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**ANNUAL REPORT FOR 1978 ON
RESEARCH, DEVELOPMENT AND DEMONSTRATION OF
NICKEL-ZINC BATTERIES FOR
ELECTRIC VEHICLE PROPULSION**
Contract No. 31-109-38-4248

by

Energy Research Corporation

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Danbury, Connecticut

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By
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Danbury, Connecticut 06810

June 1979

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SECTION I - INTRODUCTION

1.0 INTRODUCTION

The report contained herein is the first annual report which reviews the progress achieved under ANL Contract 31-109-38-4248. It covers the report period from 15 March 1978 to 15 August 1978.

The report itself is subdivided into the major areas of activity e.g., Component Development and System Engineering. The first segment of the overall program entitled, "Component Development" consists of four basic subtasks which are all proceeding in parallel. They are:

- TASK I - Nickel Electrode Development
- TASK II - Zinc Electrode Development
- TASK III - Separator Development
- TASK IV - Sealed Cell Development

Each of these subtasks is reported herein on a stand-alone basis along with its own introduction and conclusion.

The nickel electrode development program under TASK I is directed at the optimization of the electrical performance, specifically, in terms of increased cycle life. In addition, emphasis is being placed upon low cost manufacturing procedures as the ERC developed non-sintered electrode holds great promise of becoming the lowest cost nickel electrode available.

The work during this report period concentrated upon both the development of pilot plant facilities to produce nickel hydroxide and upon optimizing the manufacturing processes to produce nickel hydroxide which has high electrochemical utilization. The pilot plant is now capable of producing in excess of 100 lb/week of nickel hydroxide which is equivalent to approximately 12.5 KWH theoretical capacity.

The baseline nickel hydroxide has been characterized and is now being subjected to optimization via variations in processing e.g., variations in precipitation procedures, degree of washing, grinding, drying and aging prior to incorporation into electrodes.

Full size nickel electrodes are now being routinely manufactured in the pilot plant. It is now apparent that there are no barriers to large scale production utilizing ERC's non-sintered process. Electrodes utilizing this process have yielded 300 cycles at 85% depth of discharge in 20 AH nickel-cadmium cells during the period with no evidence of decay in performance.

During the next twelve (12) month period, efforts will center on improvement in the volumetric efficiency (AH/in³) of the nickel electrode.

The primary goal under Task II of the zinc electrode studies is to increase the cycle life of this electrode in order to achieve 400-500 deep cycles at the C/2 discharge rate. Prior ERC work on experimental Ag₀-Zn cells has established that this level of cycle life can be achieved.

This effort is primarily concentrating on the effect of additives upon shape change and cycle performance and on the mechanistic processes involved in the shape change. The diagnostic efforts to determine the rates of formation of dendrites and the basic mechanisms involved have not as yet yielded clear data. When a viable diagnostic procedure is developed, it will have the two-fold purpose of being a tool for mechanism studies and will also be useful as a practical method to conduct accelerated testing of new electrode formulations.

During the next twelve (12) months, zinc electrode tasks will center on the effects of various additives and constructional variations upon electrode stability and cycle life. Work will continue in the area of the development of laboratory procedures for screening additives and quantitative determination of shape change.

TASK III, the separator effort, has as its major goal the development of a low cost separator which exhibits stability in the electrolyte, has uniform pores which are of a sufficiently small size to impede the growth of zinc dendrites and exhibits low electrical resistance and good flexibility. ERC's efforts involve both in-house manufactured and commercially available separator materials. The in-house manufactured separators consist of self-supporting and supported composite films.

The process itself is now optimized for pilot plant manufacture; hundreds of formulations have been produced and subsequently screened in both the laboratory and in actual cells. Promising formulations are presently being subjected to additional characterization tests and life cycles. Additionally, any promising commercial separators which become available are immediately placed into screening programs.

During the next twelve months, selected formulations will be tested in full scale EV cells. Studies will be undertaken to improve the mass transport characteristics and new separators will continue to be manufactured and tested.

The goal of TASK IV, the sealed cell studies, is to determine the feasibility of sealed cell operation. This task was started later than the other studies and hence has the least amount of available data. The initial exploratory studies are being undertaken in 20 AH size cells where the rates of oxygen recombination, hydrogen generation and electrolyte concentration effects, etc. are being determined.

TASK V entitled System Engineering is the second major sub-division of this effort. It is under this task that all cells are designed and tested. Also included is the investigation of charge control devices and techniques as well as the complete analysis of all cells for failure modes.

TASK V also encompasses the accelerated testing of 20 AH size cells. To date, large numbers of these 20 AH cells have been subjected to this type of testing. These cells incorporated separator variations, active material additives and internal design variations. Cycle lives up to 150 deep cycles have been achieved under these accelerated conditions depending on design details.

ERC has developed a test facility under this task which is capable of testing large numbers of full scale EV cells under varied test regimes including the simulated J227 test. This test data is now routinely fed into our computer system for data reduction and correlation. A small number of full scale cells have been tested. To date, full size cells appear to have a lower cycle life capability than 20 AH cells. The reasons are not yet known.

Observations, thus far, include the following:

- Bonded nickel electrodes perform as well as sintered electrodes under EV test conditions.
- Coulometric charge control using pressure from a pilot Ni-H₂ cell as a signal to terminate the charge is reliable.
- Constant potential charging appears to be one of several promising methods.

SECTION II

NICKEL ELECTRODE DEVELOPMENT FOR NICKEL-ZINC CELLS - TASK I

1.0 INTRODUCTION

The goals of this phase of the ANL nickel-zinc research and development program are to reduce the cost of the bonded nickel electrode and to optimize the performance capability such that 400 deep cycles (at the C/2 rate) can be achieved in nickel-zinc cells.

This investigation is presently centered on the performance characterization of the ERC baseline Ni(OH)_2 and upon the scaling up of processes involved in the manufacture of electrodes.

Test procedures are being established to completely characterize Ni(OH)_2 and graphite powders with respect to particle size, surface area and bulk density. The electrochemical utilization of active material in finished electrodes for cell design purposes will be determined by limited cycling of Ni-Cd cells.

Experimental Ni(OH)_2 electrodes will also be fabricated and tested to improve electrochemical utilization of active material and electrode stability. This portion of the development effort will center on the preparation of Ni(OH)_2 , using several different manufacturing processes including the use of additives to the active material during preparation. Experimental electrodes will be subjected to pore size measurements before and after cycling, X-Ray analysis before and after cycling, and measurement of change in electrode thickness with cycling.

2.0 TECHNICAL DISCUSSION

2.1 Nickel Hydrate

The preparation of nickel hydrate under this program was a continuation of work being done under company sponsorship. One of the objectives was to scale up the preparation of our hydrate to yield 100 pounds per week. Briefly, the preparation is carried out by precipitating a solution of cobalt nickel sulfate with an excess of potassium hydroxide. The hydrate is then washed free of alkali and sulfate.

Additional work was done to improve the preparation and electrochemical activity of the nickel hydrate. One of the problems of hydrate preparation is the relatively long time required to dry the material. To overcome this, samples of hydrate were dried at 60, 80, 100 and 120°C to determine the temperature the hydrate could withstand and still be active electrochemically. Cells have been made from these hydrates and preliminary findings will be discussed under Cell Testing.

Recent emphasis has been directed toward improving the electrode capacity per unit volume. Improved utilization of the hydrate with graphite should allow less graphite to be used, thereby devoting a greater portion of the electrode volume to the active mass. The mode is to prepare hydrates having a portion of the graphite added during their preparation.

2.2 Ni-Cd Cell Tests

The testing of experimental nickel hydrates has been carried out in nominal 20 AH nickel-cadmium cells having 70 mil positive plates with a potassium titanate separator. With such an arrangement, it has been possible to obtain over 500 cycles at the C/2 rate before the capacity fell to 50% of the initial value. A new series of cells was made with hydrates prepared by varying washing and drying conditions and was put on test.

After 100 cycles, these cells had dropped to 60-80% of their initial capacity so the cells were set aside to determine the reason for the anomalous behavior. Cells made at the same time, but not filled with electrolyte, were taken apart and in one case the pack was tightened and in the other fuel cell asbestos was substituted for potassium titanate. Neither of these variables improved cell performance. Electrode preparation was investigated next.

In the preparation of bonded positive electrodes, nickel hydrate, graphite and Teflon are milled between rollers to develop a cohesive mass. A test was made of the amount of this mulling upon the performance of subsequent electrodes. The nickel hydrates chosen were two types.

These hydrates were used to make nominal 20 AH nickel-cadmium cells with the positive plate materials milled normal, in excess of normal and less than normal. The separator used

TABLE I
EFFECT OF MULLING OF NICKEL HYDROXIDE ACTIVE MATERIALS
20 AH Ni-Cd CELLS

DEGREE OF MULLING INITIAL CAP. AH	TYPE II			TYPE I		
	OVER 18.2	NORMAL 17.3	UNDER 17.7	OVER 17.1	NORMAL 17.9	UNDER 17.9
CELL VOLTAGE	At 1 hour/ 1 hour + 55 minutes or Capacity to 0.70 Volt					
Cycle 1	1.116/0.993	1.098/18.5	1.094/18.7	1.132/18.7	1.129/1.006	1.131/19.0
Cycle 13	1.133/1.019	1.108/0.911	1.102/0.866	1.153/1.065	1.144/1.061	1.148/1.063
Cycle 61	1.139/1.010	1.056/17.7	1.023/16.3	1.160/1.065	1.137/1.043	1.159/1.061
Cycle 106	1.135/0.986	1.029/17.5	1.018/17.2	1.164/1.063	1.133/1.036	1.168/1.067
Cycle 142	1.134/0.975	0.097/16.2	0.981/16.0	1.175/1.056	1.133/1.021	1.177/1.060
Cycle 163	1.123/0.948	0.965/15.8	0.953/15.3	1.170/1.039	1.122/0.988	1.175/1.046
Cycle 184	1.118/0.932	0.953/15.7	0.925/14.5	1.165/1.029	1.116/0.995	1.171/1.042
Cycle 205	1.116/0.892	0.924/14.8	0.883/14.0	1.168/1.032	1.122/0.995	1.174/1.044
Cycle 229	1.129/0.904	0.826/11.3	0.800/11.0	1.171/1.027	1.136/1.019	1.178/1.051
Cycle 247	1.101/0.879	---/7.7	---/8.8	1.152/1.012	1.118/1.020	1.160/1.038
Cycle 268	1.116/0.824	---/4.6	---/6.8	1.163/0.982	1.137/1.003	1.173/1.022

was nylon cloth and Pellon. These cells have been on a cycle of a six-hour charge at 3.7 amperes followed by a two-hour discharge at 10 amperes representing an 85% depth of discharge. The cells have gone through 268 discharge cycles and representative monitored cycle data is shown in the attached table. This data shows the initial improvement in capacity with cycling. The general superiority of the Type I hydrate over the Type II confirms previous observations. The Type II hydrate test cells clearly show the need for maximum mulling.

The experimental samples of Type I hydrate dried at 60, 80, 100 and 120°C were made into nominal 20 AH Ni-Cd test cells using the overmulled preparative procedure. The results show the average of the midpoint voltages at the C/2 rate was initially decreased 50 millivolts due to the higher drying temperature. With four formation cycles, this difference decreased to 20 millivolts. The total cell capacities improved gradually with cycling but are independent of drying temperature.

2.3 Ni(OH)₂ Characterization Studies

Studies were initiated to determine why Ni(OH)₂ electrodes made by rolling show a slight tendency to swell during cyclic operation.

Aging experiments were begun to determine what conditions influence the formation of beta-Ni(OH)₂ during the preparation of the active material.

Initially, precipitation experiments were set up in which Co(OH)₂ was precipitated under various conditions from CoSO₄ salt. The hydroxides of cobalt are iso-structural with beta-Ni(OH)₂ and form hydrothermally from the blue alpha-Co(OH)₂. The precipitation experiments with Co(OH)₂ therefore provide immediate visual evidence of what conditions produce the beta or the alpha hydroxide.

Table II gives the various experimental conditions under which Co(OH)₂ samples were prepared along with the visual results obtained.

The results indicate that precipitation of Co(OH)₂ at room temperature results initially in formation of blue alpha-Co(OH)₂ which changes to the pink beta form on standing in the solution. Co(OH)₂ precipitated at 80°C regardless of the KOH concentration formed the pink beta type immediately.

TABLE II

PRECIPITATION OF Co(OH)_2 UNDER VARIOUS CONDITIONS

<u>Precipitation Condition</u>	<u>Visual Observation</u>
Room Temp. 1MCoSO_4 soln. 10% KOH	Initially <u>blue</u> ppt. turning pink after 2 hours in KOH solution.
Room Temp. 10MCoSO_4 soln. 10% KOH	Initially <u>blue</u> ppt. turning pink after 2 hours in KOH solution.
Room Temp., 1MCoSO_4 soln. 45% KOH	Initially <u>blue</u> ppt. turning pink after 2 hours in KOH solution.
Room Temp., 10MCoSO_4 soln. 45% KOH	Initially <u>blue</u> ppt. turning pink after 2 hours in KOH solution.
80°C , 1MCoSO_4 soln. 10% KOH	<u>Pink</u> ppt formed immediately.
80°C , 10MCoSO_4 soln. 10% KOH	<u>Pink</u> ppt formed immediately.
80°C , 1MCoSO_4 soln. 45% KOH	<u>Pink</u> ppt formed immediately.
80°C , 10MCoSO_4 soln. 45% KOH	<u>Pink</u> ppt formed immediately.

3.0 CONCLUSIONS

Work has been in progress to determine the optimum conditions necessary for the precipitation of $\text{Ni}(\text{OH})_2$. This included the effect of washing, grinding, drying and aging on the ultimate electrochemical properties of the material. The process for preparing $\text{Ni}(\text{OH})_2$ has been scaled up to produce about 100 pounds per week.

$\text{Ni}(\text{OH})_2$ bonded electrodes have been prepared and tested in Ni-Cd cells which are capable of over 300 cycles at 80% DOD.

During the next 12 months, work will focus on improving the volumetric efficiency (AH/in^3) of the nickel electrode.

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SECTION III

ZINC ELECTRODE DEVELOPMENT FOR NICKEL-ZINC CELLS - TASK II

1.0 INTRODUCTION

The primary goal of this phase of the component study will be to develop stable zinc electrode structures which are capable of at least 400-500 deep cycles (at the C/2 rate) in nickel-zinc cells.

It will be the object of this investigation to answer the following questions related to the mechanisms of zinc shape change in a working cell:

1. How do the rates of deposition and dissolution of zinc differ from the edge to the center of the electrode?
2. How do these rates differ as a function of cycling?
3. What are the rate-controlling steps for deposition and dissolution of zinc at growth steps or nucleation sites on the electrode?
4. How is the nature of the zinc deposit affected by substrate material?
5. How do additives to the active zinc material effect shape change?
6. How does the distribution of additives change in the zinc electrode with cycling?

The effects of the various electrode construction variables on shape change will be investigated in terms of their contribution to changes in current distribution within the electrode during cycling.

Segmented electrodes will be cycled and the current distribution will be monitored during various stages of life. The use of this type of set-up will allow analysis of shape change trends since uneven current distribution will result in unequal distribution of zinc.

In addition to the individual electrode studies, full size Ag-Zn and Ni-Zn cells will be fabricated with various zinc electrode structures to determine their cyclic performance capabilities under practical conditions.

2.0 TECHNICAL DISCUSSION

A zinc electrode test was set up using segmented zinc electrodes to monitor current distribution between the sections during various stages of cell life.

Preliminary tests indicated that split zinc electrodes develop gross distortions in the normal current density patterns with cycling. This results in non-reproducible data. Because of these anomalies, split positive silver electrodes were used as counter electrodes to measure changes in current patterns with cycling.

Results after 3 months do not clearly show that this technique will give an indication of zinc electrode shape change.

2.1 Procedure

Initially four single, segmented electrode cells were constructed to perfect the mechanical assembly details and to collect some preliminary data. Each cell was constructed with bonded $\text{Ni}(\text{OH})_2$ electrodes, with one zinc electrode sandwiched between two nickel half plates. Each cell had one layer of Pellon (2506K4) on the zinc electrode and two layers of PVA (0.0015") around the nickel electrodes (Figure 1). The complete electrode assemblies were inserted into transparent polyethylene bags and placed into plexiglass stands (Figure 2) to allow visual observation of electrode changes. A 35% potassium hydroxide (KOH) solution with 1% lithium hydroxide (LiOH) was used as the electrolyte. The electrodes are the same size as those used in ERC's 250 Ah cells.

Of Cells A,B,C&D (Table I), two were constructed with the zinc electrodes split vertically into three separate sections of equal area. These sections were connected through independent shunts to a common bus bar. This permitted current and voltage measurements to be taken for each section (Figure 2A).

The four cells were cycled continuously on a regime consisting of a two-hour discharge at a 10 amp current and a six-hour charge at 3.67 amps. Cells reaching a discharge voltage of 0.80 were automatically removed from the circuit for the remainder of the discharge. Discharge current vs. time measurements were recorded for each section of the two segmented electrode cells in addition to recording voltages for all the cells.

Three additional single electrode cells (S1, S2 & S3) were built with silver positive electrodes instead of nickel electrodes (see Table II). All the cells contain the same zinc formulation; however, Cell S3 has a layer of an inert conductor and a binder pressed onto the negative electrode between the ZnO layer and the copper current collector (see Figure 3) in an attempt to help prevent zinc shape change.

A = Nickel Positive (Half) Electrode
(0.036")

B = nylon (0.002")

C = 4 layers PVA (0.006" total)

D = Pellon 2506K4 (0.007")

E = Zinc Negative Electrode
(0.026" - 0.035")

Figure 1 - Electrode Arrangement

Figure 2 - Single Electrode Cell

TABLE I - CELL DESIGN SUMMARY

CELL	A	B	C	D
<u>Positive Electrode</u>				
Number	2-half electrodes	2-half electrodes	2-half electrodes	2-half electrodes
Size	6-1/4" x 9-1/2"	6-1/4" x 9-1/2"	6-1/4" x 9-1/2"	6-1/4" x 9-1/2"
Thickness	0.036"	0.036"	0.036"	0.036"
Theoretical Capacity	23.6 AH	24.1 AH	23.8 AH	24.14 AH
<u>Negative Electrode</u>				
Number	1 full	1 full	1 split	1 split
Size	6-1/4" x 9-1/2"	6-1/4" x 9-1/2"	6-1/4" x 9-1/2"	6-1/4" x 9-1/2"
Thickness	0.026"	0.035"	0.026"	0.035"
Theoretical Capacity	41.5 AH	55.7 AH	41.0 AH	41.9 AH
Zinc Mix Density	45gm/in ³	45gm/in ³	45gm/in ³	35gm/in ³
Additive	CdO	CdO	CdO	Inert
Zn/Di Ratio	1.76	2.31	1.72	1.72

Figure 2A - SINGLE ELECTRODE CELL WITH SPLIT ZINC ELECTRODE

TABLE II
SINGLE ELECTRODE TEST CELLS

CELL	S1	S2	S3	S4	S5	S6	T1-T3	NZ-1
POSITIVE ELECTRODE	Silver	Silver	Silver	Silver	Silver	Silver	Nickel Exmet	Impregnated Nickel
NUMBER	1 Full	1 Full-Split	1 Full-Split	1 Full-Split	1 Full	1 Full-Split		2 Half
SIZE	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"
THEO. CAP.	40 Ah	40 Ah	40 Ah	40 Ah	40 Ah	40 Ah		
NEGATIVE ELECTRODE	Zinc	Zinc	Zinc	Zinc	Zinc 3% TFE	Zinc 3% TFE	Zinc 3% TFE	Zinc 3% TFE
NUMBER	2 Half	2 Half	2 Half	2 Half	2 Full	2 Full	1 Full	1 Full
SIZE	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"	6½" x 9"
THEO. CAP.	75.6 Ah	75.6 Ah	75.6 Ah	75.6 Ah	74.2 Ah	74.2 Ah	74.2 Ah	74.2 Ah
ADDITIVE	CdO	CdO	inert layer collector	CdO	inert layer collector	inert layer collector	inert layer collector	inert layer collector
SEPARATOR	FSC	FSC	FSC	FSC	FSC	FSC	PVA	PVA
NO. CYCLES	177	75	170	75	21	21	88	
PRESENT PLATEAU VOLTAGE	1.40	Disassembled 7/20/78	1.35	Off Test 8/1/78	1.48	1.40	1.09	
CAPACITY TO 0.80 (Ah)	14.1		11.6		20.3	11.3	17

A = Copper Current Collector

B = CdO + TFE

C = ZnO + CdO + TFE

FIGURE 3 - Cell S3, Zinc Half Electrode Construction

Cells S2 & S3 were constructed with the silver electrode split vertically into three sections of equal area (Figure 4). Both the positive and negative plates were covered with an absorber layer of Pellon (2506K4) and three layers of FSC as a separator (figure 5). The cells were filled with a 45% potassium hydroxide (KOH) solution with 1% lithium hydroxide (LiOH). Cells S1 and S2 were cycled continuously on a regime consisting of a two-hour discharge at a 10 amp current and a six-hour charge at 3.67 amps. A low voltage limit of 0.80V was set to remove cells with low voltage from the circuit. Cell S3 was cycled with a two-hour discharge at 8.0 amps (4.1 mA/cm^2); the reduced current density was used to duplicate the current density in the 250 Ah E.V. cell tests.

Cell S4 was constructed as a duplicate of S2. It had one full, split, positive electrode between two zinc half electrodes. Pellon (2506K4) was used as an absorber layer on both the positive and negative plates. Three layers of FSC were used as a separator. The electrolyte was a solution of 45% potassium hydroxide (KOH) and 1% lithium hydroxide (LiOH).

Three "dummy" cells (T1, T2, & T3) were constructed with one full zinc electrode sandwiched between nickel exmet which was used as a "dummy" positive electrode. The negative electrodes contained ZnO, CdO, and TFE. Each of the negative electrodes had an inert conductive layer pressed into it between the ZnO layer and the copper current collector. Pellon (2506K4) was used as an absorber layer on the negative plate. Two layers of PVA were used as a separator.

Cell S5 was built with one full silver electrode sandwiched between two zinc electrodes. The negative electrodes are the same as those in Cells T1, T2, and T3 and have an inert conductive layer pressed into the negative electrode between the ZnO and the silver current collector.

Cell S6 was built with one full, silver positive electrode between two zinc electrodes which were identical to those of Cell S5. The silver electrode was split vertically into three sections of equal area. Pellon (2506K4) was used as an absorber layer on both the positive and negative plates. Three layers of FSC were used as the main separator in both cells. The electrolyte was a 45% KOH solution. NZ-1 was constructed with one full zinc plate sandwiched between two impregnated nickel plates. The negative plate contained ZnO, CdO, TFE. It had an inert conductive layer on the current collector and was also treated. Pellon (2506K4) was used as an absorber layer on the negative electrode and nylon was the plate envelope of the positive. The separator was three layers of PVA.

2.2 Results

Upon completion of the first ten cycles, Cells A, B, C and D exhibited constant discharge performances with cell capacities ranging from 15-17.5 ampere-hours to a 1.25V cut-off

FIGURE 4. SINGLE ELECTRODE CELL WITH SPLIT SILVER ELECTRODE

A = Zinc Negative (Half) Electrode
 (0.024"-0.031")
 B = Pellon (2506 K4)
 C = 3 layers FSC
 D = Pellon (2506 K4)
 E = Silver Positive Electrode (0.020")

FIGURE 5. ELECTRODE ARRANGEMENT

point. During these early cycles the cells were limited by the capacity of the nickel electrodes which yielded between 62-72% of the theoretical active material utilization. After the tenth cycle, the cell capacities began to decline as well as the average cell voltages. Discharge curves for two of the cells are shown in Figures 6 & 7.

After 45 cycles, Cells A, B, C and D yielded only 25-45% of the theoretical nickel utilization. Cell A was removed from the circuit after 45 cycles while Cell B was removed after completion of 65 cycles. Tear-down analyses performed on these cells revealed a great degree of zinc shape change with a loss of 50-70% of the active area of the electrode geometric area. There was also a significant amount of zinc dendrite growth through the PVA separator with evidence of zinc shorting which probably contributed to the low cell capacities.

Cells C & D, the split electrode cells, were left on continuous cycle for a total of 121 cycles. Figures 8 and 9 show the current distribution among the sections of the zinc electrode for the two inert conductive additives. It can be seen that the current was shared fairly equally among the sections until about 75% of the discharge was completed at which time the center of the electrode assumed the greatest portion of the current load. This condition was more exaggerated in the later cycles as the zinc shape change became more pronounced.

Finally, the two split electrode cells were dissected in order to visually observe the electrode shape change and to determine the cause for the cell's capacity degradation. As was observed in Cells A & B, there was a large amount of zinc dendrite growth through the PVA. This resulted in some shorting of the cell and a loss in capacity. There was no shift of zinc material to the center section because the sections acted as separate zinc electrides with the active material shifting towards the center portion of each individual section.

Cell S1 has presently completed 217 cycles. The discharge voltage profile (Figure 10) illustrates that the cell capacity has been dropping.

Cell S2 completed 105 cycles before it was disassembled. Its last discharge voltage profile and section current vs. time plot are presented in Figure 11 and Figure 12. Cell S2 was disassembled after 75 cycles. The suspected short was confirmed during the dissection and the cell was reassembled. Upon reassembly it completed an additional 30 cycles with its final capacity being 10.6 Ah.

Cell S3 has presently completed 224 cycles. Its discharge voltage profile and section current information are presented in Figures 13 and 14. Its performance has dropped during cycling (See Figure 13). Its present capacity is 9.3 AH

FIGURE 6. Cell A, 10A Discharge

FIGURE 7. Cell B, 10A Discharge

FIGURE 8 - CELL C, SECTION CURRENT VS. TIME

FIGURE 9 - CELL D, SECTION CURRENT VS. TIME

FIGURE 12. CELL S2
SECTION CURRENT vs TIME

FIGURE 14. CELL S3
SECTION CURRENT vs TIME

as opposed to 22 AH during its 60th cycle. Figure 14 illustrates that there has been a consistent distribution of current between the three sections. The center section has constantly been carrying a smaller fraction of the current than either of its neighboring sections; the current load shared by the right side is also larger than that of the left section. This same current distribution was seen in split silver cells (S2 & S4).

Cell S4 was removed from test after having completed 75 cycles. A duplicate of Cell S2, Cell S4 showed a decline in performance and had a final capacity of 2 AH. Its final information is presented in Figures 15 and 16.

Cell S5 has presently completed 78 cycles. Its discharge voltage profile can be seen in Figure 17. During the first 9 cycles the performance was fairly stable; since then, its capacity has dropped.

Cell S6 has also run 78 cycles. The discharge voltage profile as well as section current data are presented in Figures 18 and 19. It can be seen that the cell capacity has dropped significantly.

Cells T1 and T2 were removed from cycle after 97 cycles. These cells showed a decline in performance during their life; this may be due to the lack of voltage cut-off as "dummy" cells. Cell S3 was removed after 111 cycles at which point it had a capacity of only 4 AH.

FIGURE 16. CELL S4
SECTION CURRENT vs TIME

FIGURE 18. CELL S6
SECTION CURRENT vs TIME

3.0 CONCLUSIONS

Based on the data obtained thus far, it appears that the use of sectioned electrodes as a tool for monitoring zinc shape change is not reliable in its present form.

During the next 12 months the zinc electrode study will center on the effects of various constructions and additives on shape change in both 20 AH and 250 AH size cells.

Experimental work on the effect of current distribution and passive layer formation will be studied at the single electrode level to determine the mechanisms of zinc shape change.

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SECTION IV

SEPARATOR DEVELOPMENT FOR NICKEL-ZINC CELLS - TASK III

1.0 INTRODUCTION

Separator degradation and its influence on zinc electrode shape change is one of the life-limiting factors of Ni-Zn cells.

The goal of this task in the component optimization program will be to develop a low-cost separator which is physically and chemically stable in KOH, is flexible, has a uniform pore size and exhibits low electrical resistivity.

The investigation will include both self-supporting and supported films utilizing various formulations. Appropriate solvent/solute and wetting agent ratios will be selected for each of the combinations.

Separators will be subjected to both physical and electrochemical screening tests to fully characterize each type of material before experimental cells are fabricated for cyclic testing. The most critical parameters will be electrical resistivity, pore size, and chemical stability.

Promising candidate separators will be evaluated in both vented and sealed Ni-Zn cells. It is important to evaluate the materials under both conditions since the properties desired of a separator for a sealed cell may be different than those required for vented cells.

2.0 TECHNICAL DISCUSSION

The separator program has been directed towards developing new separator materials as well as evaluating the best commercially available separator materials.

As part of this program several screening test methods have been and are in the process of being developed.

2.1 Self Supporting Cast Films

A number of chemically stable thermoplastics have been filled with both KOH soluble and insoluble fillers.

Techniques for filling plastics include: 1) filling with an inorganic compound which leaches out of the separator in the cell leaving minute pores for electrolyte permeability and wettability, 2) filling with a KOH stable compound which creates tortuous channels in the separator along the separator filler interface and 3) a combination of KOH leachable and stable fillers. In addition to these techniques, formulations with plasticizers and wetting agents were tested.

Data summarized in Table I indicates that KOH soluble fillers are necessary in most plastic films. The most promising filled separator developed by ERC is designated P-64.

Some one mil plastic films tend to be brittle and the incorporation of a plasticizing agent greatly enhances the flexibility of the film.

The non-hydrogen bonding methylenedichloride (MeCl_2) solvent system proved ideal for dispersion of some fillers which creates a hydrogen bonded network of its own in the solvent. Conversely other fillers with a positive charge showed a tendency to clump and resist dispersion in the solvent.

Various insoluble fillers were evaluated; particle size and chemical stability data for these fillers is contained in Table II. At this time, no best choice can be made on insoluble fillers and more work is needed for characterization. Insoluble fillers can function to enhance wettability, electrical resistance, and to reduce separator shrinkage on the carrier after casting. Attempts to produce films with emulsions of both ethylene glycol and glycerine failed, due to breakdown of the emulsion during the casting process.

In an effort to improve the wettability and electrolyte retention character of some plastic materials, a large organo-nickel complex has been added to the P-64 formulation. P-97-88 includes 1% nickel octoate. P98-88 includes 5% nickel stearate. Performance character of these films remains to be determined.

TABLE I
PHYSICAL PROPERTIES OF SEPARATOR MATERIALS

SEPARATOR MATERIAL	COMPOSITION	THICKNESS (MIL)	*MEASURED ELECTRICAL RESISTANCE (MΩ)	AGING** PERIOD	COMMENTS
A. COMMERCIALY AVAILABLE FILMS					
RAI P-22-91 40/60		1.0	95.0	4 days	
Mono-Sol PVA	Polyvinyl Alcohol	1.5	35.0	4 days	Wet Thickness - 3.0 mils
Celanese Celgard	Polypropylene	1.0	30.0		
Union Carbide F.S.C.	Cellulose	3.0	20.0		Wet Thickness - 8.5 mils
German F.S.C.	Cellulose	3.0	28.0		
DuPont Cellophane	Cellophane	1.1	20.0		Wet Thickness - 3.3 mils
S.A.C. EAHT-2016	Polyethylene-Polyacrylic Acid	2.0	20.0		Wet Thickness - 2.2 mils
B. ERC FILMS					
P-1-67	Proprietary	1.0	90.0	1 day	
P-7-67	Proprietary	2.6	70.0	7 days	3% Plasticizer (T.E.A.)
P-13-67	Proprietary		160.0	5 days	3% Plasticizer (T.E.A.)
P-24-67	Proprietary		85.0	3 days	
P-26-67	Proprietary		155.0		

*For an area of 0.78 in²

**Prior to Test

TABLE I
PHYSICAL PROPERTIES OF SEPARATOR MATERIALS
(Continued)

SEPARATOR MATERIAL	COMPOSITION	THICKNESS (MIL)	*MEASURED ELECTRICAL RESISTANCE (m Ω)	**AGING PERIOD	COMMENTS
P-28-77	Proprietary				Lacks Physical Integrity
P-31-77	Proprietary	2.0	300	7 days	
P-35-77	Proprietary	2.0	***T.H.T.R.	14 days	
P-37-87	Proprietary	1.0	1.7 Ω	7 days	
P-44-87	Proprietary	1.0	1.27 Ω	1 day	
P-60-87	Proprietary	1.0	300		
P-64-107	Proprietary	1.5	70	1 day	
P-66-107	Proprietary	1.0	T.H.T.R.		
P-69-107	Proprietary	1.2	32 Ω	2 days	
P-70-117	Proprietary				Lacks physical integrity
P-71-117	Proprietary				Unable to cast
P-72-117	Proprietary	1.5	T.H.T.R.	10 days	
P-73-117	Proprietary	1.3	T.H.T.R.	10 days	
P-78-18	Proprietary	2.0			Does not wet

* For an area of 0.78 in²

** Prior to test

*** Resistance too high to read

TABLE I
PHYSICAL PROPERTIES OF SEPARATOR MATERIALS
(Continued)

SEPARATOR MATERIAL	COMPOSITION	THICKNESS (MIL)	*MEASURED ELECTRICAL RESISTANCE (m Ω)	**AGING PERIOD	COMMENTS
P-84-28	Proprietary	1.0	9.95m Ω	2 days	Uneven film
P-86-28	Proprietary	1.1	3.9 Ω	1 day	
P-87-28	Proprietary				Lacks physical integrity
P-88-28	Proprietary	1.0			Lacks physical integrity
P-97-88	Proprietary	1.0	53	1 hour	1% Ni-Octoate
P-98-88	Proprietary	2.0	75	4 hours	5% Ni-Stearate
	Proprietary				
A-41-117	Proprietary	1.4	***T.H.T.R.	3 days	
A-50-117	Proprietary	1.2	50	1 day	
A-54-18	Proprietary	1.2	1.72 Ω	1 day	
A-55-18	Proprietary				Lacks physical integrity
A-60-28	Proprietary	0.9	1.80 Ω	4 days	
A-61-28	Proprietary	1.0	60	7 days	
A-64-28	Proprietary	1.0			Lacks physical integrity

* For an area of 0.78 in²

**Prior to test

***Resistance too high to read

TABLE I
PHYSICAL PROPERTIES OF SEPARATOR MATERIALS
(Continued)

SEPARATOR MATERIAL	COMPOSITION	THICKNESS (MIL)	*MEASURED ELECTRICAL RESISTANCE (m Ω)	**AGING PERIOD	COMMENTS
A-65-28	Proprietary	1.0	65	60 hours	
A-70-48	Proprietary	1.0	660	2 days	small pinholes
A-71-48	Proprietary	1.5	60	3 days	
A-72-48	Proprietary	1.0	100	3 days	
A-73-48	Proprietary	1.3	50	d days	
A-74-48	Proprietary	1.0	50	1 day	
A-75-48	Proprietary	1.0	70	1 day	5% Victamet 12 added
A-76-48	Proprietary	1.0	975	1 day	
A-77-48	Proprietary	3.0	170	4 days	Pinholes-course texture
A-78-48	Proprietary	1.0	115	4 days	
A-83-78	Proprietary	1.0	60	1 day	
	Proprietary				
PVB-1-78/98	Proprietary	1.0	T.H.T.R	2 hours	
PVB-2-78/98	Proprietary	1.0	35	2 hours	

* for an area of 0.78 in²

**prior to test

***electrical resistance too high to read

TABLE I
PHYSICAL PROPERTIES OF SEPARATOR MATERIALS
(Concluded)

SEPARATOR MATERIAL	COMPOSITION	THICKNESS (MIL)	*MEASURED ELECTRICAL RESISTANCE (m Ω)	**AGING PERIOD	COMMENTS
PVB-3-78/98	Proprietary	1.0	40	2 hours	
PVB-6-88/72	Proprietary	1.0	60	2 hours	
PVB-10-88/72	Proprietary	1.0	50	6 hours	
	Proprietary				
A-6-67	Proprietary	1.0	4.2 Ω		
A-31-117	Proprietary	1.2	45	10 minutes	Pinholes
A-32-117	Proprietary	2.0	560		
A-33-117	Proprietary	1.5	45		
A-39-117	Proprietary				Lacks physical integrity
FVBA	Proprietary	0.5	45	2 hours	

*for an area of 0.78 in²
**prior to test

TABLE II
AVERAGE PARTICLE SIZE AND CHEMICAL STABILITY OF FILLERS

FILLER	MANUFACTURER	DENSITY	AVERAGE PARTICLE SIZE, μm	STABILITY IN 45% KOH (HEATED 24 HOURS at 50°C)
Proprietary	Carborundum	3.18	3.13	No change in color or weight
Proprietary	Bendix	3.18	2.60	No change in color or weight
Proprietary	Bendix	3.18	0.80	No change in color or weight
Proprietary	N.L. Ind.	7.5	1.18	No change in color or weight
Proprietary	N.J. Zinc	5.6	0.33	No change in color or weight
Proprietary	ERC	4.1	0.55	No change in color or weight
Proprietary	ERC	2.5	1.60	10% weight loss-color green to brown
Proprietary	J.T. Baker	2.34	1.85	20% weight loss-color white to tan
Proprietary		5.6	2.45	
Proprietary		5.6	2.75	
Bentonite MPS-1	American Colloid Co.	2.7	0.10	55.8% weight loss
Zeolon 100	Norton Chem.		6-12	
Hydrite UF	Georgia Kaolin	2.58	0.20	55.3% weight loss
Kaophile 2	Georgia Kaolin	2.61	0.20	59.5% weight loss

TABLE II (Concluded)

AVERAGE PARTICLE SIZE AND CHEMICAL STABILITY OF FILLERS

[illegible]

Due to the absorptive properties of hydrates and ion exchange capability of clays, a number of clays were evaluated as fillers in inert plastic films. Clays such as Kaolin, Bentonite, Zeolite and Clinoptilolite were incorporated up to a 50% ratio by weight. The clays, which consist chiefly of aluminum silicate, differ greatly in crystalline structure and physical properties according to type and particle size. Particle size and chemical stability data for these clays is contained in Table II.

Four basic types of Kaolin were used (in the smallest particle sizes available) and they are designated as Hydrite U.F., (hydrated form), Glomax JDF (calcined form), Kaophile 2 (surface modified form) and Kaopaque 10 (delaminated form). Two other hydrated kaolins are Al-Sil-Ate OH and Al-Ail NCF. Natural Bentonite, which is a mineral montmorillonite, is a special form of clay. It swells only slightly in strong alkaline solution and is known to have an intercalated water.

Zeolites having the mineralogical name mordenite have a unique crystalline structure and provide remarkably uniform intercrystalline pores. Zeolon 100 molecular sieve is a synthetic zeolite which is known for strong alkaline resistance. In addition to chemical stability, Zeolon 100 has pores which can absorb molecules larger than 5Å in diameter.

All the plastic/clay formulations cast uniform and strong films except for bentonite. The film with bentonite is uniform but not strong and pinholes or large pores are visible. After 2 to 3 days in 45% KOH at 50°C the electrical resistance of these materials reached a minimum value of around 50 mΩ/in². The plastic/bentonite film, however, showed a resistance of 660 mΩ after 2 days. In addition, during wetting rate tests the resistance of this film increased while readings decreased slowly for other films at room temperature. Although bentonite swells less in MeOH than in water, it swells sufficiently in the former to shrink back when the film is dried, leaving fine pores in the film. During the wetting test in 45% KOH, the filler appeared to have expanded to maximum volume and all pores were closed up.

A common problem with plastic/clay formulations is the presence of large clumps which breakdown in the alkaline environment of the cell leaving pinholes which lead to dendritic shorting. A leading formulation at this time is designated A-61 and is composed by weight of 70% plastic and 30% Al₂O₃. Data for the various plastic formulations is contained in Table I.

2.2 Celgard As Support

Chemically stable Celgard (Type 3400) film has pores which are too large to stop dendritic migration. In order to control pore size, ERC plastic, nylon and polyox formulations as well as APN and PNF were coated onto the Celgard.

TABLE III
PHYSICAL PROPERTIES OF SUPPORTED FILM

SUPPORT	MANUFACTURER	COATING* MIL THICKNESS	DRY** THICKNESS	ELECTRICAL RESISTANCE (mΩ)	COMMENT
Celgard 3400	Celanese	PVA-0.7	2.3	T.H.T.R.***	Separates in KOH
Celgard 3400	Celanese	Cellophane 0.7	2.4	T.H.T.R.	Separates in KOH
Asbestos	NASA	PPO with fillers	15.0	T.H.T.R.	Separates in KOH
Proprietary	ERC	A-65-28 1.0	2.5	210	Excellent adhesion
Proprietary	ERC	P-50-28	--	--	No adhesion
Proprietary	ERC	A-57-28 0.8	2.3	150	Excellent adhesion
Proprietary	ERC	A-67-28 0.7	2.2	270	Good adhesion
Proprietary	ERC	A-68-28 0.6	2.1	95	Excellent adhesion
Proprietary	ERC	P-Ox.-1-38 0.3	1.8	60	Excellent adhesion
Celgard	ERC	P-64-48 1.0	2.3	T.H.T.R.	Coating material saturates Celgard
Celgard	ERC	A-65-48 1.0	2.1	T.H.T.R.	Coating material saturates Celgard
Celgard	ERC	APN	--	--	Coating wets through - unmanageable
Celgard	ERC	PNF	--	--	Coating wets through - unmanageable
Proprietary	ERC	APN	2.0	T.H.T.R.	
Proprietary	ERC	PNF	2.0	T.H.T.R.	

*dry thickness of coating ** dry thickness of separator material after coating
***electrical resistance too high to read

All of the above formulations wet through the Celgard producing films which were quite stiff except the APN and PNF coatings which remained tacky and unmanageable. Table III summarizes the characteristics of the supported films.

2.3 Screening Tests

A primary function of this separator program is the evaluation of commercially-available separators, as well as the development of tests to better characterize ERC separator materials and components.

2.3.1 Evaluation of Fillers

A number of inorganic materials were characterized with relation to particle size, specific gravity and chemical stability in 45% KOH at 50°C. Table II shows the average particle size and chemical stability of some fillers under these conditions. The chemical stability study of very fine particle fillers created some problems during filtration or centrifuging. The particles went through the fritted sintered glass filter. Alternatively, when standard filter paper was used, it was not stable enough to filter the particles in the strong alkaline solution. In addition, centrifuging could not precipitate these fine particles.

2.3.2 Evaluation of Separator Materials

Screening tests for commercial and ERC manufactured separator materials include the following:

A. Chemical Stability

Separator materials are desiccated, weighed and soaked in 45% KOH/0.1 N-KMnO₄ solution at 50°C. After appropriate time intervals samples are removed, washed free of electrolyte, dried, desiccated and weighed to determine weight loss.

The chemical stability measurements of plastic/clay materials showed 50% weight loss after they were heated at 50°C in 45% KOH solution for three days. As 100% plastic film controls showed no weight loss, this indicates that 100% of the fillers were leached out of the film. When the stability measurements of fillers were carried out in the same manner by using 3 gram samples in 125cc KOH solution, only 18% of weight loss was measured. When 1-gram samples in 100cc KOH were used, weight loss increased to 58.5%. The solubility of these clays in 45% KOH appeared to be lower than the concentration mentioned above (1gm/100cc) and yet high enough to leach 100% of the fillers from the separator materials.

B. Porosimetry Analysis

Three separator materials (commercial PVA, P-50 & P-64) were subjected to a pore volume, size and distribution study as determined by the mercury penetration method. Sample P-64 consists of 90% volume plastic and 10% volume soluble filler

FIGURE 1
PORE DISTRIBUTION CURVE OF SAMPLE P-64

FIGURE 2
PORE DISTRIBUTION CURVE OF SAMPLE P-50

FIGURE 3
DISTRIBUTION OF PORES IN SEPARATOR

FIGURE 4
DIFFUSION APPARATUS

which were leached out from the film before the analysis was conducted. Sample P-50 has 76% plastic, 7.5% soluble fillers and 16.5% insoluble fillers based on volume. The porosity of a sample of commercial PVA film could not be determined by mercury intrusion. Two sets of data for each sample are summarized in Table IV and pore size distribution curves are shown in Figures 1 and 2. Analysis of the data in Figures 1 and 2 yields distribution curves plotted in Figure 3. These resulting distribution curves represent the volume of pore for a given radius.

TABLE IV
Summary of Porosimetry Analyses on P-64 & P-50

<u>Separator Material</u>	<u>Net Pore Volume (cc/g)</u>	<u>Avg. Pore Diameter (microns)</u>
P-64	0.1808	0.06
P-64	0.2266	0.037
P-50	0.1239	0.031
P-50	0.1536	1.8

Although the data recorded is probably the best we can expect by mercury porosimetry considering the type of materials (flexible plastic membranes), this method is not accurate for materials with pores smaller than 300Å. A few other possible methods to study the porosity for submicron pores could be by Transmission Electron Microscopy and by nitrogen adsorption and desorption isotherms.

C. Electrolyte Diffusion Rate Measurements

The permeability of a membrane to an electrolyte is useful for characterizing separator materials and it can be expressed by means of the electrolyte diffusion rate.

A design for diffusion rate test cell is shown in Figure 4. The diffusion rate can be determined by measuring the hydroxyl ion concentration change of the solution on the dilute side of the membrane, per unit time, per unit area of sample. The hydroxyl ion concentration can be obtained by measuring the pH of the solution directly using a pH meter. A procedure measuring the electrolyte diffusion rate was established using a similar method described by E.L. Harris.

45% KOH solution (11.67M) was used on the strong solution side and deionized water on the low concentration side of the separator material. It was found that the effect of mixing time in the dilute side of the cell was negligible with respect to concentration gradient as long as the concentration gradient was mixed adequately before measuring pH. The diffusion rate valve can also be used to estimate the upper limiting current densities of the separator in the batteries.

Hydroxyl Ion Diffusion Through Various Separators

FIGURE 5

TABLE V
TYPICAL DIFFUSION DATA AND CALCULATIONS

SAMPLE: F.S.C. (Union Carbide)
Soaked in 45% KOH at 60°C
for 24 hrs. prior to measurement

Area of sample = .785 in²
Volume of Dilute side = 140cc
Initial concentration of strong side = 45% KOH
of weak side = D.I. H₂O

Mixing Condition = 2 minutes stirring
1 minute rest before measurement

TIME	pH	pOH	a _{OH⁻}	a _{OH}	a _{OH} mole/t	$\frac{\Delta c}{\Delta t}$ mole/t
0	11.40	2.60	10 ^{-2.60}	10 ⁻³ x 10 ⁻⁴⁰	2.512 x 10 ⁻³	
5	12.70	1.30	10 ^{-1.30}	10 ⁻² x 10 ⁻⁷⁰	5.012 x 10 ⁻²	4.761 x 10 ⁻²
10	13.09	0.91	10 ^{-.91}	10 ⁻¹ x 10 ⁻⁰⁹	1.23 x 10 ⁻²	.7288 x 10 ⁻¹
15	13.29	0.71	10 ^{-.71}	10 ⁻¹ x 10 ⁻²⁹	1.95 x 10 ⁻¹	.7200 x 10 ⁻¹
20	13.41	0.59	10 ^{-.59}	10 ⁻¹ x 10 ⁻⁴¹	2.57 x 10 ⁻¹	.620 x 10 ⁻¹
25	13.52	0.48	10 ^{-.48}	10 ⁻¹ x 10 ⁻⁵²	3.311 x 10 ⁻¹	.741 x 10 ⁻¹
30	13.60	0.40	10 ^{-.40}	10 ⁻¹ x 10 ⁻⁶⁰	3.911 x 10 ⁻¹	.670 x 10 ⁻¹

$$FLUX = \frac{\Delta M}{A \Delta t} = \frac{\Delta c}{\Delta t} \times \frac{V}{A} = \frac{.70 \times 10^{-1} \times .140}{.5 \times .785} = 2.496 \times 10^{-3} \text{ mole/min-in}^2$$

M = rate of material transfer

t = time interval

A = Area of sample

V = Volume of dilute solution

c = Concentration of hydroxide ions

TABLE VI
SINGLE ELECTRODE CELL CYCLE LIFE SUMMARY

CELL #	SEPARATOR MATERIAL	ZINC ELECTRODE A		COMMENTS Absorber
		Cycles to Approximately 1V	Cycles to Approximately 0V.	
57	PVA - Commercial	90 cycles to 0.97V	100 cycles to 0.0V	KT + Pellon
75	PVA - Commercial	85 cycles to 1.02V	100 cycles to 0.12V	KT + Pellon
95	PVA - Commercial	80 cycles to 1.06V	114 cycles to 0.0V	Pellon Rolled Ni pos.
152	PVA - Commercial	50 cycles to 1.06V	64 cycles to 0.0V	Pellon
76	P-64	52 cycles to 1.10V	55 cycles to 0.0V	KT + Pellon
116	P-64	45 cycles to 1.00V	55 cycles to 0.0V	KT + Pellon Rolled Ni pos.
79	P-50	66 cycles to 1.00V	70 cycles to 0.0V	KT + Pellon
147	PVBA	67 cycles to 1.08V	89 cycles to 0.0V	Pellon
157	PVBA	35 cycles to 0.98V	40 cycles to 0.0V	Pellon
159	PVBA-2 layers	94 cycles to 1.10V	Still on cycle	Pellon
155	A-83-78	35 cycles to 1.45V	40 cycles to 0.0V	Pellon
154	PVB-2-78/98	40 cycles to 1.08V	45 cycles to 0.0V	Pellon
162	PVB-4-88/72	35 cycles to 1.08V	40 cycles to 0.0V	Pellon
163	PVB-5-88/72	35 cycles to 1.24V	54 cycles to 0.0V	Pellon

TABLE VI

SINGLE ELECTRODE CELL CYCLE LIFE SUMMARY
(Continued)

CELL #	SEPARATOR MATERIAL	ZINC ELECTRODE B		COMMENTS Absorber
		Cycles to Approximately 1V.	Cycles to Approximately 0V.	
63	PVA	99 cycles to 1.05V	108 cycles to 0.0V	KT + Pellon
85	PVA - Commercial	105 cycles to 1.00V	128 cycles to 0.0V	Pellon
111	PVA - Commercial	208 cycles to 0.9V	242 cycles to 0.0V	Pellon
126	PVA- 2 layers Commercial	150 cycles to 1.10V	161 cycles to 0.0V	Pellon
64	P-50	120 cycles to 1.23V	135 cycles to 0.0V	KT+ Pellon
124	P-50 - 2 layers	168 cycles to 1.30V	203 cycles to 0.0V	Pellon
87	P-64	55 cycles to 1.13V	61 cycles to 0.0V	KT + Pellon
113	P-64	181 cycles to 1.08V	195 cycles to 0.0V	Pellon
119	A-67	40 cycles to 1.50V	150 cycles to 0.0V	Pellon
122	A-67	98 cycles to 1.02V	99 cycles to 0.0V	Pellon
125	A-67 - 2 layers	140 cycles to 1.26V	142 cycles to 0.0V	Pellon
120	A-61	120 cycles to 1.31V	132 cycles to 0.0V	Pellon
137	S.A.C. EAHT 2016	93 cycles to 1.08V	100 cycles to 0.0V	Pellon
148	PVBA	145 cycles to 1.15V	155 cycles to 0.0V	Pellon

TABLE VI
SINGLE ELECTRODE CELL CYCLE LIFE SUMMARY
(Concluded)

CELL #	SEPARATOR MATERIAL	ZINC ELECTRODE C		COMMENTS Absorber
		Cycles to Approximately 1V.	Cycles to Approximately 0V.	
58	Celgard	75 cycles to 1.00V	81 cycles to 0.0V	KT + Pellon
78	PVA - Commercial	40 cycles to 1.15V	42 cycles to 0.0V	KT + Pellon
103	PVA - Commercial	113 cycles to 1.38V	183 cycles to 0.0V	Pellon
107	PVA - Commercial	220 cycles to 1.08V	300 cycles to 0.0V	Pellon Rolled Ni pos.
110	A-61	198 cycles to 1.10V	281 cycles to 0.0V	Pellon
130	A-61	191 cycles to 1.01V	245 cycles to 0.0V	Pellon

Figure 5 illustrates the relationship between OH^- concentration and the diffusion rate for 4 different types of separators. Details of diffusion data and calculations are amplified in Table V.

D. Electrical Resistance Measurement

These measurements were carried out by measuring the voltage drop between two reference electrodes with and without direct current through the material in 45% KOH solution. The area of the sample being measured is 0.78 in^2 .

Electrical resistance for the separator materials is summarized in Table I.

In general, clay filled separator films showed low electrical resistance, ranging from $40 \text{ m}\Omega/\text{in}^2$ to $80 \text{ m}\Omega/\text{in}^2$, except for the plastic/bentonite film, which is over $500 \text{ m}\Omega/\text{in}^2$.

E. Zinc Penetration Test - Single Electrode Cell Test

Accelerated zinc penetration tests were carried out in cells which have been constructed with one layer of separator to test the zinc stopping ability under severe conditions where rapid failure is induced. The positive electrodes are 2 full, sintered nickel electrodes and the negative electrodes are roll bonded zinc oxide with various additives.

Type of zinc electrode made a significant difference in the life of the single electrode cells. Table VI summarizes cycle life for different separators and three zinc electrode combinations.

Not all separator materials have been evaluated with the same zinc electrodes. As such results from this test are not fully comparable for this reason, graphs of discharge end voltages shown in Table VI are referenced as to zinc electrode composition and comparisons restricted to electrode types.

F. Tensile Strength Hang Test

Observing changes in tensile strength over time at an air-electrolyte interface can give valuable information concerning chemical stability of a separator material. This is particularly important for comparing commercial PVA to filled plastic separators and other experimental materials, as the former cannot be tested by means of weight change after soaking in 0.1 N-KMnO_4 :45% KOH.

Figure 6 shows an incubator and representation of the test set up. The incubator features a glass inner door to allow for observation of test units without disturbing test conditions. This permits a constant temperature vibration-free environment.

Strips of separator material $1/16$ " wide by 2" long will be suspended in individual test tubes. Weights are constructed from 304 S.S. and designed to provide a constant 300 lb/in^2 force for cross sectional area of separator material.

FIGURE 6. TENSILE STRENGTH HANGING TEST SET-UP

45% KOH will be filled to half the length of separator sample. Test units will be placed in the oven at 65°C and observed at regular intervals. Lengths of time until the separator degrades to the breakpoint will be recorded and averaged over a given number of samples. While 1/16" samples may be subject to flaws which would significantly alter individual tests, it is expected that averaging over a number of samples will provide a reasonable characterization of each separator. This data will provide a baseline for comparisons not available from present tests.

3.0 CONCLUSIONS

During this period, several inorganic/organic separator compositions have been developed which are promising candidates for use in the nickel-zinc systems. These materials are filled and plasticized plastic P-64, PVBA and PVB.

Screening tests which include KmnO_4 oxidation, electrolyte diffusion, electrolyte resistance, and hanging strength in KOH have been developed which provide good information concerning ultimate performance in cells.

Processing techniques have been scaled up to provide film continuously at the rate of 20-200 ft/hr. depending on the material.

Plans for the next 12 months include: the determination of performance of these materials in 250 Ah size cells as well as the continuation of investigative efforts to improve the mass transport characteristics of these separators for sealed cells.

The on-going program will also include the investigation of new composite materials.

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SECTION V

DEVELOPMENT OF SEALED NICKEL-ZINC CELLS - TASK IV

1.0 INTRODUCTION

The goal of this phase of the ANL nickel-zinc research and development program will be to determine the feasibility of operating large size cells in a sealed condition.

Initial exploratory studies will be carried out in 20 Ah size sealed cells to establish baseline construction and mode of operation parameters for cells containing various separator systems and zinc electrode additives. Cells containing both bonded and sintered nickel electrodes will also be fabricated.

The sealed cell investigation will include determination of rates of oxygen recombination, hydrogen generation, effect of electrolyte concentration and quantity, cycle life as a function of depth of discharge, and effect of constant current, modified constant potential and pressure controlled types of charging.

The results of the 20 Ah cell study will then be used to design and construct 250 Ah size cells for further evaluation for electric vehicle application.

2.0 TECHNICAL DISCUSSION

A total of thirty-six 20 Ah sealed cells are being built. Fourteen of the thirty-six cells have been completed and have begun testing. The discussion presented below details the work performed during the first five months of the project.

2.1 20 Ah Sealed Cell Designs

The 36 sealed cells represent 14 different designs. The construction variables evaluated in these cells include separator system (5 levels), electrode additive (5 levels) and electrolyte concentration (4 levels). Sixteen of the cells contained sintered nickel electrodes which have been impregnated by a proprietary electrochemical method developed by ERC. The remaining 20 cells contain bonded Ni(OH)_2 electrodes. Table I summarizes the construction variables for each group.

With regard to the negative plate additives, the Ti_2O_3 and PbO binary is a mercury substitute which has proven satisfactory in 850 Ah Ag-Zn cells which have been fabricated and tested under contracts for the Naval Sea Systems Command. The inert conductive layer plus 5% CdO is a unique construction patented by ERC which has shown vastly improved cycle life in 40 Ah Ag-Zn cells. Both types of negative plates also contain a small percentage of Teflon which serves as a binder permitting the material to be rolled into continuous sheets.

The five separator systems being evaluated are listed in Table I. A major problem in sealed cell design is that the nickel-zinc system requires a microporous separator system to inhibit dendrite growth while larger pores are required for effective transport of oxygen for recombination.

Celgard is a wettable microporous polypropylene with pores that are about $200\text{\AA}$ in width and $1000\text{\AA}$ in length. This pore size is about 10-50 times greater than FSC or PVA.

The separator system containing 2 layers of FSC sandwiched between layers of Celgard was chosen as a control. The use of Celgard in this arrangement may provide some protection against oxidation of the FSC material.

Four electrolyte concentrations were selected to establish the optimum concentration for oxygen recombination and to learn how reduced zinc solubility in 25% KOH affects cycle life and shape change. Figure 1 shows a schematic of the 20 Ah sealed cell.

2.2 Test Regime

The cells are filled with excess electrolyte and allowed to soak for 3 days. They are then put through two vented cycles consisting of charging at the C/16 rate and discharging at C/2 to 1.2 volts. After charging a third time at C/16, the cells are drained of all free electrolyte and sealed, followed by a discharge at C/2 to 1.2 volts.

TABLE I
20 Ah Sealed Cell Construction Variables

Group No.	Positive Plate Type	Theo. Pos. Capacity (Ah)	Neg. Plate Additive	*Separator System	Electrolyte Concentration (% KOH)
IA	Sintered	26	1% Tl_2O_3 +2% PbO	(+)/1P/4CG/1Pt(-)	25-1% LiOH
IB	Sintered	26	"	"	30-1% LiOH
IC	Sintered	26	"	"	35-1% LiOH
ID	Sintered	26	Inert Conductive Layer + 5% CdO	"	30-1% LiOH
IE	Sintered	26	1% Tl_2O_3 +2% PbO	(+)/1P/2CG/2FSC/1CG/1Pt(-)	35-1% LiOH
IIA	Bonded	25	Inert Conductive Layer + 5% CdO	(+)/1NY/4CG/1NY(-)	30-1% LiOH
IIB	Bonded	25	1% Tl_2O_3 +2% PbO	"	30-1% LiOH
1F	Sintered	26	2% CdO+1% PbO	1P/1P-64/2-PVA/P	35-1% LiOH
1G	Sintered	26	2% CdO+1% PbO	1P/1P-64/2CN/1P	40-1% LiOH
1H	Sintered	26	2% CdO+1% PbO	1P/3 EXF SEP/2P	35-1% LiOH
2C	Bonded	25	2% CdO+1% PbO	1P/1P-64/2PVA/1P	35-1% LiOH
2D	Bonded	25	2% CdO+1% PbO	1P/1P-64/2CN/1P	40-1% LiOH
2E	Bonded	25	2% CdO+1% PbO	1P/3 EXF SEP/2P	35-1% LiOH
2F	Bonded	25	1% Tl_2O_3 +2% PbO .004" CdO layer	1P/1P-64/2CN/1P	40-1% LiOH
3A	Bonded	29	Inert Conductive Layer +5% CdO	1P/1P-64/2CN/1P	35-1% LiOH
3B	Bonded	29	Inert Conductive Layer + 5% CdO	1P/1P-64/2CN/1P	35-1% LiOH

*CG - Celgard
P - Pellon
NY - Nylon

FSC - Fibrous Sausage Casing
CN - Cellophane

Figure 1. 20 AHR SEALED Ni-Zn CELL

The procedure is different for cells with Celgard as the only separator material. To minimize dendrite growth through the larger pores of the Celgard, the cells are never run flooded but are drained and sealed before any formation cycles.

Oxygen recombination rates are determined for each cell plotting the pressure increase on charge and the pressure decrease on open circuit. This is done at successively higher rates of charge up to the C/4 rate. The cells are charged to 20 psi unless the rate of pressure increase is slow enough to warrant charging to a higher pressure.

At least two cells of each design were made, so the 34 cells will be split into two identical (at least in design) sets of cells with two test regimens for gas recombination.

The first set of cells will be tested for recombination as described above, with successively higher rates of charge, up to C/4. The cells will then be charged at C/6 to 25 psi and gas chromatograph samples will be taken to determine the amount of hydrogen evolved. Oxygen will then be introduced externally into the cells and the pressure drop recorded. This will be done at various states of charge.

The second set of cells will be tested for recombination with a slight excess of electrolyte in the cell. The electrolyte will be removed in increments to determine the effect of electrolyte quantity on performance. As in the first series, chromatographic analyses will be performed on the evolved gases and chemical recombination with oxygen will be observed.

Following the recombination experiments, the cells will be put on an automatic cycling routine consisting of 10A discharge for 2 hours (or 1.2V) and 3.67A charge for 6 hours (or 25 psi).

Two of the cell groups have 4 cells of the same design. In these groups, two of the four cells will be cycled at a greater depth of discharge to determine the effect on cycle life.

Gas recombination tests will also be performed in a pressure-tight single electrode housing which has been constructed. Single zinc electrodes will be charged in a "dummy" cell and placed in the test chamber into which 25 to 50 psi oxygen will be introduced. The device is also equipped with terminal posts so single cells can be tested for gas evolution and recombination.

2.3 Cell Test Results

2.3.1 Pressure and Voltage Characteristics on Charge

Figures 3 thru 9 show the pressure and voltage characteristics of cells from Groups 2C, IIA, 2D and 2E. The pressure curves on charge exhibit two linear portions, with a slow rate of increase early in the charge and a much more rapid increase later in the charge. The shift to the faster rate of increase

CHARGE ACCEPTED TO
20 PSI VS CHARGE
RATE

FIGURE 2. GROUP 2C, CELL IIA2

FIGURE 3. CELLS IIA2 & 2C3, VOLTAGE AND PRESSURE CHARACTERISTICS

FIGURE 4

CELLS 2C3, 2C4 & IIA2 VOLTAGE & PRESSURE
CHARACTERISTICS AT 4A CHARGE

is usually accompanied by an increase in the cell voltage as the nickel electrode accepts less charge and produces more oxygen.

In some cases the pressure continues to rise after the charge has been cut off. The pressure eventually decreases to about 5 psi and begins to rise slowly as hydrogen is generated by self discharge of the zinc electrode.

Of the cells tested so far, Group 2C exhibits the slowest rate of recombination after charge. The pressure generally rises about 5 psi after the charge has been cut off and returns to the cut off pressure after about three hours. Figures 3 and 4 show pressure and voltage data for cells from Group 2C.

Figure 3 compares the voltage and pressure data of cells IIA2 and 2C3 on charge, open circuit, and discharge. While IIA2 has a higher rate of pressure increase in charge, the rate of recombination on open circuit is greater than for cell 2C3. The pressure increases about 3 psi beyond the cutoff point, but returns to the cut off pressure after about 30 minutes.

The recombination characteristics of Group 2C and cell IIA2 are generally slow. The gas generation severely limits the amount of charge that can be given to the cells. The charge input to 20 psi for the cells at different charge rates is shown in Figure 2.

Considering the open pore structure in the Celgard separator, the poor performance of cell IIA2 is surprising. Cell IIA1 has been built and initial test results show performance superior to cell IIA2. On its second cycle, IIA1 accepted 15.3 Ah before reaching the 20 psi cut off. This is superior to both IIA2 and Group 2C.

Table II shows the pressure controlled charge data for Group 2D. While the performance is generally better than that of Group 2C or IIA2, the 3A charge curves of 2D2, 2D3, and 2D4 indicate that shorts may have been developing in the cells. The voltage and pressure curves for the 3A and the 2.2A charge are shown in Figures 5 thru 8.

TABLE II
GROUP 2D PRESSURE CONTROLLED CHARGE CHARACTERISTICS

Charge Rate	Charge Input to 20 psi (Ah)				Discharge Capacity (Ah)			
(Amperes)	2D1	2D2	2D3	2D4	2D1	2D2	2D3	2D4
2	16.6	16.6	17.4	17.8	16.7	16.4	17.2	18.0
2.2	13.4	11.4	11.7	13.4	6.2	7.5	6.5	7.5
3	11.9	9.25	8.55	9.55	10.5	8.5	8.5	8.5

FIGURE 5
CELL 2DI VOLTAGE & PRESSURE CHARACTERISTICS

FIGURE 6
CELL 2D2 VOLTAGE & PRESSURE CHARACTERISTICS

FIGURE 7. CELL 2D3, VOLTAGE & PRESSURE CHARACTERISTICS

FIGURE 8. CELL 2D4, VOLTAGE & PRESSURE CHARACTERISTICS.

FIGURE 9
CELL 2E1 3A CHARGE

TABLE III
OPEN CIRCUIT GAS GENERATION RATES

<u>CELL</u>	<u>ΔP OVER 16 HOURS (psi)</u>	<u>RATE PSI/ HOUR</u>	<u>ΔP OVER 66 HOURS</u>	<u>RATE PSI/HOUR</u>
2C1	2	.125	8	.121
2C2	2	.125	5.5	.083
2C3	5	.313	15	.227
2C4	3	.188	10	.152
IIA1	8	.500	31	.470
IIA2	11	.688	27.5	.417
KKB1	1	.063	19	.288
IIB2	1	.063	9.5	.144
2D1	3	.188	11	.167
2D2	7	.438	19	.288
2D3	2	.125	7	.106
2D4	5.5	.344	9	.136
2E1	2	.125	11	.167
2E2	5	.313	23	.348

FIGURE 10. CELL 2C2, RECOMBINATION TEST

FIGURE 11. CELLS 2C1 and IIA2, RECOMBINATION TESTS

FIGURE 12
CELLS 2D3 and 2D4, RECOMBINATION TESTS

The pressure rise on charge is usually slower for Group 2D. During the 3 amp charge, the cells were charged to 25 psi resulting in as much as 40 minutes charge time after the 20 psi point had been reached. Unlike Group 2C or IIA, the cells in Group 2D show an immediate pressure drop when the charge current is cut off.

In addition to formation cycles, Group 2E (2 cells) and Group 2B (2 cells) have each been given a 3A charge in the sealed condition. 2E1 and 2E2 accepted 12.75 and 14.0 Ah to the 20 psi cut off. 2B1 and 2B2 accepted 16.45 and 15.2 Ah respectively. Figure 9 shows voltage and pressure characteristics of cell 2E1.

2.3.2 Gas Generation on Open Circuit

A major problem with the sealed cells is the hydrogen gas generated on open circuit due to zinc corrosion. Chromatograph analysis of gases from cells left on open circuit indicates that the gas is hydrogen with traces of nitrogen and oxygen, presumably from the air initially sealed in the cell.

The pressure build-up from hydrogen generation makes regular venting of the cells necessary to prevent bursting. Table III shows the gas generation rates over 16 and 66 hour periods.

2.3.3 Chemical Recombination Tests

Cells 2C1, 2C2, 2IIA2, 2D3 and 2D4 have all been tested for direct chemical recombination by introducing 20 psi oxygen into the charged cells. Despite its poor charging characteristics, cell IIA2 performed better than the cells from Groups 2C and 2D. The pressure in IIA2 leveled off at 11.5 psi vacuum after six hours and 2C2 reached a low of 13.5 psi vacuum after 6 hours.

Group 2D performed better than Group 2C, leveling off below 10 psi vacuum after 3 hours. The data for this test is shown in Figures 10 thru 12.

3.0 CONCLUSIONS

Rates of oxygen recombination and hydrogen evolution have been determined for various 20 Ah sealed cell designs.

Removal of free electrolyte to enhance oxygen recombination also results in a loss of capacity.

During the next 12 months, work will continue on methods for improving O_2 recombination without sacrificing cell capacity. This investigation will center on the use of inexpensive recombination electrodes employing various oxygen electrocatalysts. Both 20 and 250 Ah size cells will be tested.

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SECTION VI

SYSTEM ENGINEERING - TASK V

1.0 INTRODUCTION

The goal of this phase of the ANL Program is the development of an EV type battery incorporating the advances made in component technology, manufacturing methods and design concepts.

Our attention during this reporting period was divided into design, fabrication and testing of 20 Ah and 250 Ah vented nickel-zinc cells, charge control methods, and cell modeling and data reduction using a digital computer.

The following sections present a technical discussion on our investigative efforts.

2.0 TECHNICAL DISCUSSION

CELL DESIGN, FABRICATION AND TESTING

2.1 20 AH Cells

Electrochemical designs for two types of cells, a large EV type cell and a small 20 Ah cell, were prepared. The smaller size cells are test vehicles to evaluate the design, components and electrolyte composition. Both types were positive limited and contained rectangular electrodes individually bagged in the separator material. The salient features of the design are given in Table I.

A number of cells of both types were fabricated. Furthermore, alterations were made in the baseline design with respect to the number and type of electrodes, the separator system and ampere-hour capacity of the electrode sandwich.

2.2 Cell Design

The construction of cells consisted essentially of nickel positive electrodes, zinc negative electrodes and separators. The electrodes were all of the bonded and pressed type as opposed to the conventional sintered nickel plaque electrodes. The components were assembled in a transparent polysulfone case, terminals soldered and cover ultrasonically sealed. The cells were filled with electrolyte, allowed to stand for 72 hours and tested.

Initially, about 40 cells were built with various mix formulae for the negative electrode. The cells were tested on an automatic cycler.

Each cell was tested until the discharge capacity dropped to below 12 Ah with an end voltage of 1.25V. The cell voltages were monitored continually by means of recorders. The electrolyte level was maintained by topping up with 5% KOH solution as required to compensate for electrolyte losses. At the completion of tests, sample cells were dissected to check for dendrite growth, shorts, positive swelling, negative shape change, separator degradation, etc.

In the first group of cells, the electrode size, number of electrodes per cell and separator configuration were kept the same.

The negative mix was varied by the addition of CdO, HgO, and various proprietary additives. The combinations are listed in Table IA.

An examination of Table IA shows that cycle life varies from 46 to 132. The mix containing HgO gave only 46 cycles and this has to be investigated further. Even though mix No. 1 which contained no additive gave about 80 cycles, the cell was tested immediately after it was built and it is to be expected that the same number of cycles cannot be obtained

TABLE I
DESIGN PARAMETERS

ITEM	TYPE I	TYPE II
Rated Capacity, Ah	20.00	250.00
Cell Case Material	Polysulfone	Noryl fiberglass
Cell Dimension, inches	6x1-5/16x3-9/16	7.0x12-1/2x2-3/4
Positive Plate Type	ERC Bonded	ERC Bonded
Number of Electrodes	6	16
Negative Plate Type	ERC Bonded	ERC Bonded
Number of Electrodes	7	17
Separator		
Inner Separator for Electrodes	Woven Nylon	Woven Nylon
Main Separator	Commercial PVA	Commercial PVA
Secondary Reservoir type separator	Pellon 2502	Pellon 2502

TABLE I A CYCLE LIFE OF 20 AH CELLS

Mix S.No.	Negative Mix	Number of Cells Tested	Average Number of Cycles
1	ZnO TFE	2	82
2	ZnO CdO TFE	5	58
3	Proprietary	2	66
4	ZnO CdO TFE	2	58
5	Proprietary	3	68
6	Proprietary	2	132
7	Proprietary	2	113
8	Proprietary	2	122
9	ZnO HgO TFE	2	46

after wet stand since self discharge of zinc would be critical. Cells fabricated using ERC proprietary additives displayed cycle life from 68 to 132.

A group of six (6) 20 Ah vented Ni-Zn cells (Group 1) was fabricated to test the effectiveness of the rolling procedure used in the manufacture of positive electrodes. Of the six cells fabricated, three contained positive electrodes fabricated from ERC precipitated $\text{Ni}(\text{OH})_2$ batch #54-102 and the other three contained those from batch #81-52A. All the six cells were assembled in an identical manner and were filled with the same quantity of 35% KOH and 1% LiOH electrolyte. The variable being studied in the rolling procedure is the degree of mulling. Degree of mulling may be classified into:

MAXIMUM: Mulling to the point that a small amount of cracking will occur on rolling.

NORMAL: Mulling to the point that the sheet has one less pass than required to make a satisfactory sheet.

MINIMUM: Mulling to the point that it has just enough adhesion to form a sheet.

The test procedure after cell assembly consisted of alternately charging and discharging the cells in an automatic cycler. The depth and rate of discharge amounted to 83% and C/2, respectively for each cycle. The experimental results are summarized in Table II.

Cells made from ERC $\text{Ni}(\text{OH})_2$ batch #54-102 had poorer nickel utilization and poor cycle life when the mulling was minimum but improved considerably when mulled to normal or maximum level. There was no noticeable difference in the electrochemical performance of the cells made from ERC batch #81-52A. Figures 1 and 2 show graphical representation of capacity decline with cycling for the cells.

It may be concluded from the above data that although mulling is a critical operation, minute changes in the degree of mulling do not affect the electrochemical performance, if the nickel hydroxide has the desired characteristics.

A second group of 4 cells was fabricated to test the effectiveness of a proprietary additive (B-1) as a Hg substitute in the zinc electrode. The cells, with a rated capacity of 20 Ah, were again tested for cycle life in an automatic cycler. The amp-hour capacity of the cells at each discharge cycle and the original number of cycles at which the capacity declined below 60% of the theoretical positive capacity were determined. Table III summarizes the experimental results. The results show that this proprietary additive is effective as an Hg substitute to a certain extent. Furthermore, the amount of additive in the negative electrode mixture had no effect on the cycle life. The

TABLE II
RESULTS OF MULLING EXPERIMENTS

GROUP	I			II		
Ni Type	ERC 54-102			ERC 81-52A		
Cell No.	25	26	27	28	29	30
No. of Cycles	20	55	56	68	82	70
Avg. Discharge Volts	1.34	1.43	1.37	1.56	1.55	1.55
Max. Discharge Capacity (AH)	15.0	15.6	15.6	16.9	16.9	16.9

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EFFECT OF MULLING ERC NI #54-102

FIGURE 1

EFFECT OF MULLING ERC Ni #81-52 A

FIGURE 2

TABLE III

EVALUATION OF B-1 ADDITION TO THE NEGATIVE PLATES

Cell No.	TL1	TL2	TL3	TL4
Electrode Composition				
ZnO/H-1	92-10-3	93-5-2	96-2-2	No D-1
CYCLE NO.	DISCHARGE CAPACITY, AH, TO 1.25 END V			
5	14.4	15.0	13.8	15.0
10	15.6	16.9	15.6	15.6
15	14.4	17.5	16.9	15.6
20	16.3	16.9	17.5	16.3
25	16.3	17.5	18.1	16.9
30	16.3	16.9	17.5	16.9
35	15.6	16.9	17.5	16.9
40	15.6	16.3	16.9	16.9
45	15.6	16.3	16.9	16.9
50	15.6	16.3	16.9	16.9
55	15.6	15.0	16.9	17.5
60	15.6	14.4	15.6	17.5
65	15.6	14.4	15.6	15.0
70	15.6	13.1	15.0	14.4
75	15.6	11.9	12.5	13.1
80	12.5	11.9	11.9	13.1
85	10.1	10.0	10.0	8.1
90	10.0	10.0	10.0	8.1
Avg. volts	1.55	1.50	1.55	1.50
Avg. AH	15.4	15.9	16.2	15.8

experiments are being continued to evaluate the effect of B-1 in combination with CdO.

A group of fifteen (15) 20 Ah cells was fabricated and their cycle life was determined. Table IV details the performance of these cells. Capacity decline for representative samples of this group of four cells is illustrated in Figure 3.

2.3 250 AH Cells

A total of twenty-two (22) EV type cells were fabricated. After assembly the cells were vacuum filled with an electrolyte composition consisting of 35% KOH and 1% LiOH. This was followed by a formation charge at C/12.

The cells were tested in an automatic cyler in a cycling regime consisting of Charge: Constant current at 40 Amp for 5 hours 45 minutes and Discharge: Constant current at 85 Amp for 2 hours, 15 minutes.

The cell skin temperature was allowed to rise during cycling. There are no pauses in the cycling routine and each cell goes through a total of 3 cycles per day. The duration of overcharge amounts to 17%. The corresponding depth of discharge is 75%.

During charge and discharge the variation of cell voltage with time was recorded on a Rustrak recorder. The data reduction consisted of first tabulating the cell voltage versus time, which formed the input to the computer along with discharge current, end of charge voltage and current and duration of charge. The output from the computer consisted of ampere-hour capacity versus voltage plots and performance data such as ampere-hour efficiency and watt hour efficiency. Figures 4A through 4C show discharge curves and Tables V, VI and VII illustrate the performance characteristics.

Two of the EV type cells were discharged in a J227aD pulse discharge profile which approximates the duty cycle in an operating electric vehicle. The discharge pattern is as follows:

CHARGE: 40 Amps for 5 hours, 45 minutes
DISCHARGE: 28 seconds at 200 Amps
50 seconds at 75 Amps
42 seconds at open circuit

Figures 5 and 6 show the voltage versus time recorder plots obtained for cells EV10 and EV13 respectively. The test results demonstrate the capability of ERC designed Ni-Zn cells to perform in an electric vehicle. Further, it substantiates our claims about the high current density capabilities of the non-sintered bonded Ni(OH)₂ electrodes. The capacity decline observed is not due to the degradation of the positive and negative plates. Instead, it may be due to electrolyte loss at the electrode surface which leads to

TABLE IV

BATTERY/MCNOBLOCK/CELL TESTS

CELL/ MONOBLOCK/ BATTERY DESCRIPTION	RATED CAPACITY		RATES, hr		INITIAL EFF. %		LIFE CHARACTERISTICS						REMARKS
	A-hr	W-hr	DISCH.	CHARGE	NOMINAL		DAYS	CYCLES	% DECLINE IN				
					A-hr	W-hr			CAPACITY	ENERGY	A-hr EFF.	W-hr EFF.	
#27 Vented cell	20	32.0	C/2	C/6	87	71	31	92	36	28	36	28	
#28 Vented cell	20	32.0	C/2	C/6	90	74	32	95	38	30	38	30	
#29 Vented cell	20	32.0	C/2	C/6	90	74	40	120	38	30	38	30	
#30 Vented cell	20	32.0	C/2	C/6	87	71	35	105	36	28	36	28	
#31 Vented cell	20	32.0	C/2	C/6	87	71	45	138	36	28	36	28	
#32 Vented cell	20	32.0	C/2	C/6	90	74	42	127	38	30	38	30	
#33 Vented cell	20	32.0	C/2	C/6	87	71	40	120	36	28	36	28	
#34 Vented cell	20	32.0	C/2	C/6	90	74	41	123	38	30	38	30	
#35 Vented cell	20	32.0	C/2	C/6	78	64	30	90	29	21	29	21	
#36 Vented cell	20	32.0	C/2	C/6	87	71	13	40	35	28	36	28	
#37 Vented cell	20	32.0	C/2	C/6	90	74	18	53	38	30	38	30	
#38 Vented cell	20	32.0	C/2	C/6	87	71	11	32	35	28	36	28	
#39 Vented cell	20	32.0	C/2	C/6	93	76	18	53	40	29	40	29	
#40 Vented cell	20	32.0	C/2	C/6	93	76	16	78	40	29	40	29	
#41 Vented cell	20	32.0	C/2	C/6	93	76	18	85	40	29	40	29

FIG. 3 EFFECT OF NEGATIVE ADDITIVES ON CYCLE LIFE

FIGURE 4A. DISCHARGE PERFORMANCE, Ni-Zn CELLS (EV12, EV14, EVS2)

FIGURE 4B. DISCHARGE PERFORMANCE, Ni-Zn CELLS (EV20, EV22, EV23 & EV25)

FIGURE 4C. DISCHARGE PERFORMANCE, Ni-Zn CELLS (EV27, EV28, EVS3 & ECAR-1)

TABLE V
Ni-Zn Cell EV23

Initial Amp-Hr Capacity = 191.25
Initial Amp-Hr Efficiency = 83.15

Ni-Zn CELL EV23

Cumulative percent decline in amp-hr capacity and efficiency compared to first given cycle.

FIRST GIVEN CYCLE IS CYCLE NUMBER 1.0

<u>CYCLE</u>	<u>AMP-HR. CAPACITY</u>	<u>PERCENT DECLINE</u>
5.0	191.25	0.0
11.0	184.17	3.7
19.0	191.25	0.0
27.0	191.25	0.0
34.0	183.98	3.8

Initial Watt Hr. Efficiency = 72.55

Cumulative percent decline in watt-hr efficiency in comparison to the watt-hr efficiency of the first given cycle.

<u>CYCLE</u>	<u>CYCLE EFFICIENCY</u>	<u>PERCENT DECLINE</u>
5.0	73.59	-1.43
11.0	70.41	2.95
19.0	72.78	-0.31
27.0	71.17	1.91
34.0	68.54	5.54

TABLE VI
Ni-Zn Cell EV25

Initial Amp-Hr Capacity = 170.00

Initial Amp-Hr Efficiency = 73.91

Ni-Zn Cell EV25

Cumulative percent decline in amp-hr and efficiency compared to first given cycle.

FIRST GIVEN CYCLE IS CYCLE NUMBER 1.0

<u>CYCLE</u>	<u>AMP-HR. CAPACITY</u>	<u>PERCENT DECLINE</u>
3.0	165.22	2.81
5.0	165.87	2.43
9.0	191.25	****
14.0	179.52	-5.60
16.0	177.67	-4.51
20.0	166.87	1.84
24.0	164.97	2.96
27.0	154.06	9.38
30.0	161.15	5.21

Initial Watt-Hr Efficiency = 65.04

Cumulative percent decline in watt-hr efficiency in comparison to the watt-hr efficiency of the first given cycle.

<u>CYCLE</u>	<u>CYCLE EFFICIENCY</u>	<u>PERCENT DECLINE</u>
3.0	61.61	5.28
5.0	61.90	4.04
9.0	71.01	-9.10
14.0	67.78	-4.21
16.0	65.59	-0.84
20.0	62.47	3.96
24.0	61.75	5.06
27.0	55.92	14.02
30.0	59.20	8.98

TABLE VII

Ni-Zn Cell EV22

Initial Amp-Hr Capacity = 191.25

Initial Amp-Hr Efficiency = 83.15

Ni-Zn Cell EV22

Cumulative percent decline in amp-hr capacity and efficiency compared to first given cycle.

FIRST GIVEN CYCLE IS CYCLE NUMBER 1.0

<u>CYCLE</u>	<u>AMP-HR. CAPACITY</u>	<u>PERCENT DECLINE</u>
3.0	191.25	0.0
10.0	191.25	0.0
15.0	191.25	0.0
23.0	191.25	0.0
30.0	160.13	16.27
35.0	121.55	36.44
45.0	70.83	62.96

Initial Watt-Hr. Efficiency = 70.23

Cumulative percent decline in watt-hr efficiency in comparison to the watt-hr efficiency of the first given cycle.

<u>CYCLE</u>	<u>CYCLE EFFICIENCY</u>	<u>PERCENT DECLINE</u>
3.0	70.36	-0.18
10.0	69.71	0.74
15.0	70.21	0.04
23.0	70.45	-0.32
30.0	57.03	18.79
35.0	42.98	38.80
45.0	24.68	64.86

CELL #EVT 10

CYCLE: #8

PULSES: 85

TOTAL DISCHARGE: 207 AHR

AVERAGE VOLTAGES:

180A = 1.381

75A = 1.496

0A = 1.666

FIGURE 5. J227ad ELECTRIC PROFILE, CELL EVT 10

CELL #EVT 13

PULSES: 66

TOTAL DISCHARGE: 171 AHR

AVERAGE VOLTAGES:

200A = 1.419

75A = 1.557

0A = 1.683

FIGURE 6. J227ad ELECTRIC PROFILE, CELL EVT 13

high temperatures inside the cell with subsequent oxidation of the separator. We are able to prove this fact by failure analysis.

The baseline design given in Table I does not incorporate any means to prevent electrolyte dryout. The situation may be improved by:

1. Using slightly thinner electrodes.
2. Adding reservoir type materials to the separator system.
3. Adding a vent mechanism to the cover assembly which reduces electrolyte loss during charging.
4. Using constant potential charging.

3.0 CHARGE CONTROL

3.1 Coulometric Technique

A major requirement for the successful application of Ni-Zn cells for electric vehicle propulsion is a charge control procedure and a state of charge indicating system. Recognizing this, a coulometric type charge control was designed and fabricated. The following paragraphs describe the operating characteristics of the coulometer.

Construction

The coulometer uses the pressure variations in a nickel-hydrogen cell to control charge. In other words, the Ni-H₂ cell acts as a control cell. A hermetically sealed nickel-hydrogen cell was assembled. The nickel hydroxide electrode in the control cell is of the same type as that used in the main Ni-Zn cell.

A control circuit was designed for the coulometer. The main elements of the electronic circuitry are: 1) power supply, 2) shunt, 3) amplifier, 4) pressure switch and 5) pressure gauge. A block diagram of the coulometer circuit is given in Figure 7.

Operation and Functional Features

Linearity: In order to test the circuitry the nickel-hydrogen cell was automatically charged and discharged by connecting it to ERC designed test equipment. During this experiment, the charging current and discharging current for the nickel-hydrogen cell were drawn through the shunt. First, the variation of voltage drop across the shunt with the current (charging or discharging) was determined. It was linear. Then the voltage drop across the shunt during a typical charging and discharging regime was monitored. The voltage drop remained constant as shown in Figure 8. The current through the coulometer cell was also monitored. As shown in Figure 8, a constant value for the current was obtained. During this experiment the current output from the automatic cycler was 4.0 amperes during charge and 10 amperes during discharge.

Typical Performance: A 20 Ah nickel-zinc cell was assembled and used as the test vehicle to evaluate the coulometer. The nickel-zinc cell was connected to a DC power supply through a shunt. The coulometer was connected across the shunt as shown in Figure 7. The nickel-zinc cell was charged at 4.0 amperes. Under these conditions, the charging current for the nickel-hydrogen cell was 100 milliamperes. During charge, the voltage of the Ni-Zn cell and the pressure of the nickel-hydrogen cell were monitored. The documented values for Ni-H₂ pressure and Ni-Zn voltage are plotted in Figure 9. The pressure varied linearly with time. The Ni-Zn voltage reached a value of 2.0V after 6 hours and 20 minutes.

FIGURE 7. COULOMETER CIRCUIT

FIGURE 8. CONSTANCY OF VOLTAGE DROP AND
CURRENT DURING CHARGE AND DISCHARGE

FIGURE 9 CHARACTERISTICS OF COULOMETRIC CHARGE CONTROL - CHARGE

A - VARIATION OF Ni-Zn VOLTAGE WITH TIME

B - VARIATION OF Ni-H₂ PRESSURE WITH TIME

Then, the Ni-Zn cell and the Ni-H₂ cell were discharged. The discharge current for the Ni-Zn was 6 amperes and that for Ni-H₂, 170 milliamperes. Again the variations of Ni-H₂ pressure and Ni-Zn voltage were monitored. The pressure varied linearly with time. The discharge characteristics are shown in Figure 10.

The charging and discharging were repeated. Reproducible values for pressures were obtained at the end of charge and end of discharge. From the experimental data, it is evident that values for the pressure can be selected for the end of charge and end of discharge. Charging can be terminated by an automatic pressure switch as soon as a preselected value for the pressure is reached.

3.2 Constant Voltage Charging

Since H₂ evolution on zinc on overcharge is deleterious to the stability of the zinc, constant potential charging seems appropriate. An automatic cyler was assembled consisting of power supply, electronic relays and a timer. A voltage of 1.92 was selected for the controlled potential charging. This voltage is below the over-voltage at which H₂ evolution occurs on Zn. Figure 11 gives a typical charging curve. The charging current decays from 95 amperes at the beginning of charge to 10 amperes towards the end of charge. EVS2 was cycled using controlled potential charge and constant current discharge. The performance of EVS2 is given in Figure 4A.

FIGURE 10 CHARACTERISTICS OF COULOMETER DURING DISCHARGE
 A = VARIATION OF NICKEL-ZINC VOLTAGE WITH TIME
 B = VARIATION OF NICKEL-HYDROGEN PRESSURE WITH TIME

EVT S2

FIGURE 11. CURRENT VARIATIONS DURING CONSTANT VOLTAGE CHARGING AT 1.92 VOLTS

CHARGE =
 $\int \text{AMP. HR.}$
= $4385 \times .05 \times 1$
= 219.25 Ah

4.0 DATA REDUCTION AND CELL MODELING

All efforts during the period were directed toward the dual tasks of data reduction and mathematical modeling. Both tasks make use of the computer facilities at ERC.

The goal of the data reduction task is to furnish a program for the computer which will tabulate, graph and analyze the experimental data generated by cell testing. At the same time, these sets of raw data are entered on permanent files which are added to our growing bank of cell performance data.

The main data reduction program is complete and ready for regular use. This program performs the following functions: For each cycle:

1. Lists reference information
2. Tabulates three columns of data reflecting time elapsed, voltage, and amp-hr capacity removed
3. Plots a graph of voltage vs amp-hr capacity removed. This graphing routine is an upgraded version of our previously reported routine. All data points now appear on the graph with a maximum error of .01 volt.

For each cell (using data for all available cycles):

1. Calculates initial amp-hr capacity and efficiency
2. Tabulates percent decline in amp-hr capacity and efficiency (compared to first given cycle) for each cycle.
3. Calculates initial watt-hr efficiency
4. Tabulates percent decline in watt-hr efficiency (compared to first given cycle) for each cycle.
5. Plots a graph of the entire discharge performance history for the cell. The graph plots total amp-hr capacity removed vs cycle number.

The goal of the modeling task is to produce a thermal model of battery electrodes which can be utilized to help improve cell performance and analyze cell failure. A computer program incorporating this mathematical model will show changing temperature distributions within the electrode stack as a function of time. By changing the input parameters and studying the resulting thermal effects, the designer can use the program as an optimization tool to eliminate hot spots and "tailor" the temperature gradients to prevent failure and increase cycle life.

5.0 CONCLUSIONS

It may be concluded from the preceding test data that:

1. Hg may be substituted with various proprietary additives.
2. The bonded-pressed Ni(OH)_2 electrode performs as well as the conventional sintered Ni(OH)_2 in EV type cells.
3. Constant potential charging seems quite promising as a simple means of controlling charge and overcharge.
4. The coulometric method for charge control, in which the pressure of Ni-H_2 control cell is used as a signal to terminate charging is extremely reliable.
5. For EV type cells, electrolyte dry out, separator degradation and thermal gradients are more of a problem during the first 100 cycles of life.

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