An 1 mproved Theoretical Ni-Cd Battery Performance Model

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ABSTRACT

1 'revious reports at this conference have shown how a battery model was developed using])01011s electrode theory. The model was first reported in 1991 (1). Since then the model has been upgraded and expanded. '1 'hese upgrades include oxygen reaction and positive electrode intercalation in 1991 (?). and proton diffusion in 1992 (3). The effects of additional details of the solid stale physics of the. nickel electrode will be reported herein. '1 'he. model has been used to predict performance of Ni-Cd Cells. Beyond the electrochemical aspects, hat ter y modeling aspects have been incorporated, including power sub-system interface and a thermal model in 1991 (4), and cell degradation aspects in 1993 (5,6). The previously reported theoretical models have suffered from an inability to accurately predict potentials across a range of charge. and discharge rates. This inaccuracy was traced to the nickel electrode. More specifical I y, the expression for the conductivity of the active material. A term for a Schottky junction was added to the solid phase. conductivit y expression. '1 'his term uses the hyperbolic tangent function, wh ich provides the characteristic saturation of a Schottky junction with mixed n-type / Jl-type materials. This behavior is consistent with the, NiOOH material being an n-type semiconductor on discharge and a p-type semiconductor on charge, as reported in the literature (7). Comparison of both positive electrode and cell results give. superior predictions. The results arc compared to a variety of actual data from electrodes, cells, and batteries. The results arc. discussed with respect to the model of the active material layer, and the intrinsic assumptions of the model. The ability of the model to perform spacecraft simulations is demonstrated. The implications of this work on other nickel based systems are discussed. Ni-H2, Ni-MH and Ni-Zn models will all benefit from this work.

PERFORMANCE PREDICTIONS

Boilerplate Data

Data was gmc.rated for model calibration purposes using a boilerplate cell. The details of this cell and the characterization technique have previously been reported (4).

The cell was operated at constant current rates equivalent to C/20, C/10, and C/2. Using these rates, it was charged and discharged. A series of tests were done at 0°C, 20°C, and 40°C. Without this ala, it is nearly impossible to calibrate the model. Sample cell data for three discharge and charge rates al 20°C is attached as Figures 1 and 2.

Constant Current Predictions

The constant current prediction were generated by simulating a 30 AH cdl design, and running it at the various C rates on charge and discharge. The rates are based on the nominal capacity of 26.5 AH, as used by NASA for the Gates Aerospace Batteries 43B030AB-1615 design, Predictions are attached as Figures (3) and (4).

Differences in predictions and boilerplate cell data can be analyzed by comparing Figures (1) and (3) for charge, and Figure (2) and (4) for discharge. The comparisons show potentials that are substantially different.

Mid-Plateau Potentials

To better analyze the variations of overpotentials, mid-plateau potentials were studied. These are potentials taken from the middle of the charge and discharge curves. The Mid-point potential analysis provides another comparison of the model and the boiler-pla!c test data. Only the positive electrode and the cell have been shown. The negative electrode is of less concern, because ii's smaller contribution to the total cell potential.

Figures (5) and (6) show the lltid-plateau potentials for the positive and cell potentials. The trends displayed are of insufficient overpotential. The deviation from the reversible potential of 1.30 volts for the cell or 0.40 volts versus Hg/HgO for the positive electrode is the total overpotential. Additional equation refinements are aimed at adding over-potcmlial,

Schottky Junction

Deviations in the mid-plateau potential gives a interesting overpotential versus rate relationship. The deviation in predictions and measured potentials were plotted in Figure (7). The c.1101 is assumed to be approximately zero at open circuit, since reversible potentials are fairly repeatable. However, at the al l rates, from 0.05C to 0.5C, the errors were relatively constant for charge and discharge respectively. If one assumes that there is some phenomenon not described by the equations set, the phenomenon would have. to give overpotential which saturates at fairly low current. There are wry few phenomenon in nature which show potential saturation characteristics as shown by this curve. One is the effect of a Schottky junction, as developed at a metal-oxide junction. It has previously been suggested by McBreen that such a junction exists in this system (8), and many others have suggested mixed semiconductor materials (9). Unfortunately, no references were found which experimentally characterized this junction. Despite this lack of empirical verification, a term for the oxide film equation was developed. The term uses a hyperbolic tangent function. This is a common method of representing Schottky barriers in the semiconductor device modeling field. This term was able to affect the model's performance at the mid-potential point such that the errors were less than 10 mv at every rate. tested. This is a dramatic improvement.

Following modifications to the conductivity equation, the model was characterized at various rates for charge and discharge. The charge and discharge curves for this upgraded model are attached as Figures (8 and 9). The revised mid-plateau potentials were extracted. Figures (10 and 11) show the correlation to between the model and the boilerplate mid-plateau potential for the cell and the positive. electrode respectively. The curves show a very good correlation between the boilerplate data and the simulation. This indicates the over-potential relationships are roughly correct.

More detailed comparisons can be done by comparing complete charge or discharge curve sets. It can be said in general that the model has very good fit with the exception of the beginning of charge and discharge. The model has a tendency to respond too quickly to the current turn cm. That is, the overpotentials approach a pseudo-steady-state too quickly. This same. characteristic will be seem in the flight simulations that follow.

Flight Battery Simulation

Several cases have been studied to demonstrate. the battery model's abilities for making flight or flight-like simulations. The Topex spacecraft is an earth orbiting satellite which uses the. Modular Power Subsystem (MPS). The MPS uses the NASA standard battery design, with 50 AH cells.

The subsystem operates with VT charge control in a Low Earth orbit, (LEO) regime. The mission has varying length occultation periods, creating variable. discharge periods and (DOD)'s).

The cases studied are high DOD cases. One case is from the actual spacecraft, and the other is from a ground mission simulation battery test running at JPL. Both are 112 minute orbits. The flight case is approximately a 15 Ampere charge rate, and the ground test is 25 Ampere peak rate.. The discharges are done at 10 Amperes for 34 minutes. The flight case is run at 10°C while the ground test is at 20°C. There is also a difference in the VT levels used. The spacecraft case was at VT #3 and the ground was at #4.

Figures 12 and 13 show comparisons of predictions to ground test data. The ground test data provides excellent data quality and a careful approximation of flight conditions. Figures 14 and 15 provide. comparisons to actual flight data, which has lower resolution and poorer data quality. Both data sets are acceptable for these comparisons.

The model does very well at predicting the end-of-discharge voltage for both cases. It is within 0.10 volts at the battery level for the worse of the two. It dots not do as well at the beginning and middle of the discharges, due to a different slope to the discharge curves. The other important area to study is charge current. The model dots a nearly perfect job of predicting end-of-charge current. It is less accurate at earlier charge current predictions.

Generally, after reaching some pseudo-steady state, the. model is highly accurate, but shortly after a current transition, it is much less accurate. This problem is thought to come from the positive electrode, and probably from the treatment of the active material layer.

Life Cycle Testing

Life cycle testing of the boilerplate cell has shown changes over time in the positive electrode., and to a lesser degree the negative electrode. Figure (16 , 17, 18) show the changes in the cell, positive, and negative electrodes over 100 cycles. The first cycle shows potentials very simular to the orbital predictions in Figures (13) and (15). After the first cycle, all three show a growing trend of "s"-shaped discharge curves. The "s"-shape is indicative a decreasing quantity of active mate.rial being cycled. As the cycling, capacity of the favored phase dc.creases, a wider range of states-of-chaqw arc accessed. Thermodynamically, this forces the "s"-shape to emerge. The rate of change in the potential curve implies that active material segregates very quickly. This segregation wil I ultimately lead to second plateaus on deep discharge. Identifying the characteristics of these separate phases is crucial to *modeling performance* on cycling as wel I as the severe forms of degradation seen on extended cycling.

Discussion

This model has shown that it is possible to predict beginning of life performance of the Ni-Cd cell with fairly good accuracy. In-flight simulation require better knowledge. of the effects of cycling on the nickel electrode in the active material. Since the characteristics of all of the phases present are not fill ly known, it is difficult to model them. The proton diffusion coefficient, and the conductivity effects in the oxide film are of primary importance. The transport problems may not follow classical behavior. Possible paths for improvement are the incorporation of fractal diffusion in place of ideal diffusion, incorporation a variable diffusion coefficient, accounting for active. material heterogeneity, and further refinement of the film's treatment as a semiconductor.

These advances are generic to the nickel electrode in all nickel cathode battery systems. Work on understanding the degradation processes in nickel electrodes wi I I be reflected in future models of the Ni-H$_2$, Ni-MH, and Ni-Zn systems. The degradation aspects are crucial to accurately predicting flight data. It was shown that the performance changes substantially in as few as ten cycles. This models ties the description of the fundamentals of electrode operation to the application of the batteries.

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Figure 1: Boilerplate Cell Discharge

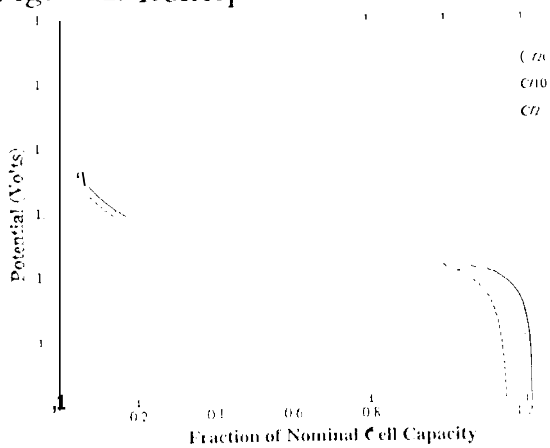

Figure 2: Boilerplate Cell Charge

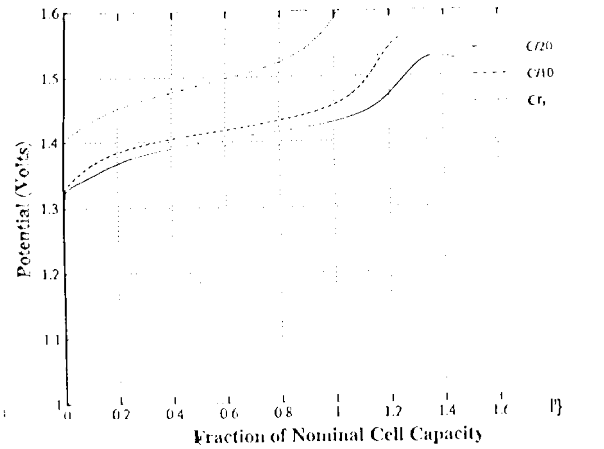

Figure 3: Predicted Cell Discharge

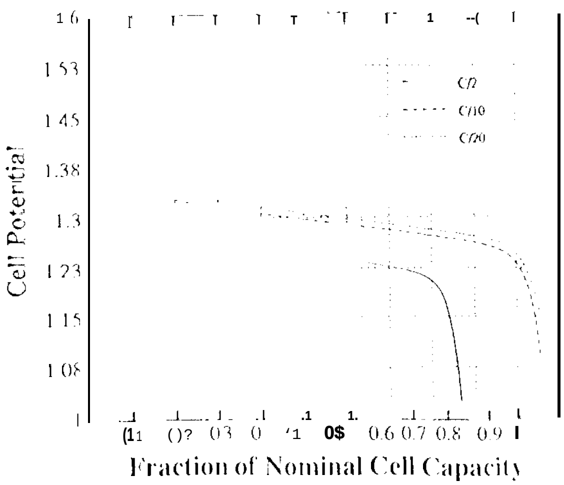

Figure 4: Predicted Cell Charge

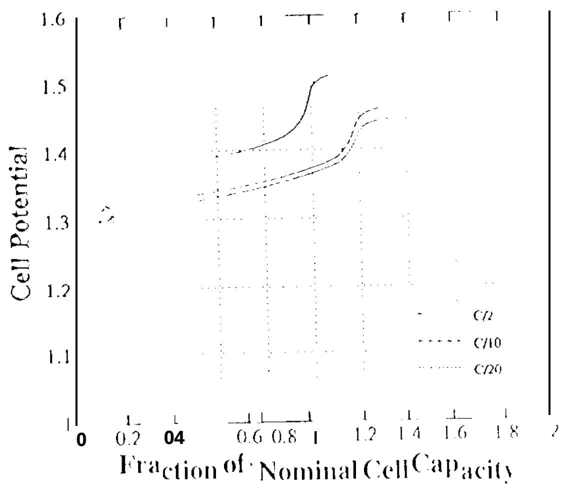

Figure 5: Mid-Plateau Cell Potentials

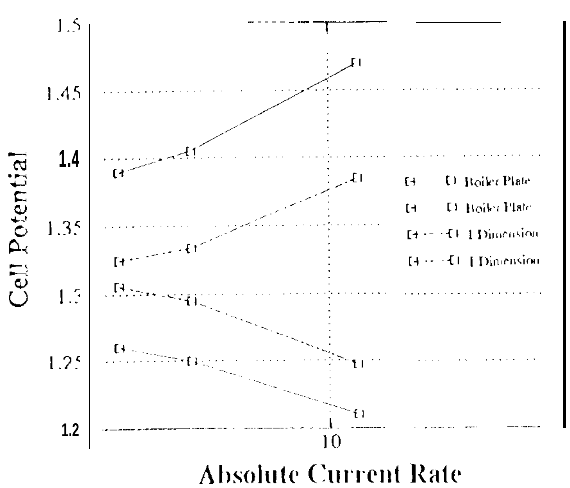

Figure 6: Mid-Plateau Positive Electrode

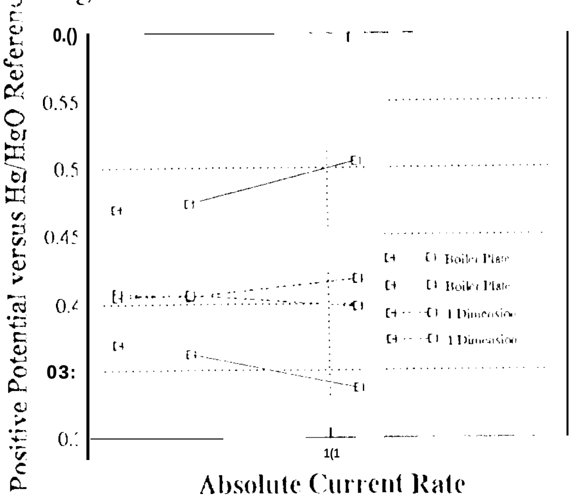

Figure 7: Potential Prediction Error Versus Rate

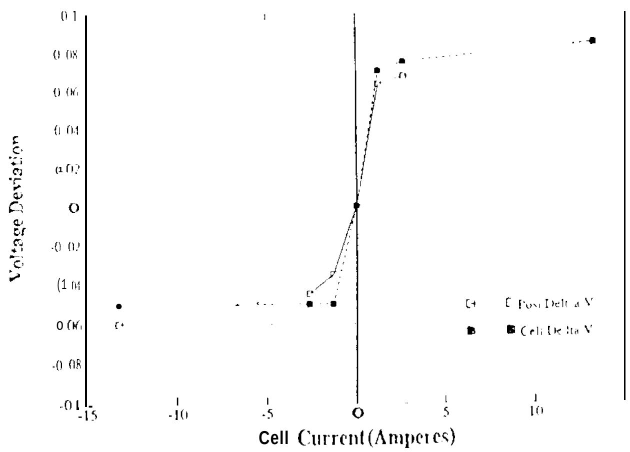

Figure 8: Updated Predictions

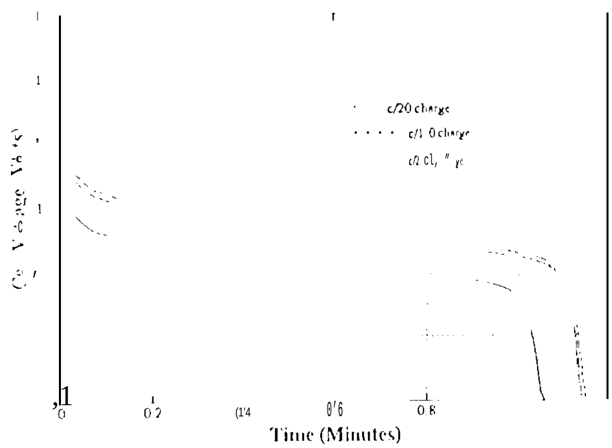

Figure 9: Updated Predictions

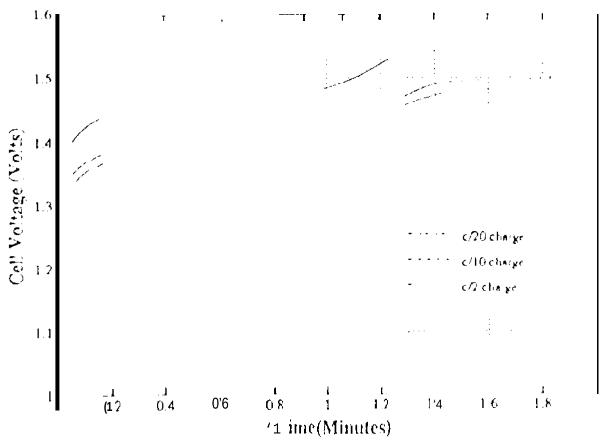

Figure 10: Updated Mid-Plateau Cell Predictions

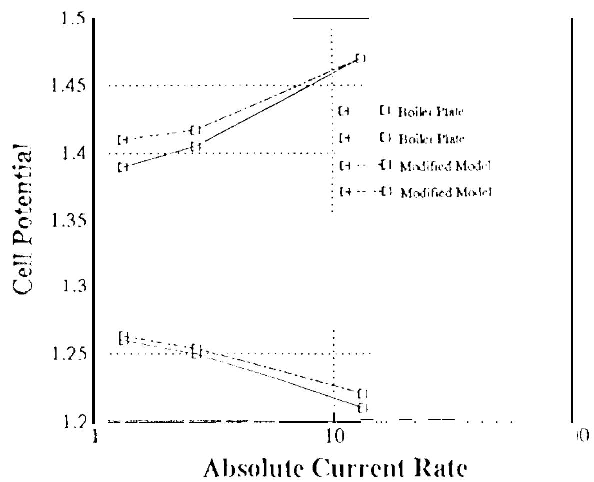

Figure 11 Updated Mid-Plateau Positive

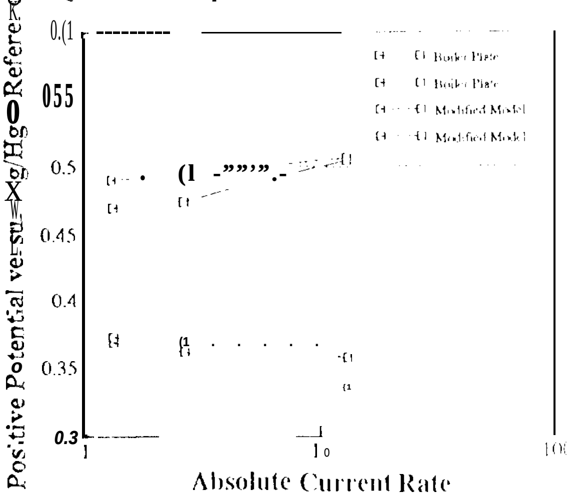

Figure 1?: Topex Ground Simulation Comparison

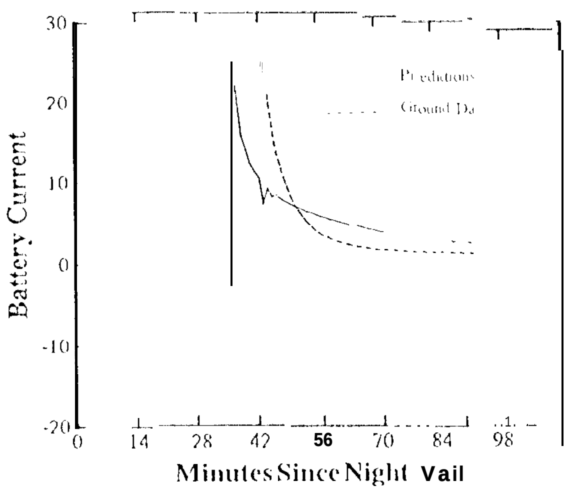

Figure 13: Topex Ground Simulation

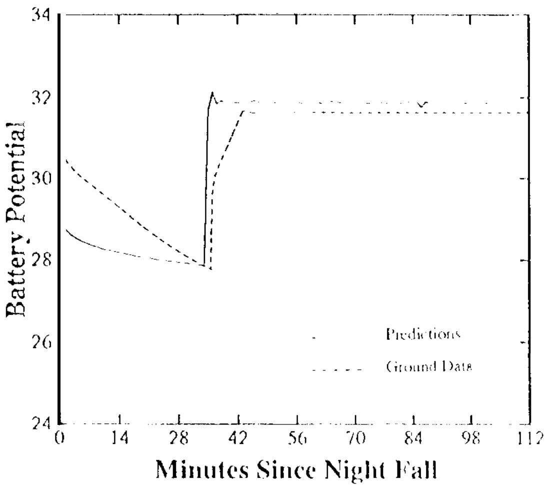

Figure 14: Topex Flight Data Comparison

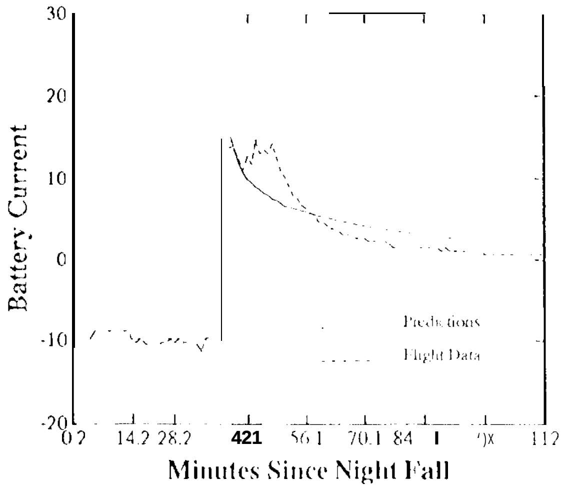

Figure 15: Topex Flight Data Comparisons

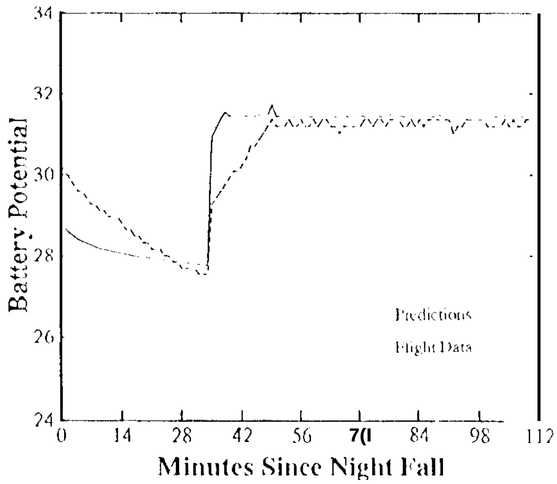

Figure 16: Effect of 100" Cycles cm Cell Potentials

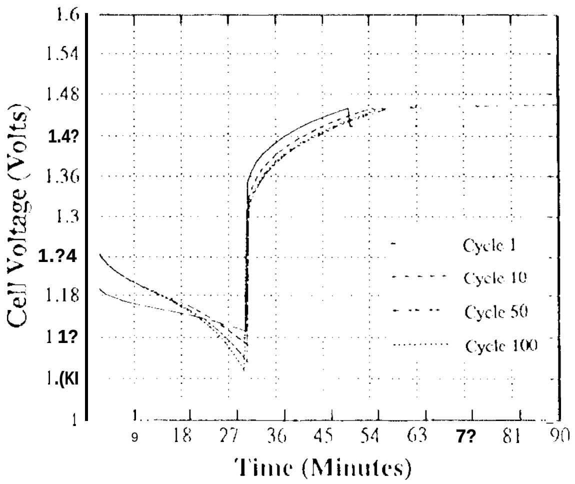

Figure 17: Effect of 100 Cycles on Positive

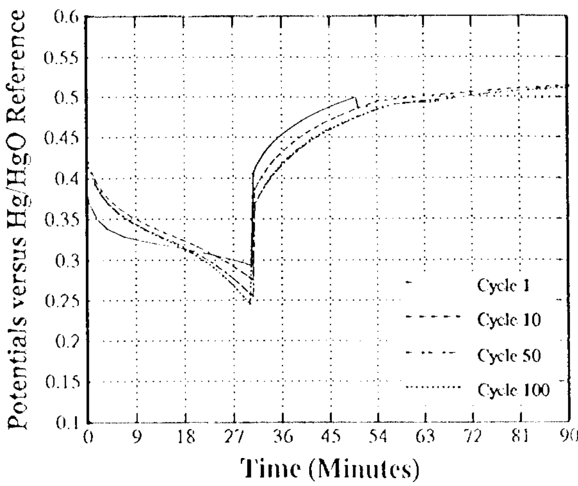

Figure 18: Effect of 100 Cycles on Negative