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### Authors

Nichols, J.T.  
McLarnon, F.R.  
Cairns, E.J.

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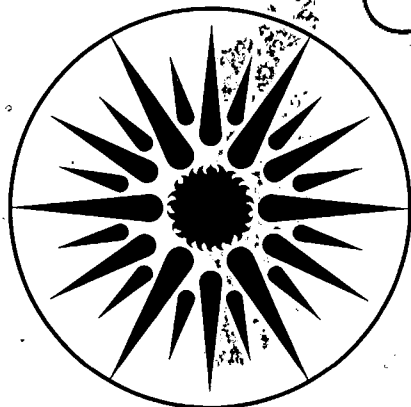
RECHARGEABILITY OF THE ZINC ELECTRODE  
IN ALKALINE ELECTROLYTE

J.T. Nichols, F.R. McLarnon, and E.J. Cairns

September 1982

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*Presented at the International Society of Electrochemistry  
Meeting, Lyon, France*

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J.T. NICHOLS, F.R. MCLARNON AND E.J. CAIRNS

ENERGY AND ENVIRONMENT DIVISION  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720  
U.S.A.

RECHARGEABILITY OF THE ZINC ELECTRODE IN ALKALINE ELECTROLYTE\*

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## SUMMARY

THE RECHARGEABILITY AND CYCLE-LIFE PERFORMANCE OF MODEL Zn/NiOOH CELLS WAS INVESTIGATED. ELECTROLYTES THAT EXHIBIT REDUCED SOLUBILITY OF ZnO DEMONSTRATED IMPROVED CAPACITY RETENTION AND LOWER RATES OF Zn MATERIAL REDISTRIBUTION AFTER APPROXIMATELY 128 CONSTANT CURRENT CYCLES. KOH + KF AND KOH + H<sub>3</sub>BO<sub>3</sub> ELECTROLYTES SHOWED THE BEST PERFORMANCE.

## INTRODUCTION

POROUS ZINC ELECTRODES ARE EMPLOYED IN SEVERAL RECHARGEABLE ALKALINE BATTERIES, SUCH AS Zn/NiOOH, Zn/AIR AND Zn/AgO. THESE SYSTEMS OFFER ATTRACTIVE SPECIFIC ENERGY AND SPECIFIC POWER CHARACTERISTICS, BUT THEY GENERALLY EXHIBIT RAPID CAPACITY LOSS, LEADING TO LIFETIMES OF ONLY 100-300 DEEP CYCLES. THIS CAPACITY DEGRADATION IS RELATED (1) TO ACTIVE MATERIAL REDISTRIBUTION (SHAPE CHANGE) OVER THE FACE OF THE ZINC ELECTRODE, AND THE PROPOSED MECHANISMS (2,3) OF SHAPE CHANGE ARE LINKED TO THE HIGH SOLUBILITY OF ZINC-BEARING SPECIES OF ALKALINE ELECTROLYTES. THE PURPOSE OF THE PRESENT STUDY IS TO EXAMINE THE RECHARGEABILITY AND CYCLE-LIFE PERFORMANCE OF MODEL Zn/NiOOH CELLS THAT EMPLOY ELECTROLYTES (4) WITH REDUCED SOLUBILITY OF ZINC.

## EXPERIMENTAL

A MODEL Zn/NiOOH CELL WAS CONSTRUCTED, AND BOTH ASSEMBLED AND EXPLODED VIEWS ARE SHOWN IN FIGURES 1 AND 2, RESPECTIVELY. SUFFICIENT ZnO WAS LOADED INTO THE NEGATIVE ELECTRODE TO PROVIDE 3 TIMES THE STOICHIOMETRIC EQUIVALENT OF THE NOMINAL 1.35 AH CELL CAPACITY. THE TWO SINTERED NiOOH ELECTRODES WERE LOADED WITH 1.41 AH OF ACTIVE Ni MATERIAL, NEARLY EQUAL TO THE NOMINAL CAPACITY. FOUR DIFFERENT ELECTROLYTES WERE TESTED, AND THEIR COMPOSITIONS ARE SPECIFIED IN THE CAPTIONS UNDER FIGURES 5 AND 6. ALL CELLS WERE CYCLED AT CONSTANT CURRENT TO COMPLETELY DISCHARGE IN < 2.5 HR TO A 1.1 V LIMIT AND TO COMPLETELY CHARGE IN < 6 HR OR WHEN A LIMIT OF 2.15 V WAS REACHED. ALL TESTS WERE TERMINATED AT 128 CYCLES.

## RESULTS

X-RAY PHOTOGRAPHS OF THE Z<sub>N</sub> ELECTRODES WERE RECORDED BOTH BEFORE AND AFTER CYCLING TO PROVIDE A MEASURE OF SHAPE CHANGE RATES. FIGURE 3 SHOWS A MODERATE Z<sub>N</sub> SURFACE AREA REDUCTION AFTER 128 CYCLES WHEN 14.4 WT% KOH IS EMPLOYED, AND FIGURE 4 ILLUSTRATES SUBSTANTIAL IMPROVEMENT IN SHAPE CHANGE RATES WHEN KF IS ADDED TO THE KOH. EXCESSIVE Z<sub>N</sub> MATERIAL REDISTRIBUTION WAS OBSERVED IN THE STANDARD 31 WT% ELECTROLYTE ("HIGHD" IN FIGURE 5).

FIGURES 5 AND 6 DISPLAY THE Z<sub>N</sub>/NiOOH CELL CAPACITY RETENTION AS A FUNCTION OF CYCLE NUMBER FOR ALL FOUR ELECTROLYTES EMPLOYED. THE THREE ELECTROLYTES WITH ~ 15 WT% KOH ("LOWA," "KFF," AND "BO3H") EXHIBIT CAPACITIES MORE STABLE THAN THAT OF ~ 31 WT% KOH ("HIGHD"), AND THE ELECTROLYTES WITH KF AND H<sub>3</sub>BO<sub>3</sub> ADDITIONS ARE SEEN TO BE SUPERIOR TO ELECTROLYTE WITH KOH ONLY.

TYPICAL CHARGE/DISCHARGE PROFILES ARE DISPLAYED IN FIGURES 7 AND 8.

## DISCUSSION

FIGURES 5-6 DEMONSTRATE THAT ELECTROLYTES EXHIBITING REDUCED Z<sub>N</sub>O SOLUBILITY (4) SHOW Z<sub>N</sub>/NiOOH CELL CAPACITY RETENTION. THERE IS ALSO A CLEAR CORRELATION BETWEEN STABLE CELL CAPACITY (E.G., CURVE KFF IN FIGURE 6, KOH + KF ELECTROLYTE) AND REDUCED Z<sub>N</sub> ELECTRODE SHAPE CHANGE RATES (FIGURE 4). THESE RESULTS ARE NOT UNEXPECTED BECAUSE OF THE ESTABLISHED RELATIONSHIP (2, 3) BETWEEN SHAPE CHANGE RATES AND Z<sub>N</sub> SOLUBILITY.

THE IMPROVEMENT IN CAPACITY RETENTION OBSERVED WHEN KF (OR H<sub>3</sub>BO<sub>3</sub>) IS ADDED TO 15 WT% KOH (COMPARE THE DOTTED CURVE WITH THE DASHED CURVE IN FIGURE 5) IS APPARENTLY LINKED TO ENHANCED CHARGE ACCEPTANCE BY THE NiOOH ELECTRODE. A COMPARISON OF THE NiOOH ELECTRODE POTENTIAL DURING THE CHARGING PORTION OF FIGURES 7 AND 8 INDICATES SUBSTANTIALLY LOWER OVERPOTENTIALS FOR KOH + KF ELECTROLYTE. THE Z<sub>N</sub> ELECTRODE OVERPOTENTIALS ARE NEGLIGIBLE BY COMPARISON.

## REFERENCES

1. J. MCBREEN AND E.J. CAIRNS, IN ADVANCES IN ELECTROCHEMISTRY AND ELECTROCHEMICAL ENGINEERING, H. GERISHER AND C.W. TOBIAS, EDS., VOL. 11, PP. 273-352 (1978).
2. J. MCBREEN, J. ELECTROCHEM. SOC. 119, 1620 (1972).
3. K.W. CHOI, D.N. BENNION, AND J. NEWMAN, J. ELECTROCHEM. SOC. 123, 1616 (1976).
4. R.F. THORNTON AND E.J. CARLSON, J. ELECTROCHEM. SOC. 127, 1448 (1981).

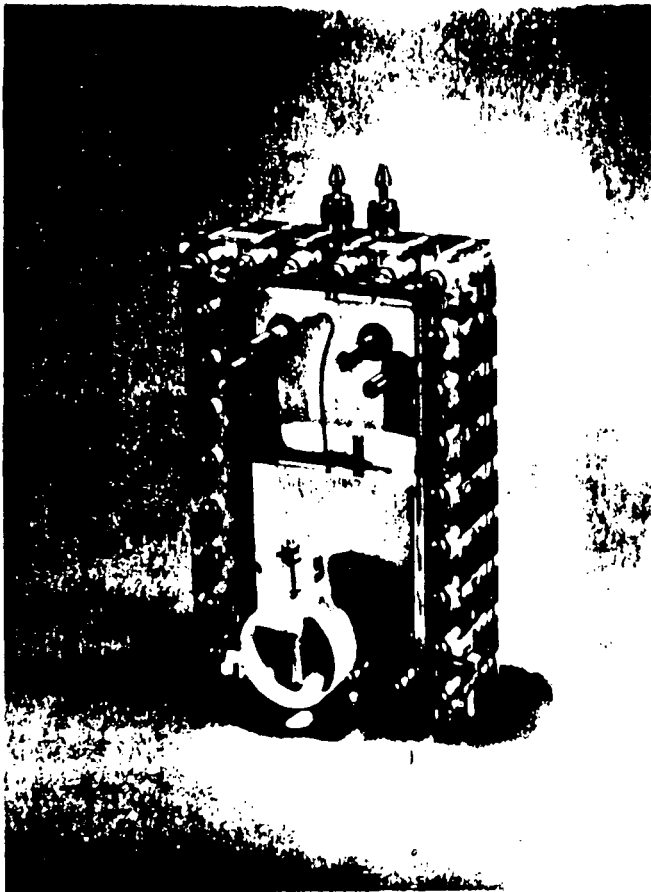


FIGURE 1  
ASSEMBLED MODEL ZINC/NICKEL OXIDE CELL

### CELL SPECIFICATIONS

1 NEGATIVE ELECTRODE: 94%  $ZnO$ , 2%  $PbO$ , 4% PTFE. 1.35 AH NOMINAL CAPACITY, LOADED TO 3X STOICHIOMETRIC  $ZnO$  EQUIVALENT  $Cu$  SCREEN CURRENT COLLECTOR ELECTROPLATED WITH  $Pb$ .

2 POSITIVE ELECTRODES: SINTERED  $NiOOH$  ELECTRODES SUPPLIED BY EAGLE-PICHER CO. 1.41 AH NOMINAL CAPACITY, 16  $MAH/CM^2$ .

SEPARATOR SYSTEM: 3 LAYERS OF CELGARD 3401 SEALED AROUND NEGATIVE ELECTRODE.

WICK: PELLON 2502K4 WRAPPED AROUND BOTH POSITIVE ELECTRODES.

REFERENCE ELECTRODE:  $Hg/HgO$  ELECTRODE WITH CAPILLARY LOCATED AT BACK SIDE OF A POSITIVE ELECTRODE.

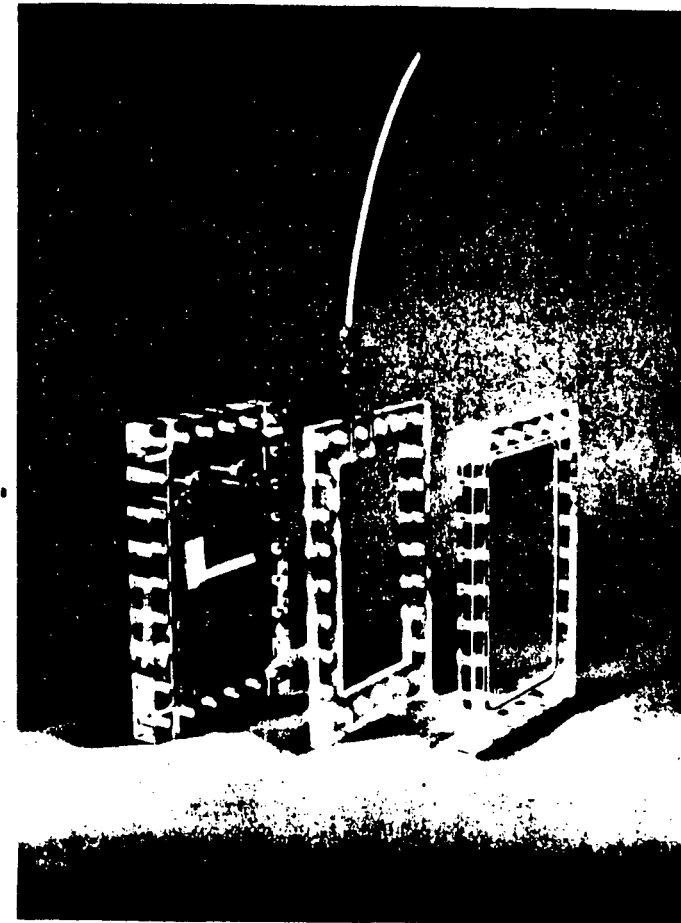


FIGURE 2  
EXPLODED VIEW OF  
MODEL ZINC NICKEL OXIDE CELL



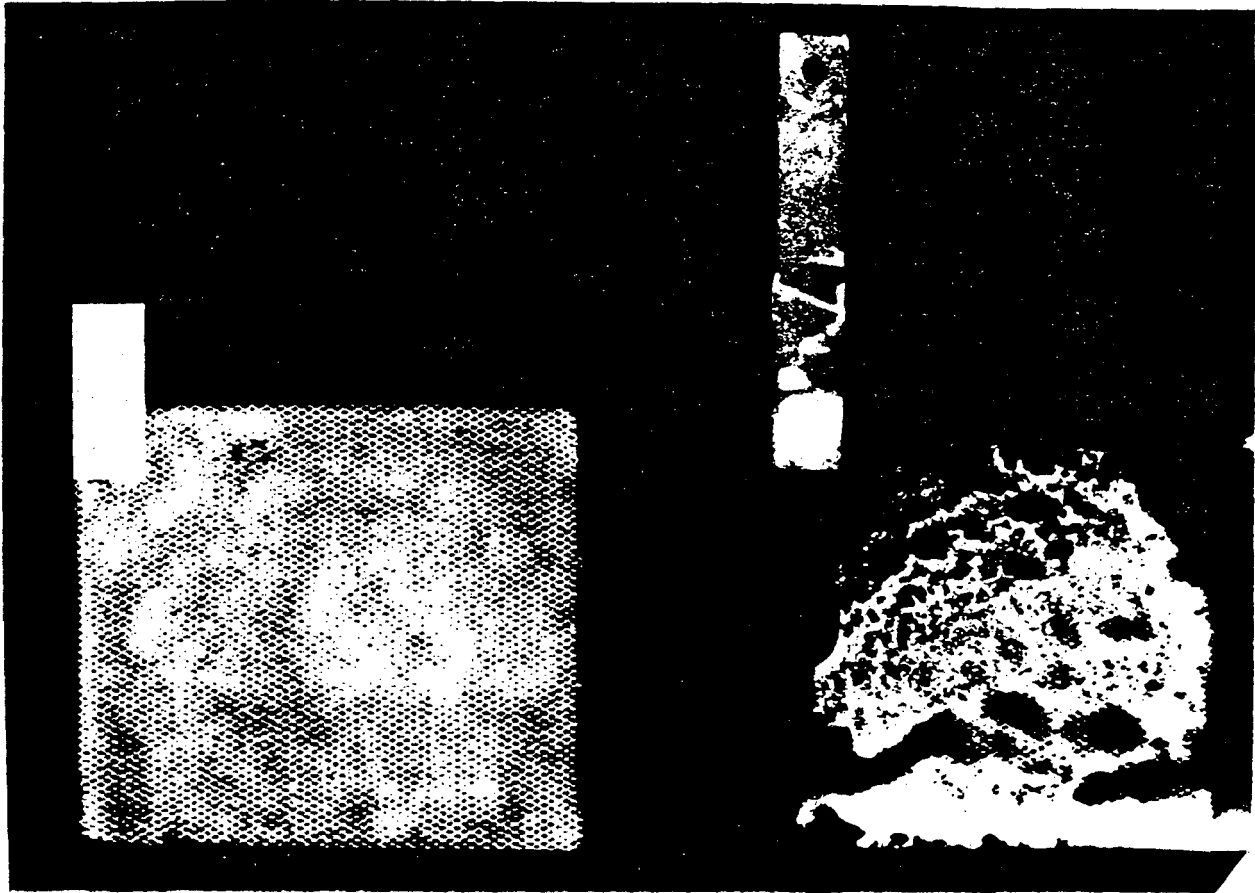


FIGURE 3

X-RAY PHOTOGRAPH OF ZINC ELECTRODE BEFORE AND  
AFTER 128 CYCLES IN KOH ELECTROLYTE

ELECTROLYTE COMPOSITION: 14.4 WT% KOH  
(DESIGNATED "LOWA" 1.1 WT% LiOH  
IN FIGURE 5) SATURATED WITH ZNO

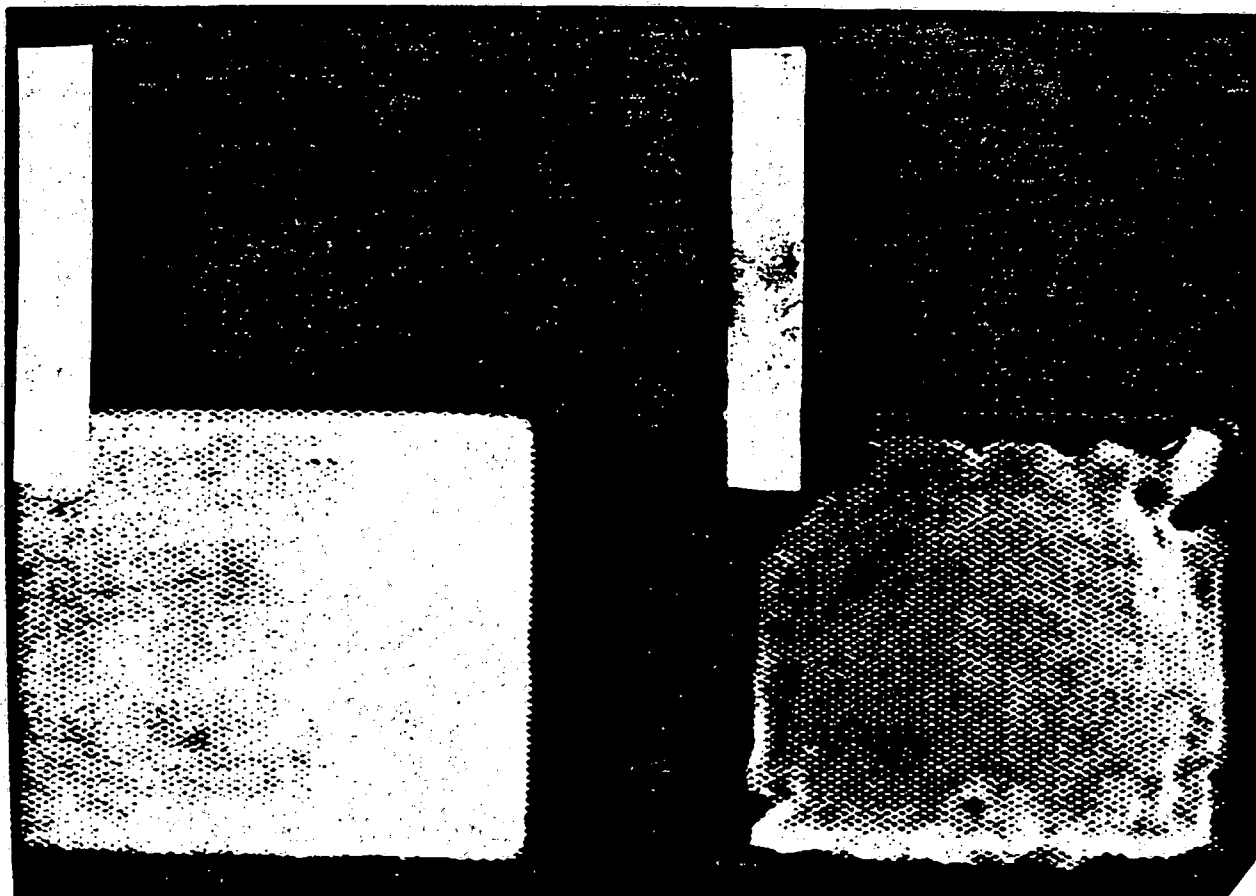


FIGURE 4  
X-RAY PHOTOGRAPH OF ZINC ELECTRODE BEFORE AND  
AFTER 128 CYCLES IN KOH + KF ELECTROLYTE  
ELECTROLYTE COMPOSITION: 15.3 wt% KOH  
(DESIGNATED KFF 15.0 wt% KF  
IN FIGURE 6) 0.0002 wt% LiOH  
SATURATED WITH ZNO

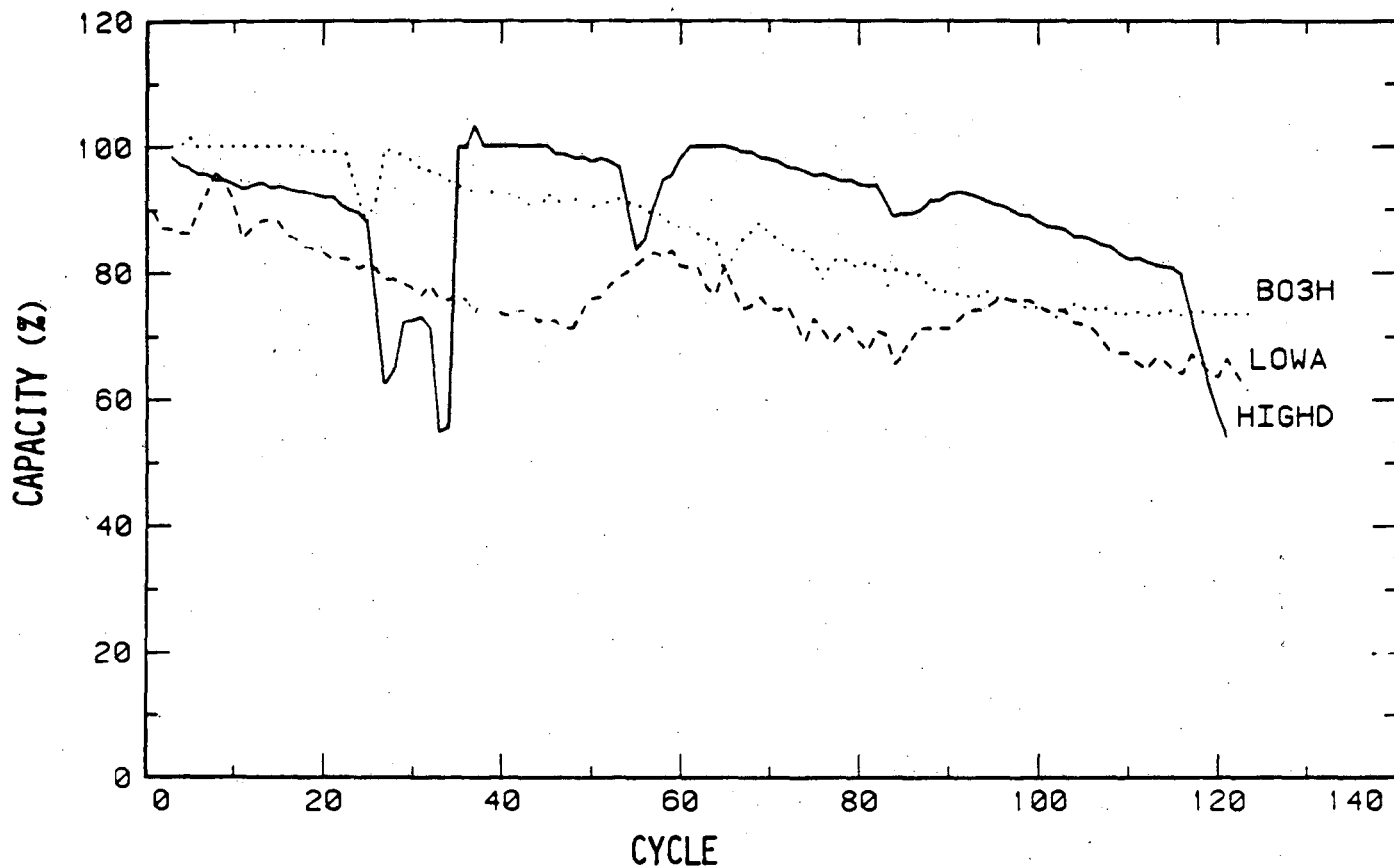


FIGURE 5

CAPACITY VS CYCLE NUMBER FOR KOH AND KOH + H<sub>3</sub>BO<sub>3</sub> ELECTROLYTES

"HIGHD" ELECTROLYTE: 30.0 wt% KOH  
 1.0 wt% LiOH  
 SATURATED WITH ZnO

"LOWA" ELECTROLYTE: 14.4 wt% KOH  
 (SEE FIG. 3, 7) 1.1 wt% LiOH  
 SATURATED WITH ZnO

"BO3H" ELECTROLYTE: 20.6 wt% KOH  
 8.4 wt% H<sub>3</sub>BO<sub>3</sub>  
 1.0 wt% LiOH  
 SATURATED WITH ZnO

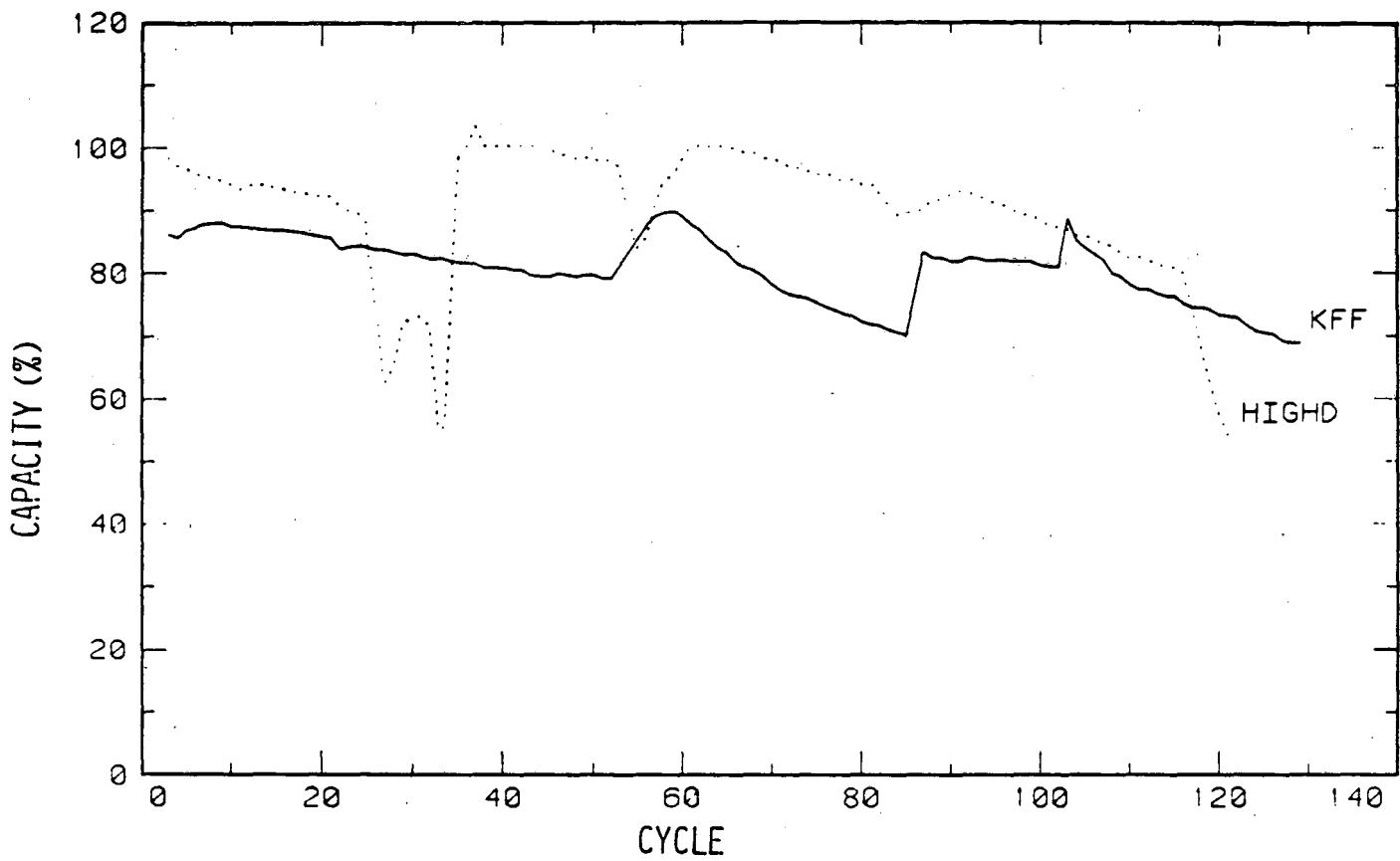


FIGURE 6

CAPACITY VS CYCLE NUMBER FOR KOH AND KOH + KF ELECTROLYTES

"HIGHD" ELECTROLYTE: SEE FIGURE 5

"KFF" ELECTROLYTE: 15.3 WT% KOH  
 15.0 WT% KF  
 0.0002 WT% LIOH  
 SATURATED WITH ZNO

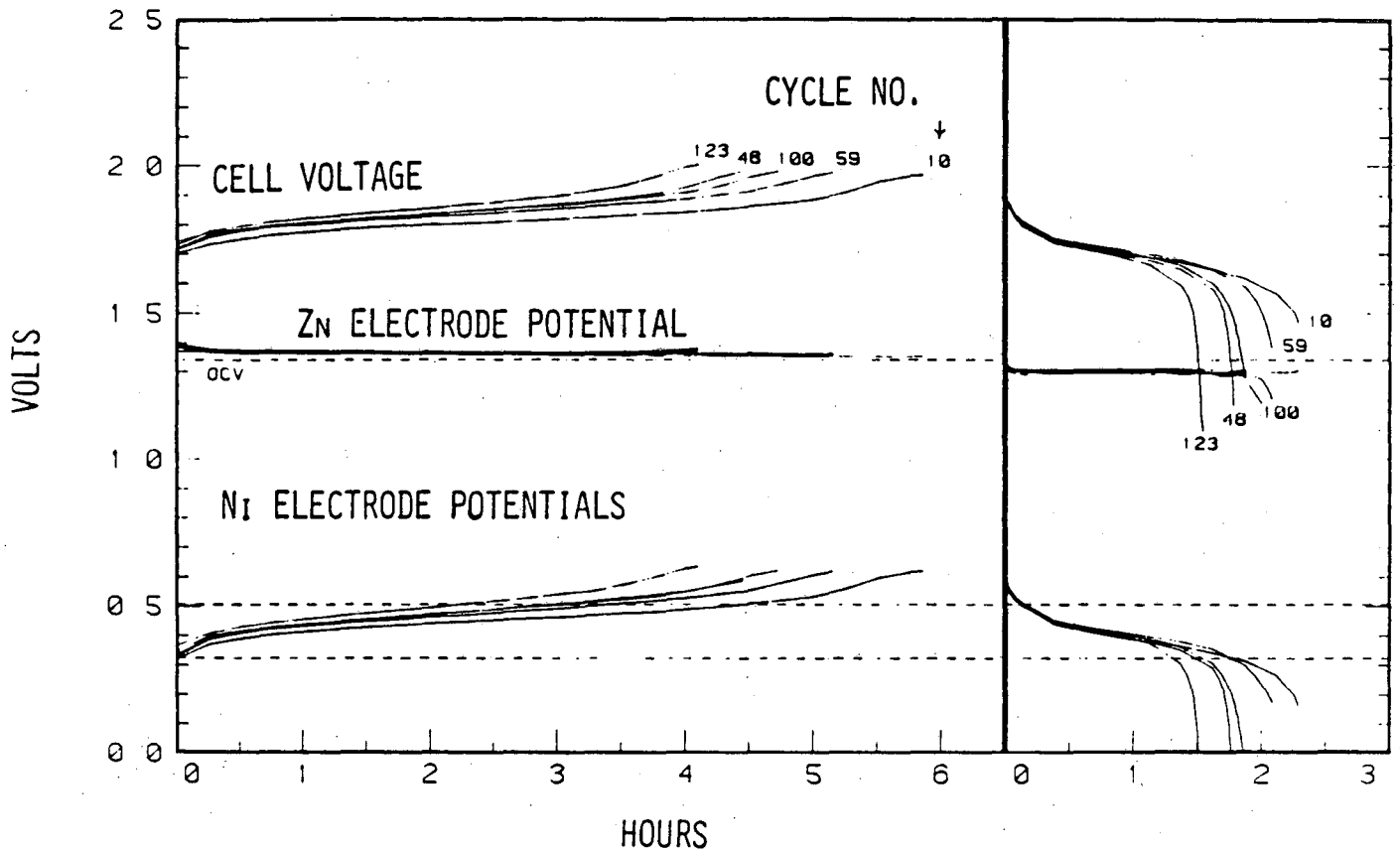


FIGURE 7

CELL POTENTIALS VS TIME DURING CONSTANT-CURRENT CHARGE AND DISCHARGE IN KOH ELECTROLYTE

ELECTROLYTE COMPOSITION: 14.4 wt% KOH  
 1.1 wt% LiOH  
 SATURATED WITH ZNO

CELL VOLTAGE (UPPER CURVE), Hg/HgO-Zn POTENTIAL, AND NiOOH-Hg/HgO POTENTIALS ARE SHOWN AS THE UPPER, MIDDLE, AND LOWER SETS OF CURVES, RESPECTIVELY. CHARGE IS ON THE LEFT-HAND SIDE, AND DISCHARGE IS ON THE RIGHT-HAND SIDE.

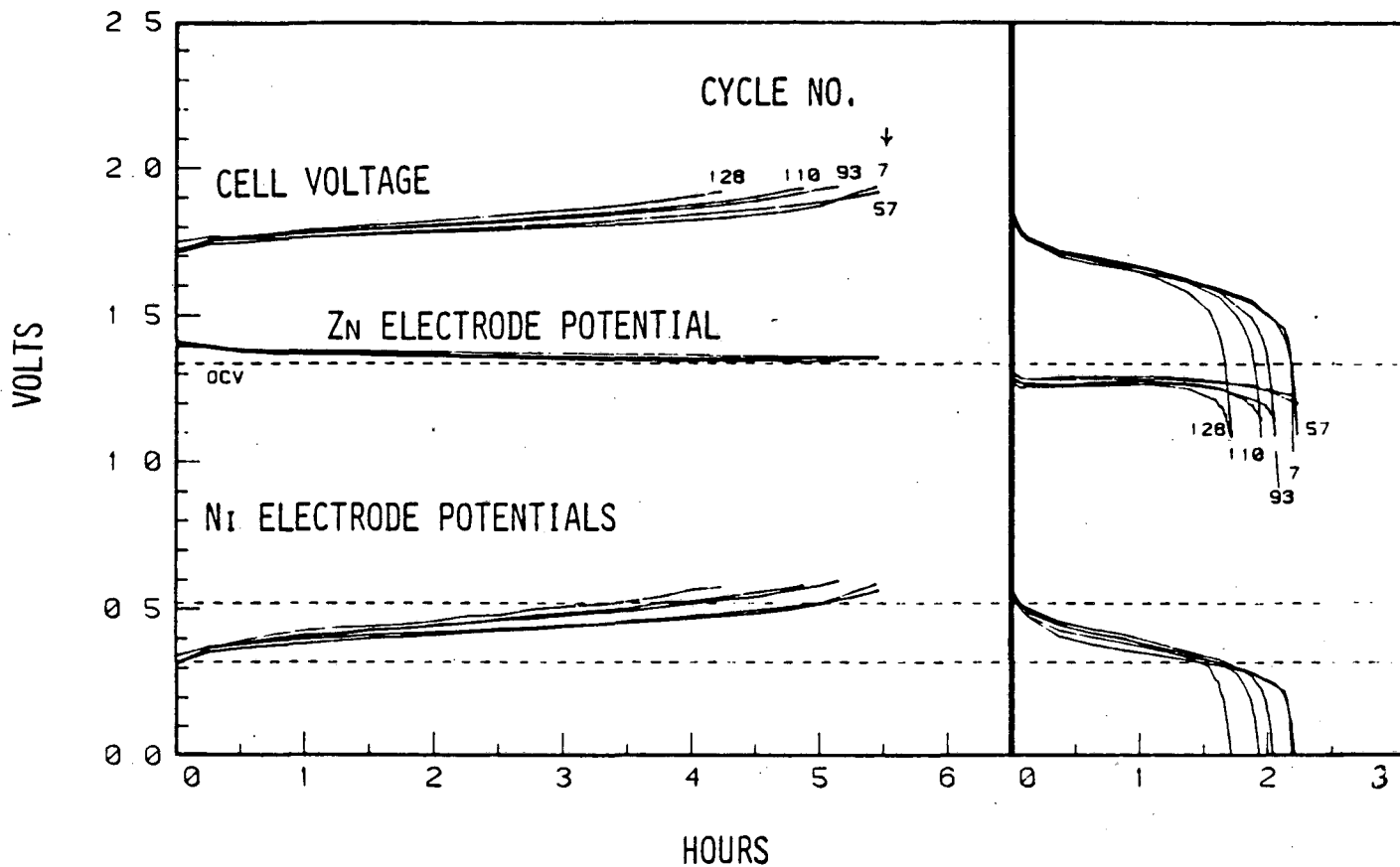


FIGURE 8

CELL POTENTIALS VS TIME DURING CONSTANT-CURRENT CHARGE AND DISCHARGE  
IN KOH + KF ELECTROLYTE

ELECTROLYTE COMPOSITION: 15.3 WT% KOH  
(DESIGNATED "KFF" IN 15.0 WT% KF  
FIGURE 6) 0.0002 WT% LiOH  
SATURATED WITH ZnO

DESIGNATIONS AS IN FIGURE 7.

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