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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_3BO_3 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 A_H CELL CAPACITY. THE TWO SINTERED NiOOH ELECTRODES WERE LOADED WITH 1.41 A_H 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 Zn ELECTRODES WERE RECORDED BOTH BEFORE AND AFTER CYCLING TO PROVIDE A MEASURE OF SHAPE CHANGE RATES. FIGURE 3 SHOWS A MODERATE Zn 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 Zn MATERIAL REDISTRIBUTION WAS OBSERVED IN THE STANDARD 31 wt% ELECTROLYTE ("HIGHD" IN FIGURE 5).

FIGURES 5 AND 6 DISPLAY THE Zn/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_3BO_3 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 ZnO SOLUBILITY (4) SHOW Zn/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 Zn ELECTRODE SHAPE CHANGE RATES (FIGURE 4). THESE RESULTS ARE NOT UNEXPECTED BECAUSE OF THE ESTABLISHED RELATIONSHIP (2, 3) BETWEEN SHAPE CHANGE RATES AND Zn SOLUBILITY.

THE IMPROVEMENT IN CAPACITY RETENTION OBSERVED WHEN KF (OR H_3BO_3) 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 Zn ELECTRODE OVERPOTENTIALS ARE NEGLIGIBLE BY COMPARISON.

REFERENCES

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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.

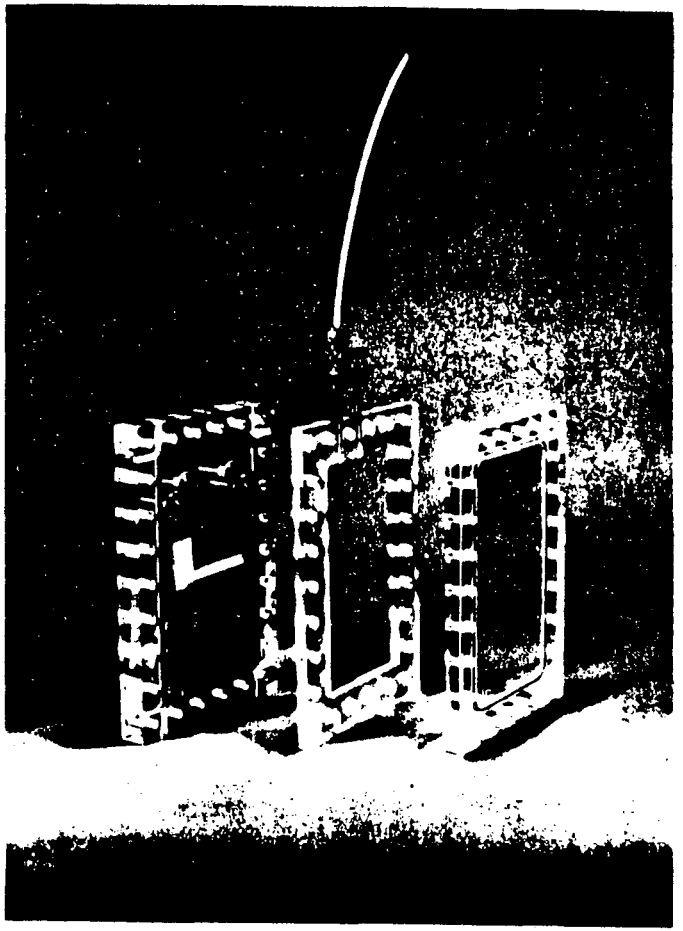

FIGURE 2
EXPLODED VIEW OF
MODEL ZINC NICKEL OXIDE CELL

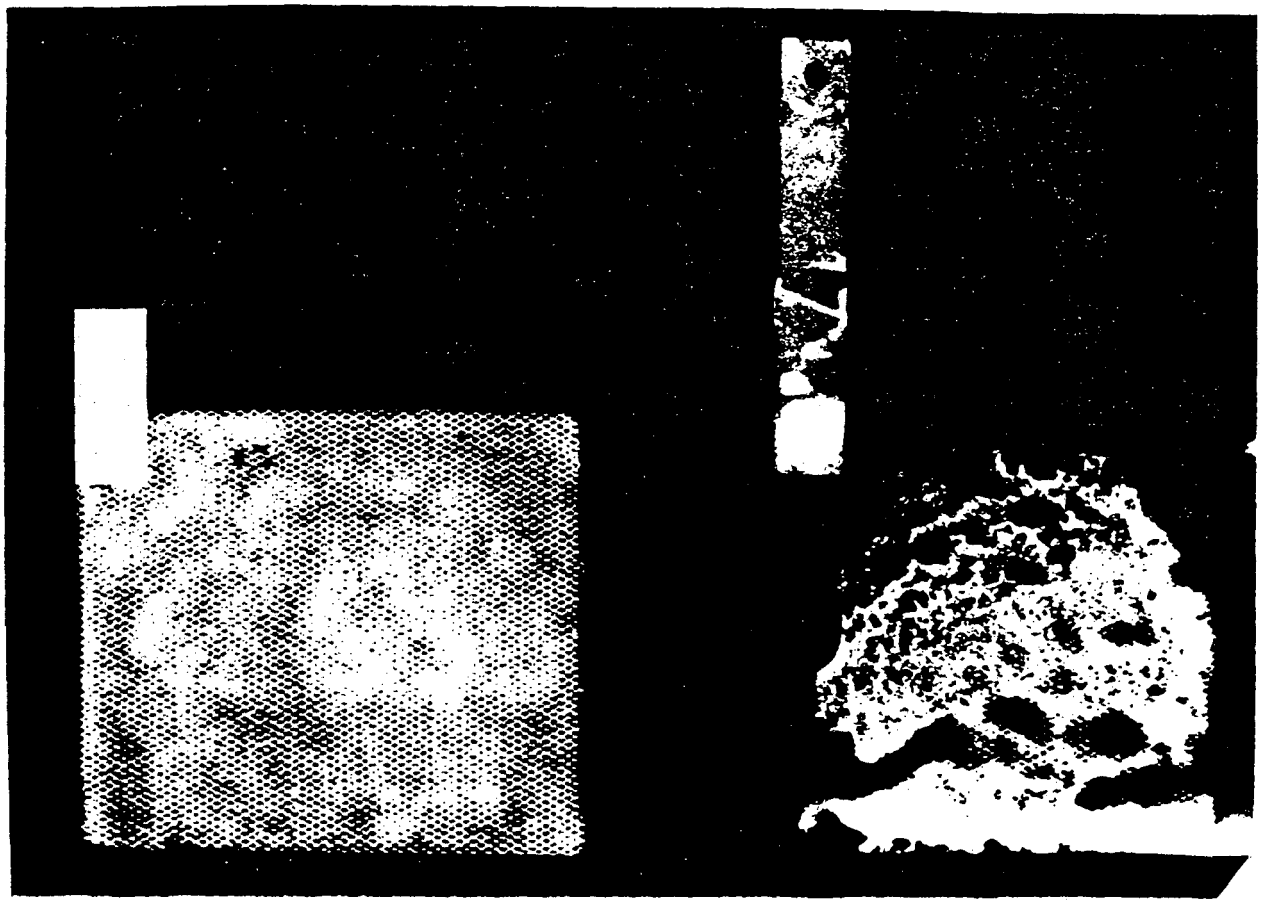

FIGURE 3

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

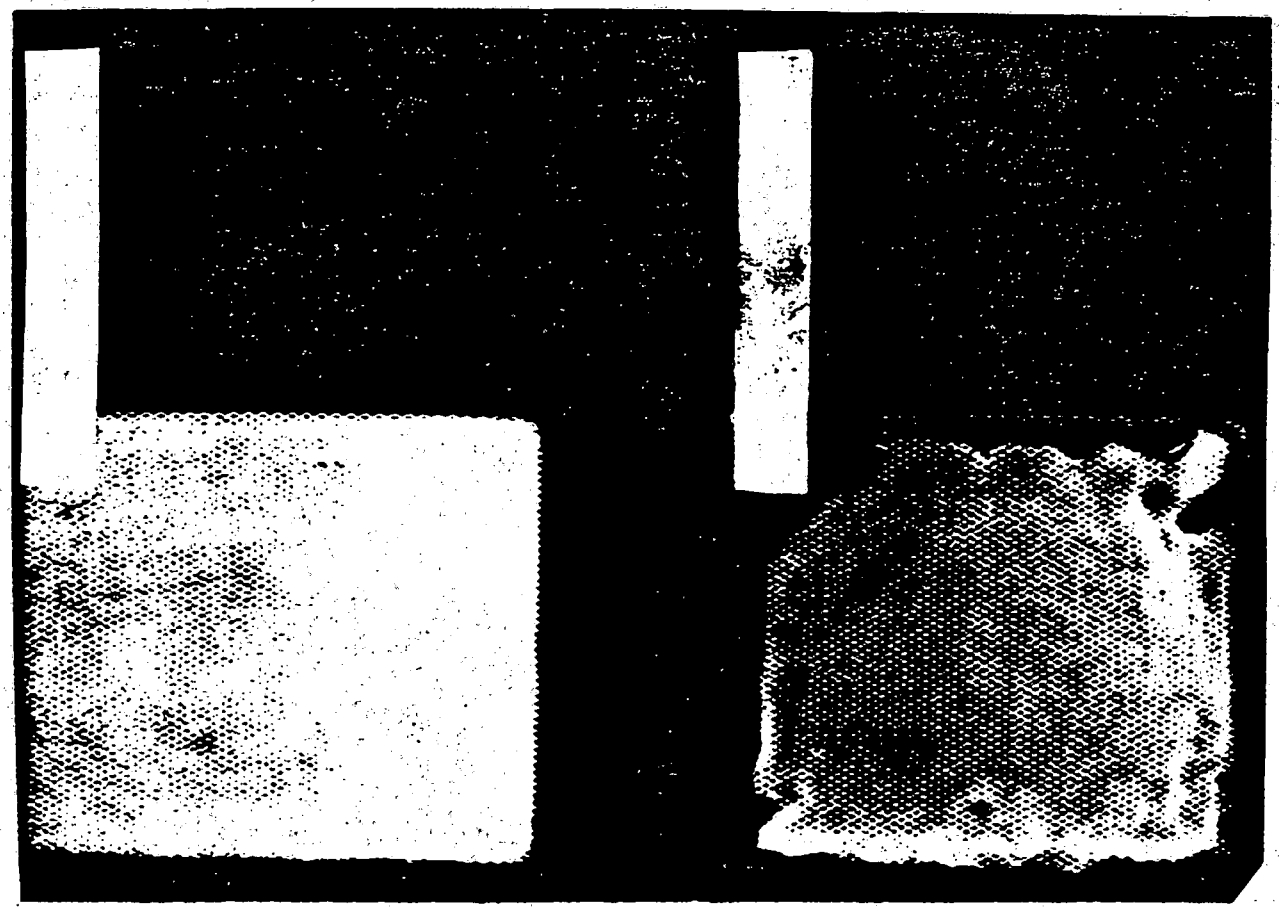

FIGURE 4

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

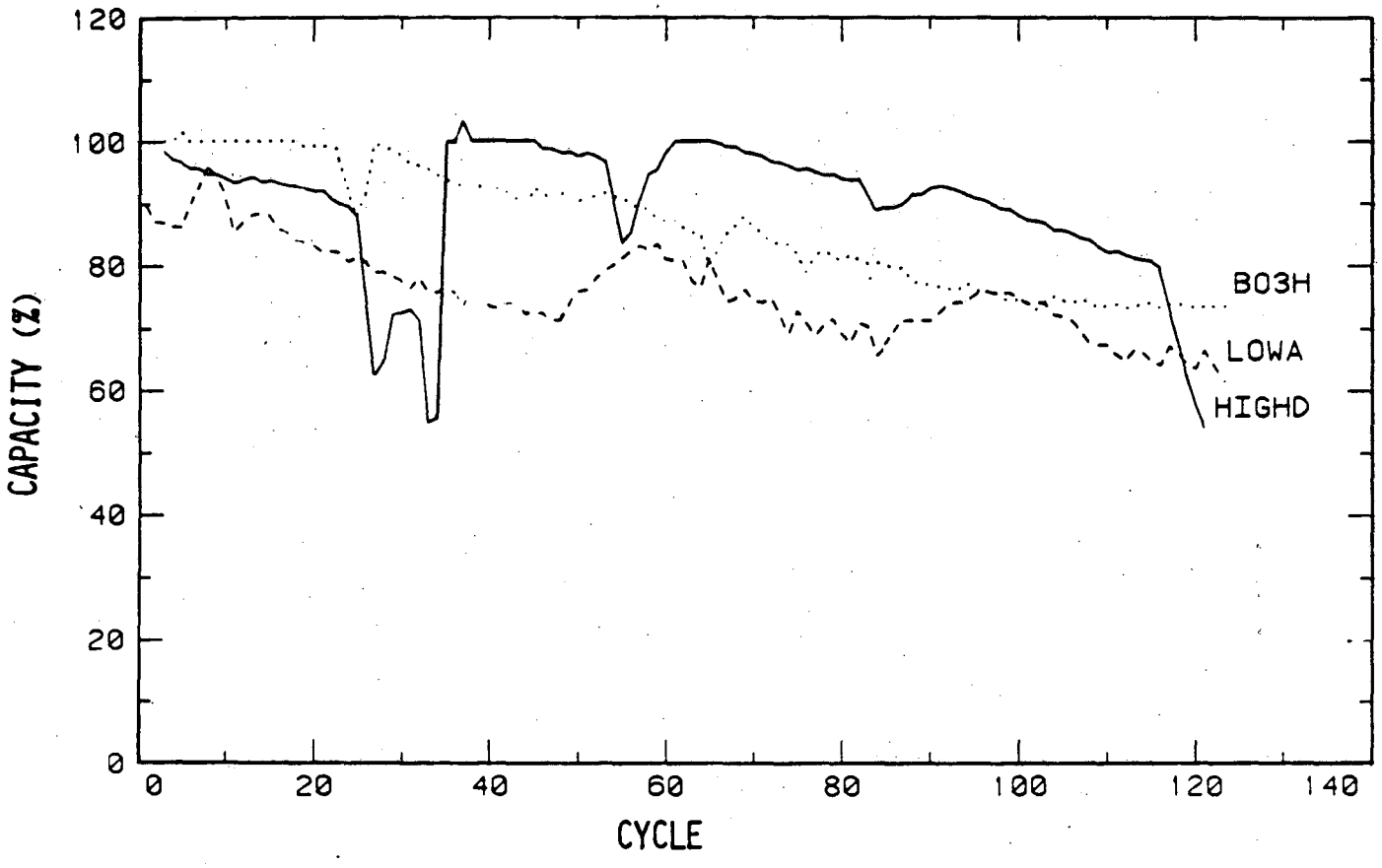

FIGURE 5

CAPACITY VS CYCLE NUMBER FOR KOH AND KOH + H_3BO_3 ELECTROLYTES

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

"BO3H" ELECTROLYTE: 20.6 wt% KOH
8.4 wt% H_3BO_3
1.0 wt% LiOH
SATURATED WITH ZnO

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

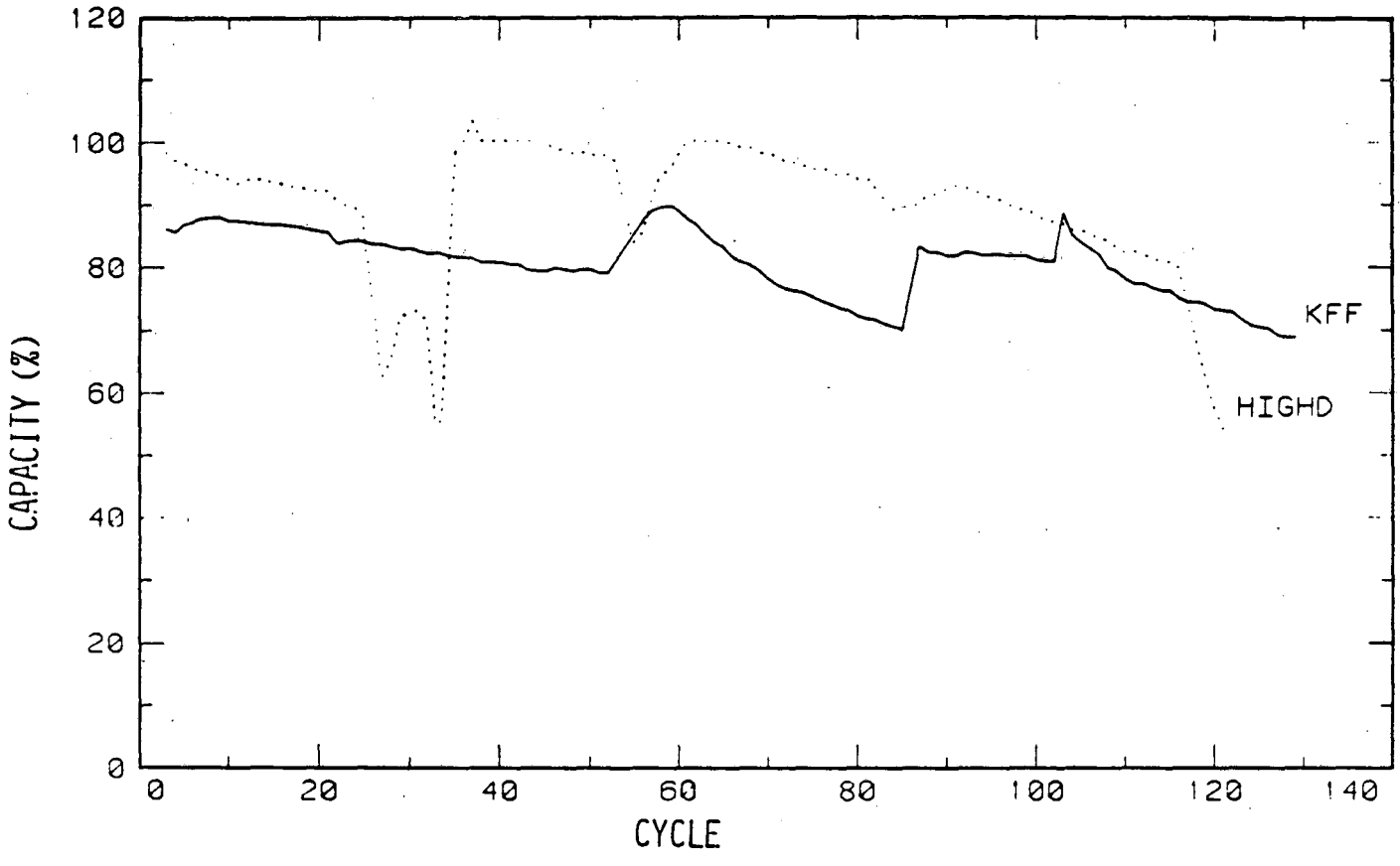

FIGURE 6

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

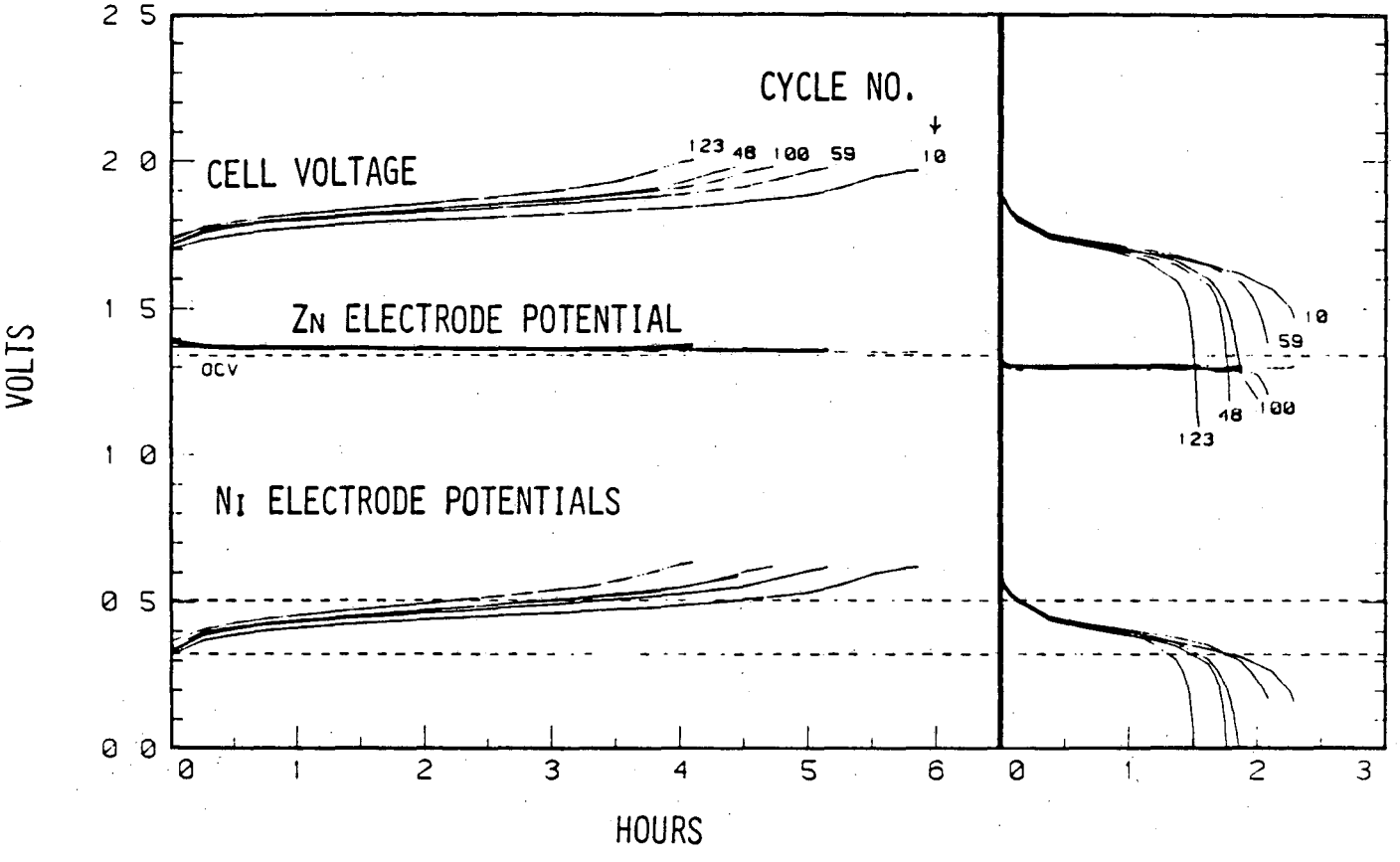

FIGURE 7

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.

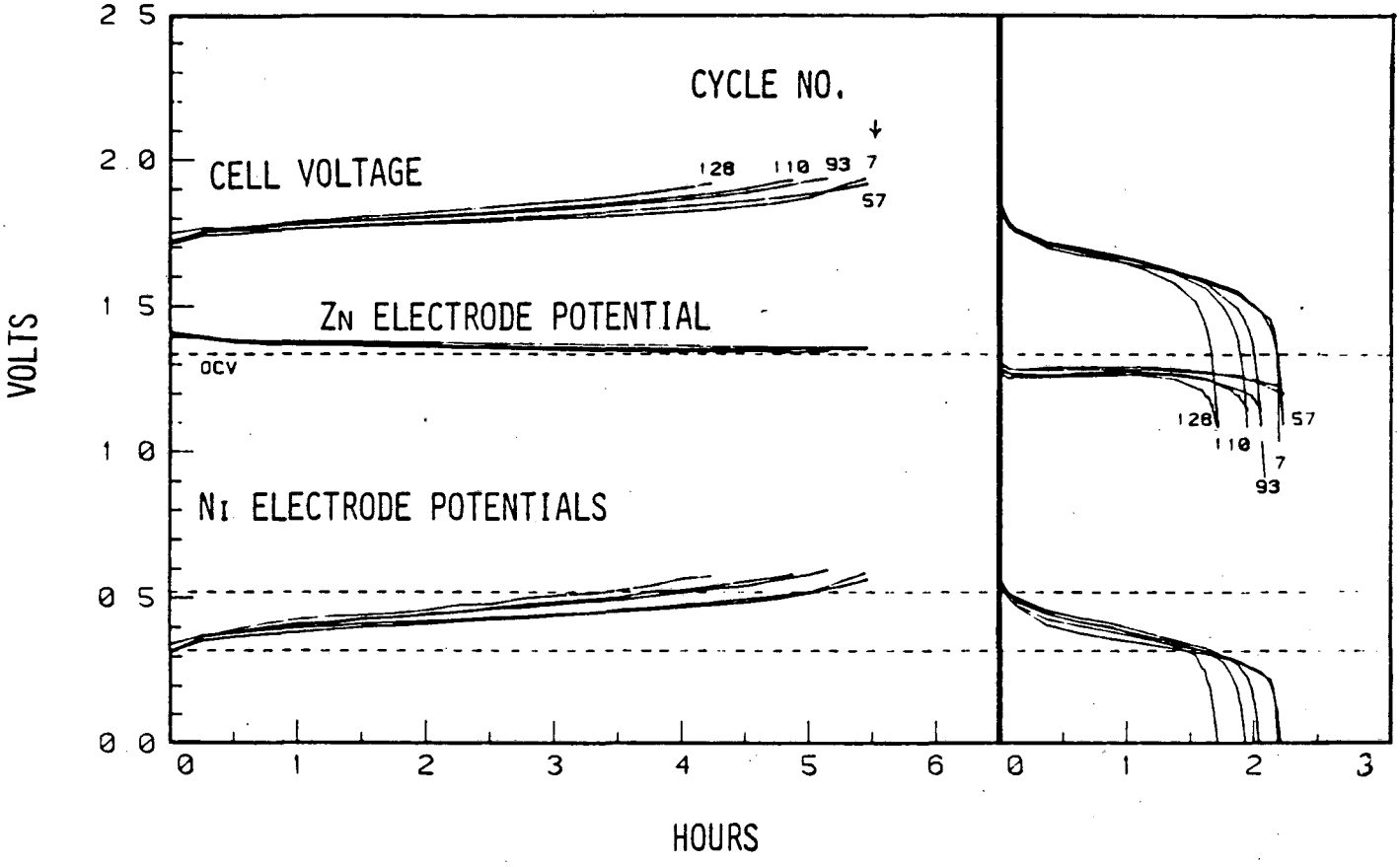

FIGURE 8

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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