) increases with an increase in cycle number i.e., with progressive cycling, less and less Zn is deposited at the edges. Now, during the anodic process, the Zn dissolution occurs with greater efficiency at the center than at the edges, as indicated by the anodic overvoltage data. Thus more Zn and ZnO are produced at the center, leading to so-called shape change.

The migration of dissolved zincate from the edges to the center occurs during the cathodic process (charging) since the predominant reaction at the center is reduction of zincate with no competition from the H_2 evolution reaction. On the contrary,

the edges support the H_2 evolution reaction right from the beginning of charge.

According to our theory, the lower the anodic shift of OCV and overvoltage during polarization, the lower the shape change. The experimental data obtained from electrode P-IVA, which exhibited minimum shape change after 80 cycles, showed a very low anodic shift and ability to polarize. As further proof, a zinc electrode composition identical to P-IVA displayed a cycle life of 260 in a 20 Ah tri-electrode cell.

3.0 CONCLUSIONS

A new theory for shape change, based on pH gradient and ability of the electrode to polarize is proposed which can explain some of the correlations between battery operating parameters and shape change.

REFERENCES

1. Klein, M. et al, Proceedings 14th Intersociety Energy Conversion Engineering Conference, Boston, 1979, pg. 646.
2. McBreen, J. and Cairns E.J. Advances in Electrochemistry and Electrochemical Engineering, Vol. II, Gerischer, H. and Tobias, C.W. Eds., Wiley, 1978.
3. Baker, B.S., Klein, M., U.S. Patent 3,898,099.
4. McBreen, J., U.S. Patent 3,876,470
5. Gibbard, H.F. et al., Extended Abstracts, No. 118, The Electrochemical Society, Fall 1979 Meeting, Los Angeles, October, 1979.
6. Bockris, J.O'M., et al. J. Electrochem. Soc., 119, 285; 1972.
7. Liu, Ming-Biann, Cook, G.M., and Yao, N.P., Report No. ANL/OEPM-80-1, prepared for DOE under Contract W-31-109-Eng-38; May 1980.
8. Powers, R.W., and Breiter, M.W., J. Electrochem. Soc., 116, 719, 1969.

APPENDIX A

TABLE A.1
ELECTRODE P-IIB

(in 35% KOH with 1% LiOH)

COMPOSITION: 98% ZnO, 2% TFE

		η , mV at:					
SECTION NO.	PROCESS	i _o , A/cm ² x 10 ⁴	m , mV/decade of i	4 mA/cm ² & 1.670 mA/cm ² (cathodic)	12 mA/cm ² & 1.392 mA/cm ² (anodic)	OCV , v	
BEFORE CYCLING							
3	Cathodic	~2.5-4	30-42	~35 (29)	22 (18)	1.349	
3	Anodic	~6	39-40		>250 (68) 17 (7)	1.340	
3	Cathodic	~5	~25	~20	12	1.349	
5	Cathodic	~4.2	~20	~17 (25)	8 (19)	1.356	
5	Anodic	~4	32-33		~250 (52) 19 (9)	1.340	
5	Cathodic	~4.4	28-29	~25	18	1.302	
AFTER 11 CYCLES							
3	Cathodic	~6.3	~30	~35 (15)	15 (9)	1.330	
3	Cathodic	~6.8	~40	~32 (29)	15 (15)	1.339	
3	Anodic	~5.8	~32		~130 (25) 13 (5)	1.334	
5	Cathodic	~9.5-10	27-28	~17 (18)	7 (8)	1.262	
5	Cathodic	~9.5	~30	~20 (32)	8 (14)	1.276	
5	Anodic	~9.4	~33		~90 (35) 7 (6)	1.273	
AFTER 43 CYCLES							
3	Cathodic	~6.3	~45	45	22	1.336	
3	Anodic	5.0-7.4	33-50		140	15	1.354
3	Cathodic	~6.0	~52	41	23		1.352
3	Anodic	~6.0	~59		170	21	1.368
5	Cathodic	~7.5	~30	22	10		1.267
5	Anodic	~9.1	~41		100	8	1.285
5	Cathodic	5.7-7.1	37-48	32	18		1.311
5	Anodic	5.1-5.9	45-66		180	20	1.358
AFTER 57 CYCLES							
3	Cathodic	~6.2	~52	45	21.5		1.361/2
3	Anodic	~4.5	~44		~170	21	1.361
3	Cathodic	~4.8	~45	49	24		1.323
3	Anodic	~4.9	~47		~195	16	1.320
5	Cathodic	~5.0	~42	40	21.5		1.360/1
5	Anodic	~5.0	~45		~135	30	1.354
5	Cathodic	~6.8	~30	23	13		1.271
5	Anodic	7.8-9.2	48-56		~135	10	1.259
AFTER 69 CYCLES							
3	Cathodic	3.7-9.8	32-90	~50	21		1.351
3	Anodic	4.6-8.7	40-96		~190	19	1.362
3	Cathodic	~4.2	40	~51	25		1.342
5	Cathodic	~4.3	40-~31.5	~39	18.5		1.331
5	Anodic	4.9-6.8	40-~62		~185	17-18	1.354
5	Cathodic	8.2	39	~25	12		1.273

* P-IIA (in same electrolyte) appears in parentheses under first two categories.

† See Figure II.1 for explanation of sections.

TABLE A.2
ELECTRODE P-IIC
(in 20% KOH with 1% LiOH)
COMPOSITION: 98% ZnO, 2% TFE

SECTION NO.	PROCESS	$i_0, \text{A/cm}^2 \times 10^4$	$ m , \text{mV/decade of } i$	$\eta, \text{mV at:}$				$ OCV , \text{V}$
				4 mA/cm ² & 1.670 mA/cm ² (cathodic)		12 mA/cm ² & 1.392 mA/cm ² (anodic)		
BEFORE CYCLING								
3	Cathodic	5.1-6.1	34-46	41	19			1.311
3	Anodic	~ 9.5	~ 38			60	9	1.311
3	Cathodic	~ 4.2	~ 25	25	17			1.305
3	Anodic	~ 7.6	~ 32			60	9	1.308
5	Cathodic	~ 4.9	~ 35	34	18			1.301
5	Anodic	5.5-9.5	15-20			22	6	1.300
5	Cathodic	~ 5.8	~ 21	22	15			1.296
5	Anodic	~ 8.8	~ 30			50	7	1.300
AFTER 12 CYCLES								
3	Cathodic	6-7.5	27-39	39	14			1.299
3	Anodic	~ 8.6	~ 45			80	11	1.301
3	Cathodic	~ 5.6	~ 33	29	17			1.298
3	Anodic	~ 6.6	~ 35			95	11	1.304
5	Cathodic	7-8.4	36-46	28	12			1.300
5	Anodic	~ 7.5	~ 35			73	10	1.294
5	Cathodic	~ 8.3	~ 35	23	14			1.285
5	Anodic	~ 7.5	~ 35			86	10	1.295
AFTER 32 CYCLES								
7	Cathodic	~ 4.5 or ~ 8.0	~ 23 or $\sim 37-40$	24	14			1.296
7	Anodic	9.4	32			112	6	1.314
7	Cathodic	5.8	~ 41	21	18			1.315
7	Anodic	6.3-11.5	39-92			135	13	1.324
9	Cathodic	5.2	20	17	11			1.298
9	Anodic	~ 5.6 or 10.2	~ 25 or ~ 63			89	11	1.308
9	Cathodic	6.1 or 6.7	~ 22 or ~ 24	18	10			1.308
9	Anodic	6.1 or 9.8	~ 34 or ~ 64			88	12	1.323
5	Cathodic	5.38	24	19	12			1.295
5	Anodic	9.1 or 13.3	~ 40 or ~ 62			81	8	1.307
5	Cathodic	4.3 or 5.8	~ 21 or ~ 24	21	11			1.314
5	Anodic	6.1 or 9.8	34 or 64			92	12	1.322
AFTER 43 CYCLES								
7	Cathodic	11	43	22	8.5			1.331
7	Anodic	7-11	41-83			100	12.5	1.323
5	Cathodic	9.0	29	19	8.5			1.326
5	Anodic	6.2- ~ 10.5	34-69			85	12.0	1.321
AFTER 57 CYCLES								
7	Cathodic	11	54	39	11			1.347
7	Anodic	7.4	70			115	14	1.328/9
7	Cathodic	5.0-7.0	38-52	30	17			1.316
7	Anodic	6.6-11.5	28-67			121	9	1.341
5	Cathodic	8.4-9.0	42-50	43	15			1.330
5	Anodic	8.4	75			190	12.5	1.320
5	Cathodic	5.6	35	40	20			1.305
9	Anodic	7.6-10.5	47-78			162	13	1.332
AFTER 69 CYCLES								
7	Cathodic	9.8 or ~ 12	79 or 105-119	80	18			1.352
7	Anodic	11.5	122			155	13	1.345
7	Cathodic	15-33	62-124	25	9			1.342
7	Anodic	10.5	99			122	16	1.329
6	Cathodic	8-13	63-125	72	21			1.333
6	Anodic	10.5-12.5	119-155			~ 265	20	1.342
6	Cathodic	19-38	54-101	19	9			1.334
6	Anodic	10.5-12	94-119			125	17	1.329

TABLE A.3
ELECTRODE P-IIID
(in 6% KOH with 1% LiOH)
COMPOSITION: 98% ZnO, 2% TFE

SECTION NO.	PROCESS	$i_0, A/cm^2 \times 10^4$	$ m $		$ n , mV$		i		$ OCV , v$
			mV/decade	of i	4 mA/cm ² & 1.670 mA/cm ² (cathodic)	12 mA/cm ² & 1.392 mA/cm ² (anodic)			
BEFORE CYCLING									
3	Cathodic	2.3 or 3.5-4.0	57 or 85	89	55				1.215/6
3	Anodic	4.4 or 6.1	54 or 75			332	27		1.242
3	Cathodic	3.75 or 4.1	57.5 or 62	63	37				1.235
3	Anodic	5.5 or 7.0	62 or 80			173	25		1.256
5	Cathodic	3.3 or 4.0	67 or 80	75	49				1.202
5	Anodic	4.0 or 6.2	59.5 or 55			376	10		1.233
5	Cathodic	3.5 or 5.3	41 or 51	36	26				1.215
5	Anodic	5.9 or 7.3	51 or 64			154	19		1.240
AFTER 12 CYCLES									
3	Cathodic	4.0 or 5.1	32 or 40	35	20.5				1.262
3	Anodic	6.2	41			107	15		1.242
5	Cathodic	4.9 or 5.3	37.6 or 40	33	20				1.262
5	Anodic	9.5	41			78	10		1.214
AFTER 32 CYCLES									
3	Cathodic	6.2	42	35	18				1.202
3	Anodic	8.6	60			150	15		1.199
3	Cathodic	6.0	65	54	29				1.213
5	Cathodic	6.6	19	16	11				1.131
5	Anodic	14	47			100	5		1.127
5	Cathodic	5.2	30	25	14				1.153
AFTER 43 CYCLES									
3	Cathodic	4.6	53	65	28				1.227
3	Anodic	5.2	50			300	20		1.243
5	Cathodic	7.0	55	45	21				1.212
5	Anodic	7.6	45			100	12		1.210
AFTER 57 CYCLES									
6	Cathodic	6 - 9.6	40 - 80	55	19				1.220
6	Anodic	33	106			60	9		1.194
9	Cathodic	8	73	52	26				1.221
9	Anodic	13	113			122	18		1.262
5	Cathodic	9.6	58	35	14				1.207
5	Anodic	30	91			57	10		1.179
5	Cathodic	4.5 - 6	49 - 79	54	29				1.210
5	Anodic	14	114			130	17		1.253
AFTER 69 CYCLES									
9	Cathodic	-	-	-	-				1.193
7	Anodic	11	125			155	24		1.242
7	Cathodic	6.2 or 16	68 or 120	55	29.5				1.184
7	Anodic	14 - 23	100 - 185			280	16		1.204
5	Cathodic	9 or 28	60 or 119	40	19				1.185
5	Anodic	20	135			123	16		1.208
5	Cathodic	5.6 or 23	49 or 108	41	23				1.184
5	Anodic	25	137			240	9		1.187

TABLE A.4
ELECTRODE P-IIIE
(in 11% KOH with 1% LiOH)
COMPOSITION: 98% ZnO, 2% TFE

		$ n , mv \text{ at}$					
SECTION NO.	PROCESS	$i_0, A/cm^2 \times 10^6$	$ m , mv/decade \text{ of } i$	4 mA/cm ² 1.670 mA/cm ² (cathodic)	12 mA/cm ² & 1.392 mA/cm ² (anodic)	$ OCV , v$	
<u>BEFORE CYCLING</u>							
3	Anodic	5.6	57		262*	23	1.277
3	Cathodic	4.4	47	45	29		1.263
3	Anodic	9.6	59		120	13	1.275
3	Cathodic	4.8	61	57	37		1.273
3	Anodic	7.2-9	72-89		218	22	1.293
5	Anodic	5.6	60		228*	21	1.268
5	Cathodic	6.4-8.4	34-47	26	15		1.222
5	Anodic	8.4	35		78	10	1.233
5	Cathodic	4.8	43	30	18		1.227
5	Anodic	9.6	59		147	13	1.247
<u>AFTER 14 CYCLES</u>							
3	Cathodic	7.0	65	45	23		1.261
3	Anodic	19-40	79-136		54	8	1.285
5	Cathodic	7.4	50	23	21		1.247
5	Anodic	32	94		65	10	1.279
<u>AFTER 32 CYCLES</u>							
3	Cathodic	7.6	56	47	18		1.274
3	Anodic	18	122		101	15	1.271
3	Cathodic	8.8	61	40	17		1.281
5	Cathodic	11	57	37	13		1.264
5	Anodic	23	117		91	11	1.261
5	Cathodic	13.5	61	29	13		1.271
<u>AFTER 43 CYCLES</u>							
3	Cathodic	8-11	56-83	50	17		1.291
3	Anodic	17	139		140	16	1.288
3	Cathodic	6.6	62	49	24		1.282
5	Cathodic	10	53	35	12		1.280
5	Anodic	22	140		105	11	1.280
5	Cathodic	11	57	32	17		1.272
<u>AFTER 57 CYCLES</u>							
3	Cathodic	9.2	73**	55	18		1.292
3	Anodic	13.5	113-130		130	17	1.294/5
3	Cathodic	7	61	46	22.5		1.292
3	Anodic	21	220†		162	14.5	1.295/6
5	Cathodic	13.5	73†	35	14		1.288
5	Anodic	17.5	120		83	13	1.290
5	Cathodic	13.5	65	30	14.5		1.282
5	Anodic	21.5	168†		132	10.5	1.291/2
<u>AFTER 69 CYCLES</u>							
3	Cathodic	6.8	67	113**	25		1.322
3	Anodic	11 or 7.2	117 or 68		196	20.5	1.306
3	Cathodic	6.2	64	55	228		1.310
3	Anodic	16.5	82		309	21	1.308/9
5	Cathodic	7.0	35	73**	13		1.317
5	Anodic	16 or 10.8	122 or 70		110	13	1.305
5	Cathodic	10	53	31	16		1.294
5	Anodic	18	102		210	10.5	1.304/5

* High values probably due to high degree of self discharge. Before measurements, cell had been at open circuit for ~ 60 hrs.

** For this experiment, the rise in voltage with increase in current was more pronounced than usual, even at low currents.

† Values seem higher than they should be probably due to reactant depletion.

TABLE A.5
ELECTRODE P-IIIA

(in 35% KOH with 1% LiOH)
COMPOSITION: 93% ZnO, 5% CdO, 2% TFE

		$ n , mV \text{ at}$						
SECTION NO.	PROCESS	$i_0, A/cm^2 \times 10^4$	$ m , mV/decade \text{ of } i$	4 mA/cm^2		12 mA/cm^2		$ OCV , V$
				1.670 mA/cm^2 (cathodic)		1.392 mA/cm^2 (anodic)		
<u>BEFORE CYCLING</u>								
3	Cathodic	34	23	23	10.5			1.341/2
3	Anodic	21 or 45 *	52 or 140 *			78	5.5	1.337/8
3	Cathodic	37	45	22	15			1.335
3	Anodic	19 or 32 *	52 or 98 *			80	6.5	1.337
5	Cathodic	45 or 350 *	31 or 152 *	18	8.5			1.328/9
5	Anodic	41	101 **			71	6	1.325/6
5	Cathodic	10.5 **	25	16	12			1.317
5	Anodic	12 or 35 *	44 or 85 *			75	7.5	1.323/4
<u>AFTER 12 CYCLES</u>								
3	Cathodic	13.5†	59†	27	12.5			1.304/5
3	Anodic	24.5	~135			110	10.5	1.302/3
3	Cathodic	8-14.5	50-113	33	10			1.307
3	Anodic	17.5	119			142	13	1.319/20
5	Cathodic	35-40†	59-75†	12	5.5			1.227/8
5	Anodic	32	108-122			70	5	1.218
5	Cathodic	22-40	42-70	16	7.5			1.222
5	Anodic	18	106			145	11	1.305
<u>AFTER 32 CYCLES</u>								
3	Cathodic	7.4-10.2	52-70	40	9(uncertain)			1.342
3	Anodic	14.4	119			200	16.5	1.336/7
1	Cathodic	13	52	41	23			1.324
1	Anodic	13	97			~315	15	1.342
5	Cathodic	9	58	37	18			1.325/6
5	Anodic	13.4	107			188	14	1.323
5	Cathodic	9-19.5	42-80	25	14.5			1.291/2
5	Anodic	15.5	105			202	12.5	1.327/8
<u>AFTER 43 CYCLES</u>								
1	Cathodic	6.4	61	50	25.5			1.339/40
1	Anodic	8 or 17	77 or 200			230	20.5	1.341
1	Cathodic	5.6-8.8	44-59	35	20			1.340
1	Anodic	8.8-16.2	72-156			255	17.5	1.346
5	Cathodic	8.2-9.4	50-55	34	17			1.333
5	Anodic	8.6 or 18.2	67 or 190			227	17	1.332
5	Cathodic	8.4-17	38-53	25	14			1.324
5	Anodic	11.5-21	75-160			148	11.5	1.339
<u>AFTER 57 CYCLES</u>								
1	Cathodic	3.9-7.6	40-75	62	26			1.333
1	Anodic	4.5-7.8	45-84			335	22.5	1.318/9
1	Cathodic	4.5	31	50	30.5			1.313/4
1	Anodic	3.8-7.2	36-67			272	20	1.312
5	Cathodic	8.8	54	38	17			1.302/3
5	Anodic	7.8-13	37-77			233	13.5	1.243
5	Cathodic	7.0	43	32	18.5			1.264/5
<u>AFTER 69 CYCLES</u>								
1	Cathodic	4.1	44	62	27			1.335
1	Anodic	4.4	50			355	25.5	1.336/7
1	Cathodic	3.2	42	58	30.5			1.322
1	Anodic	4.7 (estimated)				~370	25.5	1.333
5	Cathodic	6.0	31	25	14.5			1.331
5	Anodic	7.4	51			320	16	1.333
5	Cathodic	8-11.5	40-50	27	16			1.280
5	Anodic	5.8	41			~320	15	1.319

* These values depend on the points chosen to determine the Tafel Slope.

** The Tafel area was probably not reached at the values of current densities used in this study, or, a short developed.

† A sharp rise in voltage occurred prematurely and thus very few points could be used in the determination of the Tafel Slope.

TABLE A.6
ELECTRODE P-IVA

(in 35% KOH, 1% LiOH)

COMPOSITION: 85% ZnO, 13% Mixed Oxides and 2% TFE

		η , mV at					
SECTION No.	PROCESS	i _o , A/cm ² x 10 ⁴	m , mV/decade of i	4 mA/cm ² & 1.670 mA/cm ² (cathodic)	12 mA/cm ² & 1.392 mA/cm ² (anodic)	ocv , v	
<u>BEFORE CYCLING</u>							
3	Cathodic	12*,12	67	37	14.5	1.353/4	
3	Anodic	23-36*,32	80		55	6 1.339	
3	Cathodic	35*	-†	12	6	1.339	
3	Anodic	300-380*	-†		5	1 1.339	
5	Cathodic	14*,11	60	33	13	1.352	
5	Anodic	33*, 47	105		41	5.5 1.336	
5	Cathodic	262*	-†	9	4	1.338	
5	Anodic	247*	-†		5	1 1.338	
<u>AFTER 12 CYCLES</u>							
3	Cathodic	86.7*,86	16	6	2	1.349/50	
3	Anodic	141.9*,140	97		11	1 1.348	
5	Cathodic	142.6*	-	3.5	1.5	1.346/7	
5	Anodic	179.3*,220	99		9	0.5 1.339	
<u>AFTER 32 CYCLES</u>							
3	Cathodic	63.2*,30-68	38-83	8	2	1.356	
3	Anodic	44.2*	-		23	1.5 1.358/9	
3	Cathodic	17.7*,17.5	46	21	12.5	1.346/7	
3	Anodic	16.2*,18	49		45	10.5 1.345	
5	Cathodic	38.4*,40-96	30-53	9	5.5	1.340/1	
5	Anodic	71.7*, 170	127		15	2.5 1.344	
5	Cathodic	18.3*,13-45	21-31	16	11.5	1.333/4	
5	Anodic	23.8*,29	68		44	7.5 1.339/40	
<u>AFTER 43 CYCLES</u>							
3	Cathodic	19.1*,10.5-24	39-80	21	10.5	1.349/50	
3	Anodic	32.9*,32	62		10	5 1.349	
3	Cathodic	14.6*, 9.5	39	27	14.5	1.344/5	
3	Anodic	32.6*, 17-23	68-93		75	11.5 1.350/1	
5	Cathodic	35.3*,43	32	12	6	1.345	
5	Anodic	47.1*,38-48	48-60		7	3.5-4 1.345/6	
5	Cathodic	27.1*	-	11	7	1.341	
5	Anodic	40.2*,30-68	44-115		28	4.5 1.343/4	
<u>AFTER 57 CYCLES</u>							
3	Cathodic	12.5	48	24	11	1.347	
3	Anodic	42.3*,23-64	30-52		20	3.5 1.352/3	
5	Cathodic	58	46	15	9	1.339/40	
5	Anodic	67.6*, 68	42		15	2.5 1.343/4	
<u>AFTER 69 CYCLES</u>							
3	Cathodic	8.4	40	28	12	1.351	
3	Anodic	14.4*,7.4-14	40-75		35	11 1.355/6	
3	Cathodic	13.8*,7-16	40-74	30	15.5	1.338/9	
5	Cathodic	16-24	40-53	13	5	1.307	
5	Anodic	28.3*,13-28	35-92		17	6.5 1.347/8	
5	Cathodic	23.3*, 32	37	16	9.5	1.333/4	

* These values were obtained from the plots of E vs i as opposed to the usual E vs $\log i$. In this case, for low values of η , the slope is equal to $RT/nF i_o$, and thus i_o can be calculated from the value of the slope.

† The Tafel region was probably not reached at the currents used in this study (all values of η were less than about 20 mV)

TABLE A.7
ELECTRODE P-VA

(in 35% with 1% LiOH)

COMPOSITION: 89% ZnO, 7% CdO, 1% Fe₂O₃ and 3% TFE

SECTION NO.	PROCESS	i_o , A/cm ² $\times 10^4$	$ m $ mV/decade of i	$ n $, mV at		$ ocv $, v	
				4 mA/cm ² & 1.670 mA/cm ² (cathodic)	12 mA/cm ² 1.392 mA/cm ² (anodic)		
<u>BEFORE CYCLING</u>							
3	Cathodic	35.8 - 50.9*	-	10	6	1.340	
3	Anodic	38.3*, 27	42		28	5	1.344
5	Cathodic	34.7*	-	11	6.5		1.347
5	Anodic	39.9*, 18-40	40-56.		28	4	1.343
<u>AFTER 12 CYCLES</u>							
3	Cathodic	13	40	24	4.5		1.351/2
3	Anodic	35.1*, 35	48		27	5.5	1.345/6
3	Cathodic	25.7, 41	32	13	8.5		1.331/2
5	Cathodic	23-32	35-75	9	1.0		1.356/7
5	Anodic	58.4*, 52	23		12	3.0	1.345
5	Cathodic	25.2*	-	13	8.5		1.331/2

* These values were obtained from plots of E vs i , where, for low values of η , the slope is equal to $RT/nF i_o$.

TABLE A.8

COMPARISON OF POLARIZATION DATA BEFORE CYCLING

ELECTRODE	[OH ⁻], M	SECTION NO.	EXP. NO.	CATHODIC PROCESS		ANODIC PROCESS			
				$ \eta , \text{mV at:}$		$ \eta , \text{mV at:}$			
				4 mA/cm ²	1.670 mA/cm ²	OCV , V	12 mA/cm ²	1.392 mA/cm ²	OCV , V
P-IIB	9.1	3	1	22	12	1.349	90*	4	1.352
			2	35 (29)	22 (18)	1.348	>250* (68)	17 (7)	1.340
			2	23	18	1.302	300* (52)	19 (9)	1.340
P-IIA given (9.1) in parenthesis		5	1	15 (25)	8 (19)	1.356	20	5	1.354
			2	23	18	1.302	300* (52)	19 (9)	1.340
			2	23	18	1.302	300* (52)	19 (9)	1.340
P-IIIA	9.1	3	1	23	10.5	1.341/2	78	5.5	1.337/8
			2	22	15	1.335	80	6.5	1.337
		5	1	18	8.5	1.328/9	71	6	1.325/6
			2	16	12	1.317	75	7.5	1.323/4
			2	16	12	1.317	75	7.5	1.323/4
P-IVA	9.1	3	1	37	14.5	1.353	55	6	1.339
			2	12	6	1.339	5	1	1.339
		5	1	33	13	1.352	41	5.5	1.336
			2	9	4	1.338	5	1	1.338
P-VA	9.1	3	1	10	6	1.348	28	5	1.344
			1	11	6.5	1.347	28	4	1.343
P-IIC	4.8	3	1	41	19	1.311	60	9	1.311
			2	25	17	1.305	60	9	1.308
		5	1	34	18	1.301	22	6	1.300
			2	22	15	1.296	50	7	1.300
			2	22	15	1.296	50	7	1.300
P-IIIE	2.64	3	1	-	-	-	262**	23	1.277
			2	45	29	1.263	120	13	1.275
			3	57	37	1.273	218	22	1.293
		5	1	-	-	-	228**	21	1.268
			2	26	15	1.222	78	10	1.233
			3	30	18	1.227	147	13	1.247
			3	30	18	1.227	147	13	1.247
P-IID	1.6	3	1	89	55	1.215/6	332	27	1.242
			2	63	37	1.235	173	35	1.250
		5	1	75	49	1.202	276	18	1.222
			2	36	26	1.215	154	19	1.240
			2	36	26	1.215	154	19	1.240

* Very sharp drops were observed in these cases after approximately 6 mA/cm², probably due to reactant depletion. These results are not considered valid.

** See note under * for Table A.4, this report.

TABLE A.9
COMPARISON OF POLARIZATION DATA AFTER INITIAL CYCLING

ELEC- CYCLE TRODE COMPL.	[OH ⁻], M	SECTION NO.	EXP. NO.	CATHODIC PROCESS		ANODIC PROCESS			
				η , mV at:		η , mV at:			
				4 mA/cm ²	1.670 mA/cm ²	OCV , V	12 mA/cm ²	1.392 mA/cm ²	OCV , V
P-IIB 11	9.1	3	1	35	15	1.330	~130	13	1.334
			2	32	15	1.339	"	"	"
		5	1	17	7	1.262	~90	7	1.273
			2	20	8	1.276	"	"	"
P-IIIA 12	9.1	3	1	21	12.5	1.304/5	110	10.5	1.302/3
			2	35	18	1.297	142	13	1.319/20
		5	1	12	5.5	1.227/8	70	5	1.218
			2	16	7.5	1.222	145	11	1.305
P-IVA 12	9.1	3	1	6	2	1.349/50	11	1	1.348
		5	1	3.5	1.5	1.346/7	9	0.5	1.339
P-VA 12	9.1	3	1	24	4.5	1.351/2	27	5.5	1.345/6
		3	2	13	8.5	1.331/2	-	-	-
		5	1	9	1.0	1.356/7	12	3.0	1.345
		5	2	13	8.5	1.331/2	-	-	-
P-IIC 12	4.8	3	1	39	14	1.299	80	11	1.301
			2	29	17	1.298	95	11	1.304
		5	1	28	12	1.300	73	10	1.294
			2	22	14	1.285	86	10	1.295
P-IIIE 14	2.64	3	1	45	23	1.261	54	8	1.285
		5	1	23	21	1.247	65	10	1.279
P-IID 12	1.6	3	1	35	20.5	1.262	107	15	1.242
		5	1	33	20	1.262	78	10	1.214

TABLE A.10
COMPARISON OF POLARIZATION DATA AFTER 32 CYCLES

ELECTRODE	[OH ⁻], M	SECTION NO.	EXP. NO.	CATHODIC PROCESS		ANODIC PROCESS			
				$ \eta $, mV at:		$ \eta $, mV at:			
				4 mA/cm ²	1.670 mA/cm ²	OCV, V	12 mA/cm ²	1.392 mA/cm ²	OCV, V
P-IIC	4.8	7	1	24	14	1.296	112	6	1.314
		7	2	21	18	1.315	135	13	1.324
		9	1	17	11	1.298	89	11	1.308
		9	2	18	10	1.308	88	12	1.323
		5	1	19	12	1.295	81	8	1.307
		5	2	21	11	1.314	92	12	1.322
P-IIIE	2.64	3	1	47	18	1.274	101	15	1.271
			2	40	17	1.281	-	-	-
		5	1	37	13	1.264	91	11	1.261
			2	29	13	1.271	-	-	-
P-IIID	1.6	3	1	35	18	1.202	~150	15	1.199
		3	2	~52	29	-	-	-	-
		5	1	16	11	1.131	~100	5	1.127
		5	2	24	14	-	-	-	-
P-IIIA	9.1	3	1	40	9(uncertain)	1.342	200	16.5	1.336/7
		1	2	41	23	1.324	~315	15	1.342
		5	1	37	18	1.325/6	188	14	1.323
		5	2	25	14.5	1.291/2	202	12.5	1.327/8
P-IVA	9.1	3	1	8	2	1.356	23	1.5	1.358/9
		3	2	21	12.5	1.346/7	45	10.5	1.345
		5	1	9	5.5	1.340/1	115	2.5	1.344
		5	2	16	11.5	1.333/4	44	7.5	1.339/40

TABLE A.11
COMPARISON OF POLARIZATION DATA AFTER 43 CYCLES

ELECTRODE	[OH ⁻], M	SECTION NO.	EXP. NO.	CATHODIC PROCESS		ANODIC PROCESS			
				$ \eta $, mV at:		$ \eta $, mV at:			
				4 mA/cm ²	1.670 mA/cm ²	OCV , V	12 mA/cm ²	1.392 mA/cm ²	OCV , V
P-IIB	9.1	3	1	45	22	1.336	140	15	1.354
			2	41	23	1.352	170	21	1.368
		5	1	22	10	1.267	100	8	1.285
			2	32	18	1.311	180	20	1.358
P-IIIA	9.1	1	1	50	25.5	1.339/40	230	20.5	1.341
		1	2	35	20	1.340	255	17.5	1.346
		5	1	34	17	1.333	227	17	1.332
		5	2	25	14	1.324	148	11.5	1.339
P-IVA	9.1	3	1	21	10.5	1.349/50	10	5	1.349
		3	2	27	14.5	1.344/5	75	11.5	1.350/1
		5	1	12	6	1.345	7	3.5	1.345/6
		5	2	11	7	1.341	28	4.5	1.343/4
P-IIC	4.8	7	1	23	8.5	1.331	~105	12.5	1.323
		5	1	19	8.5	1.326	~90	12.0	1.321
P-IIIE	2.64	3	1	50	17	1.291	140	16	1.288
			2	49	24	1.282	-	-	--
		5	1	35	12	1.280	~105	11	1.280
			2	32	17	1.272	-	-	--
P-IID	1.6	3	1	65	28	1.227	>300	20	1.243
		5	1	45	21	1.212	100	12	1.210

TABLE A.12
COMPARISON OF POLARIZATION DATA AFTER 57 CYCLES

ELECTORDE	[OH-] M	SECTION NO.	EXP. NO.	CATHODIC PROCESS			ANODIC PROCESS		
				η , mV at:			η , mV at:		
				4 mA/cm ²	1.670 mA/cm ²	OCV , V	12 mA/cm ²	1.392 mA/cm ²	OCV , V
P-IIB	9.1	3	1	45	21.5	1.362/1	120	21	1.361
			2	49	24	1.323	195	16	1.320
		5	1	40	21.5	1.360/1	135	20	1.354
			2	23	13	1.271	135	10	1.259
P-IIIA	9.1	3	1	62	26	1.333	335	22.5	1.318/9
		3	2	50	30.5	1.313/4	272	20.0	1.312
		5	1	38	17	1.302/3	233	13.5	1.243
		5	2	32	18.5	1.264/5	165	9.0	1.212
P-IVA	9.1	3	1	24	11	1.347	20	3.5	1.352/3
		5	1	15	9	1.339/40	15	2.5	1.343/4
P-IIC	4.8	7	1	39	11	1.347	115	14	1.328/9
			2	40	20	1.316	121	9	1.341
		5	1	43	15	1.330	190	12.5	1.320
		5(Cath.)	2	30	17	1.305	162	13	1.332
		9(An.)							
P-IIIE	2.64	3	1	55	18	1.292	130	17	1.294/5
			2	46	22.5	1.292	162	14.5	1.295/6
		5	1	35	14	1.288	83	13	1.290
			2	30	14.5	1.283	132	10.5	1.291/2
P-IIID	1.6	6	1	55	19	1.220	60	9	1.194
		9	2	52	26	1.221	122	18	1.262
		5	1	35	14	1.207	57	10	1.179
			2	54	29	1.210	130	17	1.253

TABLE A.13
COMPARISON OF POLARIZATION DATA AFTER 69 CYCLES

ELECTRODE	[OH ⁻], M	SECTION NO.	EXP. NO.	CATHODIC PROCESS			ANODIC PROCESS		
				η , mV at:		OCV , V	η , mV at:		OCV , V
				4 mA/cm ²	1.670 mA/cm ²		12 mA/cm ²	1.392 mA/cm ²	
P-IIB	9.1	3	1	~50	21	1.251	~190	19	1.362
		3	2	~51	25	1.342	-	-	-
		5	1	~39	18.5	1.331	~185	17-18	1.354
		5	2	~25	12	1.273	-	-	-
P-IIIA	9.1	3	1	62	27	1.335	355	25.5	1.336/7
		3	2	58	30.5	1.322	~370	25.5	1.333
		5	1	25	14.5	1.331	320	16	1.333
		5	2	27	16	1.280	~320	15	1.319
P-IVA	9.1	3	1	28	12	1.351	35	11	1.355/6
		3	2	30	15.5	1.330/9	-	-	-
		5	1	13	5	1.307	17	6.5	1.347/8
		5	2	16	9.5	1.333/4	-	-	-
P-IIC	4.8	7	1	80*	18*	1.352	155	13	1.345
		7	2	25	9	1.342	112	16	1.329
		6	1	72*	21*	1.333	~265	20	1.342
		6	2	19	9	1.334	125	17	1.329
P-IIIE	2.64	3	1	113†	25	1.322	196	20.5	1.306
		3	2	55	~28	1.310	309	21	1.308/9
		5	1	73	13	1.317	110	13	1.305
		5	2	31	16	1.294	210	10.5	1.304/5
P-IIID	1.6	9(Cath) 7(Anod)	1	-	-	1.193	155	24	1.242
		7	2	55	29.5	1.184	200	16	1.204
		5	1	40	19	1.185	123	16	1.208
		5	2	41	23	1.184	240	9	1.187

* Early gassing is presumed to have caused the high η value (compare with result from Experiment No. 2).

** See note under ** for Table A.4, this report

SECTION IV
SEPARATOR DEVELOPMENT FOR
NICKEL-ZINC CELLS - (TASK III)

1.0 INTRODUCTION

Separators which are used in secondary batteries have two primary functions; To keep positive and negative plates physically apart so electronic current will be constrained to flow outside the cell; and to allow ionic transport in the electrolyte between plates, as necessary. These functions lead to the following requirements and objectives for the separator:

- physically and chemically stable in the cell environment,
- low electrical resistance,
- retards shape change of the zinc electrode and dendritic growth.

To meet the first requirement, organic or inorganic material proposed for the separator should be chemically inert and not swell in the electrolyte. To satisfy the second requirement, it is necessary to have material which swells in the electrolyte or possesses a large pore size. The mechanism of shape change of the negative electrode and zinc dendritic growth are not fully understood but it is possible to formulate two main properties for the separator material which are desirable: To prevent zinc diffusion through the separator; and create conditions for uniform zinc deposition on the negative electrode during battery charging. Reduction of the zinc diffusion rate can be achieved by a separator material which swells in electrolyte. In this case the separator works as a selective membrane. Another way to prevent zinc penetration is to produce the separator material with a uniform pore size which is smaller than the diameter of $\text{Zn(OH)}_4^{=}$ ions and larger than OH^- ion.

ENERGY RESEARCH CORPORATION

Analysis of these requirements indicates that the material should possess properties which are not necessarily compatible:

- to swell and have high chemical and physical stability
- to be easily permeable for OH^- and impermeable for the ZnO_2^- ion; however the ions are almost the same size ($\text{OH}^- = 15\text{\AA}$; $\text{ZnO}_2^- = 20$ to $25\text{\AA}$).

Therefore attempts to produce separator material focused on three areas:

1. To make a wettable separator, with membrane type permeability which can prevent rapid zinc penetration but which is not stable in an electrolyte environment (cellulosics and PVA separators).
2. To produce microporous non-wettable separator material with capillary type permeability. This class of separator materials is stable in the electrolyte environment but cannot prevent zinc penetration, (polyethylene (polypropylene-based separators).
3. To produce a family of separator materials which combines properties of both classes. This was achieved by grafting or coating wettable polymer on a non-wettable porous matrix. These separator materials exhibit improved properties but are much more expensive and are still limited in durability by degradation of the wettable layer.

ERC production of separator materials has concentrated on several areas:

- improving the chemical and physical stability of PVA material by crosslinking with different reagents.
- formation of a microporous separator which has excellent stability in the electrolyte environment.
- creating a polymer-based separator material which has uniform properties.

ERC has found a new way to produce material possessing the overall desired properties: The separator is formed as a thin film from a polymer blend solution which contains a polymer matrix, and uniformly incorporated in this matrix is a wettable polymer. Variation of composition and formation parameters allows production

ENERGY RESEARCH CORPORATION

of films with a wide range of properties.

ERC has concluded that, together with creating a separator material, it is necessary to design a separator system which can combine all the desired properties and will not be expensive to produce.

Optimum design of the separator system and separator material should be based on an understanding of the processes occurring in the battery over a large number of cyclic tests under real cell conditions.

Basic work in developing several new compositions and in improving existing materials to meet requirements for separator films in Ni-Zn batteries has already been reported. The most important laboratory tests for evaluation of the separator materials were also developed.

The goals of research efforts during this year were:

- improvements in composition and production technology of the separator materials previously developed.
- study of the work conditions and failure modes of various Ni-Zn cells containing different components.
- creation of new separator systems which substantially increase the cycle life of Ni-Zn cells.

2.0 TECHNICAL DISCUSSION

2.1 IMPROVED COMPOSITION AND PRODUCTION TECHNOLOGY FOR CROSS-LINKED PVA SEPARATOR FILMS

Commercially available PVA films which are used in alkaline batteries show low electrical resistance but poor long-term stability in the electrolyte environment. Attempts to improve the chemical stability by crosslinking have led to increased brittleness and cracking of the separator film. Therefore,

employing a crosslinking agent which can correct the chemical deficiencies and not aggravate mechanical properties of PVA should increase the cycle life of the cell.

2.1.1 Various Compositions for Improved Crosslinked PVA Separator

Crosslinked PVA films were prepared by film casting on a metal sheet utilizing doctor blades. PVA was crosslinked by reaction with:

1. A mixture of dimethylol urea (DMU) and boric acid
2. Only boric acid
3. Only DMU
4. Heating in open air

Films were evaluated for various properties prior to testing in cells with only one layer of separator film. Results of the evaluation are given in Tables III.1 through III.3. Stability of mechanical properties in KOH for PVA based films was also determined. Different films were tested before and after exposure in KOH. Tensile strength and deflection were measured (see Table III.3).

Results of testing PVA based separator films (Table III.3) indicated that the best properties are obtained with PVA films which were crosslinked by a mixture of DMU and boric acid. PVA crosslinked only by DMU exhibited excessive swelling. Both of the films show an increase in cycle life in cells with only one layer of separator.

Another variation was tested in which PVA was crosslinked by reaction with sucrose and DMU and by heating in air. A filler was added to reduce swelling and wrinkling of PVA films in KOH. Another method¹ was used for crosslinking a PVA and sucrose blend.

ENERGY RESEARCH CORPORATION

TABLE III.1
CHARACTERISTICS OF VARIOUS PVA FILMS

COMPOSITON	ELECTRICAL RESISTANCE DATA†		DEGREE OF CROSSLINKING %	MEASURING CONDITIONS	COMMENTS
	ELECTRICAL RESIS., $m\Omega \cdot in^2/mil.$	COMMENTS			
PVA + DMU 90% 10%	40-60	Film Turns Brown	85-90	Heated at 130°C in Vacuum oven for 3 hrs.	Not soluble in water, only swells.
PVA + BA* 87% + 13%	40-50	Turns less brown	Soluble in water	"	Dissolved in water
PVA + DMU + BA 87% + 8.5% + + 4.5%	50-75	Turns less brown	85-90	"	Not soluble in water, only swells.
COMMERCIAL PVA	30-50	Turns brown	70-80	Heated at 130°C until it turned brown	"

* Boric Acid

† All films had a dry thickness of 2.0-2.5 mil. and were aged at 50°C for 4 days.

ENERGY RESEARCH CORPORATION

TABLE III.2
TESTING OF VARIOUS PVA FILMS

COMPOSITION	TENSILE HANGING TEST		WATER ABSORPTION TEST		
	NO. OF DAYS	COMMENTS	% WT. GAIN	CONDITIONS	COMMENTS
COMMERCIAL PVA	3-4	Film turned brown	40.90	Heated at 135°C until it turned brown.	Not soluble in water, only swells.
PVA + DMU 90% + 10%	8-9	Film turned brown	32.83	Heated at 135°C for 2 to 3 hrs.	Swells but not soluble.
PVA + BA* 87% + 13%	3-6	Film turned less brown	Soluble in water	Heated at 135°C for 2 to 3 hrs.	Dissolved in water. Film very brittle.
PVA + DMU + BA 87% + 8.5% + 4.5%	8-9	Film turned less brown.	34.79	Heated at 130°C in oven for 2 to 3 hrs.	Swells only. Not soluble.

* Boric Acid

† Conditions: 45% KOH at 65°C; hanging length of film was 1-1/2 to 2 inches.

TABLE III.3
TENSILE STRENGTH AND DEFLECTION OF VARIOUS PVA FILMS

COMPOSITION	THICKNESS	BEFORE EXPOSURE		AFTER EXPOSURE		CONDITION AFTER SOAKING IN KOH FOR 60 HOURS:
		FORCE lb.	DEFLECTION in.	FORCE, lb.	DEFLECTION in.	
PVA + BA	2.4	8.96 7.28 6.24 <u>4.55</u>	0.028 0.050 0.030 <u>0.042</u>	1.97 2.45 2.64 <u>1.80</u>	0.144 0.202 0.193 <u>0.148</u>	The film with 1 gm BA was physically less stable than in its original state.
AVERAGE:		6.76	0.039	2.22	0.172	
PVA + 15% BA	2.4	9.69 5.87 13.41 <u>16.30</u>	0.062 0.031 0.070 <u>0.090</u>	2.53 2.84 2.75 <u>2.74</u>	0.178 0.277 0.230 <u>0.200</u>	The film with 1.5 gm BA was physically less stable than in its original state.
AVERAGE:		11.32	0.063	2.72	0.221	
PVA + 10% DMU	2.6	11.42 10.70 12.68 <u>9.71</u>	0.069 0.072 0.065 <u>0.069</u>			The film with DMU showed good physical properties under tensile strength test. Film's elasticity was very high.
AVERAGE:		11.13	0.069			
PVA + 15% DMU	2.2	11.42 13.08 8.69 <u>9.68</u>	0.098 0.103 0.130 <u>0.090</u>			The film with DMU showed the same results as above when tested for tensile strength.
AVERAGE:		10.72	0.105			

A PVA film containing 5% sucrose was post-treated and cross-linked by the following method: 200g of Na_2SO_4 was added to one liter of water along with 20 cc of H_2SO_4 . The film was treated with this solution for 15 minutes, then washed thoroughly with water and dried at room temperature. Because the film swells somewhat during washing and wrinkles during drying, it is difficult to make bags from this film. Therefore, the zinc electrode was coated with PVA solution + 5% sucrose.

Measurements of electrical resistance and durability in KOH for PVA based films are given in Tables III.5 and III.6. Results obtained indicate that the degree of crosslinking was low for all films tested. Electrical resistance and stability in KOH is almost the same for different PVA based compositions.

Cells with these separator films were tested and the results, given in Table III.4, indicate that the shape change of the Zn electrode depends on the degree of swelling of the separator material. Addition of the filler resulted in reduction of the degree of swelling and shape change in the Zn electrode. But cycle life of the cells did not increase because zinc dendrites grew through the separator. This fact is probably related to low adhesion between PVA polymer and filler. Therefore, space for zinc dendrites to grow was created around the particles of the filler.

In another attempt to increase chemical stability, PVA was crosslinked by reaction with glutaraldehyde and p-phenylenediamine.

TABLE III.4
TEST RESULTS FOR SMALL CELLS

<u>ELECTRODE TYPE & NO.</u>	<u>ELECTRODE SIZE/IN.</u>	<u>THEO. ZINC CAP(AH)</u>	<u>SEPARATOR CONFIGURATION</u>	<u>DISCHARGE</u>	<u>CHG/ DSCH. RATIO, %</u>	<u>CYCLE</u>	<u>FAILURE MODE</u>	<u>COMMENTS</u>
(1) 2 Full Sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	H-3-7/8" W-2-7/8" T-.07"	14.4	Commercial PVA - 1 layer	2.5A x 1 hr.	120	42	Pinhole	Excessive swelling film, turned brown. Shape of zinc electrode has been changed, dendrite growth.
(2) SAME	SAME	SAME	PVA cross- linked with 15% Boric Acid	SAME	SAME	42	Small Pinhole	Film swells less than commercial PVA. Turned slightly brown, cracked from edges.
(3) SAME	SAME	SAME	PVA cross- linked with 10%-20% DMU	SAME	SAME	60	One small pinhole	Swells, turned slightly brown but still had good strength. Zinc electrodes shape changed in a way and film swelled.
(4) 2 Full Sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	H-3-7/8" W-2-7/8" T-.07"	14.4	One layer 2 mil thick PVA cross-linked with 12% Boric Acid	2.5A x 1 hr.	120	52	Dendrite Growth	Film looks brittle. No change in color.
(5) SAME	SAME	SAME	1.8 mil thick film - one layer of PVA. vis.(28-32 cp)	SAME	SAME	45	Dendrite Growth through sides	Film swells, little change in color
(6) SAME	SAME	SAME	1 layer 1.9 mil thick PVA cross- linked with 15% Boric Acid and filtered before casting	SAME				
(7) SAME	SAME	SAME	1.7 mil thick - 1 layer of high mol.wt. PVA, vis. (52-65 cp)	SAME	SAME	56	Very small one pinhole	Swells less, turns less brown, little change in shape of zinc electrode.

TABLE III.4
TEST RESULTS FOR SMALL CELLS

<u>ELECTRODE TYPE & NO.</u>	<u>ELECTRODE SIZE/IN.</u>	<u>THEO. ZINC CAP. (AH)</u>	<u>SEPARATOR CONFIGURATION</u>	<u>DISCHARGE</u>	<u>CHG/ DSCH. RATIO, %</u>	<u>CYCLE</u>	<u>FAILURE MODE</u>	<u>COMMENTS</u>
(8) 2 Full Sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	H-3-7/8" ⁺ 1/16 W-2-7/8" ⁺ 1/16 T-.07" ⁺ .002"	14.4	One layer of commercial PVA	2.5A x 1 hr.	120	60	Pinhole in film	Film swells, turns brown. Shape of zinc electrode was changed, zinc dendrites grow.
(9) SAME	SAME	SAME	PVA + DMU One layer 90% + 10%	SAME	SAME	75	SAME	Shape change observed in zinc electrode. Film swells. Zinc dendrites grow through separator.
(10) SAME	SAME	SAME	One layer of (PVA + Boric Acid) 87% + 13%	SAME	SAME	68	Pinhole in film	Film looks brittle. Film swells. Zinc dendrites grow through edges and separator. Shape change in zinc electrode.
(11) SAME	SAME	SAME	One layer of (PVA + Boric Acid + DMU) 87% + 4.5% + 8.5%)	SAME	SAME	85	There was a big hole in sepa- rator:	Film looks in good condition but swells and does not turn brown. Zinc dendrites grow through them. Shape change in zinc electrode.
(12) SAME	SAME	SAME	One layer of PVA on neg- ative plate PVA + filler 70% + 30%	SAME	SAME	45	There was a pinhole	Film does not shrink or swell much. Looks good in strength. There was not any shape change in negative electrode.

TABLE III.5
ELECTRICAL RESISTANCE OF PVA-BASED FILMS

COMPOSITION	THICKNESS MIL.	DAYS IN KOH	ELECTRICAL RESISTANCE $M\Omega \cdot \text{in}^2/\text{mil}$
PVA + sucrose 88% + 12%	2.0-2.5	4	10
PVA + filler 70% + 30%	1.5	7	15
PVA + DMU + filler 65% + 5% + 30%	2.5	5	25
PVA + DMU 88% + 12%	2.5	5	25
Brown, post-treated Commercial PVA	1.5	5	35
PVA + filler 75% + 25%	1.9	1	25
PVA + filler + DMU 75% + 20% + 5%	2.0	2	45
PVA + Sucrose 95% + 5%	1.5	1	15

TABLE III.6

TENSILE HANGING TEST FOR PVA-BASED FILMS

COMPOSITION	TIME IN KOH	COMMENTS
Post-treated brown Commercial PVA	4 days	stretched
Commercial PVA	3-4 days	stretched
PVA + filler 75% + 25%	4 days	stretched
PVA + filler + DMU 75% + 20% + 5%	4-5 days	stretched slightly

ENERGY RESEARCH CORPORATION

The following method of crosslinking was used: 25g of high molecular weight PVA was dissolved in 500 cc of water at 50°C and cooled to 20°C. Then 0.1g of gluteraldehyde was added as 5% aqueous solution and 0.1g of p-phenylenediamine anti-oxidant. The ph was adjusted to 2 with H₂SO₄. The film was cast on a glass sheet and dried in an oven at 100°C for 15 minutes. The PVA film obtained is not soluble but swells in water.

Electrical resistance of these crosslinked PVA films was measured and is given in Table III.7. Results obtained show that the degree of crosslinking is not high and the quality of the film is not good. Data from the tensile hanging test (see Table III.8) verify these observations.

2.1.2 Zinc Penetration Test

The zinc penetration test was established for better characterization of the separator materials.

Apparatus and Procedure²

The test equipment consists of a cell assembly which holds the separator being investigated between two zinc electrodes: One serves as the anode, the other as the cathode. The use of zinc instead of silver for the anode avoids possible silver attack and contamination, and provides for replenishment of the zincate as the plating proceeds. Current is passed between the electrodes at a controlled current density until a zinc trail traverses the separator; for a single test, this distance traversal can be detected optically, but for mass testing, it is more conveniently detected electronically.

TABLE III.7

ELECTRICAL RESISTANCE OF PVA FILMS
CROSSLINKED WITH GLUTARALDEHYDE
AND P-PHENYLENEDIAMINE

COMPOSITION	THICKNESS, Mil.	DAYS IN KOH	ELECTRICAL RESISTANCE $\text{m}\Omega \cdot \text{in}^2 / \text{mil.}$
ERC PVA + Glutaraldehyde + P-phenylenediamine	1.5	2	20
		5	5
		11	45
		12	55
		14	20
		17	5
		19	5
		20	5

TABLE III.8

TENSILE HANGING TEST FOR PVA FILMS
CROSSLINKED WITH GLUTARALDEHYDE
AND P-PHENYLENEDIAMINE

COMPOSITION	TIME STAYED
Film Commercial PVA	6 days
ERC PVA PVA + Glutaraldehyde + P-Phenylenediamine	5 days
ERC Polymer Blend	> 2 weeks

ENERGY RESEARCH CORPORATION

Figure III.1 shows the test cell. In preparation for a test, a disc of paper is die cut and the separator is cut along a template to the shape shown in segment A of the figure. The separator and disc are soaked for 24 hours in a solution prepared by adding 76.5g of zinc oxide (USP) to a liter of 44% KOH solution.

To start the assembly, a sheet of zinc (99.9% grade) is inserted in the notch in the anode compartment and the wet piece of Viskon paper is lifted with tweezers from the soaking vessel and placed on the inner end of the cylindrical zinc cathode. The four threaded rods are put through the anode compartment which is then placed with outer face downward on the table. Sections are successively placed in position in the order shown in the exploded view (Segment A). The wet separator is handled by the edges with two pairs of tweezers to avoid marring the test area.

After assembly, the test cell is placed in the upright position and the anode compartment is filled with the above solution. It should be noted that the only electrolyte in the cathode compartment is that held by the paper.

The assembly, even when tightly compressed, is not completely liquid-tight. Each test cell is thereafter placed in a separate plastic dish for the obvious purpose of holding the leakage, but also to eliminate the possibility of stray current from cell to cell. Segment C of the figure shows the wiring diagram.

Results of zinc penetration test are given in Table III.9. Comparison of time for zinc penetration through PVA-based and nylon-based separators proved that PVA has better zinc-stopping

TABLE III.9

TIME OF ZINC PENETRATION
FOR PVA-BASED SEPARATOR FILMS

COMPOSITION	THICKNESS, mil	ELECTRICAL RESISTANCE $\text{m}\Omega \cdot \text{in}^2/\text{mil}$	TIME, HOURS
PVA + DMU + filler	2	30	10.0
PVA + DMU	1.5	25	7.5
PVA	1.5	20	7.0
ERC Polymer Blend	1.5	85	4.0

ENERGY RESEARCH CORPORATION

A. (Exploded View)

Side View of Zinc Cathode Plate

B.

C. Wiring Diagram

FIGURE III.1 ZINC PENETRATION TEST CELL

ability.

2.1.3 The Permeability Mechanism Through PVA Films

Study of the permeability mechanism through PVA films was continued for better understanding of the criteria to develop improved separator materials.

PVA is a hydrophilic polymer and transport of electrolyte through hydrophilic films was the object of extensive study. The theory that transport of electrolytes through hydrophilic polymers is a process of diffusion permeability⁸ has found general recognition. The process of permeability consists of three stages: sorption, diffusion in polymer, and desorption. The basic principle is that the electrolyte should be dissolved in polymer for the process of permeability to occur. Transport of electrolytes can be described by the permeability coefficient P .⁴

$$P = DK \quad (1)$$

Where:

D = diffusion coefficient

K = distribution constant, which determines concentration of electrolyte in the polymer

Solubility of salts in hydrophilic polymers is related to presence of water in the polymer.⁵ Therefore concentration and distribution of water in polymer are very important for the permeability process.^{6, 7} Concentration of electrolyte in the polymer becomes equal to concentration of electrolyte in external solution at a high concentration of water in the polymer.⁵ The coefficient of electrolyte diffusion is also a function of concentration of water in the polymer. Theory of free (void) volume was the basis for deducing the following formula,^{5, 8}

which correlates the coefficients of electrolyte diffusion in water (D_0) and in the polymer (D).

$$\log D = \log D_0 - K \left(\frac{1}{H} - 1 \right) \quad (2)$$

Where:

K = constant which does not depend on the nature of the polymer

H = concentration of water in the polymer (v.p.)

According to Eq. 2, the diffusion coefficient should monotonically decrease with an increase in the quantity of water in the polymer film.

Variation in the electrical resistance (permeability) of PVA films as a function of exposure time in aqueous electrolyte was studied. Experimental data show a very sharp decrease of electrical resistance during the first three to four days (see Figure III.2). A further four to five months in KOH does not essentially change the electrical resistance of PVA. The results obtained indicate that electrolyte (which had been absorbed for three to four days), created conditions in PVA for equilibrium permeability. The same effect has been achieved during formation of PVA film from aqueous solution by variation of the temperature or time of drying. Such variation results in a different quantity of residual solvent (water) in film and different electrical resistance (see Table III.10). These data indicate that electrical resistance of PVA depends on the quantity of residual water in the film: An increase in quantity of water results in a sharp decrease in electrical resistance. This dependence is valid up to the quantity of residual solvent equal to ~6%. A further increase in quantity of water in PVA film does not in-

TABLE III.10

CONCENTRATION OF RESIDUAL SOLVENT
AND ELECTRICAL RESISTANCE OF PVA FILMS

NO.	CONDITIONS OF DRYING		RESISTANCE $m\Omega \cdot \text{in}^2/\text{mil}$	RESIDUAL SOLVENT, %
	Temp. °C	Time, Min.		
1	70	180	Very high	2.7
2	70	166	Very high	3.1
3	70	130	1000	3.5
4	70	110	315	4.1
5	70	80	40	6.7
6	70	75	45	8.6
7	70	60	43	8.9

fluence the electrical resistance (permeability) which reaches an equilibrium value for this film.

After these experiments, dry film (with approximately 1 to 1.5% residual water) and wet film (with more than 6% residual water) were tested for 10 days in KOH (see Table III.11). Variation in value of electrical resistance during the first ten days of aging in KOH has the same character as shown in Figure III.2. Electrical resistance of wet film (6% water) does not change during this period.

According to the data, dry PVA film absorbs aqueous KOH solution. Presence of water in PVA creates the conditions for higher permeability of the film to ionic flow. This results in a decrease of electrical resistance during the first days up to a certain equilibrium level, which does not change over the next five to six months. Therefore low electrical resistance of the PVA films can be achieved by employing two methods: 1) preliminary exposure of PVA film in aqueous electrolyte for three to four days, and 2) production of wet PVA films containing more than 6% residual water.

Production parameters for PVA films with a definite quantity of residual water can be calculated by the following equation:⁹

$$t = B \exp \left[\frac{Q_0 - \alpha \log C}{R} \left(\frac{1}{T} - \frac{1}{T_p} \right) \right] \quad (3)$$

Where; t = time of film formation

Q_0 = activation energy of solvent diffusion

B = constant

α = constant of polymer-solvent system

T = temperature of film formation, K

T_p = constant of polymer-solvent system

C = concentration of the residual solvent in film

TABLE III.11

VARIATION IN ELECTRICAL RESISTANCE OF PVA FILMS
CONTAINING DIFFERENT QUANTITIES OF RESIDUAL SOLVENT

NO.	CONDITIONS OF DRYING		DRY THICKNESS, mil	ELECTRICAL RESISTANCE, m Ω ·in ² /mil	TIME IN KOH @ 23°C, days	RESIDUAL SOLVENT, %
	Temp., °C	Time, min				
1	70	130	1.8	very high 45 45	1 4 10	2.7
2	70	166	2.0	very high 47 47	1 4 10	3.1
3	70	110	1.8	315 45 45	1 4 10	4.1
4	70	80	2.1	40 40 40	1 4 10	6.7
5	70	75	2.0	45 44 44	1 4 10	8.6
6	70	60	1.9	43 42 42	1 4 10	8.9

FIGURE III.2 EFFECT OF EXPOSURE TIME IN KOH
ON THE ELECTRICAL RESISTANCE OF PVA FILMS

R = gas constant

Constants of Eq. 3 for PVA based systems tested are presented in Table III.12.

Eq. 3 can be used up to about 20% residual solvent in the film for all systems tested. Existence of the concentration limit is related to a change of the diffusion mechanism at the region of about 20% solvent in a polymer. Eq. 3 describes the last stage of film formation when solvent bonded with the polymer takes part in the diffusion process. Approximately 20% of the solvent is necessary to localize intermolecular interaction in the polymer.¹⁰ So if the concentration of the solvent in the polymer is higher than 20%, transference of the solvent to the evaporation surface is carried out by self-diffusion of the solvent. The process of self-diffusion proceeds with an activation energy, which is essentially lower than the value of Q_0 in Eq. 3 and does not depend on concentration of the solvent in the polymer.¹¹

The permeability mechanism of aqueous electrolytes through the PVA membrane has the same solvent-polymer character. Therefore, by analogy with the desorption process, there are two periods of diffusion transfer which should occur during electrolyte permeability through the hydrophilic polymers:

- 1) Non-equilibrium permeability which is controlled by diffusion of water bonded with the polymer. Transport of the electrolyte is realized by formation and breakdown of intermolecular bonds between the polymer and solvent. Activation energy of diffusion depends on quantity of water absorbed in the polymer according to the following equation:

$$Q = Q_0 - \alpha \log C$$

Where

Q = effective activation energy of diffusion

TABLE III.12

CONSTANTS OF EQUATION (3) FOR PVA-BASED SYSTEMS

SYSTEM	Q_0 , $\frac{\text{Kcal}}{\text{mol}}$	Q , $\frac{\text{Kcal}}{\text{mol}}$	T_p , $^{\circ}\text{C}$	B , min	$C_{\text{lim},\%}$	Correlation Coefficient
PVA (88-89% hydrolyzed) + Water	32.0	23.45	100	17.2	23	0.978799
PVA (88-89% hydrolyzed) + Water	32.5	23.87	98	19.0	23	0.978072
PVA (88-89% hydrolyzed) + Water + Methanol (75:25) ($T < 65^{\circ}\text{C}$)	31.6	23.21	82	24	23	0.986987
PVA (88-89% hydrolyzed) + Water + Methanol (75:25) ($65^{\circ}\text{C} < T < 100^{\circ}\text{C}$)	14.9	10.94	100	24	23	0.987168
PVA (99-100% hydrolyzed) + Water	37	27.21	100	15.9	23	0.993685
PVA (99-100% hydrolyzed) + Water + Boric Acid (10%)	37.3	27.39	98	33	23	0.981097
PVA (99-100% hydrolyzed) + Water + Methanol (75:25) ($T < 65^{\circ}\text{C}$)	36.5	26.8	82	27	23	0.987345
PVA (99-100% hydrolyzed) + Water + Methanol (75:25) $65^{\circ}\text{C} < T < 100^{\circ}\text{C}$	18.0	13.22	100	27	23	0.952007

While increasing the quantity of absorbed water (decreasing the effective activation energy of diffusion), the intermolecular interaction in polymer weakens and the rate of diffusion increases. This process will continue until the local concentrations of water reach the level when the intermolecular interaction is neutralized in certain amorphous regions, and

- 2) The process of diffusion transport changes near this concentration from diffusion of molecules bonded with a polymer to self-diffusion of the solvent which is not attached to the polymer. Self-diffusion has low activation energy which does not depend essentially on the concentration of water in polymer. Non-equilibrium permeability transforms into equilibrium permeability, which can be described by Fick's laws. The rate of diffusion is not dependent on quantity of absorbed or residual water if this quantity is higher than the quantity necessary to reach the equilibrium permeability (self-diffusion) level.

The amount of water which should be obtained in the polymer to achieve the self-diffusion level is different for the process of film formation and for electrolyte diffusion. Such difference is related to the fact that aqueous electrolyte is not a solvent for PVA and, therefore, the diffusion process occurs mostly through the channels in amorphous regions where the local concentration of water is higher than in the bulk film.

Dependence of electrolyte permeability on quantity of residual water in the film is not an individual property of PVA. Other polymers which absorb water or can be dissolved in water or solvent mixtures containing water exhibit similar properties. Some polymers do not have the ability to absorb water from aqueous electrolyte solutions. Therefore another way to increase their permeability is to leave a certain quantity of residual water in film during production of these membranes from the solution containing water. For example, polyethylene oxide or polyamides do not absorb or lose water in an electrolyte environment and permeability properties formed during the production process are fixed in the membrane. Consequently, it is possible to regulate permeability

properties of plastic films for aqueous solutions simply by changing the quantity of residual water in film.

Correctness of Eq. 3 for different polymer-solvent systems⁹ shows that permeability of any polymer membrane for any solution can be increased if the polymer membrane contains a certain quantity of solvent which is employed in the solution. Solvents present in the film other than those used in solution intended for permeation do not essentially influence the rate of permeability.

2.1.4 Failure Mode Observation of Cells Containing PVA Based Separator Films

As indicated in Table III.4, the shape change of the Zn electrode depends on degree of swelling of the separator film. Addition of a filler or supporting layer resulted in considerable reduction of degree of swelling and shape change in the Zn electrode. But cycle life of the cells did not increase because zinc dendrites grew through the separator.

Work carried out with PVA separators thus far allows the conclusion that PVA material has high stopping ability for zinc dendrites because it works as a selective membrane. Increasing the chemical stability of PVA by crosslinking permitted an increase in the cycle life of the cell by 1.5 to 2 times but did not solve the problem of shape change of the zinc electrode. Decrease of swelling and wrinkling of PVA separator film leads to decreasing shape change of the negative electrode but did not increase cycle life of the cell.

Crosslinking increases mechanical strength and chemical stability of the PVA based films which results in reducing the

danger of dendritic growth through the separator. However crosslinking could not reduce shape change of the negative electrode and, therefore, does not substantially increase cycle life of the cell: Cycle life of the cells with both modes of failure is almost identical. Acceleration of the shape change process in cells containing PVA based separators can probably be explained by specific properties of the PVA separator as a selective membrane which creates high concentration gradients and causes reduction and precipitation of metallic zinc and zinc oxide from the separator bag and zinc electrode. Consequently crosslinking of PVA increases the probability of cell failure by the shape change mode and reduces the hazard of zinc penetration but does not result in a substantial increase in cycle life of the cells. These results necessitate that ERC look for a combination microporous/membrane type material combined in one separator system.

2.2 IMPROVED COMPOSITION FOR POLYMER-BLEND SEPARATOR FILMS

Chemically stable polymer-blend compositions with low electrical resistance were developed during the first year of work under the program. Use of these polymer-blend separators in Ni-Zn cells, resulted in reduction of shape change of the Zn electrode but did not result in an increase in cycle life of the cells up to the required level. Therefore, attempts to improve the composition were continued during the second year of work.

2.2.1 Evaluation of Polymer-Blend Films as a Separator Material

Continuing work this period included measurement of the stability of electrical resistance and appearance of the films as a function of exposure time in KOH (Table III.13). According to results obtained, electric resistance and appearance of the film did not change during a six month exposure in 45% KOH solution.

Tensile strength of polymer-blend films was measured for different compositions of solutions. The results presented in Table III.14 indicate that strength and elasticity of the polymer-blend films are in the range which could be considered acceptable for separator materials in Ni-Zn cells. Such a conclusion is based on stability in KOH environment and on electrical tests of the material in a number of cells. Degradation of polymer-blend films was not observed in cells which have been taken apart after cycling.

Results of the zinc penetration test given in Table III.15 show that variation in the zinc penetration time of several samples taken from one piece of film is between one and six hours. Such large differences indicate non-uniformity of the properties in films made by a doctor blade. Comparison of zinc penetration time in PVA-based and polymer-blend separators proved that PVA has better zinc-stopping ability. Therefore, employment of polymer-blend and PVA-based materials together in a separator system results in reducing shape change (by the polymer-blend separator component) and increasing zinc-stopping ability (by the PVA coating).

TABLE III.13
ELECTRICAL RESISTANCE OF NYLON-BASED FILMS.
DURING EXTENDED EXPOSURE TIME IN KOH

COMPOSITION	THICKNESS, mil	RESISTANCE, $m\Omega \cdot \text{in}^2/\text{mil}$					
		INITIAL	AFTER 2 MOS.	AFTER 3 MOS.	AFTER 4 MOS.	AFTER 5 MOS.	AFTER 6 MOS.
Pa + Po + Vic + CeO ₂ 30: 10: 6: 4:	2.5	25	30	32	20	25	30
Pa + SiO ₂ + CeO ₂ + Vic + Po 35: 6: 4: 6: 3:	3	185	175	190	170	180	160
Pa + SiO ₂ + CeO ₂ + Vic + Po 35: 6: 4: 6: 3:	3	15	25	30	20	25	20
Pa + SiO ₂ + CeO ₂ + Vic + Po 35: 6: 4: 6: 4:	3.5	85	40	50	60	70	55
Pa + Po + Vic 30: 10: 3:	2.2	20	25	30	35	20	25
Pa + Po + Vic + CeO ₂ + TEA 30: 10: 6: 4: 2:	3.5	45	50	40	45	35	40

TABLE III.14

TENSILE STRENGTH OF POLYMER-BLEND FILMS

THICKNESS, mil	FORCE, lbs.	DEFLECTION, in.	σ lb/in ²
Standard film .020" blade			
0.9	0.91	4.263	2022
0.9	0.98	4.398	2177
1.0	1.27	4.958	2540
1.1	1.36	5.010	2472
1.0	1.11	4.352	2220
0.8	0.93	4.742	2320
0.8	0.93	4.155	2320
0.9	0.99	4.834	2200
0.9	1.12	4.831	2490
0.9	1.11	5.484	2470
Standard film .040" blade			
1.9	1.70	3.484	1789
1.8	1.66	4.375	1844
1.8	1.60	3.155	1778
1.8	1.74	4.214	1933
1.7	1.48	3.574	1741
1.7	1.44	Average	1694
1.8	1.44	deflection	1600
1.8	1.59	≈ 4	1766
1.8	1.54		1711
1.4	1.09		1557
The tensile strength of the .040" standard film was slightly higher but not significantly.			
Pure polymer was tried on the tester but stretched beyond the capacity of the machine.			

TABLE III.15

COMPARISON OF ZINC PENETRATION TIME FOR
POLYMER-BLEND AND PVA-BASED SEPARATOR FILMS

COMPOSITION, g.	THICKNESS, mil	ELECTRICAL RESISTANCE, $m\Omega \cdot \text{in}^2/\text{mil}$	TIME, hours
1	2.6	625	4.75
	2.4		2.00
	2.7		5.50
	2.3		3.00
	2.7		6.00
	2.3		1.00
	2.4		1.50
2	1.5	100	1.75
3	1.4	320	2.0
PVA + DMU + Filler			10.0
PVA + DMU			7.5
4	1.5	85	4.0

An attempt was made to find a correlation among various methods of testing and the properties of separator materials.

Three methods were evaluated:

- The rate of OH^- ion diffusion (see Table III.16)
- Electrical resistance, and
- Time of zinc penetration through the separator.

Polymer-blend films were produced with different resistances. An OH^- diffusion test was conducted for the same films, then zinc penetration time through the films was measured. The data obtained are presented in Table III.17 and in Figure III.3. According to the results obtained, there is some correlation between electrical resistance of the film and its permeability to OH^- . However, the data are not linear which would be expected as a result of the similarity of test conditions.

Time of zinc penetration does not correlate with electrical resistance of the film, or the rate of OH^- diffusion. This can be explained by the difference in sensitivity of the tests: Electrical resistance and rate of diffusion relate to average porosity of the sample while the time of zinc penetration depends on the largest pore of the sample. Therefore, if different films have different pore size distributions, variations in diffusion rate and electrical resistance will result. The same films can have the same largest pore diameter and time of zinc penetration does not vary (see Table III.17).

TABLE III.16

ELECTROLYTE DIFFUSION RATE MEASUREMENTS

SAMPLE (2N) Polymer-Blend A= .785 in² Initial Concentration of Strong Side = 45%
 ER (85 to 105 $\frac{\text{m}\Omega \cdot \text{in}^2}{\text{mil}}$) V= 140cc Initial Concentration of Weak Side = 0

TIME	pH	p ^{OH}	a _{OH⁻}	a _{OH⁻}	<u>STIRRING CONDITION</u>	
					a _{OH} mol/l	$\Delta c / \Delta t$ mol/t
8:50	11.92	2.08	10 ^{-2.08}	10 ⁻³ x 10 ^{.92}	8.318 x 10 ⁻³	
9:00	13.01	0.99	10 ^{-.99}	10 ⁻¹ x 10 ^{.01}	1.023 x 10 ⁻¹	9.398 x 10 ⁻²
9:10	13.60	0.40	10 ^{-.40}	10 ⁻¹ x 10 ^{0.60}	3.981 x 10 ⁻¹	2.958 x 10 ⁻¹
9:20	13.75	0.25	10 ^{-.25}	10 ⁻¹ x 10 ^{-.75}	5.630 x 10 ⁻¹	1.649 x 10 ⁻¹
9:30	13.85	0.15	10 ^{-.15}	10 ⁻¹ x 10 ^{.85}	7.680 x 10 ⁻¹	1.450 x 10 ⁻¹
9:40	13.91	0.09	10 ^{-.09}	10 ⁻¹ x 10 ^{.91}	8.128 x 10 ⁻¹	1.048 x 10 ⁻¹
9:50	13.98	0.02	10 ^{-.02}	10 ⁻¹ x 10 ^{.98}	9.550 x 10 ⁻¹	1.422 x 10 ⁻¹

$$\frac{\Delta M}{A \Delta t} = \frac{\Delta c}{\Delta t} \times \frac{V}{A} = \frac{.140 \times 1.3208 \times 10^{-1}}{.785 \times 10} = 2.3555 \times 10^3 \text{ mol/min. in}^2$$

TABLE III.17

RESULTS OF TESTING DIFFERENT POLYMER-BLEND FILMS

ELECTRICAL RESISTANCE, $\text{m}\Omega \cdot \text{in}^2/\text{mil}$	$(\text{OH})^-$ DIFFUSION, $\frac{\text{mol}}{\text{min.}} \cdot \text{in.}^{-2} \times 10^{-5}$	ZINC PENETRATION, hrs.
50 to 90	272.47	-
80 to 100	230.12	-
105	235.55	-
235	70.92	20
300 to 340	75.68	19
400	37.62	19
460	26.37	19
570 to 600	8.50	23

FIGURE III.3 ELECTRICAL RESISTANCE VS OH⁻ DIFFUSION FOR
(2N) POLYMER-BLEND

Pore size distribution in the polymer-blend film was measured by mercury-porosimeter and initial results are given in Figure III.4 and Table III.18.

Quantity of residual solvent in the separator film also has an influence on the properties of the material and, therefore, parameters of polymer-blend film formation were determined. Results of measuring the quantity of residual solvent in films formed under different conditions are given in Table III.19. After completing this part of the work, the properties of polymer-blend films can be compared under similar conditions (the same quantity of residual solvent in film).

2.2.2 Testing of Cells Containing One Layer of Polymer-Blend Separator Films

For the purpose of studying the interaction between the zinc electrode and the separator system, several polymer-blend separators with different electrical resistances were prepared and Ni-Zn cells with one layer of these materials were built and tested. Some of the cells were terminated on cycle test before they failed in order to learn how failure progresses during cycling.

Test Conditions:

Charge	3 hours at 1.2A
Discharge	1 hour at 3A
Overcharge	20%
Depth	75%

FIGURE III.4 PORE SIZE DISTRIBUTION OF POLYMER-BLEND FILM

TABLE III.18

CUMULATIVE PORE SIZE DISTRIBUTION OF POLYMER-BLEND FILM

***** MERCURY POROSIMETRY *****

-----CUMULATIVE PORE SIZE DISTRIBUTION-----

TEST NO. PT-14

SAMPLE WEIGHT, (GRAMS) .640

DATE 6/8/80

OPERATOR MICHAEL MOHNERA

ENGINEER M. DODIN

PRESSURE(KG/CM²)*DIAMETER(MICRONS)=12.46

(CONTACT ANGLE=130 DEGREES, SURFACE TENSION=484 DYNES/CM)

ABS. PRESS, (KG/CM ²)	DISPLACEMENT, (CM)	PORE DIAMETER, (MICRONS)	% OF TOTAL VOLUME, (%)	PORE VOLUME, (CM ³ /G)
.051795	0.000000	240.363750	0.000000	0.000000
.141573	.050000	89.011124	.239866	.000552
.321129	.090000	38.800606	.431758	.000994
.587010	.150000	21.226212	.719597	.001657
.700959	.180000	17.775646	.863516	.001988
1.058345	.220000	11.773102	1.055409	.002430
1.340000	.220000	9.298508	1.055409	.002430
2.360000	.532500	3.279660	2.554569	.005881
3.040000	.720000	4.098684	3.454065	.007952
3.720000	.845000	3.349463	4.053730	.009333
4.400001	1.157500	2.831818	5.552890	.012784
6.100000	1.470000	2.042623	7.052051	.016236
6.780000	1.782500	1.837758	8.551212	.019607
11.000000	3.470000	1.132727	16.646679	.038325
21.000000	4.595000	.593333	22.043659	.050750
41.000000	5.532500	.303902	26.541138	.061105
61.000000	7.595000	.204262	36.435600	.083884
81.000000	9.469999	.153827	45.430550	.104593
100.000000	11.219999	.124600	53.825859	.123921
200.000000	14.907499	.062300	71.515930	.164648
400.000000	18.845001	.031150	90.405350	.208137
600.000000	19.595001	.020767	94.003357	.216420
800.000000	20.157501	.015575	96.701843	.222633
1000.000000	20.845001	.012460	100.000030	.230226

TABLE III. 19

QUANTITY OF RESIDUAL SOLVENT IN POLYMER-BLEND FILMS

(Thickness of the film, δ = 2.5 mil)

NO.	TEMP. OF FORMATION, °C	TIME, Min.	QUANTITY OF RESIDUAL SOLVENT, %
1	23	20	35.57
2	23	35	35.52
3	23	30	27.40
4	23	35	39.64
5	23	40	20.28
6	23	45	21.92
7	23	50	17.13
8	23	55	14.68
9	40	20	35.14
10	40	25	34.48
11	40	30	29.98
12	40	35	29.26
13	40	40	23.07
14	40	45	18.40
15	40	50	10.11
16	40	55	7.02
17	60	20	32.80
18	60	25	30.63
19	60	30	25.85
20	60	35	23.65
21	60	40	22.04
22	60	45	17.90
23	60	50	9.35
24	60	55	4.03

ENERGY RESEARCH CORPORATION

Discharge Rate C/1.5

Cycle Time 4 hours

The separator and zinc electrode were examined after the cells were disassembled. Results of the tests, given in Table III.20, indicated that different separator materials (PVA and polymer-blend) interact with the zinc electrode in different ways and that the design of the separator system also influences the cycle life of the cell. Results obtained demonstrate that cycle life of the cells varied from 11 to 106 cycles for one composition of film. Such variation is a function of electrical resistance and uniformity of components and pore size distribution in the separator. The last factor is probably the most important. By using one layer of low electrical resistance and uniform polymer-blend film, it is possible to achieve more than 100 cycles during accelerated test conditions and a drop of only 75% of initial cell capacity. Moreover, polymer-blend separators are considerably more stable in KOH than crosslinked PVA tested under the same conditions.

The second task was to compare the performance of the Celgard K-307 separator material with ERC type polymer-blend separators. Celgard K-307 is cellulose acetate coated Celgard 2400 with a total thickness about 1.5 mil. The coating was applied on both sides of the polypropylene film. Cells with one and two layers of Celgard K-307 were prepared and two cells with one layer of polymer-blend separator were tested for comparison. The thickness of the polymer-blend film was about 3 mils. These single electrode cells were all tested under the same conditions. The results, presented in Table III.21 (cells 1 through 4), indicate

TABLE III.20

INFLUENCE OF SEPARATOR DESIGN ON THE ZINC ELECTRODE AND ON CYCLE LIFE OF THE CELL

Electrode Type & No.	Electrode Size/In.	Theo. Zinc Cap. (Ah)	Separator Resistance	Charge/ Disch. Ratio, %	Cycle	Failure Mode	Comments
1) 2 Full Sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TPE - 2%	H-3-7/8" ± 1/16 W-2-7/8" ± 1/16 T-.007" ± .002	14.4 Ah		2.5A x 1 hr.	120	26	Pinholes in film. Film does not swell. Zinc electrode does not change shape. Separator is clear. No zinc out of separator.
* R = 10							
2) Same	Same	Same	* R = 220	Same	Same	12	Cell did not fail. Dendrites grow but did not short yet. Big dendrites start to grow through the separator. Voltage trace had a peak at the end of charge. No shape change.
3) Same	Same	Same	* R = 840	Same	Same	11	Several small dendrites. Several small dendrites shorted the battery. No shape change. No zinc in the separator except dendrites.
4) Same	Same	Same	Same * R = 1400	Same	Same	40	One large dendrite No shape change. Separator clean. Voltage trace did not have a peak.
5) Same	Same	Same	* R = 2300	Same	Same	11	Cell did not fail. Voltage trace had a peak at the end of charge. A lot of zinc in separator with uniform distribution. No zinc outside of separator.
6) Same	Same	Same	* R = 50 On Ni electrodes Perlon on Zn electrode. Separator was the same composition.	Same	Same	67	Several small dendrites. A lot of zinc on the walls of cell. Edges of zinc electrode denuded of Zn. Zinc shows good electrochemical utilization. Distribution of zinc in separator is not uniform. Most zinc at the top of separator.
7) SAME	SAME	SAME		SAME	SAME	78	Small pinholes Film looks very good. Small zinc dendrites, no shape change of zinc electrode.
* R = 550							
8) SAME	SAME	SAME	* R = 50	SAME	SAME	106	Very small traces of Zn in top part of separator. Film was very uniform and many small dendrites grow and dissolved during charge and discharge. Capacity dropped only to 75%.
*Electrical Resistance (R) in $\frac{m\Omega \cdot in^2}{mil}$							

that the cells with the Celgard K-307 separator lasted 120 cycles regardless of whether one or two layers of the film were employed. The failure mode was shape change of the zinc electrode for both cells. The cells did not short and a lot of zinc particles were outside the separator bag. Cells with one layer of polymer-blend separator film, cycled 132 and 138 times, also failed as a result of shape change. The cells did not short and all zinc was inside the separator bags. Comparison of cell performance shows that cycle life and failure mode are very similar for cells with one layer of polymer-blend film and with one or two layers of composite material like Celgard K-307.

The dependence of cell capacity and the end of discharge voltage on number of cycles is presented in Figure III.5. Comparison of the curves related to Celgard K-307 and polymer-blend separators shows that capacity of the cells with Celgard K-307 starts to decline after 80 cycles and drops very sharply. Cells with polymer-blend separators begin to decline in capacity after 60 cycles but the capacity decline is much slower and cells worked a little longer until 60% of nominal capacity was reached.

As a result of this work, a polymer-blend composition for separators is being developed for further use in Ni-Zn batteries. The film combines properties of selective and microporous membranes and, therefore, cells with one layer of this separator could work more than 100 cycles. Such results essentially exceed cycle life of cells with any commercially available separator material under the same testing conditions. However, technology of production has not been perfected yet and uniformity of the properties must be improved before development of a reliable

TABLE III.21

COMPARISON OF K-307 AND POLYMER-BLEND SEPARATORS

THEORETICAL ZINC CAPACITY (AH) = 14.4 A

ELECTRODE SIZE: H - 3-7/8" $\pm$ 1/16"

DISCHARGE = 2.5A x 1 hr.

W - @-7/8" $\pm$ 1/16"

CHARGE/DISCHARGE RATIO (%)=120%

T - .07" $\pm$.002"

ELECTRODE TYPE & NO.	SEPARATOR CONFIGURATION	CYCLE	FAILURE MODE	COMMENTS
(1) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of K-307 on negative plate	120	Shape change	Separator looks good. There were no pinholes Separator was some- what brittle and there was shape change in zinc plate.
(2) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	Two layers of K-307 on negative plate and Pellon on the plates	120	Shape change	Separator looks somewh. brittle but still good There was shape change and too much zinc goes through separator.
(3) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of (2N) polymer-blend on negative plate. Only Pellon on the plates.	132	Shape change	Separator looks good. There was no zinc den- drite coat on the sepa- rator or in cell. Cel dried because of shape change.
(4) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of (2N) polymer-blend on negative plate	138	Shape change	Cell was too tight. N electrode swelled and compressed the zinc pl Zinc was on Pellon absorbers.

FIGURE III.5 DEPENDENCE OF CELL CAPACITY AND END-OF-DISCHARGE VOLTAGE ON NUMBER OF CYCLES

separator material can be achieved. Cycle life of the cells can probably be increased if uniform polymer-blend films can be produced on a casting machine. The new separator material reduces shape change of the negative electrode and does not degrade in the cell environment. Appearance and dimensions of film do not change significantly during the cycle life of the cell. So, the new separator material may withstand 500 deep cycles without chemical and mechanical degradation. But it is difficult to assume that any simple single layer or multi-layer separator system can prevent zinc penetration or shape change of the negative electrode for such a long cycle life in a Ni-Zn battery. Therefore several attempts were made to design a special separator system for preventing zinc shorting the cell.

2.3 DESIGN AND TEST RESULTS OF THE IMPROVED SEPARATOR SYSTEM

2.3.1 Small Cell Testing of Various Separator Systems

As discussed earlier, PVA-based separators can be classified as selective membranes which prevent zinc penetration but do not retard shape change of the negative electrode. Polymer-blend separators are a combination of perm-selective and microporous materials, which prevent shape change but zinc dendrites grow through the films with cycling. To achieve both desirable properties, several approaches were evaluated:

1. A duplex separator consisting of the polymer-blend layer which was cast on the top of the PVA film.
2. A separator system consisting of a coating on the negative electrode of PVA in combination with one layer of polymer-blend film on the same electrode.
3. A separator system was prepared with three layers of polymer-blend films. Two external layers had the same composition. The internal layer contained a conductive powder in an amount of 50 wt% of the polymer-blend. The internal layer was rendered somewhat electro-conductive (discharging metallic zinc dendrites).

Before fabrication of cells, the separator films were tested for zinc penetration time. Test results are given in Table III.22. According to the data obtained, duplex material (PVA + polymer-blend) exhibited very good zinc stopping properties in comparison with crosslinked PVA which gave the best results prior to this test. The separator system with three layers of polymer-blend films also showed a substantial increase in zinc penetration time. This experiment indicates that the combination of polymer-blend material and PVA materials increases time to zinc penetration.

Several cells were made and tested to examine the idea described above. Cycle life and results of failure analysis for several cells are given in Table III.23.

A cell with a duplex PVA and polymer-blend separator lasted 145 cycles until the capacity dropped to 60%. The presence of the polymer-blend layer reduced swelling and wrinkling of PVA film and, therefore, substantially decreased shape change of the negative electrode. Zinc penetration was slowed by the PVA layer. The cell worked much longer than cells with two layers of polymer-blend separator or two layers of PVA-based separator which both shorted after 56-70 cycles.

The second design was a combination of PVA coating and one layer of polymer-blend formed as a bag on the negative electrode. The electrode was coated with solutions of the polymer-blend composition and PVA; the best result was the PVA coating. The cell performed for 146 cycles up to 80% of initial capacity which dropped very slowly. The PVA swelled but did not wrinkle and improved resistance to zinc penetration. Small amounts of zinc

TABLE III.22

TIME OF ZINC PENETRATION FOR IMPROVED SEPARATOR SYSTEM

<u>COMPOSITION</u>	<u>TIME, Hrs.</u>
Commercial PVA	7
PVA + Filler 75% 25%	8
PVA + Filler + DMU 75% 20% 5%	11
Multi-Layer (PVA + Polymer-Blend)	170 (~1 wk)
Polymer-Blend + (Polymer-Blend + Conductive Filler) + Polymer-Blend	62
Polymer-Blend + (Polymer-Blend + Conductive Filler) + Polymer-Blend	14

TABLE III.23

EFFECT OF SEPARATOR CONFIGURATION ON CYCLE LIFE AND FAILURE MODE

Theo. Zinc Cap. (AH) = 14.4 Ah

Electrode Size - H - 3-7/8" $\pm$ 1/16"W - 2-7/8" $\pm$ 1/16"T - .07" $\pm$.002"

Discharge = 2.5 A x 1 hr

Charge Discharge Ratio (%) = 120%

ELECTRODE TYPE & NO.	SEPARATOR CONFIGURATION	CYCLE	FAILURE MODE	COMMENTS
2 Sintered Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	Two layers of polymer-blend film on Zn plate. PVA solution was put in between two polymer-blend layers.	175		Zinc went in sol'n and a lot of zinc remains on PVA gel, shape change.
Same	One layer of combination (PVA & Polymer-blend) on Zn plate.	145	Pinholes	Zinc dendrites grew through film. There was some shape change.
Same	PVA coating on negative plate and one polymer-blend film on it.	146	Pinholes. Shorted at three, four places.	There were small zinc dendrites all over the separator and pellaon (absorber). Capacity at the end of discharge was about 80% after 146 cycles.
Same	Two layers of polymer-blend separator on negative plate.	65	Small hole, resistance is very high.	Film looks good, but zinc dendrites grew through separator. There was zinc spread all over on separator, little shape change.
Same	Three layers of polymer-blend on negative plate. Two outside layers were Std. polymer-blend and in between was one layer of Std. polymer-blend with conductive filler.	75	Pinholes, resistance is high.	Film looks good, but all zinc gone in sol'n. There was shape change in the electrode.

ENERGY RESEARCH CORPORATION

which could grow through the PVA coating were uniformly distributed in the polymer-blend separator so zinc did not form large dendrites.

The cell with PVA solution between two layers of polymer-blend films worked 175 cycles until the capacity dropped to 60%. Failure analysis showed that a uniform layer of metallic zinc was deposited on PVA film (solution dried out) but PVA film did not swell or wrinkle at all. Therefore if the polymer-blend layer uniformly distributes zinc which penetrates the film, the PVA layer stops the penetration of zinc. The external layer of polymer-blend prevents PVA from excess swelling and wrinkling. This combination resulted in the longest cycle life; and shape retention of the negative electrode was excellent.

Cells with three layers of separator material were tested in several different combinations:

1. Two polymer-blend external layers had the same composition. The internal polymer-blend layer contained a conductive filler in addition to components in the external layers.
2. The same two external layers of polymer-blend film but the internal layer contained PVA with 50% conductive filler.
3. One external polymer-blend layer, an internal layer with PVA + 50% conductive filler and one external layer with PVA.

Different cells tested with this separator system containing three layers of polymer-blend films did not exhibit promising results: Cycle life did not exceed 75 cycles. The main reason for such low performance was the high electrical resistance of the separator system. Cells with cellulose acetate coatings were tested and the results are given in Table III.24. The coating lost its physical integrity and dendrites

TABLE III. 24

TEST RESULTS FOR CELLS WITH VARIOUS SEPARATOR SYSTEMS

THEORETICAL ZINC CAPACITY (AH) = 14.4 AH

ELECTRODE SIZE: H - 3-7/8" $\pm$ 1/16"

DISCHARGE = 2.5A x 1 hr.

W - 2-7/8" $\pm$ 1/16"

CHARGE/DISCHARGE RATIO (%) = 120%

T - .07" $\pm$.002"

ELECTRODE TYPE & NO.	SEPARATOR CONFIGURATION	CYCLE	FAILURE MODE	COMMENTS
(1) 2 Full sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of cross-linked PVA on negative plate. Plate was coated with Cellulose Acetate	52	Pinholes Cell shorted	Zinc dendrites grow through separator. There was shape change.
(2) 2 Full sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	Negative plate was coated with polymer-blend solution and Pellon wrapped on both plates	46	Cell shorted	There were zinc dendrites. Coating was not thick enough.
(3) 2 Full sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	Three-throw separator film. One layer of standard polymer-blend. The second layer of standard polymer-blend + conductive filler. The third layer is standard polymer-blend.	75	Very high resistance shape change cell did not short	The separator film was too thick
(4) 2 Full sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	The first layer is standard polymer-blend. The second layer is polymer blend + conductive filler. The third layer is PVA.	156	Several small dendrites shorted the cell	Polymer-blend layer was adjacent to the Zn electr. Separator looks good. PVA does not swell. Not a lot of Zn was outside of separator bag. Shape change but not too much.
(5) 2 Full sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	The first layer is standard polymer-blend. The second layer is polymer-blend + conductive filler. The third layer is PVA	120	Shape change cell did not short	PVA layer was adjacent to the Zn electr. A lot of Zn was outside of the separator bag. Cell lost capacity because of shape change

TABLE III.24

TEST RESULTS FOR CELLS WITH VARIOUS SEPARATOR SYSTEMS

THEORETICAL ZINC CAPACITY (AH) = 14.4 AH

ELECTRODE SIZE: H - 3-7/8" $\pm$ 1/16"

DISCHARGE = 2.5A x 1 hr.

W - 2-7/8" $\pm$ 1/16"

CHARGE/DISCHARGE RATIO (%) = 120%

T - .07" $\pm$.002"

ELECTRODE TYPE & NO.	SEPARATOR CONFIGURATION	CYCLE	FAILURE MODE	COMMENTS
(6) 2 Full sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of standard polymer-blend on the negative plate. Plate was coated with (PVA + BA + DMU) solution	114	Zinc made a bridge over the separator. Cell shorted.	Zinc went to the plate through wire and shorted it. There was shape change. Zinc remains on film. It was uniformly distributed.
(7) 2 Full sintered Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of PVA (PVA + DMU) on negative plate and plate was coated with a polymer-blend solution.	162	A small pinhole	It shorted. There was less shape change. Film looks good. Color of PVA did not change, it swelled less.
(8) 2 Rolled Ni 1 Zinc ZnO - 93% CdC - 5% TFE - 2%	Two layers of polymer-blend. Pure PVA solution was inside the polymer-blend bag.	72	Cell increased the internal resistance	PVA solution dried up and made the gap between the electrodes. There was shape change.

ENERGY RESEARCH CORPORATION

grew through the separator. The coating consisting of a thin layer of polymer-blend without the separator bag was not sufficient to prevent zinc penetration and the cell shorted. Employing a polymer-blend coating and a one layer bag of crosslinked PVA resulted in increased cycle life up to 162 cycles (see Cell 7).

Three cells were fabricated with a separator system which contained a layer of polymer-blend film filled with a conductive filler. Separator systems were made in three layers and electrically conductive standard polymer-blend film with conductive filler comprised the internal layer. The cell with this separator system worked for 75 cycles and lost capacity because of shape change. The cell did not short but the resistance of the separator system became very high. The second separator system contained one external layer of standard polymer-blend, an internal layer of standard polymer-blend with a conductive filler, and one external PVA layer. This system was tested in two variations. A layer of standard polymer-blend, or PVA was in contact with the zinc electrode (see Cells 4 and 5, accordingly). The cell in which the layer of standard polymer-blend contacted the zinc electrode lasted 156 cycles and small dendrites grew through the separator. Very little Zn was outside of the separator bag. Shape change of the zinc electrode was not significant. The cell with the separator bag in which the PVA layer contacted the zinc electrode worked for 120 cycles and lost capacity as a result of shape change. Almost all zinc was outside of the separator bag and the cell was not shorted.

The cell with PVA coating on the negative plate and one layer of standard polymer-blend shorted after 114 cycles but zinc grew along the lead and created a bridge over the separator. The

separator film looked very good; zinc did not penetrate through the polymer-blend film.

A zinc penetration test was performed on commercial separator systems. Two commercially available separator materials were tested: Celgard K-307 (polypropylene microporous film coated on both sides by cellulose acetate) and Celgard K-317 (similar to K-307 but the coating on one side is cellulose acetate to which Ni powder is added as a filler). Results obtained were compared with data of zinc penetration time for ERC-developed separator systems (see Table III.25).

As indicated in the table, the zinc stopping ability of the polymer-blend film is higher than that of Celgard K-307 and two layers of polymer-blend film with PVA solution between lasted twice as long as Celgard K-317.

As discussed above, several separator systems developed at ERC allow an increase in cycle life of Ni-Zn cells (approximately two to three times greater than any other separator system with two or three layers of commercial material under the same cycling conditions). Development of more uniform polymer-blend film, with optimum properties of component and production technology for separator systems will permit a substantial increase in the cycle life of the Ni-Zn battery. Only after optimization of the properties for the described systems will it be possible to determine which separator system is the best for Ni-Zn batteries. Moreover, performance differences between small and large cells will require changes in separator system properties.

Separator systems were also tested to examine optimum combinations and ability to reproduce materials. Three systems

TABLE III.25

Zn PENETRATION TIME FOR
ERC-DEVELOPED AND COMMERCIALY AVAILABLE SEPARATOR SYSTEMS

<u>COMPOSITION</u>	<u>TIME IN HRS.</u>
1. PVA solution inside	110
2. K-317 (Celgard)	24
3. K-307 (Celgard)	11.5
4. One layer polymer-blend	24

ENERGY RESEARCH CORPORATION

tested were:

1. Crosslinked PVA coating and one layer of polymer-blend separator bag on the zinc electrode.
2. Crosslinked PVA coating on two positive electrodes and one layer of polymer-blend separator bag on the zinc electrode.
3. Two-layer bag of polymer-blend separator film on the zinc electrode and crosslinked PVA solution between the layers of the polymer-blend film.

The cycle life and failure modes of the cells tested are given in Table III.26 (for Cells 1 thru 9). The cycle life of cells employing one layer of polymer-blend separator and PVA + boric acid + DMU coating on the negative electrode varied from 162 to 276 cycles, indicating that the combination tested has high potential to increase the durability of the Ni-Zn batteries. However, the optimum properties of coating and the polymer-blend film must first be determined.

The second combination was one layer of polymer-blend separator bag on the negative electrode and PVA + boric acid + DMU coating on the two positive electrodes. Cells with this system worked for 78 and 84 cycles. The reason for short cycle life of the cells was that too thick of a coating was used on the Ni electrodes. Therefore, electrical resistance of the separator system was too high. Experiments with this separator system will be continued.

The last combination was two layers of polymer-blend separator film and crosslinked PVA solution between the polymer-blend layers. Cells with this configuration lasted 150 and 301 cycles. Two other cells performed for 310 and 440 cycles. The cell with an aqueous polymer solution worked for 310 cycles and maintained 100%

TABLE III.25

EFFECT OF OTHER SEPARATOR CONFIGURATIONS ON CYCLE LIFE AND FAILURE MODE OF THE CELLS

THEORETICAL ZINC CAPACITY (AH) = 14.4 AH

ELECTRODE SIZE: H - 3-7/8" $\pm$ 1/16"W - 2-7/8" $\pm$ 1/16"T - .07" $\pm$.002"

DISCHARGE = 2.5A x 1 hr.

CHARGE/DISCHARGE RATIO (%) = 120%

ELECTRODE TYPE & NO.	SEPARATOR CONFIGURATION	CYCLE	FAILURE MODE	COMMENTS
(1) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of (2N) polymer-blend on negative plate and the positive plate was coated five times with (PVA + DMU + BA) solution.	78	High Resistance	Separator looks good. There was shape change in negative plates. Plates was dried, resistance was too high.
(2) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of (2N) polymer-blend on negative plate and the positive plate was coated five times with (PVA + DMU + BA) solution.	84	High Resistance	Shape change evident. Coating swells and dries the plate.
(3) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of (2N) polymer-blend on negative plate. Plate was coated with (PVA + DMU + BA) solution.	162	Shape Change	Separator looks good. There was shape change. All zinc was gone in solution. Cell was too light.
(4) 2 Full Sintered Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of NPB on negative plate. Plate was coated with (PVA + BA + DMU) solution. Pellon on the plates.	276	Shape Change	There was zinc in cell. Shape change observed. Separator was good.
(5) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	Two layers of polymer-blend on negative plate with pure PVA solution inside the bag.	150	High Resistance	Resistance was too high. Solution dried up and made a thick layer of PVA. Zinc remains on PVA film. There was shape change.

TABLE III. 26

EFFECT OF OTHER SEPARATOR CONFIGURATIONS ON CYCLE LIFE AND FAILURE MODE OF THE CELLS

THEORETICAL ZINC CAPACITY (AH) = 14.4 AH

ELECTRODE SIZE: H - 3-7/8" $\pm$ 1/16"W - 2-7/8" $\pm$ 1/16"T - .07" $\pm$.002"

DISCHARGE = 2.5A x 1 hr.

CHARGE/DISCHARGE RATIO (%) = 120%

<u>ELECTRODE TYPE & NO.</u>	<u>SEPARATOR CONFIGURATION</u>	<u>CYCLE</u>	<u>FAILURE MODE</u>	<u>COMMENTS</u>
(6) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	Two layers of polymer-blend with (PVA + BA) solution inside on negative plate. Pellon on the plates.	301	Shape Change	There was shape change of zinc electrode. All zinc remains on the lower half of plate. There were some pinholes. Solution dries up and took the form of thick layer.
(7) 2 Rolled Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	Two layers of polymer-blend with polymer solution inside the bag on negative plate. Pellon on the plates.	310	Shape Change. Pinholes	There was some shape change. All zinc remains on the lower half of plate. There were some pinholes. Solution inside the bag dried up and took the form of thick layer. Too much zinc on that layer.
(8) 2 Rolled Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of NP _{B2} on negative plate was coated with (PVA + BA) solution. Pellon on the plates.	92	Cell Dried Up. Shape Change.	Ni plates swell and dry zinc plate. There was shape change. Zinc dendrites grow through separator.
(9) 2 Rolled Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	Two layers of polymer-blend on negative plate (PVA + BA + DMU) solution inside the bag. Pellon on the plates.	440	Shape Change	Separator looks good. There was shape change. All zinc went in solution. There was very less zinc on plate.

ENERGY RESEARCH CORPORATION

capacity up to 100 cycles. A cell with an aqueous PVA + boric acid + DMU solution lasted 440 cycles with over 375 cycles above 75% of initial capacity. The cell which lasted 150 cycles was made with an extra quantity of the solution. Therefore, the internal resistance of the cell increased when the solution dried up. Data obtained show that the separator system containing a liquid yields the longest cycle life thus far and reproducibility of the results is very good.

Test conditions for small Ni-Zn single electrode cells were changed in order to achieve a greater acceleration of the test. The discharge current was increased from 2.5 to 3 amperes for the same discharge time (one hour). The charge remained at 120%. Cells which were under test during this changeover adjusted their performance after 3 to 4 cycles and show almost the same capacity after an additional 50 cycles.

The dependence of cell capacity and the end of discharge voltage on number of cycles is presented in Figures III.6 thru III.8. Comparison of the curves of cells containing different separator systems shows that several cells which worked for more than two hundred cycles had a second step on the curves in coordinates capacity versus number of cycles. The capacity started to decline after 60 or 80 cycles like previous curves. But at a certain level, the capacity stopped decreasing and did not change during the next 120 to 200 cycles. Understanding the nature of the second step and gaining the ability to produce cells having long second steps at high capacity levels can probably solve the problem of durability for Ni-Zn batteries.

Results obtained with two layers of microporous separator

FIGURE III.6 DEPENDENCE OF CELL CAPACITY AND END-OF-DISCHARGE VOLTAGE ON NUMBER OF CYCLES, CELLS 6 AND 8

O - Capacity to 1.25V

X - End-Of-Discharge Voltage

FIGURE III.7 DEPENDENCE OF CELL CAPACITY AND END-OF-DISCHARGE VOLTAGE ON NUMBER OF CYCLES, CELLS 9 AND 10

FIGURE III.8 DEPENDENCE OF CELL CAPACITY AND END-OF-DISCHARGE VOLTAGE ON NUMBER OF CYCLES, CELL 9

film and polymer solution between the layers show promise in improving cycle life of Ni-Zn small cells. The problem is to immobilize the polymer solution which is used in liquid form between two layers of microporous separator film. The presence of a liquid layer in the separator system creates difficulties in assembling the cells and in obtaining reproducibility of results. To keep the liquid layer entrapped in a form which wash suitable for cell assembly, several highly porous materials were used: nylon net, fibrous glass mat, porous carbon sheet and fibrous nickel mat. Cells containing two layers of polymer-blend film and highly porous material impregnated in aqueous an polymer solution were made and tested. Results are given in Table III.27. According to the data obtained, introduction of an additional porous layer impregnated in liquid solution resulted in a sharp increase in electrical resistance of the separator system and in loss of substantial cycle life of the cells. Other methods for immobilizing the liquid layer are presently being investigated.

Development of a more uniform duplex separator film comprised another part of the development studied. Duplex separator material containing a polymer-blend film cast on top of improved PVA film has more uniform properties. Electrical resistance of the separator film is between 100 and 135 $m\Omega$ -in²/mil and zinc penetration time is about 92 hours (almost three times higher than for Celgard K-317).

TABLE III.27

CYCLE LIFE OF THE CELLS CONTAINING IMMOBILIZERS FOR LIQUID LAYER IN SEPARATOR SYSTEM
THEORETICAL ZINC CAPACITY (AH) = 14.4 AH

ELECTRODE SIZE: H - 3-7/8" $\pm$ 1/16"

DISCHARGE = 2.5 A x 1 hr

W - 2-7/8" $\pm$ 1/16"

CHARGE DISCHARGE RATIO(%) = 120%

T - .07" $\pm$.002"

<u>ELECTRODE TYPE & NO.</u>	<u>SEPARATOR CONFIGURATION</u>	<u>CYCLE</u>	<u>FAILURE MODE</u>	<u>COMMENTS</u>
(1) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	Two layers of polymer-blend and PVA solution in the bag on negative plate. Pellon on the positive plates.	30	Very high resistance	Made a very thick spongy layer of PVA. Resistance was high.
(2) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	Two layers of polymer-blend and polyurethane net and polymer solution was in bag on negative plate. Pellon on the positive plate.	24	High resistance	Polyurethane net does not have any resistance against KOH. It dissolved and made a thick layer with polymer solution. Resistance was too high.
(3) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	(2N) polymer-blend bag on negative plates. Polymer solution and (nylon net) was in the bag. Pellon on negative plates.	24	High resistance	Net combines with solution.
(4) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	(2N) polymer-blend bag on negative plates. Polymer solution and a film with fibrous glass were inside the bag.	24	High resistance	Net looks very sticky.
(5) 2 Rolled Ni 1 Zinc ZnO - 93% CdO - 5% TFE - 2%	(2N) polymer-blend bag on negative plate and nickel net was inside the bag. Pellon on positive plates.	48	High resistance	Zinc dendrites grow and stay in net.

Results presented in this section prove that specially designed separator systems have better properties than any single separator material or simple multi-layer separators. For example:

<u>Cell Description</u>	<u>Maximum Cycle Life</u>
1. With one layer of crosslinked PVA	85 cycles
2. With one layer of polymer-blend separator	138 cycles
3. With two layers of crosslinked PVA	89 cycles
4. With two layers of polymer-blend separators	105 cycles
5. With two layers of Celgard K-307 (Celgard is the best commercially available separator material so far).	120 cycles

Employing a combination of a polymer-blend separator material and crosslinked PVA results in an increased cycle life of the Ni-Zn small cells up to 250 cycles. The use of ERC separators with liquid semi-permeable membranes results in cells which can perform for more than 300 reproducible cycles. However, data obtained during cycling small cells do not always correlate with testing results for large cells. Therefore, assembling and testing of small cells were discontinued and full size, single electrode cells have been produced.

2.3.2 Testing Different Separator Systems in Full Size, Single Electrode Cells

Several separator systems which showed promise in small cells were tested in full size, single electrode cells containing one negative and two positive electrodes.

ENERGY RESEARCH CORPORATION

Cell Design

2 Full Rolled Ni Plates

1 Full Zinc Plate

Ni Plate: H - 9" $\pm$ 1/16"
 W - 6-1/2" $\pm$ 1/16"
 T - .082" $\pm$.002"

Zinc Plate: H - 9" $\pm$ 1/16"
 W - 6-1/2" $\pm$ 1/16"
 T - .053" $\pm$.002"

Theoretical Capacity of Ni: 24.4 Ah

Theoretical Capacity of Zn: 80 Ah

Test Conditions

1. Charge at 4 amp. for 6 hours
2. Discharge at 10 amp. for 2 hours
3. Overcharge 20%
4. Depth of Discharge on Negative 25%
5. Rate of Discharge C/2

Test results are given in Table III.28. A cell with one layer of polymer-blend separator worked for 96 cycles, down to 60% of initial capacity. The failure mode was shape change of the zinc electrode and no traces of zinc penetration through the separator were visible. The second cell tested contained one layer of duplex PVA + polymer-blend film and two positive plates were coated by PVA + BA. The cell lasted 105 cycles and the failure mode was also shape change. The positive electrodes swelled and the center of the negative electrode dried out in both cases and essentially reduced the working area of the electrodes and the capacity of the cell. Very similar results could be seen after Cells 3 and 4 were taken apart. The first preliminary conclusions

TABLE III.28

CYCLE LIFE OF FULL SIZE SINGLE ELECTRODE CELLS

THEORETICAL NI CAPACITY (AH) = 24 AH

ELECTRODE SIZE: H - 9" $\pm$ 1/4"W - 6-1/2" $\pm$ 1/4"T - .082" $\pm$.002"

<u>ELECTRODE TYPE & NO.</u>	<u>SEPARATOR CONFIGURATION</u>	<u>CYCLE</u>	<u>FAILURE MODE</u>	<u>COMMENTS</u>
(1) 2 Rolled Ni 1 Full Zinc ZnO - 88% Bi ₂ O ₃ - 10% TFE - 2%	(2N) Polymer-blend on negative plate and Pellon on the positive plates.	96	Shape Change	Separator looks good. There was no pinhole in it. Ni plates swell too much and dries up the plate.
(2) 2 Rolled Ni 1 Full Zinc ZnO - 93% CdO - 5% TFE - 2%	One layer of NPB on negative plate and Pellon on positive plate. The positive plates were coated with (PVA + BA) solution.	105	Shape Change	There was significant shape change of zinc plate. Ni plates swell and dries the zinc plate.
(3) 2 Positive Rolled Ni 1 Full Zinc(negative) ZnO - 88% Bi ₂ O ₃ - 10% TFE - 2%	One layer of polymer-blend on neg. plate. Plate was coated with PVA solution. Only Pellon on the plate. Only Pellon on the positive plates.	75	Shape Change	Separator looks good. There was shape change. Separator looks strong without any pinholes.
(4) 2 Positive Rolled Ni 1 Full Zinc(negative) ZnO - 88% Bi ₂ O ₃ - 10% TFE - 2%	Three layers separator & polymer-blend film. Inside layer was filled with a conductive filler.	75	Shape Change	A lot of zinc outside of the separator bag. Too high electrical resistance of the separator system.

to be made from these tests are that large zinc electrodes are more sensitive to shape change than small electrodes, and pressure developed in big cells is much higher than in small cells.

Several full size, single electrode cells were produced with the most promising separator systems (see Table III.29). A cell with two layers of polymer-blend film and PVA + BA + DMU solution worked 105 cycles down to 60% of initial capacity. The failure mode was shape change of the zinc electrode. The positive electrodes swelled and squeezed the solution out of the negative which dried up the center of the plate. Swelling of the positive electrodes reduced the electrode working area and the capacity of the cell. The dependence of cell capacity on number of cycles (see Figure III.9) started to decline after 30 cycles and did not exhibit a second step as found in small cells with the same separator system.

The cell with two layers of polymer-blend film and a polymer solution between the layers of separator film worked for 90 cycles and showed 67% of initial capacity (see Figure III.10). A cell with two sintered positive electrodes had 100% capacity up to 60 cycles and showed about 80% of initial capacity after 84 cycles. Only one layer of polymer-blend separator film was used in the last cell. These facts indicate that the swelling phenomenon influences full-size cell performance much more than cycle life of small cells since sintered positive plates do not swell to any great extent.

Negative electrodes are now being developed which are much less sensitive to the pressure exerted by the positive electrodes. Several cells with the improved zinc electrode and different

FIGURE III. 9

DEPENDENCE OF CELL CAPACITY ON NUMBER OF CYCLES

FIGURE III.10

DEPENDENCE OF CELL CAPACITY ON NUMBER OF CYCLES

TABLE III. 29
CYCLE LIFE OF THE FULL SIZE CELLS CONTAINING LIQUID LAYER IN THE SEPARATOR SYSTEM
THEORETICAL Ni CAPACITY (AH) = 24 AH

ELECTRODE SIZE: H - 9" $\pm$ 1/4"
W - 6-1/2" $\pm$ 1/4"
T - .082" $\pm$.002"

<u>ELECTRODE TYPE & NO.</u>	<u>SEPARATOR CONFIGURATION</u>	<u>CYCLE</u>	<u>FAILURE MODE</u>	<u>COMMENTS</u>
(1) 2 Rolled Ni 1 Zinc ZnO - 88% Bi ₂ O ₃ - 10% TFE - 2%	PVA solution inside polymer- blend bag.	105	Shape Change	Solution dried up and there was shape change. Ni plates swell too much, separator looks a little brittle.
(2) 2 Sintered Ni 1 Zinc ZnO - 88% Bi ₂ O ₃ - 10% TFE - 2%	(2N) polymer-blend bag on negative plate. Polymer solution was in the bag. Pellon on positive plates.	90	Pinholes	There were too many zinc dendrites on separator. It had pinholes, solution dried and made thick layer of polymer.
(3) 2 Rolled Ni 1 Zinc ZnO - 95% CdO - 1% PbO - 2% TFE - 2%	(2N) polymer-blend bag on negative plate. PVA solution in the bag.	98	Shape Change	Solution dried and made thick layer. Zinc dendrites were all over the layer.
(4) 2 Rolled Ni 1 Zinc ZnO - 95% PbO - 2% TFE - 2% CdO - 1%	(2N) polymer-blend on negative plate. Pellon on positive plates.	115	Shape Change.	There was shape change but more uniform.
(5) 2 Rolled Ni 1 Zinc ZnO - 95% PbO - 2% TFE - 2% CdO - 1%	(2N) polymer-blend bag on negative plate. Polymer solution was in the bag. Pellon on positive plates.	115	Zinc Dendrites grow at positive terminal.	

TABLE III. 29

CYCLE LIFE OF THE FULL SIZE CELLS CONTAINING LIQUID LAYER IN THE SEPARATOR SYSTEM

THEORETICAL Ni CAPACITY (AH) = 24 AH

ELECTRODE SIZE: H - 9" $\pm$ 1/4"W - 6-1/2" $\pm$ 1/4"T - .082" $\pm$.002"

<u>ELECTRODE TYPE & NO.</u>	<u>SEPARATOR CONFIGURATION</u>	<u>CYCLE</u>	<u>FAILURE MODE</u>	<u>COMMENTS</u>
(6) 2 Rolled Ni 1 Zinc ZnO - 88% Bi ₂ O ₃ - 10% TFE - 2%	One layer of K-317 and one layer of K-307 on negative plate. PVA solution was inside two layers. Pellon on positive plates.	92	Shape Change	Solution dried. There was too much zinc on film. Ni coating comes off from the film.
(7) 2 Sintered Ni 1 Zinc ZnO - 88% Bi ₂ O ₃ - 10% TFE - 2%	Two layers of (2N) polymer- blend on negative plate. Polymer solution was inside the bag. Pellon on positive plates.	92	Shape Change	Separator looks good. Zinc dendrites grow and remain on film. There was shape change.

separator systems were produced and they are now on test.

According to data obtained, cells with different separator systems had almost the same cycle life (between 90 and 115 cycles). This fact indicates that other limiting factors exist. Comparison of dependencies of capacity on number of cycles for small and full size single electrode cells shows that the number of cycles attained before capacity decline is about equivalent and the rate of this decline is almost the same. Therefore, average cycle life is about 100 to 120 cycles. However, in small cells it was possible to get a second capacity plateau for the dependence of capacity on number of cycles by employing a liquid membrane type separator. Only cells having a second plateau worked for more than 200 cycles. Conditions for obtaining a second plateau in performance for full-size cells have not been determined thus far.

Attempts were continued to immobilize the polymer solution, which is used in liquid form between two layers of microporous separator film. Plastic bags were constructed from microporous Celgard film; and PVA or other polymer aqueous solutions were put in the bags which were then sealed on top. The bags were then put in a freezer to immobilize the polymer solution. Frozen flat bags with polymer solution were used as a separator in the cells. Cells with one negative and two positive electrodes containing one layer of Celgard K-306 or polymer-blend film and one frozen bag on each side of the negative electrode were assembled and tested. The cells performed for 90 and 80 cycles to 60% of initial capacity (see Table III.30). The capacity of the cells started to decline after 40 cycles (see Figures III.11 and III.12). Post-failure examination has shown that all solution was squeezed out

TABLE III. 30

TEST RESULTS OF THE FULL SIZE CELLS CONTAINING DIFFERENT SEPARATOR SYSTEMS

THEORETICAL CAPACITY OF CELL = 24 AH

ELECTRODE SIZE: H - 9"

W - 6-1/2"

T - .082 ⁺ .002"

<u>ELECTRODE TYPE & NO.</u>	<u>SEPARATOR CONFIGURATION</u>	<u>CYCLE</u>	<u>FAILURE MGDE</u>	<u>COMMENTS</u>
1) 2 Rolled Ni 1 Zinc ZnO - 95% PbO - 2% CdO - 1% TFE - 2%	One layer of K-306 and bag of K-306 with polymer solution inside on the negative plate. Pellon on the plates.	90	Shape Change	Excessive zinc dendrites were in the cell. Celgard turned brown at some places. Polymer solution dried up. There was shape change.
2) 2 Rolled Ni 1 Zinc ZnO - 95% PbO - 2% CdO - 1% TFE - 2%	One layer of (2N) polymer- blend on positive plates. Two bags of K-306 and polymer solution inside the bag.	80	Shape Change	Rolled Ni swelled considerably and put pressure on negative plate, it dried up in middle. Shape change zinc plate.
3) 2 Rolled Ni 1 Zinc ZnO - 95% PbO - 2% CdO - 1% TFE - 2%	One layer of NPB on negative plate. Pellon on the positive plates.	78	High Resistance	Cell dried up. There was no KOH in cell. Separator looks brittle.

TABLE III. 30

TEST RESULTS OF THE FULL SIZE CELLS CONTAINING DIFFERENT SEPARATOR SYSTEMS

THEORETICAL CAPACITY OF CELL = 24 AH

ELECTRODE SIZE: H - 9"

W - 6-1/2"

T - .082 ⁺ .002"

<u>ELECTRODE TYPE & NO.</u>	<u>SEPARATOR CONFIGURATION</u>	<u>CYCLE</u>	<u>FAILURE MODE</u>	<u>COMMENTS</u>
(5) 2 Rolled Ni 1 Zinc ZnO - 95% PbO - 2% CdO - 1% TFE - 2%	One layer of (2N) polymer- blend and one layer of K-306 on negative plate. Pellon on positive plates.	120	Cell Dried, Shape Change	Cell dried up. Special middle part of both positive and negative electrode was too dry. Most of the zinc was on pellon and separator. Almost all zinc was gone from plate. Shape change.
(6) 2 Rolled Ni 1 Zinc ZnO - 95% PbO - 2% CdO - 1% TFE - 2%	Three layers of Celgard on negative plate. Pellon on positive plates.	126	Shape Change	
(7) 2 Rolled Ni 1 Zinc ZnO - 95% PbO - 2% CdO - 1% TFE - 2%	Three layers of Japanese PVA on negative plate. Pellon on positive plates.	47	Shape Change	Separator swells. Shape change in zinc electrode.

ENERGY RESEARCH CORPORATION

from the space between the electrodes and therefore the use of a polymer solution layer in a separator system of full-size cells does not result in increasing the cycle life of the cells.

The problem of optimum void space in the cell case relates to optimum pressure in the cell during cycling. Three similar cells were assembled with three layers of Celgard K-306 on the negative plates. The difference was only in the number of shims which filled the void space in the case. The cell with eight shims represented normal assembling conditions. The second cell had seven shims with 1/16" more void space than the first cell. The third cell contained six shims of 1/8" more void space than the first cell. The cells were assembled and tested during this month.

The cell with 1/8" void space could not be charged up during eight manual cycles and was disassembled. The negative electrode was not charged up at all. The cells with normal void space and with 1/16" extra void space were charged up after four manual cycles and were put on automatic cycling. During the first 48 to 50 cycles the cells performed identically but after that the cell with 1/16" extra void space started to decline whereas the cell which represented normal assembling conditions continued to show 100% of capacity. After 80 cycles, the "normal" cell was still yielding 100% of capacity but the cell with extra void space was showing only 60% of initial capacity. The cell with normal pack pressure performed 160 cycles down to 60% of initial capacity.

This experiment shows that lack of pressure in cell case is probably as detrimental as excessive pressure.

Two cells containing three layers of Celgard K-306 as a

FIGURE III.11

CELL 1

DEPENDENCE OF CELL CAPACITY ON NUMBER OF CYCLES

FIGURE III.12

CELL 2

DEPENDENCE OF CELL CAPACITY ON NUMBER OF CYCLES

separator in one cell and one layer of Celgard K-306 with two layers of nylon-based separator film in another showed 126 and 120 cycles, relatively, in full-size, 20 Ah cells (see Table III.30 and Figures III.13 and III.14).

3.0 CONCLUSIONS

3.1 PVA-BASED SEPARATOR MATERIALS

- PVA crosslinked by using a mixture of DMU and boric acid has shown improved chemical stability in an alkaline environment.
- Evaluation of crosslinked PVA indicates that it has improved mechanical and physical properties. Cycle life of the cells with one layer of separator increased the 85 cycles compared to the 60 cycles of commercial PVA.
- Attempts to increase the degree of crosslinking by using other reagents did not result in improvement of the properties in comparison with PVA crosslinked by DMU and boric acid.
- The mechanism of electrolyte permeability in PVA films was studied. The presence of non-equilibrium and equilibrium conditions for electrolyte permeability of PVA films containing aqueous KOH solution or residual water was explained from the view point of changing the diffusion mechanism of permeability.
- Diffusion of the electrolyte through the relatively dry polymer is realized by formation and breaking down of intermolecular bonds between the polymer and solvent. Activation energy of diffusion depends on the quantity of residual or absorbed solvent in the film. Change in this quantity results in variation of permeability properties and causes a non-equilibrium period of permeability.
- Diffusion of the electrolyte through the wet polymer is realized by the mechanism of solvent self-diffusion. Activation energy of self-diffusion is low and does not depend on quantity of solvent in the film. Therefore, permeability through the wet polymer has an equilibrium characteristic.
- Usually about 20% of the solvent is necessary to localize intermolecular interaction in the polymer and proceed from concentration-dependent diffusion to self-diffusion of the solvent. Local concentration of water in PVA is much higher than the average concen-

FIGURE III.13

CELL 5

DEPENDENCE OF CELL CAPACITY ON NUMBER OF CYCLES

FIGURE III.14

CELL 6

DEPENDENCE OF CELL CAPACITY ON NUMBER OF CYCLES

and, therefore, only 6% of the average weight concentration of water is enough to create conditions for equilibrium electrolyte permeability through PVA membranes.

- Crosslinking PVA as a separator material increases the probability of cell failure by shape change and reduces the hazard of zinc penetration.

3.2 POLYMER-BLEND SEPARATOR MATERIALS

- Properties of polymer-blend separator film were improved considerably during the period under review.
- Electrical resistance of the film is in the range of 30 to 150 m⁻ⁱⁿ²/mil and can be regulated. Employing polymer-blend films in Ni-Zn cells results in a substantial reduction of shape change in the negative electrode.
- Comparison of cycle life of cells containing Celgard K-307 (cellulose acetate coated on both sides of Celgard 3400) and polymer-blend separator film shows that the cells with one layer of polymer blend film achieved 132 and 138 cycles. Cells with one and two layers of Celgard K-307 lasted 120 cycles regardless of whether one or two layers of the film were employed.

3.3. DESIGN AND TEST RESULTS OF THE IMPROVED SEPARATOR SYSTEM

- Duplex separator material consisting of the polymer-blend layer which was cast on the top of the PVA film results in an increase in cell life up to about 200 cycles.
- The combination of one layer of polymer-blend film with a PVA coating on the negative electrode results in an increase in the cycle life of Ni-Zn cells up to 150 cycles.
- A separator system with three layers of PVA and polymer-blend films in which the inner polymer-blend layer (in addition to the normal components) contains a conductive filler amount of 50%, gives a maximum of 156 cycles.
- The best results were obtained with a separator system containing two layers of polymer-blend film and polymer solution in a liquid form placed between the polymer-blend layers. Reproducible results were obtained in the range of 300 to 400 cycles.
- Any improved separator system allows achievement of longer cycle life compared to simple multi-layer systems of similar materials.

4.0 FUTURE WORK

During this period, several improved separator systems were developed and tested. These systems are promising candidates for use in full size Ni-Zn cells. Therefore the tasks for the next period of work will include:

- a) Detailed evaluation of performance in large plate, 20 Ah and 250 Ah size cells.
- b) Improvement of the separator system to achieve maximum cycle life of full-size cells.
- c) Development of the production technology for polymer-blend and PVA base separator films.
- d) Study of long-term stability of separator materials.

REFERENCES

1. Philipp, W.H. and Hsu, Li Chen, "Method for the In-Situ Cross-linking of Polyvinyl Alcohol Films for Battery Separator Application in KOH Electrolyte", paper presented at 156th Electrochemical Society Meeting, Los Angeles, CA, October, 1979.
2. Design of the zinc penetration test cell and description of apparatus and procedure were taken from the book "Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries", Edited by J.E. Cooper and Arthur Fleischer.
3. Lonsdale, H.K., Merten, U., Riley, R.L., J. Appl. Polymer Sci., 4, 1341, 1965.
4. Reitlinger, S.A. "Pronitsaemost' Polimernykh Materialov", Khimiya, Moskva, 1974.
5. Yasuda, H., Lamaze, C.E., Ikenberry, L.D., Makromol Chem., 19, 118, 1968.
6. Vieth, W., Douglas, A.S. Am. Chem. Soc., Polymer Prepr., 9, 1556, 1968.
7. Riley, R.L., Lyons, C.R., Merten, U., Desalination, 2, 177, 1970.
8. Rosenbau, S., Mahon, J.J., Cotton, O., J. Appl. Polymer Sci., 10, 2041, 1967.
9. Dodin, M.G., ACS 179th National Meeting, Houston, Texas, March 1980.
10. Tager, A.A., "Physical Chemistry of Polymers" Khimiya, Moskva, 1968.
11. Chalykh, A.E., Vasenin, R.M., Vysokomolekulyarhye Soedineniya, Seriya A., 8, No. 11, 1966.

SECTION V.
DEVELOPMENT OF SEALED
NICKEL-ZINC CELLS - (TASK IV)

1.0 INTRODUCTION

The goal of this phase of the ANL nickel-zinc program is to determine the feasibility of operating large size cells in a sealed condition. Exploratory studies are being carried out in 20 Ah size cells to establish baseline construction and mode of operation parameters for sealed cells. The benefits of running Ni-Zn cells sealed include low maintenance and extended life due to oxygen recombination, which reduces zinc electrode state-of-charge, thereby inhibiting dendrite growth.

Early work in the program had developed 20 Ah cells which had good initial performance but poor cycle stability. Major problems which have inhibited cycle performance are electrolyte redistribution and hydrogen gas build-up. The hydrogen buildup has been solved with the development of catalytic recombination devices. To improve cell wetting, work has been done in the past year with experimental separator and absorber materials, as well as sealed cell designs which are run with an excess of electrolyte. This report presents the progress and results achieved over the past year in the program.

ENERGY RESEARCH CORPORATION

2.0 TECHNICAL DISCUSSION

2.1 EXPERIMENTAL SEPARATOR AND ABSORBER DESIGNS

Early in the year, the best separator design tested in sealed cells consisted of four layers of Celgard 3401 separator interspersed with layers of Pellon polyamide absorber felt. The importance of the extra layers of absorber is due to the fact that the cells are run electrolyte-starved.

Cells with the Celgard/Pellon separator design exhibited good initial performance, but were limited to about 30 cycles due to electrolyte redistribution during cycling. Over the past year, new materials from Celanese, Kimberly-Clark, and in-house were tested in sealed cells.

Experimental polymer-blend made at ERC was tested in sealed cells with separator designs as follows:

Cell 2W

Woven 2 layers
(+)Nylon Bag/ ERC Film/Pellon///Pellon/ERC Film/Pellon(-)

Cell 2X

Same separator system but with Pellon absorber on (+) plate

The ERC material had exhibited good performance in small cell testing performed under the separator development task of this project. However Cells 2W and 2X showed high voltages and gassing rates on charge, accepting less than 6 Ah charge input before pressure built up to 20 psig. Cell voltages at the end-of-charge were above 2V for both cells. The performance of these cells suggests that the polymer-blend film does not wet sufficiently for use in electrolyte-starved cells.

ENERGY RESEARCH CORPORATION

Sealed cells were also tested with three variations of Celgard separator materials. Cell CE-1 was built with a Celgard/cellophane laminate, CE-2 contained cellulose-acetate coated Celgard (coated on one side), and CE-3 contained Celgard coated on both sides with cellulose acetate. Each cell contained three layers of the Celgard film, with Pellon absorber wraps on the positive and negative electrodes. Flooded formation cycles were run on the cells prior to sealed testing, with the following results:

Cell	Separator	Flooded Formation Capacity, Ah	Charge Input To 20 psig, Ah	Drained Sealed Capacity, Ah
CE-1	Celgard/Cellophane Laminate	20	14.3	0
CE-2	Cellulose Acetate Coated Celgard (1 side)	19.2	20.9	12.2
CE-3	Cellulose Acetate Coated Celgard (2 sides)	20	18.1	17.0

Capacity for Cell CE-1 did not improve in subsequent tests and the cell was not cycle tested. When drained and sealed, the cell exhibited charge voltages in excess of 2.5V and delivered no capacity, indicating that the laminate film did not retain enough liquid for use in electrolyte starved cells.

Cells CE-2 and CE-3 were cycle tested with platinum catalyst packets in the cells to recombine hydrogen and oxygen. The cells were equipped with pressure switches which terminated charge when cell pressure reached 20 psig. The cells were

charged at 3.67 amps to 20 psig (or 22 Ah) and discharged at 10 amps to 1.25V (or 20 Ah). Test results are given in Table IV.1.

While the cell with the coating on one surface never delivered more than 13.8 Ah capacity, Cell CE-3 with Celgard coated on both sides ran for 32 cycles before capacity fell below 60% of nominal (12 Ah). This cycle performance is comparable to cells with a Celgard/Pellon separator system and indicates that the cellulose acetate coating significantly improves wetting of the Celgard material.

The three CE cells contained 5% CdO zinc electrode additive. Three more cells were made with the coated Celgard film (designated K-306) and zinc electrodes with 2% PbO and 1% CdO binary additive. As in the CE cells, 3 layers of K-306 were used with Pellon electrode wraps. Two cells, designated S-1-1 and S-1-2, were built with sintered positive electrodes. A third cell, S-2 was built with rolled, pressed electrodes. Formation and cycle test data for these cells are given in Table IV.2.

During flooded, vented formation cycles, the cells delivered more than 20 Ah. On the second cycle the electrolyte was drained from the cells and they were sealed prior to the discharge. The only cell to be adversely affected by the electrolyte removal was S-2, with the rolled positive electrodes. This indicates that the rolled positive plate is more sensitive to reduced electrolyte inventory than is the sintered plate.

TABLE IV.1
CYCLE TEST RESULTS OF CELLS WITH
COATED CELGARD FILM

CELL CE-2			
CYCLE #	CHARGE INPUT TO 20 PSI (Ah)	ECV	CAPACITY (Ah)
1	15.1	2.00	13.8
3	14.2	1.97	12.5
5	13.3	2.01	10.0
7	12.4	2.01	8.8
9	12.4	2.02	8.8
11	12.0	2.05	8.3
13	11.5	2.05	8.1

CELL CE-3			
CYCLE #	CHARGE INPUT TO 20 PSI	END OF CHARGE VOLTAGE	DISCHARGE CAPACITY TO 1.25V
1	13.3	1.90	11.2
3	14.2	1.95	10.2
5	22	1.95	16.9
7	22	1.92	17.5
9	22	2.00	18.1
11	22	1.97	18.1
13	22	1.95	17.5
15	22	1.95	17.5
17	21	1.95	15.0
20	19	1.95	14.3
24	18	1.92	13.8
28	16.5	1.92	12.5
32	16.0	1.92	11.8
35	15.5	1.90	10.0

TABLE IV.2
PERFORMANCE DATA FOR SEALED CELLS
S-1-1, S-1-2, and S-2

CELL NO.:		S-1#1		S-1#2		S-2	
Positive Electrode		Sintered		Sintered		Rolled-Pressed	
		Capacity ECV to 1.25V		Capacity ECV to 1.25V		Capacity ECV to 1.25V	
ALL DISCHARGES AT 10AMPS							
Flooded formation cycle 32Ahr charge		1.923	23.8	1.931	22.2	1.879	21.3
Flooded 32Ahr charge. Sealed, starved 10Amp discharge		1.939	23.3	1.940	22.6	1.973	19.3
Sealed 4Amp charge, 32.5Ahr input		1.920	22.7	1.911	21.2	1.850	8.5
Automatic cycle: 3.67Amp charge x 6Hrs; 10Amp discharge x 2Hrs.							
CYCLE NO.	1	1.75	18.9	1.79	17.9	1.75	19.0
	5	1.85	18.6	1.90	19.1	2.00	>20Ahr 1.4 EDV
	10	1.88	17.6	1.90	18.1	1.91	14.5
	15	1.90	18.5	1.90	16.0	1.90	13.0
	20	1.90	12.8	1.90	16.0	1.95	16.1
	25	1.90	11.8	1.87	15.0	1.96	14.0
	30			1.90	12.0	1.90	11.5

FIGURE IV.1 PRESSURE AND VOLTAGE ON A 4A CHARGE FOR CELLS S-1-1, S-1-2 & S-2

ENERGY RESEARCH CORPORATION

The cells were then given a 4 amp charge in the sealed condition which lasted for 8.1 hours. Only one cell had built up pressure to 20 psig at this point. The pressure in Cell S-2 rose to only 3.4 psia (from a 25 in. Hg vacuum) during charge. After this, the cell delivered only 8.5 Ah, but capacity improved during cycling, with the cell eventually delivering a full 20 Ah discharge.

Cell S-1-1 developed 19 psia during charge and delivered 22.7 Ah capacity. Cell S-1-2 developed 33.5 psia on charge and delivered 21.2 Ah capacity. Figure IV.1 shows the pressure and voltage behavior of these cells during charge. Immediately following charge, the pressure decayed in Cells S-1-1 and S-1-2 at 15.7 and 10.7 psi/hour, respectively. Pressure increased in Cell S-2 just after charge at a rate of 0.65 psi/hour.

Following this test, the cells were put on the automatic cycle test described above. Relief valves set at 20 psig were used to allow full charge input. The cycle results are given in Table IV.2. Between Cycles 10 and 15, an equipment malfunction caused the cells to receive a 100% overcharge. The cells were then conditioned by discharging them to 0.0V, but the overcharge probably accelerated their failure.

In terms of cycle life (number of cycles with capacity more than 12 Ah) the three cells were similar, although the cells with sintered plates exhibited a more stable capacity. Following the cycle test, the cells were refilled, and tested vented to determine the extent to which dry-out had caused failure. Cell performance did not improve significantly and the data indicated that the cells were short-circuited. Open circuit voltage of the cells declined significantly with time and end-of-charge voltages were low, indicating the presence of shorts.

2.2 CELLS WITH Ag-HgO RECOMBINATION ELECTRODE PARTITIONS

A major problem in developing sealed Ni-Zn cells has been their poor performance in the electrolyte starved condition. (The cells are run starved to allow oxygen transport for recombination.) One approach to this problem is running the cell pack flooded, with auxiliary electrodes used for the oxygen recombination reaction. A design was evolved in which Ag-HgO recombination electrodes were run along the sides of the cell pack with one side wet by electrolyte and the other side exposed to the cell gas. The side of the electrode exposed to gas is laminated with a layer of 2 mil unsintered Teflon film to prevent flooding of the electrode. A diagram of the cell is shown in Figure IV.2.

The first cell built with this design, Cell 2R-5, contained 2% CdO + 1% PbO zinc additive and 3 layers of PVA separator. Pellon was used as the electrode absorber wrap.

Initial performance of the cell was very good. Vented capacity was 19.7 Ah after a 24 Ah charge. Figure IV.3 shows the pressure rise and recombination current on the first sealed charge. After 30.3 Ah of charge the cell was 4 in. of Hg below atmospheric pressure (the cell was at 25 in. Hg vacuum at the start of charge). Discharge capacity of the cell was 21.2 Ah.

The recombination current on charge is a measure of the positive electrode charge efficiency at any point during the charge. It represents the proportion of the charge current lost in oxygen production at the positive electrode. Figure IV.4 shows the charge efficiency curve for Cell 2R-5, with efficiency calculated as:

FIGURE IV.2
Ni-Zn CELL WITH RECOMBINATION
ELECTRODE PARTITION

FIGURE IV.3 PRESSURE AND RECOMBINATION CURRENT CN 4A CHARGE FOR CELL 2R-5.

FIGURE IV.4 CHARGE EFFICIENCY ON CHARGE FOR CELL 2R-5 (BASED ON O₂ RECOMBINATION CURRENT)

ENERGY RESEARCH CORPORATION

$$\text{Charge Efficiency} = \frac{\text{Charge Current} - \text{Recombination Current}}{\text{Charge Current}}$$

The average charge efficiency over the 30.3 AH charge (Cell S-1-2 in Figure IV.1) was 83%. The actual efficiency ($\frac{\text{discharge capacity}}{\text{charge input}}$) was 70%. This is a lower figure because it includes capacity lost due to self-discharge during the time between charge and discharge.

During the 15.6 hour open circuit stand following the first sealed charge, cell pressure rose from a 4 in. Hg vacuum to 18.5 psig (the Ag-HgO electrode was not connected). At this point the recombination electrode was connected and the pressure began to decay as shown in Figure IV.5. The high rate of recombination indicates that much of the gas generated on open circuit was oxygen due to self-discharge of the highly charged positive electrode. Assuming that all of the oxygen was consumed over the 45 minutes shown in Figure IV.5, the cell gases, before connection of the Ag-HgO electrode, were composed of 7.25 psia hydrogen (22%) and 23.5 psia oxygen (71%), with the remaining gas being nitrogen from the 2.49 psia of air that was in the cell before the charge. The 23.5 psia of oxygen corresponds to about a 3.5 Ah positive plate capacity loss, which accounts for the difference in the efficiency estimates discussed above.

The results shown in Figure IV.5 were used to determine the dependence of recombination current on oxygen partial pressure. This relationship, shown in Figure IV.6, appears to be linear, with some limiting of the reaction rate occurring above 6 amps.

CURRENT
(AMPERES)

FIGURE IV.5 OPEN CIRCUIT OXYGEN RECOMBINATION FOR CELL 2R-5

FIGURE IV. 6

RELATIONSHIP BETWEEN RECOMBINATION RATE AND
OXYGEN PRESSURE DURING OPEN CIRCUIT RECOMBINATION, CELL 2R-5

ENERGY RESEARCH CORPORATION

While initial pressure behavior and discharge capacity were good, performance declined with cycling. The cell was cycle tested with pressure switches set to terminate charge at 20 psig. Platinum catalyst packets were used in the cell to prevent hydrogen build up. The cycling results were as follows:

Charge Number	Charge Input To 20 psi, Ah	End-of-Charge Voltage, Volts	Discharge Capacity to 1.25V, Ah
1	22.0	1.89	15.0
3	19.5	1.80	10.0
5	22.0	1.87	13.1
7	14.5	2.05	10.0
8	12.8	2.10	9.4
9	11.0	2.12	8.1

Following the cycle test, the cell was given a vented 24 Ah charge. Discharge capacity was 16 Ah.

The cell was dissected to determine why capacity had fallen so quickly. The separator material was generally in good condition although the PVA at the electrode edges was wrinkled and darkened due to occasional high current densities and high temperatures near the Ag-HgO electrode. Very little zinc penetration was found; however the zinc electrodes exhibited severe shape change. Shape change appears to be accelerated by the recombination electrodes, which discharge the zinc electrode non-uniformly at the edges to a greater extent than the inner portion of the electrode.

Design modifications were made to allow more uniform utilization of the zinc electrode. In one design, the ZnO

ENERGY RESEARCH CORPORATION

active material at the electrode edges was replaced by strips of CdO electrode material, shifting much of the recombination discharge to an insoluble active material. Another approach involved replacing the PVA separator system with Celgard materials with more open pore structures, allowing greater mass transport of electrolyte to the inner portion of the cell pack. The Celgard/Pellon system and the 3 layer K-306 separator system were used.

Cell 2R-6 was built with the Celgard/Pellon system and electrode designs identical to Cell 2R-5. Cell 2R-7 contained the same electrode formulations and a separator system consisting of 3 layers of K-306 with an extra layer of Pellon absorber inserted between two of the layers. Woven nylon was used as the positive plate wrap in both cells to allow room for the extra Pellon layers. Cell 2R-8 contained the same separator system as Cell 2R-5 (3 layers PVA) but was built with zinc electrodes in which 1/2 inch strips on each side had been replaced with active material composed of 94% CdO, 5% Ag powder and 1% Teflon binder. Data for these cells on vented formation cycles are given in Table IV.3.

Discharge capacities for Cell 2R-6 were low. Dissection analysis indicated that much of the Celgard had not wet and zinc penetration was severe in the areas that had wet. Failure of the cell was due to the poor wetting of the 3500 film (earlier cells with the Celgard/Pellon system were built with 3401, which contains an improved wetting agent).

Cells 2R-7 and 2R-8 were cycle tested with relief valves set to vent at 30 psig. The cells were charged at 4 amps for

CELL NO.	DESIGN FEATURES	FIRST CYCLE		SECOND CYCLE		
		End of Charge Voltage	Discharge Capacity to 1.25V	End of Charge Voltage	Discharge Capacity to 1.25V	Discharge Midpoint Voltage
2R-6	Celgard Separator: Nylon/3400 /Pellon/2xCelgard/Pellon/Celgard///Pellon 2% CdO + 1% PbO additive	1.987	6.8	1.984	8.2	1.32
2R-7	(+)Nylon/2xK306/Pellon/K-306//Pellon(-) 2% CdO + 1% PbO additive	1.865	20.2	1.895	24.0	1.59
2R-8	(+)Pellon/2PVA///1PVA/Pellon(-) 2% CdO + 1% PbO + Cd strips on electrode edges	1.849	5.2	1.909	16.2	1.59

TABLE IV.3

FORMATION DATA FOR CELLS WITH RECOMBINATION ELECTRODES

6 hours and discharged at 10 amps to 1.25V for 2 hours. The recombination electrodes were connected to the negative electrode through a shunt resistor, through which current readings could be taken.

Cycling results for these cells are given in Table IV.4.

The pressure, voltage and recombination current monitored during Cycle 7 are shown in Figures IV. 7 and IV.8. It is apparent in both cells that recombination current reaches a maximum and then drops as the relief valve vents and oxygen partial pressure decreases (due to increasing rates of hydrogen generation). In Cell 2R-7, recombination current reached a maximum of 3.8 amps, or 95% of the charge current. In Cell 2R-8, recombination current reached a maximum of only 2.2 amps, or 55% of charge current. This difference in recombination current, an indication of positive electrode efficiency, is consistent with the discharge capacity data.

Prior to being placed on automatic cycle, Cell 2R-7 was tested to determine the characteristics of the recombination electrodes. The cell was vacuumed and then filled with various pressures of pure oxygen. Pressure was maintained by a regulator, which continuously fed oxygen to the cell. The readings at higher pressures were taken first. Equilibrium current values were reached fairly quickly (within two minutes) at each pressure. Figure IV.9 shows a linear relationship between reaction rate and O_2 pressure up to about 21 psia (6.3 psig), where current becomes limited. Because this test involved sustained reaction rates, the current values are lower than in Figures IV.5 and IV.6 (with Cell 2R-5). The limitations in recombination rate seen in Figures IV.6 and IV.9

TABLE IV. 4
 Cycle Performance of Sealed Cells with
 Recombination Electrodes

Cycle #	CELL 2R7		CELL 2R8	
	End of Charge Voltage	Discharge Capacity To 1.25V	End of Charge Voltage	Discharge Capacity to 1.25V
	(Volts)	(Ampere Hours)	(Volts)	(Ampere Hours)
3	1.90	18.1	1.91	18.0
5	1.89	14.4	1.89	14.8
7	1.90	13.8	1.98	16.0
9	1.91	13.0	2.12	16.0
11	1.97	14.9	2.15	16.9
13	2.00	15.2	2.15	17.5
15	1.90	13.8	2.12	16.0
17	1.90	11.8	2.05	14.2
19			2.00	13.2
21			1.90	11.2
23			1.80	8.0

All Charges: 4 Amps x 6 hours

All Discharges: at 10 Amps

FIGURE IV. 7 PERFORMANCE OF CELL 2R7 ON CYCLE #7

FIGURE IV.8
PERFORMANCE OF CELL 2R8 ON CYCLE #7

FIGURE IV.9 CELL 2R7 RECOMBINATION RATE VS O₂ PRESSURE

are due to limitations in ion transport from the plates through separator wraps to the recombination electrode.

While initial performance of Cells 2R-7 and 2R-8 was good, the data in Table IV.4 show a rapid decline in capacity during cycling, with both cells failing within 20 cycles. Dissection of 2R-7 showed considerable shape change and zinc penetration throughout the center portion of the separator wrap. The separator was wet and had not lost much strength. Zinc had saturated the center portion of the Pellon wrap, which was fused to the plate.

Shape change was also evident in the negative plates in Cell 2R-8, but it was not as severe as in Cells 2R-7 or 2R-5. The cadmium strips were intact and showed a change in color toward the edges, indicating a variation in the state of charge. The PVA separator had oxidized considerably, losing much of its strength and appearing black near the electrode edges. Zinc penetration could be seen throughout the separator area covering the zinc portion of the negative plates.

The performance of cells with the recombination electrode partition indicates that the benefits provided by the flooded cell pack may be outweighed by the uneven utilization of the zinc electrode. Cycle test performance in these cells was inferior to cells run electrolyte-starved, where the recombination reaction was more evenly distributed on the zinc electrode.

3.0 CONCLUSIONS AND FUTURE WORK

The potential benefits of the sealed cell configuration have not yet been realized in Ni-Zn cells. The two best sealed cell designs (containing Celgard/Pellon or coated Celgard separator systems) are limited to about 30 cycles. This result has been achieved in cells with charge-terminating pressure switches as well as cells with relief valves which allow a full charge input.

The predominant failure mechanism in the cells is dry-out, due to electrolyte redistribution during cycling. One approach to this problem, using the recombination electrode partition, increased the shape change problem by distributing the oxygen recombination reaction unevenly over the zinc electrode to the plate edges.

Another approach is to improve the electrode retention capability of the separator layers, absorber wraps and electrodes. Future work in the sealed cell task should focus on this approach.

Future work should also include evaluation of various electrode constructions, such as split zinc electrodes and low density electrodes that may improve cell wetting. Separator systems combining the K-306 film with membrane dendrite barriers and nickel-coated Celgard film should also be evaluated to determine if the increased dendrite protection can extend cell life. Because of budget limitations in FY 1981 work in this area will be discontinued.

SECTION VI
SYSTEM ENGINEERING (TASK V)

1.0 INTRODUCTION

The objective of this phase of the ANL nickel-zinc program is the optimization of the Ni-Zn electric vehicle battery. Included in the effort are the design and testing of EV type Ni-Zn cells incorporating advances made in component technology, manufacturing methods, and design concepts. The system engineering task also includes the development of charging procedures and charge control techniques.

Three test vehicles have been used to evaluate variations in cell design. Before testing design concepts in full-size cells, it is advantageous to have a less expensive, accelerated test to screen experimental designs. Small cells of 20 Ah nominal capacity have been used for this purpose. Because these cells fail to provide information on the scale-up problems encountered in larger cells, more recent testing has been done in single electrode test cells. The single electrode cell consists of a full-size positive electrode between two negative plates. The cells provide test data which have been found to be more indicative of large cell performance.

The most promising design concepts are tested in full-size cells of 250 Ah nominal capacity. Full-size cells have undergone constant current and constant voltage cycle tests, as well as J-227D vehicle simulation tests.

This section of the report will present data from 20 Ah full-size, single electrodes and 250 Ah cells on constant current cycle tests. Results of 250 Ah cells on constant voltage, two step charge and vehicle simulation tests will also be given.

2.0 TECHNICAL DISCUSSION

2.1 TESTING OF 20 AMPERE-HOUR CELLS

Evaluation of various zinc electrodes and electrolytes was performed on 20 Ah nickel-zinc cells. The cells consisted of six pairs of 3-7/8 x 2-7/8 in. electrodes. The separator design used in the cells was as follows:

(+) Nylon/ 3 layers PVA/ Pellon (-)

To accelerate the accumulation of data, the cells were tested on a 100% depth of discharge cycle test. The cells were discharged at 10 amps for two hours or until cell voltage dropped to 0.8V. The cells were charged at 3.67 amps for 6 hours.

2.1.1 Zinc Electrode Tests

A series of 20 Ah cells were built with various additives in the zinc electrode. The results of these tests are given in Table V.1, which lists the cycle life and half life capacity of the cells.

The cell with the longest cycle life was Cell 117, with 2% PbO + 1% CdO zinc electrode additive. This cell and the cells with 10% Bi₂O₃ delivered the most capacity while on cycle test (the best of the three cells delivered a maximum of 19.4 Ah at some point in their cycle life).

At the time of these tests, the 10% Bi₂O₃ additive was the baseline zinc electrode formulation. Cells were built with lower and higher concentrations of Bi₂O₃ and cycle tested. The results, given in Figure V. 1, show an improvement in performance with higher concentrations of Bi₂O₃ in the negative plate. The

TABLE V.1

EVALUATION OF ZINC ELECTRODE ADDITIVES IN
20 AH Ni-Zn CELLS

CELL NO.	ZINC ADDITIVE	CYCLE LIFE* Cycles	CAPACITY AT 1/2 CYCLE LIFE, Ah	AVERAGE CYCLE LIFE AND DATA RANGE, Cycles
103-1	5% CdO	56	18.2	51.5 $\pm$ 4.5
103-2	" "	47	18.5	
107-1	10% Bi ₂ O ₃	55	19.3	63.5 $\pm$ 8.5
107-2	" "	72	18.7	
112-1	2% PbO + 1% Tl ₂ O ₃	53	16.0	64 $\pm$ 11
112-2	" " " "	75	18.5	
115-1	2% CdO + 1% Tl ₂ O ₃	60	18.7	66 $\pm$ 4
115-2	" " " "	72	18.5	
116-1	1% PbO + 1/2% CdO	51	18.7	55.5 $\pm$ 4.5
116-2	" " " "	60	18.0	
117	2% PbO + 1% CdO	95	18.7	95

*Number of cycles a cell ran before capacity fell to 12 Ah.

FIGURE V.1
CYCLE PERFORMANCE OF CELLS WITH
 Bi_2O_3 ADDITIVE

improvement in performance is most pronounced below the 3% level. Above this level, cycle life continues to improve with increased Bi_2O_3 concentration, but at a diminishing rate. Despite this, the cells with 25% Bi_2O_3 did not cycle as well as the cell with 2% PbO /1% CdO additive.

An experimental zinc plate with an electrode mix consisting of 1.25% filler + 98.75% ZnO was tested in 20 Ah cells. The mix was heat-treated at 900°C for 4 hours before being mixed with a binder (2% Teflon) and made into electrodes. Figure V.2 compares the cycle data of this cell with a control cell containing 10% Bi_2O_3 additive.

The results show that while initial capacity for the cell with heat-treated ZnO was low, this eventually improved and cycle life was finally greater than for the control cell. However, additional testing of this mix in larger cells did not produce good results. This may have been due to reduced resistance of the heat-treated material to the pressures in the larger cell pack.

To evaluate the effect of scale-up on the performance of various cell designs, more recent testing of zinc electrode variables has been done in the full-size, single electrode test cells described in Section 2.2.

2.1.2 Investigation of Alternate Electrolytes

A series of 20 Ah cells were built for the evaluation of various electrolytes. The standard electrolyte consists of an aqueous solution (35% KOH and 1% $\text{Li}(\text{OH})$ by weight). Two electrolytes with reduced zinc solubility were tested: one with 20% KOH and 1% $\text{Li}(\text{OH})$ and another with 35% KOH , and 1% LiOH , and 6%

FIGURE V.2
CYCLING: HEAT-TREATED ZnO

boric acid. An electrolyte with a higher concentration of KOH (45%) was used to determine if a higher utilization of the positive electrode could be achieved. The potential disadvantage of these electrolytes is that the lower KOH concentration may increase zinc degradation while the higher KOH concentration may increase zinc dissolution and shape change. A fifth electrolyte that was tested consisted of a plating agent added to 35% KOH in an attempt to reduce the formation of dendritic zinc.

The results of this test, given in Table V.2, indicate a superiority of the bromide salt additive. The 20% KOH and borate electrolytes did show improved cycle life over the cell with standard electrolyte, but with lower initial capacity due to reduced concentration of hydroxyl ions. The 45% KOH showed good initial capacity but shorter cycle life than the 20% KOH or borate electrolytes.

These tests were performed on cells with a PVA separator and Bi_2O_3 zinc additive. The current effort in this program task has centered on the evolution of a new baseline design with a PbO/CdO additive to the zinc electrode and coated Celgard separator. While the 35% KOH + 1% LiOH has remained the standard electrolyte, future plans call for re-evaluating alternate electrolytes in the newer type cells.

2.2 FULL-SIZE, SINGLE ELECTRODE TESTS

One disadvantage of the 20 Ah cell tests is that the results obtained provide no information on scale-up problems. As a result, many design variations which perform well in 20 Ah cells perform poorly when used in 250 Ah cells. A full-size, single electrode test was developed to provide rapid information while

TABLE V.2
ALTERNATE ELECTROLYTE MIXES IN 20 AH Ni-Zn CELLS

	CELL NO.							
	1	2	3	4	5	6	7	8
CYCLE #	ELECTROLYTE							
	35% KOH (STD.)	20% KOH		45% KOH		35% KOH 6% Boric Acid		35% KOH + .01 Molar Tetrabutyl Ammonium Bromide
5	>20	17.5	20.0	>20.0	>20.0	15.0	15.0	>20.0
15	17.5	16.8	15.0	>20.0	>20.0	16.8	16.8	20.0
25	17.5	15.0	15.0	18.8	20.0	17.5	17.5	17.5
35	17.5	15.0	15.0	17.5	17.5	16.3	16.8	18.0
45	13.0	15.0	15.0	16.5	17.5	15.0	15.0	18.0
50	12.5	15.0	15.0	16.3	16.3	15.0	15.6	16.9
60	--	15.0	15.0	13.8	13.8	15.0	No data	15.0
70	--	15.0	15.0	11.3	11.3	13.1	13.1	15.0
85	--	13.8	13.8	--	--	12.0	11.9	12.5
95	--	11.9	11.9	--	--	--	--	12.0

addressing the problems of scale-up in fabricating 250 Ah cells.

The test involves cycling one set of 250 Ah size electrodes in a reusable test fixture. One positive plate is placed between two negative plates. In the first cells tested, two zinc half plates were used. Performance of these cells was poor and it was found that the cells would be more indicative of 250 Ah performance if full-size electrodes were used. In this configuration, the zinc active material on the outer side of the copper collector is not utilized. A comparison of the PVA separator/ Bi_2O_3 additive design in four different test vehicles is shown in Figure V.3.

The single electrode test has been used to evaluate variations in zinc electrode and separator design. The cells, which have a theoretical capacity of 24.3 Ah, are tested on the 20 Ah test regime described above, with the automatic voltage cut-off raised from 0.80 to 1.25V. Design evaluations conducted in the single electrode test have led to significant improvements in 250 Ah cell design.

2.2.1 Evaluation of Zinc Electrode Designs

The zinc electrode studies in single electrode cells have centered on finding a zinc design with good electrochemical properties and sufficient mechanical strength to resist compression from the expanding positive plate.

Table V.3 gives the cycle data for 5 cells with PVA separator and various zinc electrode designs. In addition to the heat-treated mix and binary additives which were tested in 20 Ah cells, a single electrode cell was built with PbO/CdO additive and 5% potassium-titanate (KT). The KT was added to the zinc

FIGURE V.3
STANDARD Ni-Zn DESIGN IN
DIFFERENT TEST CELL CONSTRUCTIONS
ALL ON CONSTANT CURRENT CYCLE

TABLE V.3
CYCLING OF CELLS WITH PVA SEPARATOR AND
ZINC ADDITIVE VARIATIONS

CYCLE NO.	CELL NO.									
	SE-1		SE-7		SE-8		SE-37		SE-38	
	ZN ADDITIVE									
	10% Bi ₂ O ₃		1.25% filler Heat Treated Mix		5% PbO + 2% Ti ₂ O ₃		2% PbO + 1% CdO + 5% KT		2% PbO + 1% CdO	
	ECV	AH	ECV	AH	ECV	AH	ECV	AH	ECV	AH
5	2.01	15.0	2.02	19.1	1.93	17.0	2.01	16.2	2.05	20.1
10	2.05	15.9	2.05	18.6	1.95	16.6	2.05	17.0	2.08	20.0
20	2.05	15.6	2.26	16.7	1.90	14.9	2.00	16.5	2.06	17.5
30	2.09	14.1	2.29	15.0	1.92	14.8	2.00	16.4	2.14	16.3
40	2.30	13.6	2.20	13.4	1.95	14.3	2.00	15.0	2.12	13.8
55	2.26	14.7	2.11	12.2	1.95	14.2	2.00	14.5	2.02	12.0
60	2.19	13.8	2.05	12.0			2.00	14.2		
70	2.10	12.0			1.85	14.2	2.00	14.1		
90					2.01	15.9	2.09	15.6		
100					1.92	11.4	2.02	14.2		
130							2.00	12.0		

Aho = Capacity to 1.25V

ECV = End-of-charge voltage

mix to provide the plate with additional strength to resist compression from the positive electrode.

The data indicate that the KT was significant in improving cycle performance. A comparison of SE-38 and SE-37 shows that the KT additive also resulted in lower charge voltage in cells with PbO/CdO additive. The tests conducted in single electrode cells with a PVA separator indicated that bulking additives and the binary zinc additives were superior to the 10% Bi₂O₃ formulation.

Investigations of zinc additives were also conducted in cells with cellulose acetate coated Celgard (K-306). Three layers of the material were used with Pellon polyamide absorber on the positive electrodes and asbestos absorber on the negative plates. (Pellon absorber was used on both plates in cells with PVA separator, in Table V.3.

Cycling results for several zinc electrode variations are given in Table V.4. In addition to the PbO/CdO and PbO/Tl₂O₃ binary additives, data are also shown for cells with 5% CdO additive and a .004 in. layer of CdO (with TFE binder) on the negative collector. In two of the cells with this construction, the negative plates were heat-treated at 280°C for 7 minutes. The plates with PbO/Tl₂O₃ additive in SE-12 were also heat-treated. Also presented are data for cells with HiJell ^(TM), a bentonite clay from Georgia Kaolin Corporation, which was evaluated as a bulking additive.

The data for Cells SE-68, 69 and 70 indicate that the clay additive is not an appropriate bulking agent. Higher concentrations of the material improved cycle life (over the cells with

TABLE V.4

CYCLE TEST DATA FOR CELLS WITH CELGARD K-306
SEPARATOR AND ZINC ADDITIVE VARIATIONS

CELL NO.	ZINC ADDITIVE	Cycle:	CAPACITY TO 1.25V, Ah AT CYCLE													
			5	10	20	30	40	50	70	80	100	150	175	200	243	265
SE-12	5% PbO + 2% Tl_2O_3 Heat Treated		17.6	17.5	16.5	16.9	16.6	17.5	17.2	16.7	15.8	13.6	12.0			
SE-40-A	2% PbO + 1% CdO		19.5	19.0	18.0	17.4	17.5	18.0	17.5	17.2	18.2	16.1	15.0	14.0	12.0	
SE-40-B	" " " " "		17.5	17.5	17.5	17.7	17.8	17.1	17.0	16.8	19.0	17.9	16.8	14.7	12.8	11.8
SE-68	2% PbO + 1% CdO + 5% Hi Jell		19.3	19.8	15.0	10.7										
SE-69	2% PbO + 1% CdO + 10% Hi Jell		15.0	15.3	15.3	14.5	14.2	12.8								
SE-70	2% PbO + 1% CdO + 20% Hi Jell		15.4	15.0	15.2	15.0	14.8	13.0	12.3	12.0						
SE-71-1	5% CdO + CdO Layer		18.2	16.2	11.8											
SE-71-2	" " " " "		19.8	19.8	17.3	12.6	11.6									
SE-72-1	" " " " Heat Treated		18.3	18.3	18.5	17.8	16.5	14.8	12.2	11.6						
SE-72-1	" " " " "		17.1	17.7	18.2	17.0	15.8	14.6	12.6	11.8						

only 5% HiJell), but at the expense of lowering cell initial capacity.

A comparison of Cells SE-71 and SE-72 indicates that the heat treatment had a significant effect on cycle life. The two SE-72 cells ran for about 80 cycles, while the SE-71 cells (not heat-treated) ran for 20 and 40 cycles. Cycle life was considerably better for the cell containing heat-treated negative plates with the $\text{PbO/Tl}_2\text{O}_3$ binary additive. This cell, SE-12, ran for 175 cycles before delivering less than 12 Ah (60% of nominal capacity).

The best cycle performance achieved in single plate cells was in the SE-40 cells with PbO/CdO binary additive. The two cells ran for 243 and 265 cycles. Voltage and capacity data for Cells SE-12 and SE-40 are shown in Figures V. 4 and V. 5.

Single electrode test cells usually exhibit a rise in the end-of-charge voltage (ECV) early in the cycle test. The ECV reaches a maximum and then begins to decrease. This decrease is usually accompanied by a decline in discharge capacity. Figures V. 4 and V. 5 both show this pattern but in the SE-40 cells, the rise in ECV was delayed until late in the cycle test. The SE-40 cell also achieved higher utilization than SE-12, delivering more than 20 Ah at one point.

Zinc electrode testing in cells containing K-306 separators has produced the highest cycle life achieved to date in the single electrode test. As found in the cells with a PVA separator, the tests have demonstrated the superiority of the binary additives.

2.2.2 Evaluation of Separator System Design

The single electrode test has been used to evaluate various

Discharge
Capacity to
1.25V, Ah

Page No. 198

FIGURE V.4
CYCLE DATA FOR CELL SE-12

FIGURE V.5 CYCLE DATA FOR CELLS WITH PbO/CdO ADDITIVE

separator systems with the goal of finding a separator design with good zinc penetration resistance and stability in concentrated KOH. The single electrode test also provides a good measure of the system's resistance to dryout under the gassing and high pressure conditions of large cell geometry.

The best performing separator system in the single plate tests is the cellulose acetate coated Celgard K-306 (3 layers) combined with asbestos negative absorber wrap and Pellon polyamide positive electrode wrap. Cells with this separator and PbO/CdO zinc additive have run for over 240 cycles before delivering less than 60% of nominal capacity. A comparison of this separator system and the PVA separator can be made with cells discussed in the previous section. Cell SE-8, with the PVA separator, ran for 98 cycles while Cell SE-12, with K-306 separator, ran for 175 cycles. Subsequent cell tests have continued to demonstrate the superiority of the K-306 film. The section on large cell tests will present data which demonstrate the importance of the asbestos absorber wrap.

Cells with several other separator systems are detailed in Table V. 5. The best separator in this series is the combination inorganic film and cellophane in Cell SE-17. The inorganic film is a 5 mil Teflon bonded, rolled sheet. In addition to being a very good electrolyte reservoir, the material may also limit dendrite growth by reacting with zincate to form insoluble zincates.

Additional evaluation of promising design variables such as the K-306 film, inorganic film and PbO/CdO zinc electrode additive has continued in 250 Ah cells. A discussion of these

TABLE V.5
CYCLE DATA FOR CELLS WITH Bi₂O₃
ZINC ADDITIVE AND VARIOUS SEPARATOR SYSTEMS

CELL NO.	SEPARATOR SYSTEM	Cycle:	CAPACITY TO 1.25V (AMPERE-HOURS)									
			10	20	30	40	50	60	70	80	90	100
SE-1	(+)Pel/3 x PVA/Pel(-)		15.9	15.6	14.1	13.6	15.3	13.8	12.0			
SE-14	(+)Pel/2 x PVA/1 x Inorganic layer/Pel(-)		15.2	14.3	13.8	13.3	12.5	11.9				
SE-15	(+)Pel/1 x PVA/2 x Inorganic layers/Pel(-)		18.8	16.6	16.3	14.7	13.8	13.4	12.5	11.9		
SE-16	(+)Pel/3 x Inorganic layers/Pel(-)		10.2	6.5								
SE-17	(+)Pel/4 x Cell/1 x Inorganic layer/Pel(-)		18.0	17.0	16.0	15.8	15.2	14.8	14.1	13.4	12.3	11.6
SE-18	(+)Pel/3 x Cell/2 x Inorganic layers/Pel(-)		18.5	17.5	16.6	16.1	16.0	15.6	15.0	12.8	11.9	
SE-14	(+)Pel/3 x K701/Asbestos(-)		17.0	17.0	16.8	16.5	16.0	15.3	14.0	13.2	12.0	

Pel: PellonTM Absorber

Ca(OH)₂: 5 mil Ca(OH)₂ film

Cell: Cellophane

Grc Abs: Grace Absorber #114

Grc Sep: Grace 4 mil separator

K701: Celgard/Cellophane Laminate

tests is presented in the next section.

2.3 250 AH CELL TESTS

Full-size, EV type, 250 Ah cells are used to evaluate variations in component design, charge procedures, and cell geometry. Most cells are tested on a constant current cycle, although two-step charge, constant potential charge and pulsed discharge have been under investigation.

2.3.1 Cell Test with PVA Separator and Bi₂O₃ Zinc Electrode Additive

Early in the year large cell testing was conducted on cells containing a PVA separator (3 layer), Pellon polyamide absorber on both electrodes, and 10% Bi₂O₃ in the zinc electrode. The standard cell design consists of 14 positive and 15 negative plates. This design has been found to reproducibly deliver about 55 cycles (at 77% DOD and without reconditioning during the cycle test) before cell capacity falls to 60% of nominal. Dissection analysis of failed cells has indicated that separator degradation and zinc shorting throughout the inner portion of the plates contributed to cell failure. Drying out of the center portions of the negative plates has consistently been seen in cells with this design.

Two approaches were tried to reduce gas entrainment in the cell pack, which accelerates dryout and separator degradation. A cell was built with the standard design, but only 13 plate pairs, to reduce pack compression. A second design included grooved positive and negative electrodes to improve gas and liquid transport in the cell pack.

The cells were put through a cycle test consisting of a 37.2 amp charge for 5.75 hours (214 Ah) followed by a 2.25 hour discharge at 85 amps (191.25 Ah). This represents a 12% over-charge, 77% DOD test in 250 Ah cells. The test results of the three designs are shown in Figure V.6.

Neither design modification produced better results than the standard. The cycle performance of the cell with grooved plates was stable for 35 cycles; however, the end of discharge voltage was low as indicated by a plateau in the discharge curve. This second plateau was due to the use of contaminated nickel-hydroxide and has been eliminated by washing the active material prior to electrode fabrication.

Because the negative electrode and separator design have been identified as the components most in need of development, the majority of testing in the past year has utilized a standardized positive electrode. Active material from a commercial source containing 95% $\text{Ni}(\text{OH})_2 \cdot 1/4 \text{H}_2\text{O}$ and 1.5% $\text{Co}(\text{OH})_2$ was usually used. ERC active material (also with 1.5% $\text{Co}(\text{OH}) \cdot 1/4 \text{H}_2\text{O}$) was evaluated in cells with PVA separator along with Bi_2O_3 as the negative additive. The test results, given in Table V.6, indicate that the commercial and ERC materials perform equivalently in cells with PVA and Bi_2O_3 .

The early baseline design was also used to evaluate two alternate charge procedures. One cell was put on cycle test with a two-step charge consisting of 5-1/2 hours of charge at 34.4 amps followed by 4-12 hours of charge at 6 amps. Another

FIGURE V.6
CYCLE TEST RESULTS OF CELLS WITH
PVA SEPARATOR AND Bi_2O_3
ZINC ADDITIVE

TABLE V.6
CYCLE PERFORMANCE OF CELLS WITH ERC
AND COMMERCIAL $\text{Ni}(\text{OH})_2/\text{Co}(\text{OH})_2$ POSITIVE ACTIVE MATERIAL

GROUP 137-II COMMERCIAL Ni, ASBURY GRAPHITE				
CYCLE #	CELL 137-II-1		CELL 137-II-2	
	ECV	EDV	ECV	EDV
4	1.923	1.53	1.92	1.54
15	1.94	1.49	1.93	1.49
20	1.98	1.52	1.91	1.49
24	1.98	1.50	1.90	1.46
30	2.05	1.39	1.99	1.40
35	2.10	1.10	2.01	1.10
50	2.15	1.00	2.11	1.15

GROUP 137 ERC Ni, ASBURY GRAPHITE				
CYCLE #	CELL 137-1		CELL 137-2	
	ECV	EDV	ECV	EDV
5	1.88	1.54	1.88	1.55
15	2.02	1.53	2.03	1.54
20	2.03	1.52	1.99	1.48
25	2.06	1.50	2.04	1.45
30	2.12	1.31	2.04	1.25
35	2.12	1.26	2.00	1.20
49	1.98	0.85	1.86	0.30

ECV = Voltage at end of 214 Ah charge

EDV = Voltage at end of 191.25 Ah discharge

Zinc additive in all cells: Bi_2O_3

Separator in all cells: PVA

cell was put on cycle test with a modified constant potential charge that limited charge current as the cell voltage. All discharges were at 85 amps. The two-step cycle represents 12% overcharge, as does the standard constant current test. On the modified constant potential test, charge input on a fresh cell was 214.2 Ah, representing about a 12% overcharge.

Results for three cells evaluated on different regimes are shown in Figure V. 7. The data indicate that of the three charging methods tested, the constant current charge was superior.

2.3.2 Cell Tests with Advanced Separator and Electrode Designs

Design developments during the past year have significantly improved cell performance over the earlier PVA/Bi₂O₃ design. As described above, full-size single electrode cells with improved components have delivered in excess of 240 cycles at 100% DOD. The general direction of recent developments has been away from membrane separators, such as PVA, and toward more stable microporous films, such as Celgard materials. Zinc electrode development has focused on binary additives such as CdO/PbO and PbO/Tl₂O₃.

Test results and dissection analyses in PVA/Bi₂O₃ cells have demonstrated a need for an improved absorber wrap on the negative electrode. Several experimental materials have been studied, but the only material found to be significantly better than Pellon was 10 mil thick fuel cell grade asbestos. Cycle data for cells with asbestos and Pellon negative absorber wraps are shown in Figure V.8. The figure includes voltage at the end of each 191.25 Ah discharge as a function of cycle number.

FIGURE V.7
Ni-Zn CYCLE TEST WITH VARIOUS CHARGE PROCEDURES
PVA SEPARATOR AND Bi_2O_3 ADDITIVE

CYCLE PERFORMANCE OF CELLS WITH PELLON AND ASBESTOS ABSORBER

FIGURE V. 8

ENERGY RESEARCH CORPORATION

The negative electrode designs in all cells in Figure V.8 were the same, with 5% potassium-titanate bulking additive. Results indicate that in these cells, the asbestos wrap was necessary to prevent early failure from dryout of the separator and zinc electrodes. The data also show that the separator design with three layers of coated Celgard had comparable performance to cells with five layers of the film. This may be due to the reduced DOD on the cells with fewer layers (DOD is 7% less for the cells with fewer layers because space is available for an extra pair of plates. However, it does indicate that the three-layer design is acceptable within the limits of this test.

The effect of the asbestos absorber in cells with the PbO/CdO zinc additive is shown in Figure V.9, which presents cycle data for cells with Pellon and asbestos absorbers. Cell 159 is a scale-up of the single electrode cells which exceeded 240 cycles. Cell 163 is a similar design in which the asbestos wrap was replaced by Pellon, allowing room for more active material. Test results show that despite its higher capacity and zinc ratio, the cell with Pellon absorber failed earlier than the cell with asbestos.

Another design which had shown promise in full-size, single electrode tests was the combination of membrane films with ERC's 5 mil inorganic film. A combination of cellophane and the inorganic film had given good performance in these tests. A series of similar designs were tested in 250 Ah cells and the longest life was achieved in Cell 118, with 2 layers of PVA combined with the inorganic film. The cell also had negative plates made with a heat-treated ZnO/inorganic filler mix,

CELL	SEPARATOR DESIGN	CYCLE LIFE *
159	(+) PELLON / 3 x K306 /// ASBESTOS (-)	130
163	(+) PELLON / 3 x K306 /// PELLON (-)	90

* CYCLE LIFE = NUMBER OF CYCLES WITH CAPACITY MORE THAN 60% OF NOMINAL

FIGURE V.9
250 AH CYCLE DATA

which had performed well in 20 Ah cell tests.

Cycling of Cell 118, along with an early baseline design cell and more advanced designs, are shown in Figure V.10. While cell 118 ran for more cycles than the early baseline cell, the newer designs had even longer cycle life.

Cell 151 contained positive electrodes 19% less dense than standard, and negative plates 17% less dense than standard. This design was built to determine if the electrodes' lower densities would reduce cell pack compression and improve performance.

Cell 157 was built with another approach for reducing pack compression. The cell contained a standard density electrode but was built in a long, thin geometry. The cell is only four plate pairs thick with plates that measure 6 in. high x 31-1/4 in. long. This design was fabricated to determine if a reduction in the compression, wetting and thermal problems in the cell pack was possible.

As indicated in Figure V.10, the low density and long geometry cells performed about the same. A comparison with Figure V.9 shows that these cells performed better than Cell 159, with standard density plates and Pellon absorber, but not as good as Cell 163, with asbestos negative plate absorber.

The effect of the longer cell geometry on cell temperature can be seen in Figures V.11 and V.12, which present voltage and temperature data for Cells 157 and 151 on cycle test. The figures show that the long cell ran up to 13°C cooler during discharge than the standard geometry design.

2.3.3 Simulated Vehicle Use Test

A test regime has been established for 250 Ah cells

Cell	Zn Additive	SEPARATOR
▲ 95	Bi ₂ O ₃	(+) PEL/3PVA/PEL (-)
× 118	Inorganic	(+) PEL/2PVA/Inorganic (-) Heat treated ZnO/Inorganic filler mix
■ 151	PbO+CdO	(+) PEL/3 K-306/PEL (-) Low density electrodes
● 157	PbO+CdO	(+) PEL/3 K-306/PEL (-) Long thin geometry

FIGURE V.10
250 AH CELL CYCLE TEST DATA

FIGURE V.11
CELL 151-1
VOLTAGE AND TEMPERATURE
DATA FOR CYCLE 59

FIGURE V.12
CELL 157
LONG CELL
VOLTAGE AND
TEMPERATURE DATA
FOR CYCLE 55

which will simulate a certain pattern of electric vehicle use. The test regime is based on trip distribution for trips of 100 miles and under. Based on information from the Federal Highway Administration, a trip distribution model was generated which approximates the maximum electric vehicle use for 75% of all operators. This distribution is given in Table V.7. The mileage shown for 25-mile trips is actually a total of all trips 25 miles or less.

For the discharge portions of the test, it was decided to use the J227AD GE-Chrysler vehicle current profile derived at ANL. Each time this profile, shown in Figure V.13, is run, 2.187 Ah is removed from the battery and 0.95 miles of driving is simulated. After each discharge, the cells are recharged at 38 amps to a charge input of 10% more capacity than was removed.

The weekly test sequence is shown in Figure V.14. Each week the test simulates 1645 miles and every six weeks, one year's operation (9870 miles according to the model).

Testing was started on a 250 Ah cell with the CdO/PbO additive and K-306 separator. The cell design included an excessively tight pack to accommodate a higher zinc ratio. This has been found detrimental to performance and duplicates of this cell (Design 162) have only delivered about 30 cycles on the 77% DOD test. On the vehicle simulation test, the cell ran the equivalent of 12,700 miles before its range fell to 60 miles.

Test results for the cell during 25 and 100 mile discharges are shown in Figure V.15. After being tested for the equivalent of 4500 miles, the cell began to deliver less than

TABLE V.7

ANNUAL ELECTRIC VEHICLE TRIP
DISTRIBUTION FOR 75TH PERCENTILE OPERATOR

Trip Mileage	Number of Trips	Annual Mileage
25	228	5700
35	42	1470
50	24	1200
75	12	900
100	6	<u>600</u>
TOTAL		9870

FOUR CURRENT STEPS TO PROVIDE A SIMPLIFIED APPROXIMATION TO THE J227AD/DOE-GE-CHRYSLER VEHICLE (WITH REGENERATIVE BRAKING)

FIGURE V.13

FIGURE V.14

TIME
WEEKLY VARIABLE DEPTH
TEST SEQUENCE

FIGURE V.15

SIMULATED EV USE TESTING OF CELL 162

the 230 Ah removed in the 100-mile discharge. The decay in the cell range, in miles, with cumulative equivalent mileage is shown in Figure V.16.

These results indicate that an early design capable of only 30 cycles at 77% DOD had an equivalent range of 100 miles after 4500 cumulative miles use and 60 miles after 12700 miles use. This result is promising in terms of the suggested potential of more advanced designs on this test.

3.0 CONCLUSIONS

The work done during the past year under this task of the project has centered on improving the performance of full-size EV cells. By replacing small cells with full-size single electrode cells, the design optimization effort was concentrated more on the problems of large cell performance. The development work has led to significant improvements in zinc electrode and separator system design.

The tests conducted on various zinc electrodes have led to the selection of electrode designs which are superior to the Bi_2O_3 additive in electrochemical performance and physical stability in large cells. The CdO/PbO binary additive is currently considered the best design tested up to this point.

The separator system design studies have led to the selection of cellulose acetate coated Celgard K-306 as the most promising separator tested to date. In addition to being more stable than PVA, the microporous K-306 also allows greater mass transport than PVA, preventing the establishment of concentration gradients which impede cell performance. The tests have also demonstrated the need for an improved negative electrode ab-

VARIABLE DEPTH LIFE TEST

sorber wrap, and asbestos has given the best results to date.

Earlier in the year, cells with PVA separator and Bi_2O_3 negative additive were capable of delivering 55 cycle on a 77% DOD cycle test without reconditioning during the test. In the full-size single electrode test, the design ran 70 cycles. Cells with K-306 separator, asbestos negative plate absorber and CdO/PbO zinc additive have delivered more than 240 cycles in the single electrode test and 130 cycles in 250 Ah cells. These cycle results were achieved without reconditioning and with periodic electrolyte addition the only periodic maintenance procedure.

4.0 FUTURE WORK

The system engineering effort during the next year will focus on determining the reproducibility of the cycle test performance in cells with optimized components. In addition, testing will determine characteristics of the new design, such as open circuit capacity loss, thermal response, and performance on the vehicle use simulation test.

The vehicle simulation test will become an integral part of EV cell design evaluation. Testing will be conducted to determine life on the constant current test and performance on the vehicle simulation test.

Of the various charge procedures examined, constant current charging produced the best results. The charge technique currently preferred is constant current charging controlled by a metal-gas coulometer. Future work will include running the coulometer with 250 Ah cells on the vehicle simulation regime to provide data on the long-term accuracy of the pilot cell.

ENERGY RESEARCH CORPORATION

Evaluation of new component technology will continue in single electrode and 250 Ah cell tests. Commercial and in-house separator materials will be evaluated as they are developed. Zinc electrode development will continue, with emphasis on stable electrode constructions. The long cell design has shown promising cycle performance as well as improved thermal behavior and will be studied further.

Distribution for ANL/OEPM-80-13

Internal:

J. J. Barghusen	D. Fredrickson	W. Miller
D. Barney	B. R. T. Frost	P. A. Nelson
M. H. Bhattacharyya	E. C. Gay	M. V. Nevitt
C. Bean	J. Geller	E. G. Pewitt
E. S. Beckjord	M. Genge	D. Poa
M. Bernard	D. Graczyk	J. Rajan
E. C. Berrill	E. Hayes	J. J. Roberts
R. Biwer	L. Hill	M. F. Roche
A. Brown	F. Hornstra	H. Shimotake
L. Burris	C. C. Hsu	R. K. Steunenbergh
G. Chapman	V. Kolha	C. Swoboda
A. A. Chilenskys	J. Klinger	Z. Tomczuk
C. C. Christianson	V. Kremesec	A. Tumillo
G. Cook	A. B. Krisciunas	R. Varma
D. Corp	M. Kronenberg	P. D. Vashishta
P. Cunningham	S. J. LaBelle	D. R. Vissers
E. Creamer	T. S. Lee	D. S. Webster
S. A. Davis	M. Liu	F. Williams
W. DeLuca	R. Loutfy	F. Wyant
R. C. Elliott	W. Massey	N. P. Yao (44)
M. Farahat	J. Meisenhelder	ANL Contract File
P. R. Fields	J. Miller	ANL Libraries
F. Foster		TIS Files (6)

External:

DOE-TIC, for distribution per UC-94ca (318)
Manager, Chicago Operations and Regional Office, DOE
Chief, Office of Patent Counsel, DOE-CORO
V. Hummel, DOE-CORO
R. Gariboldi, DOE-CORO
Argonne Universities Association:
President
C. B. Alcock, U. of Toronto
W. L. Worrell, U. of Pennsylvania
W. Ahmad, KW Battery, Skokie, IL
R. Alkire, University of Illinois, Urbana
M. Allen, Mechanical Technology Inc., Latham, NY
E. T. Ames, TRW Systems, Redondo Beach, CA
L. Andrews, Electric Vehicle Council, Washington, DC
S. J. Angelovich, Mallory Battery Co., Tarrytown, NY
G. M. Arcand, Idaho State University, Pocatello
R. Aronson, Electric Field Propulsion Corp., Troy, MI
G. N. Ault, NASA Lewis Research Center
J. D. Baker, Stewart Warner Corp., Chicago
W. Bales, Jet Industries, Inc., Austin
H. Balzan, Chattanooga, TN
K. F. Barber, DOE, Office of Transportation Programs, Washington

T. Barber, Jet Propulsion Laboratory, Pasadena
 R. J. Barkley, Compass Industries Inc., Hermosa Beach, CA
 T. M. Barlow, Lawrence Livermore Laboratory
 J. H. Hampton Barnett, Tennessee Valley Authority, Chattanooga
 R. Barnstead, Aerospace Corporation, Washington DC
 D. Barron, Delco-Remy Div., GMC, Anderson, IN
 R. Bassett, Sandia Laboratory, Albuquerque
 W. Bauer, Hittman Associates Inc., Columbia, MD
 W. Bauer, KW Battery, Skokie, IL
 E. Baumann, LILCO, Mineola, NY
 W. C. Beasley, Union Carbide Corporation, New York, NY
 H. Bell, Arizona Public Service Co., Phoenix
 J. Bellack, Cleveland Electric Illuminating Co., Cleveland
 L. Belove, Marathon Battery Corp., Waco, TX
 W. R. Benn, Great Lakes Carbon Corporation, New York
 D. Bennion, Brigham Young University, Provo, UT
 C. Berger, Electrochemical & Water Desal. Technology, Santa Ana, CA
 D. Bergmann, GM Transportation Systems Center, Warren, MI
 L. Berkowitz, Esso Research Co., Linden, NJ
 C. Berlsterling, C. Franklin Research Institute, Philadelphia
 J. Birk, Electric Power Research Institute, Palo Alto
 W. S. Bishop, Air Force Aero Propulsion Lab, Wright-Patterson AFB
 D. P. Boden, C&D Batteries, Plymouth Meeting, PA
 D. Borrello, Die Mesh Corporation, Pelham, NY
 A. Borucka, Borucka Research Co., Livingston, NJ
 P. Bowen, C&D Batteries, Plymouth Meeting, PA
 D. Bowman, United States Postal Service, Washington
 J. C. Boylan, Electric Dynamics Corp., Plainwell, MI
 B. J. Bragg, Bell Laboratories, Murray Hill, NJ
 J. Brennand, General Research Corp., Santa Barbara
 A. F. Brewer, Malibu, CA
 D. C. Briggs, Philco-Ford Corp., Palo Alto
 P. Bro, P. R. Mallory & Co., Inc., Burlington, MA
 J. Broadhead, Bell Laboratories, Murray Hill, NJ
 E. P. Broglio, Eagle-Picher Industries, Joplin, MO
 A. D. Brown, EVE Electric Motor Car, Inc., East Lansing, MI
 P. J. Brown, DOE, Office of Transportation Programs, Washington
 R. A. Brown, Eagle-Picher Industries, Joplin, MO
 B. S. Brummer, EIC Corporation, Newton, MA
 J. Bucci, C&D Batteries, Plymouth Meeting, PA
 R. Buchholz, Honeywell Corp., Minneapolis
 A. J. Burgess, Lucas Industries, Inc., Troy, MI
 H. Burghart, Cleveland State University, Cleveland
 D. Burns, Onan Corporation, Minneapolis
 B. W. Burrows, Gould Inc., Rolling Meadows, IL
 M. Burtgon, Delco-Remy Div. of GMC, Anderson, IN
 J. D. Busi, USA Foreign Science & Tech. Center, Charlottesville, VA
 E. Buzzelli, Westinghouse Electric Corp., Pittsburgh
 W. P. Cadogan, Emhart Corp., Hartford, CT
 E. Cairns, Lawrence Berkeley Lab.
 E. Campbell, Electric Vehicle Consultants, Inc., New York, NY
 P. Campbell, University of Southern California, Los Angeles
 J. Campbell, DOT/UMTA, Washington, DC
 L. T. Carpenter, Kimberly Clark Corp., Neenah, WI

T. V. Carvey, Hughes Aircraft Corp., Culver City, CA
 A. Charkey, Energy Research Corp., Danbury, CT
 L. D. Christian, General Electric, Gainesville
 R. C. Chudacek, McGraw Edison Co., Bloomfield, NH
 R. Clark, Sandia Labs., Albuquerque
 J. E. Clifford, Battelle Memorial Institute, Columbus
 J. A. Consiglio, Solva-Tek Associates, Topsfield, MA
 A. R. Cook, ILZRO Inc., New York
 K. E. Cooper, Trojan Battery Co., Santa Fe Springs, CA
 G. Coraor, E. I. DePont de Nemours & Co., Inc., Wilmington, DE
 R. E. Corbett, Lockheed Missiles & Space Co., Sunnyvale
 D. Crane, United States Postal Service, Washington
 R. A. Crawford, PPG Industries, Barberton, OH
 C. Dacres, White Oak, Silver Spring, MD
 R. H. Dare, Batronic Truck Corp., Boyertown, PA
 D. Davis, Lawrence Livermore Laboratory
 R. J. Dawson, Exide Management and Technology Co., Madison, WI
 G. A. DeBari, INCO, Sterling Forest, Suffern, NY
 J. Devitt, Denver, CO
 A. N. Dey, P. R. Mallory & Co. Inc., Burlington, MA
 W. J. Dippold, DOE, Office of Transportation Programs, Washington, DC
 T. P. Dirske, Calvin College, Grand Rapids, MI
 D. DiVirgilio, Lockheed Missiles and Space Co. Inc., Sunnyvale
 D. Douglas, Electric Power Research Institute, Palo Alto
 D. Dow, Detroit, MI
 D. Dunoye, Reston, VA
 T. Dwyer, Corning Glass Works, Corning, NY
 E. F. Echolds, AiResearch Manufacturing Co., Torrance, CA
 M. Eisenberg, Electrochimica Corp., Mountain View, CA
 D. B. Eisenhaure, Charles Stark Draper Lab., Inc., Cambridge, MA
 T. Eissenberg, Oak Ridge National Lab.
 M. W. Ellison, Hughes Aircraft Corp., El Segundo
 D. Elson, Black and Decker Inc., Towson, MD
 C. English, University of New Mexico, Albuquerque
 R. English, General Battery Co., Reading, PA
 B. Enserik, Dynamic Science, Phoenix
 R. Enters, McGraw Edison Co., Bloomfield, NJ
 H. Espig, Gould Inc., Rolling Meadows, IL
 E. C. Essig, Long Island Lighting Co., Mineola, NY
 A. Ewing, DOE, Office of Transportation Program, Washington
 G. Farbman, Westinghouse Electric Corp., Pittsburgh
 D. W. Fedor, Bell Laboratories, Murray Hill, NJ
 R. Fedora, Gould Inc., Rolling Meadows, IL
 W. Feduska, Westinghouse Electric Corp., Pittsburgh
 W. H. Fengler, Meteor Research Limited, Roseville, MI
 F. Feres, KW Battery Co., Skokie, IL
 R. Ferraro, Electric Power Research Institute
 D. T. Ferrell, Exide Management and Technology Co., Yardley, PA
 E. Fiss, Duke Power Co., Charlotte, NC
 A. Fleischer, Orange, NJ
 C. W. Fleischmann, C&D Batteries, Plymouth Meeting, PA
 R. F. Fogle, North American Rockwell, Anaheim
 R. T. Foley, American University, Washington, DC
 F. Fontana, Consolidated Edison Co., Astoria, NY

L. R. Foote, Vehicle Systems Department, Ford Motor Co., Dearborn, MI
 J. S. Fordyce, NASA Lewis Research Center
 H. A. Fuggiti, Exide Management and Technology Co., Yardley, PA
 T. Fujita, Pasadena, CA
 B. Ganji, KW Battery Co., Skokie, IL
 G. Gelb, Advanced Ground Systems, Long Beach, CA
 J. H. B. George, George Consulting International Inc., Concord, MA
 S. Geppert, Eaton Corporation, Southfield, MI
 L. J. Gerlach, United States Postal Service, Rockville, MD
 J. A. Gilchrist, Chloride America, Tampa
 W. Gillespie, Structural Plastics Inc., Tulsa
 J. R. Gilmore, Ford Motor Co., Dearborn, MI
 C. Glassman, Transportation Research Center, East Liberty, OH
 H. Glixon, Chevy Chase, MD
 M. Globerman, General Services Administration, Washington
 W. Goldman, Electric Vehicle Engineering, Lexington, MA
 G. Goodman, Globe Battery Division, Milwaukee
 R. E. Goodson, Purdue University
 J. Gould, Unique Mobility Inc., Englewood, CO
 L. B. Gratt, IWG Corp., San Diego
 G. Greenberg, Electric Vehicle Battery Technology, Stamford, CT
 H. Grepke, TurElec Inc., Bradenton, FL
 D. Griter, Solar Centra, Mechanicsburg, OH
 E. E. Grough, Lucas Industries Inc., Troy, MI
 R. Guess, General Electric Research Lab., Schenectady
 R. G. Gunther, General Motors Research Labs., Warren, MI
 M. Hadden, Billing Energy Corp., Provo, UT
 G. Hagey, DOE, Division of Technology Overview, Washington
 H. Hamilton, University of Pittsburgh
 W. Hamilton, General Research Corp., Santa Barbara
 B. Hamlen, Exxon Enterprises Inc., Florham Park, NJ
 D. Hanify, Fiat, Chicago
 K. L. Hanson, General Electric Co., Philadelphia
 W. Harhay, Electric Vehicle Associates, Cleveland
 J. H. Harrison, Naval Ship R&D Center, Annapolis, MD
 G. Hartman, Exide Management and Technology Co., Yardley, PA
 J. Hartman, General Motors Research Labs., Warren, MI
 C. Hayden, General Telephone and Electronics, Stamford, CT
 E. A. Heintz, Airso Speer Carbon Graphite, Niagara Falls, NY
 E. V. Hellman, Gould Inc., Langhorne, PA
 R. Heppenstall, Penn Jersey Suburu Inc., Pennsauken, NJ
 A. Himy, Naval Sea Systems Command, Washington
 V. Hlavin, NASA Lewis Research Center
 G. Hobbib, Exide Management and Technology Co., Cleveland
 M. Hodgman, General Electric, Gainesville
 R. Hoenburg, Mechanical Technology Inc., Latham, NY
 R. Hudson, Eagle-Picher Industries, Joplin, MO
 J. R. Huff, US Army Mobility Equipment R&D Command, Fort Belvoir, VA
 H. L. Hughes, Oklahoma State University, Stillwater
 W. Hull, USPS Research and Development Laboratory, Rockville, MD
 B. Iseard, Freeport, Bahamas
 H. R. Ivey, Wood-Ivey Systems Corp., Winter Park, FL
 J. Jacus, Moore Haven, FL
 M. A. Jansen, Allegheny Power Service Corporation, Greensburg, PA

G. H. Jantz, Rensselaer Polytechnic Institute
 A. W. Johnson, General Electric Co., Philadelphia
 L. Jokl, MERADCOM, Fort Belvoir, VA
 K. R. Jones, Thiensville, WI
 W. J. Jones, Westinghouse Electric Corp., Pittsburgh
 R. E. Jordan, Omega Motors Corp., Garden Grove, CA
 D. Kane, National Motors Corp., Lancaster, PA
 E. Kanter, Gulton Battery Corp., Metuchen, NJ
 N. Kaplan, Harry Diamond Laboratories, Washington
 V. Kapur, Arco Solar Inc., Chatsworth, CA
 R. Kaylor, Kaylor Energy Products, Menlo Park
 J. Keith, Kaman Sciences, Colorado Springs, CO
 J. J. Kelley, Exide Corporation, Yardley, PA
 H. C. Kelly, OTA, U.S. Congress, Washington
 J. G. Kennard, NASA Lewis Research Center
 R. L. Kerr, Aero Propulsion Lab., Wright Patterson AFB
 J. A. Kerrella, Delco-Remy Division/GMC, Anderson, IN
 R. A. Keyes, Robert A. Keyes Associates, Martinsville, IN
 R. A. Kingery, Oconomowoc, WI
 R. S. Kirk, DOE, Office of Transportation Programs, Washington
 M. Klein, Energy Research Corporation, Danbury, CT
 G. B. Kliman, General Electric Co., Schenectady
 G. B. Klinean, General Electric Co., Schenectady
 R. C. Knechtli, Malibu, CA
 R. A. Knight, AMF Inc., Stamford, CT
 O. R. Kozak, American Battery Corp., Long Beach, NY
 J. G. Krisilas, Aerospace Corporation, El Segundo, CA
 P. E. Krouse, Exide Management & Technology Co., Yardley, PA
 R. R. Kubalek, St. Joe Lead Co., Clayton, MD
 L. Kulin, Whirlpool Corp. Benton Harbor, MI
 C. M. Langkau, Union Carbide Co., Cleveland
 H. Lauve, Electric Auto Corporation, Troy, MI
 E. Lawlor, Membrana Incorporated, Chicago, IL
 J. Lee, RAI Research Corp., Hauppauge, NY
 I. J. Levine, Consolidated Edison, New York
 K. Levine, St. Joe Minerals Corp., Pittsburgh
 H. Lim, Hughes Research Lab., Malibu, CA
 D. Linden, Little Silver, NJ
 E. L. Littauer, Lockheed Palo Alto Research Laboratory
 A. Long, Zeonics Corp., Fairfax, VA
 E. Long, St. Joe Minerals Corp., Monaca, PA
 P. Lu, Westinghouse Electric Corporation, Pittsburgh, PA
 J. T. Lundquist, W. R. Grace & Co., Columbia, MD
 T. Lynch, Fiber Materials, Inc., Biddeford, ME
 E. N. Mabuce, Union Electric Co., St. Louis
 J. MacDougall, AT&T, Basking Ridge, NJ
 D. E. Mains, Naval Weapons Support Center, Crane, IN
 J. Mader, Electric Power Research Institute, Palo Alto, CA
 J. Maisel, Cleveland State University, Cleveland
 J. S. Makulowich, Electric Vehicle Council, Washington
 V. Manson, National Aeronautics and Space Adm., Washington
 L. Mapa, KW Battery, Skokie, IL
 L. S. Marcoux, Hughes Aircraft Company, Los Angeles
 T. W. Martin, United States Postal Service, San Bruno, CA

J. Masson, Martin Marietta Corp., Denver, CO
 C. E. May, NASA Lewis Research Center
 E. Meeks, Derl Manufacturing Co., Compton, CA
 J. D. Meiggs, Kaman Sciences Corp., Colorado Springs
 P. Mighdoll, Booz-Allen & Hamilton, Cleveland
 R. P. Mikkelsen, General Dynamics, San Diego
 D. G. Miley, U.S. Naval Ammunition Depot, Crane, IN
 H. Miller, Department of Transportation, Cambridge, MA
 D. K. Miner, Copper Development Associates, Birmingham, MD
 L. G. Morin, Tarrytown, NY
 F. Morse, Silver Spring, MD
 A. Moss, Leeson Moos Laboratories, Warwick, RI
 R. Mueller, University of California, Berkeley
 J. H. Muir, Dimension V Inc., Indialantic, FL
 J. P. Mullin, National Aeronautics & Space Administration, Washington
 G. Murphy, Northwestern University
 N. T. Musial, Nasa Lewis Research Center
 B. McCormick, Los Alamos Scientific Lab.
 L. R. McCoy, Energy Systems Group, Canoga Park
 A. H. McCutcheon, Texas State University, Waco, TX
 R. McKee, McKee Engineering, Palatine, IL
 F. McLarnon, Lawrence Berkeley Lab.
 J. N. McNamara, Northrup Corporation, Hawthorne, CA
 P. McRay, ILC Technology, Sunnyvale
 W. J. Nagle, NASA Lewis Research Center
 L. Nalley, Creative Research Co., Roebuck, SC
 J. Newman, Univ. of California, Berkeley
 J. S. Newton, Newton Engineering Co., Glen Ellyn, IL
 A. O. Nilsson, NIFE Incorporated, Lincoln, RI
 J. Norberg, Exide Management & Technology Co., Philadelphia
 A. C. Occhipinti, Kenner, LA
 L. G. O'Connell, Lawrence Livermore Lab.
 G. Odom, Georgia Power Company, Atlanta, GA
 R. Oglesby, GM Transportation Systems Ctr., Warren, MI
 L. Omohundro, Kingery Research & Development, Wake Forest, NC
 E. I. Onstott, Los Alamos Scientific Lab
 R. Osteryoung, State University of New York at Buffalo
 B. N. Otzinger, North American Aviation, Downey, CA
 J. P. Overman, Hammond Lead Products Inc., Hammond, IN
 J. E. Oxley, Gould Inc., Rolling Meadows, IL
 E. Papandreas, REI, Lake Worth, FL
 J. S. Parkinson, Johns-Manville R&D Center, Manville, NJ
 J. M. Parry, Arthur D. Little Inc., Cambridge, MA
 E. Patagalia, General Services Administration, Washington
 S. Pauling, Naperville, IL
 J. E. Pavolsky, NASA/Lyndon B. Johnson Space Ctr., Houston
 C. Pax, DOE, Office of Transportation Programs, Washington
 E. Pearlman, Exide Management and Technology Co., Yardley, PA
 J. P. Pemsler, Castle Technology Corp., Lexington, MA
 G. F. Pezdirtz, DOE, Office of Advanced Conservation Technology, Washington
 A. Pivec, Public Service Electric and Gas, Newark, NJ
 A. G. Plunkett, General Electric R&D Center, Schenectady
 R. A. Powers, Union Carbide Corp., Cleveland
 V. J. Puglisi, Yardney Electric Corp., Pawcatuck, CT

E. Ramirez, Amectran, Dallas
 A. D. Raynard, AiResearch Manufacturing Co., Torrance, CA
 E. C. Read, Exxon Enterprises, Linden, NJ
 H. L. Recht, Atomics International Division, Canoga Park
 C. Ridgway, Walt Disney World Co., Lake Buena Vista, FL
 W. Rippel, Jet Propulsion Laboratory, Pasadena
 E. Rizkalla, DOE, Office of Controller, Washington
 R. A. Rizzo, Globe Battery Division, Milwaukee
 R. Robert, The MITRE Corporation, McLean, VA
 F. T. Rooney, Bureau of Automotive Maintenance, Norfolk, VA
 L. Rosenblum, NASA Lewis Research Center
 N. Rosenberg, Department of Transportation, Cambridge, MA
 R. Rosey, Westinghouse, Pittsburgh
 J. Rossmon, Cornell University
 G. Rowland, General Electric, Schenectady
 J. Ruhenzer, NASA Ames Research Center, Moffett Field
 P. H. Rubic, Electric Passenger Cars, Inc., San Diego
 H. E. Ruskie, Naval Intelligence Support Center, Washington
 A. J. Salkind, Rutgers Medical School, Piscataway, NJ
 R. T. Schneider, RTS Laboratories, Gainesville, FL
 L. W. Schopen, NASA Lewis Research Center
 H. J. Schwartz, NASA Lewis Research Center
 W. R. Scott, TRW Systems Inc., Redondo Beach
 H. Seigel, South Coast Technology Inc., Santa Barbara, CA
 H. Seiger, Harvey Seiger Associates, Waterford, CT
 J. Seliber, Fluid Drive Engineering Co., Wilmette, IL
 E. Seo, Gates Energy Products, Denver, CO
 L. Shahnasarian, Elcar Corp., Elkhart, IN
 R. C. Shair, CENTREC Corporation, Fort Lauderdale
 H. Shalit, ARCO Chemical Corp., Glendolden, PA
 D. W. Sheibley, NASA Lewis Research Center
 G. L. Silverman, Ford Motor Co., Dearborn, MI
 E. Small, Amectran Corporation, Washington
 G. A. Smith, Englehard Industries, Iselin, NJ
 S. Smith, St. Joe Minerals Corp., Monaca, PA
 V. Smith, Delco-Remy Div. GMC, Anderson, IN
 J. Smits, Nevada Operations Office, Las Vegas
 I. J. Soloman, IIT Research Institute, Chicago
 W. C. Spindler, Electric Power Research Institute, Palo Alto
 J. S. Stanley, U.S. Army Foreign Sci. & Tech. Center, Charlottesville, VA
 E. J. Steeve, Commonwealth Edison Co., Chicago
 I. Stein, Jet Propulsion Laboratory, Pasadena
 T. A. Stoneham, Marathon Battery Company, Waco, TX
 R. Strauss, Communications Satellite Corp., Clarkshurg, MD
 W. E. Strawbridge, Caterpillar Tractor Co., Peoria, IL
 R. L. Strombotne, DOE, Department of Transportation, Washington, DC
 S. Sudar, Rockwell International, Canoga Park
 P. C. Symons, Birmingham, MI
 F. Tepper, Catalyst Research Corp., Baltimore
 R. Thacker, General Motors Research Labs, Warren, MI
 C. E. Thomas, Chrysler Corporation, New Orleans, LA
 F. Thomas, Grumman Aerospace Corp., Bethpage, NY
 M. Thorpe, Towson, MD
 G. M. Thur, DOE, Office of Transportation Programs, Washington

W. H. Tiedemann, Globe Battery Division, Milwaukee
 C. W. Tobias, University of California, Berkeley
 A. Topouzian, Ford Motor Co., Dearborn, MI
 W. Toth, Society of Automotive Engineers, Inc., Warrendale, PA
 H. Toulmin, Bloomfield, MI
 I. Trachtenberg, Texas Instruments, Dallas
 J. C. Trocciola, United Technologies Corp., South Windsor, CT
 G. W. Tuffnell, The International Nickel Co., Troy, MI
 D. Turford, Western Mining Corp., Pittsburgh
 G. H. Turney, Western Research Industries, Las Vegas, NV
 E. A. Ulrich, Creative Automotive Research, Whittier, CA
 R. L. Ulrich, General Services Administration, Washington
 T. Ulrich, McGraw-Edison Co., Bloomfield, NJ
 G. Underhill, A. D. Little, Cambridge, MA
 H. B. Urbach, Naval Ship R&D Center, Annapolis, MD
 H. Vaidyanathan, Energy Research Corp., Danbury, CT
 C. J. Venuto, C&D Batteries, Plymouth Meeting, PA
 S. W. Vreeland, General Dynamics, Convair Division, San Diego
 A. Waddell, EBCO Battery Co., Columbus, GA
 E. H. Wakefield, Linear Alpha Inc., Evanston, IL
 R. Walker, University of Florida, Gainesville
 C. H. Waterman, C. H. Waterman Industries, Althol, MA
 G. Way, Troy, MI
 W. Webster, DOE, Office of Advanced Conservation Technology, Washington
 R. D. Wehrle, Sandia Labs, Albuquerque, NM
 S. A. Weiner, Ford Motor Co., Detroit, MI
 C. Weinlein, Globe Battery Division, Milwaukee
 M. Weinreb, Con Edison, New York
 E. Y. Weissman, GASF Wyandotte Corp., Wyandotte, MI
 I. Wender, Bureau of Mines, Pittsburgh, PA
 H. B. West, McGraw-Edison Company, Bloomfield, NJ
 J. H. Whitmore, Binghamton, NY
 M. E. Wilke, Burgess Battery Company, Freeport, IL
 R. Wilks, Lavelle Aircraft Co., Newton, PA
 C. F. Williams, Teledyne Isotopes, Timonium, MD
 H. R. Williams, Detroit Edison Co., Detroit
 J. M. Williams, E. I. duPont de Nemours & Co., Wilmington, DE
 E. Willhnganz, C&D Batteries, Plymouth Meeting, PA
 N. L. Willmann, Delco Remy Div. of GMC, Anderson, IN
 J. F. Wing, Booz-Allen & Hamilton Inc., Bethesda, MD
 G. A. Wooldrige, Boeing Aerospace Co., Seattle
 V. Wouk, Petro-Electric Motor Ltd., New York
 R. A. Wynveen, Life Systems Inc., Cleveland
 L. Yanni, Booz-Allen and Hamilton, Bethesda, MD
 L. S. Yao, University of Illinois, Urbana
 H. Yoder, Batronic Truck Corp., Boyertown, PA
 M. Yontar, Jersey City, NJ
 R. Zalosh, Factory Mutual Research, Norwood, MA
 J. E. Zanks, NASA Langley Research Center, Hampton, VA
 M. Zlotnick, Division of Conservation Research and Technology, Washington, DC