NASA Technical Memorandum 88803

A Mathematical Approach for Evaluating Nickel-Hydrogen Cells

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Prepared for the
1986 Fall Annual Meeting of the AIChE
Miami, Florida, November 2-7, 1986

NASA

A MATHEMATICAL APPROACH FOR EVALUATING NICKEL-HYDROGEN CELLS

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E-3114

ABSTRACT

A mathematical equation is presented which gives a quantitative relationship between time-voltage discharge curves, when a cell's ampere-hour capacity is determined at a constant discharge current. In particular the equation quantifies the initial exponential voltage decay; the rate of voltage decay; the overall voltage shift of the curve and the total capacity of the cell at the given discharge current. The results of 12 nickel-hydrogen boiler plate cells cycled to 80 percent depth-of-discharge (DOD) are discussed in association with these equations.

INTRODUCTION

The shape of a cell's discharge determination (100 percent DOD) is the result of complex interactions of several rate limiting processes. These processes may be physical or chemical in nature and changeable during the life of the cell. The anode, cathode or electrolyte phase may be responsible individually or in combination for the shape of the cell's discharge curve. Although specific tests have been designed to illucidate certain isolated characteristic of the discharge curve, the customary practice of displaying complete discharge curves is still used to show changes in cell behavior during life and differences between cells.

The changes associated with discharge curves give insight to the electrochemist as to the gross properties of the cell. However; when many cells are being investigated the data processing and trend analysis procedure become unmanageable without the use of mathematical techniques. By the use of an equation that describes the various characteristics of the discharge shape it is possible to assign definitive attributes to the discharge curve. This then reduces the amount of information to be assimilated to a manageable amount. This information now being in numerical form allows the use of other mathematical procedures to further illucidate the changes in the curves.

Two related mathematical equations are used to compare changes occurring during cycling as well as differences between cells for 12 nickel-hydrogen cells. The numerical values from the equations are further analyzed with respect to cycle life.

EXPERIMENTAL DATA

Nineteen nickel-hydrogen boiler plate cells were constructed and life cycled by Hughes Research Laboratories (Ref. 1). These cells were constructed from nickel plaque having three different bend strengths and three different pore sizes. Nickel electrodes were prepared from these plaques having three different loadings of active material. Table I shows the cell number and its respective design characteristics. Initial performance tests included 12 consecutive capacity measurements to characterize the cells. To facilitate experimental cycling the cells were divided into three rated capacity groups of 2.7, 3.0, and 3.3 A-hr. This grouping allowed for cycling all cells using a constant time for charge and discharge with three different currents, dependent upon the rated capacity.

The cells were life cycled at 23 °C to 80 percent depth-of-discharge (DOD) of the rated capacities using a 45 min cycle regime. The cycling regime consisted of a 2.74 C rate discharge for 17.5 min and a 1.92 C rate charge for 27.5 min. Thus, as near as possible normalizing the test conditions. The life cycling regime was interrupted periodically for capacity measurements after approximately every 1600 cycles. Capacity measurement data at cycles 1700, 3100, 5000, and 6100 were available as strip chart recordings of voltage-time curves for the 1.37 C discharge rate. The data was transformed into numerical voltage-time points by digitizing the strip chart using a Hewlett-Packard 9111A Graphics Tablet. The accuracy of this process was found to be ±2 mV and ±0.1 min. This results in a maximum uncertainty of ±0.002 A-hr.

The conversion from voltage-time to voltage-DOD was performed so as to further normalize the variation in cell capacity. The pre-cycling capacity at 1.37 C rate discharge was used in this normalization process since the test data was also at the 1.37 C rate. Equation (1) describe the conversion.

$$DOD = \frac{(\text{time (min)} * \text{current (A)})}{60 \text{ min/hr} * \text{cap @ } 1.37 \text{ C (A-hr)}} \qquad (1)$$

EQUATION

It was found (Ref. 2) that Eq. (2) describes the typical s-shaped discharge profile

$$E = K - \frac{1}{Ln(C)} * Ln\left[\frac{Ln(X)}{-exp(1)}\right] + A_0 * Exp(-A_1 * DOD) \qquad (2)$$

where

X DOD/A

A Capacity of the cell at the specified discharge conditions (DOD)

Ln(C) is proportional to the slope of the discharge curve (volts^{-1})

A_0 Maximum height of the voltage drop at the start of discharge (volts).

A_1 the voltage drop duration at the start of discharge (DOD^{-1})

K Intercept of the voltage plateau with the voltage axis taken at DOD = Exp(-1) (volts)

These relationships are shown in Fig. 1.

Equation (2) can be expanded to describe the discharge profile of a two plateau curve as shown in Eq. (3).

$$E = K - \frac{1}{Ln(C)} * Ln\left[\frac{Ln(X)}{-exp(1)}\right] + A_0 * Exp(-A_1 * DOD)$$
$$+ K' - \frac{1}{Ln(C')} * Ln\left[\frac{Ln\left(\frac{DOD-A}{A'-A}\right)}{-exp(1)}\right] + A_0' * Exp(-A_1' * (DOD-A)) \qquad (3)$$

where: All parameters have the same significance as in Eq. (1). The (') parameters are associated with the second plateau.

The digitized voltage-DOD data was fit to Eq. (3) by using a nonlinear regression procedure on a Hewlett-Packard 9845C desk top computer. The regression program follows the Marquardt procedure to obtain estimates for the parameter.

If only one plateau is present in the voltage-DOD curve Eq. (2) can be used. However, all cells exhibited two plateau discharge characteristics, to various degrees between open circuit and 0.4 V. Therefore, Eq. (3) was used. Figure 2(a) shows the result of boiler plate cell number 12 at the 5000 cycle capacity check which has a very small second plateau (A'-A = 0.068 DOD). Figure 2(b) shows the result of boiler plate cell number 14 also at the 5000 cycle capacity check which has a moderate well formed second plateau (A'-A = 0.152 DOD). Figure 2(c) is a plot of the difference between the experimental potential and the results of Eq. (3) for each DOD point digitized for cell number 14 at the 5000 cycle capacity check. As can be seen the equation provides a good representation of the data. The average of the potential differences for 23 data points is -2.5 mV with a standard deviation of 6.5 mV.

ANALYSIS OF DATA

The cycle life data as shown in Table I varies from 2330 to 12 960 cycles. This decade of variance, however, cannot be attributed to any of the experimental design characteristics (bend strength, pore size or loading) since no statistically significant ($1-\alpha = 0.9$) difference could be found using analysis of variance techniques. With a cycle life variation of over 10 000 cycles and no effect due to experimental design it is unlikely that cell cycle life is 6185 with a standard deviation ±3054 cycles. It is therefore necessary to look elsewhere for the cause of variation.

Data (E-DOD) was available for 12 of the 19 cells at capacity determination cycles 1700, 3100, 5000, and 6100.[1] Boiler plate cells number 23, 24, and 25 were early failures (approximately 2300 cycles) and therefore were not used. Boiler plate cells number 16, 18, 19, and 26 were available for only one or two capacity determination cycles and were also excluded. All 12 boiler plate cells had capacity check data for capacity measurements at cycles 1700, 3100, and 5000; however, six cells had cycle lives long enough to have a capacity measurement at cycle 6100. All 42 capacity determinations were fitted to Eq. (3) and the parameters of the equation used as a means of evaluating cycle life.

H.S. Lim (Ref. 1) attempted to fit the cycle life of cells to the percent DOD (based on the theoretical capacity). Although a trend was observed the amount of scatter was too large to draw conclusive results. The use of the theoretical DOD would have to assume that cells would behave identically during their early lifetime i.e., gain or lose capacity at the same rates during formation. Also, reported by Lim was the appearance of the second plateau that varied in magnitude in a unrecognizable manner during life.

From the information obtained by fitting the data to Eq. (3) it is apparent that A' varies during life. This indicates that the capacity of the cells are neither constant nor decreasing uninformally during their cycle lives. For cells with short cycle lives, A' tends to continually decrease over life. For cells of intermediate life (4000 to 5000 cycles) the trend is towards no change in the first two capacity checks (1700 & 3100) and then a decrease in capacity at the 5000 cycle/check. For cells with long life, (6000 and more cycles) the trend is for an increase in A' and then a decrease.

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[1]No capacity determinations were performed beyond the cells cycle life. If a cell failed at cycle 3000 capacity determination at 3100 was the last measurement.

In addition to the 10 equation parameters obtained from the nonlinear data fit to Eq. (3) two additional quantities were used. These additional quantities are the DOD's to which the cells were actually cycled and the ratio of A-hr at the capacity determination cycle to the cell's theoretical A-hr capacity (utilization). Both of these values are based upon the parameter A' from Eq. (3) and are shown in Eqs. (4) and (5).

$$\text{Ampere-hour ratio (Ut)} = \frac{A' * \text{capacity (1.37 C)}}{\text{theoretical capacity}} \quad (4)$$

$$\text{cycling DOD (Cy DOD)} = \frac{0.8 * \text{rated capacity}}{A' * \text{capacity (1.37 C)}} \quad (5)$$

where capacity (1.37 C) = pre cycling capacity at 1.37 C discharge rate.

Figure 3 shows how the capacity of the cells have increased above the theoretical capacity at capacity determination cycle 1700 and then decreases as cycle life progresses. This increase is not phenomenal or unexpected. It is a well observed fact that nickel electrodes increase capacity during initial cycling (Refs. 3 and 4). This change in capacity alters the actual DOD of a cell during cycling and is shown in Fig. 4. As can be seen from Fig. 4 the increase in capacity has lowered the actual DOD of cycling to about 65 percent at capacity determination cycle 1700. From the capacity determinations at cycles 3100 and 5000, the variation in cell cycling DOD increases to three times that at cycle 1700 (0.1 to 0.311). Since cycle life is strongly dependent upon DOD this variation in actual DOD phenomena should effect cycle life.

In order to determine the impact of the changing discharge curve on cycle life the 10 parameters from Eq. (3) along with the two quantities describing the A-hr ratio (Ut) and cycling DOD (Cy DOD) were regressed to cycle life using a stepwise forward linear regression procedure (Ref. 5). Equations (6) to (9) show the results of the linear regression for each of the capacity determination cycles.

Capacity determination at cycle 1700:

$$Life = 102\,902 - 16\,840 * A - 36\,903 * Ut - 63\,969 * Cy\ DOD \quad (6)$$

Capacity determination at cycle 3100:

$$Life = 123\,073 - 33\,931 * A - 34\,298 * Ut - 76\,707 * Cy\ DOD \quad (7)$$

Capacity determination at cycle 5000:

$$Life = 61\,155 - 31\,927 * A_0 - 23\,699 * Ut - 37\,461 * Cy\ DOD \quad (8)$$

Capacity determination at cycle 6100:

$$Life = 29\,558 - 54\,821 * A_0 - 17\,666 * Cy\ DOD \quad (9)$$

As can be seen from Eqs. (6) to (9) actual DOD of cycling is the major contributor in all but the capacity determination at cycle 6100. Figures 5(a) to (d) show plots of how well Eqs. (6) to (9) predict cycle life. Although Eqs. (6) to (9) do not produce a perfect fit to cycle life, as portrayed by the doted line, 88, 90, 90, and 99 percent of the variability in cycle life can be accounted for by Eqs.(6) to (9) respectively. Table II lists the difference between the actual and predicted cycle lives for the four capacity determination cycles. With the exception of boiler plate cell number 20 the difference is acceptable as a predictor of cycle life. Table III lists the percentage difference between the actual and predicted cycle lives. Boiler plate cell number 20 is shown to be in error by over 50 percent for all three capacity determination cycles. The mean of the percent residuals with boiler plate cell number 20 excluded is only -2, -3, -1, and -2 percent for capacity determinations at cycles 1700, 3100, 5000, and 6100 respectively. The reason boiler plate cell number 20 is so much different than the other is not known.

Examination of Eqs. (6) to (9) show some rather interesting trends. Parameter A which is a measure of the capacity available at the higher potential is a predictor early in life of cycle life while parameter A_0 which is a measure of the potential drop from open-circuit is not. This trend reverses itself after capacity determination cycle 3100. The ampere-hour ratio (utilization) decreases in importance as cycle life increases droping to zero at capacity determination cycle 6100. The actual cycling DOD is the only contributor for predicting cycle life needed in all capacity determination cycles.

CONCLUSIONS

Although the response variable, cycle life, showed no significant dependence upon the experimental variables bend strength, pore size or loading level, the discharge curves of capacity measurements during life, are related to cycle life.

It was shown that:

1. Discharge curves can be represented by an equation even when there are two plateaus.

2. Parameters from the equation describing the discharge curve are related to cycle life.

3. Cell cycling depth-of-discharge and Ah ratio (utilization) are very important characteristics which can be obtained from the equation describing the discharge curve.

4. The capacity obtained during cell characterization is not a reliable indicator of cell capacity during life testing.

5. The capacity of the higher potential plateau is important in predicting cycle life early in cycle testing.

6. The exponential potential drop is important in predicting cycle life in the latter part of cycle testing.

The single most important type of information needed to understand this set of cells, and probably all nickel-hydrogen cells, are the processes that lead to the increase of cell capacity over an extended period of cycling.

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TABLE I. - NICKEL ELECTRODE CHARACTERIZATION PLAN AND CYCLE LIFE

Loading, g/cc	Bend strength, psi						
	400			550		700	
	Pore size, μ						
	10	12	14	10	12	10	12
1.40	[a]16 [b]3509	12 3450	25 2330	22 3349	17 3664	---- ----	10 3729
1.55	[a]15 [b]7919	13 12960	24 2580	21 6426	19 4632	18 4276	9 8936
1.70	[a]14 [b]4790	11 5167	23 2340	20 4259	26 4993	---- ----	8 9572

[a]First line denotes cell number.
[b]Second line denotes cycle life.

TABLE II. - DIFFERENCE BETWEEN ACTUAL AND PREDICTED CYCLE LIFE

Cycle Difference, Actual-Predicted

Cell number	Capacity determination cycle				Actual cycle life
	1700	3100	5000	6100	
8	-763	-169	923	-29	9 572
9	43	-94	-678	-64	8 936
10	-992	-350	783	----	3 729
11	746	20	-669	-182	5 167
12	468	-175	-130	----	3 450
13	1531	337	820	-57	12 960
14	-30	213	-477	----	4 790
15	-103	1345	134	-419	7 919
17	255	318	-417	----	3 664
20	-2377	-2414	-2172	----	4 259
21	1300	1341	1067	-86	6 426
22	197	-372	818	----	3 349

TABLE III. - PERCENTAGE ERROR OF PREDICTED CYCLE LIFE

Percent Error 100*, Actual-Predicted/Actual

Cell number	Capacity determination cycle				Actual cycle life
	1700	7100	5000	6100	
8	-8	-1.8	9.6	-0.3	9 572
9	0.5	-1.1	-7.6	-0.7	8 936
10	-26.6	-9.4	21	----	3 729
11	14.4	0.4	-12.9	-3.5	5 167
12	13.6	-5.1	-3.8	----	3 450
13	11.8	2.6	6.3	-0.4	12 960
14	-0.6	4.4	-10	----	4 790
15	-1.3	17	1.7	-5.3	7 919
17	7	8.7	-11.4	----	3 664
20	-55.8	-56.7	-51	----	4 259
21	20.2	20.9	16.6	-1.3	6 426
22	5.9	-11.1	24.4	----	3 349
Mean[a]	-2	-3	-1	-2	

[a]Cell number 20 not used in mean calculation.

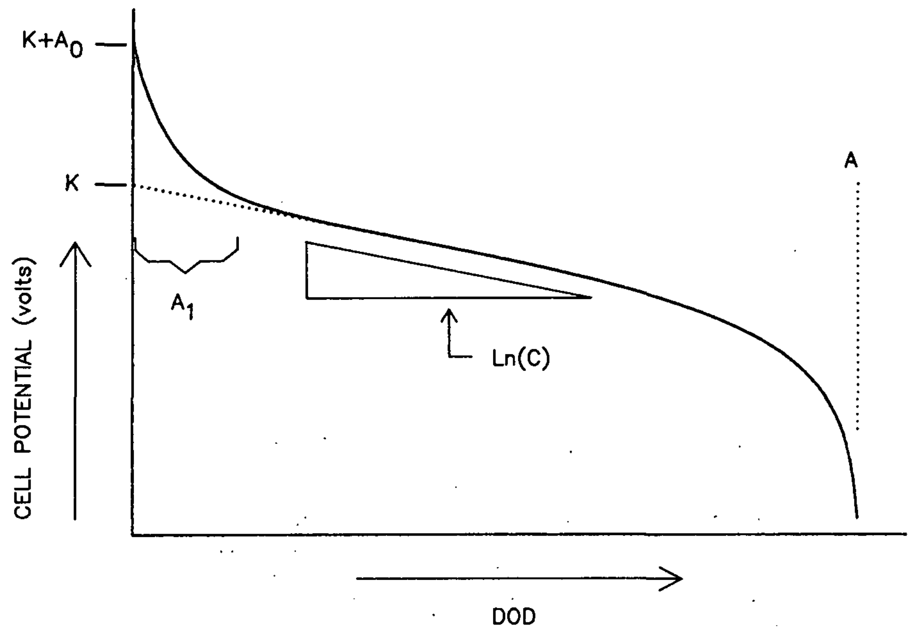

FIG. 1 Significance of parameters used in describing discharge curves.

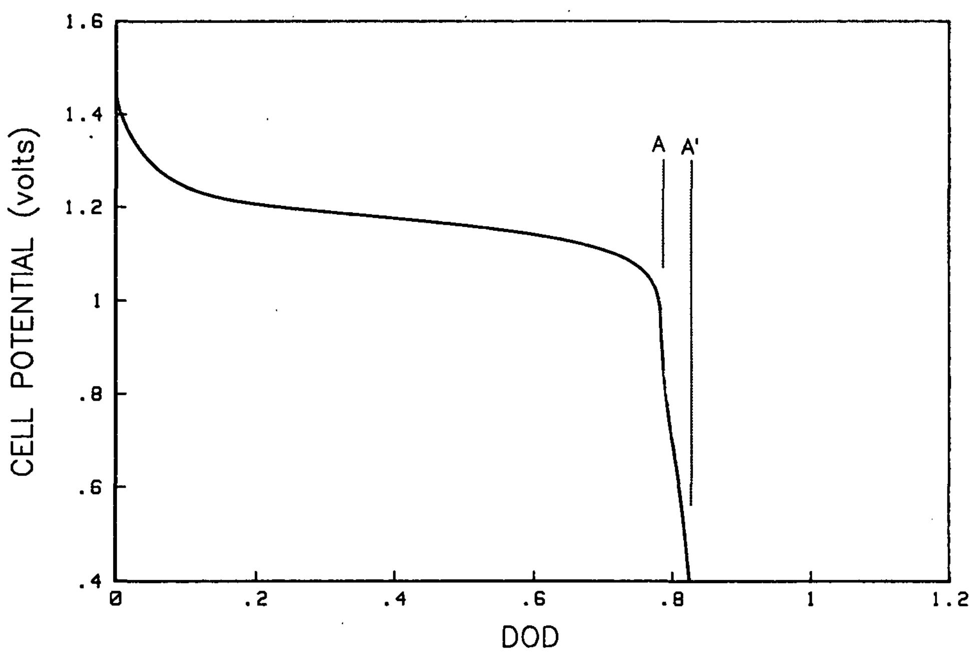

FIG. 2a Fit of discharge data having a small second plateau. Cell #12, cycle 5000, A'–A=0.068

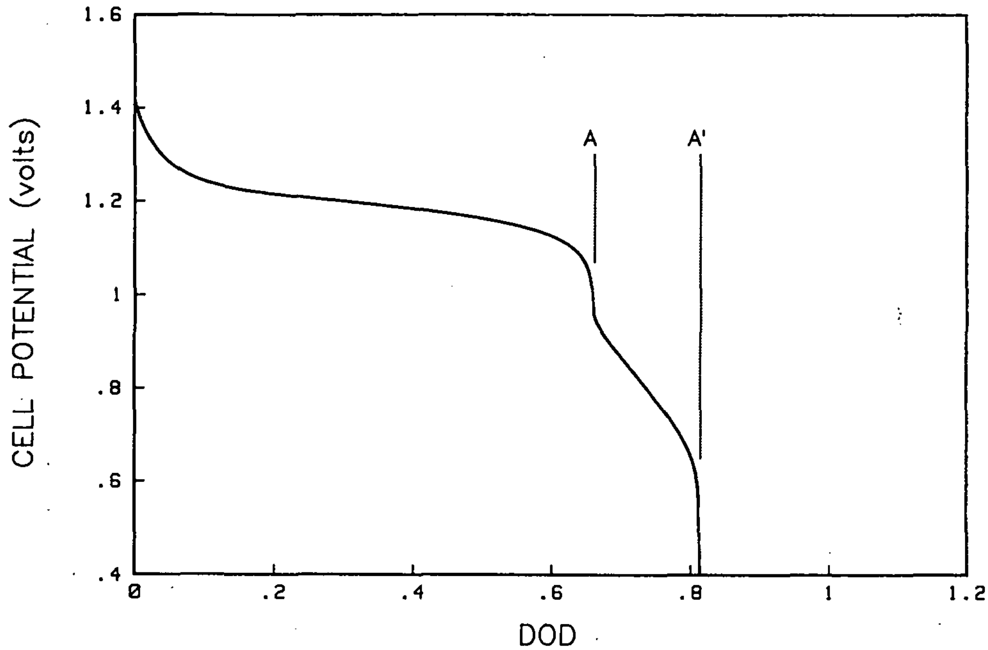

FIG. 2b Fit of discharge data having a moderate second plateau. Cell #14, cycle 5000, A'−A=0.152

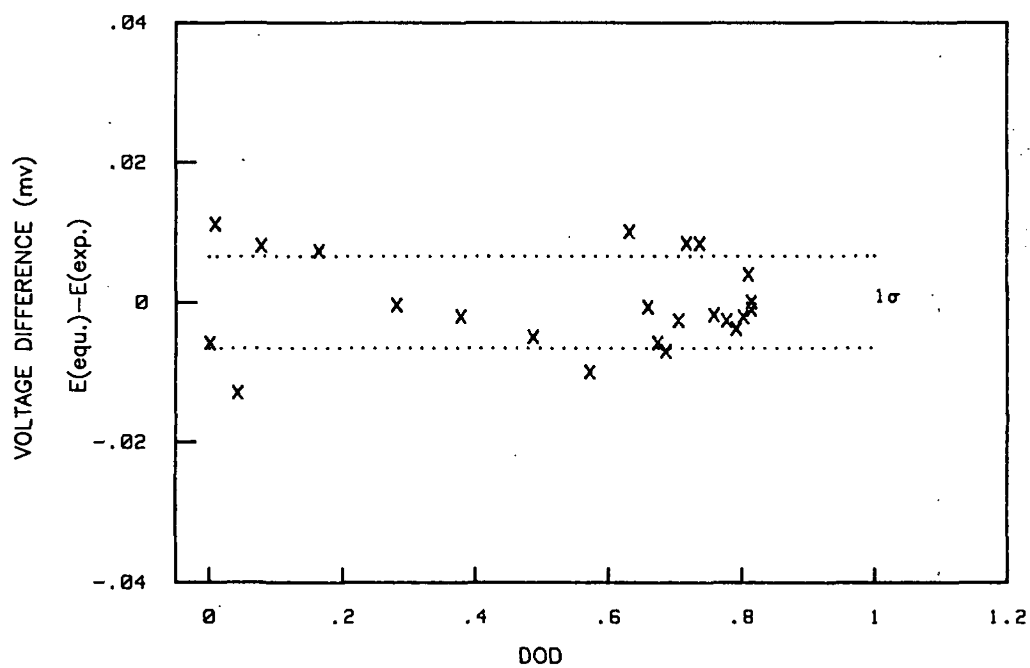

Fig. 2c Difference between equation and experimental data. Cell #14, cycle 5000, sigma 6.5 mv.

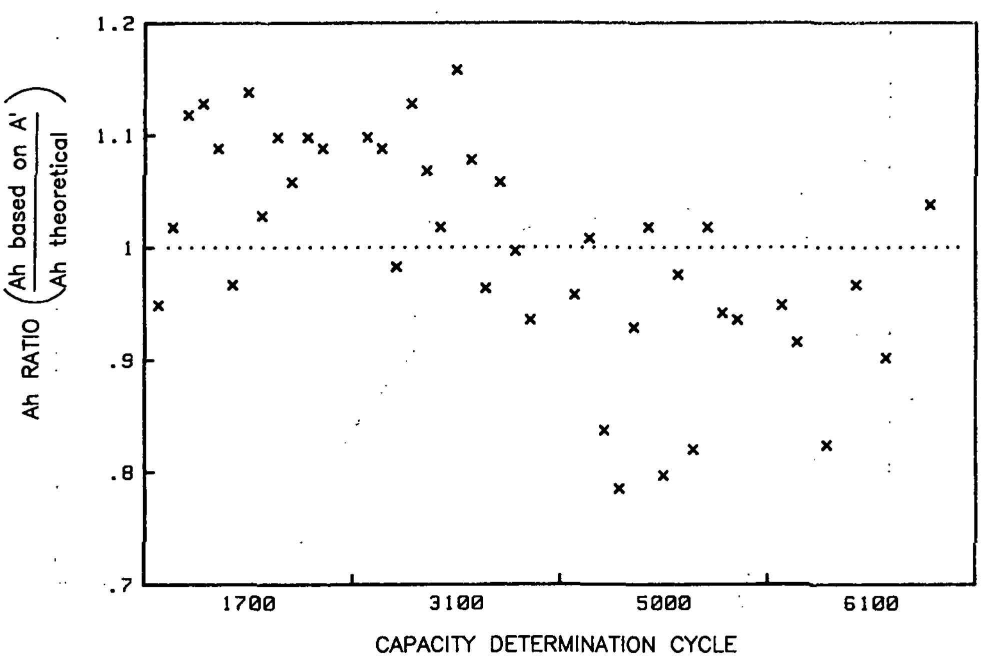

FIG. 3 Ratio of cell actual capacity to theoretical capacity.

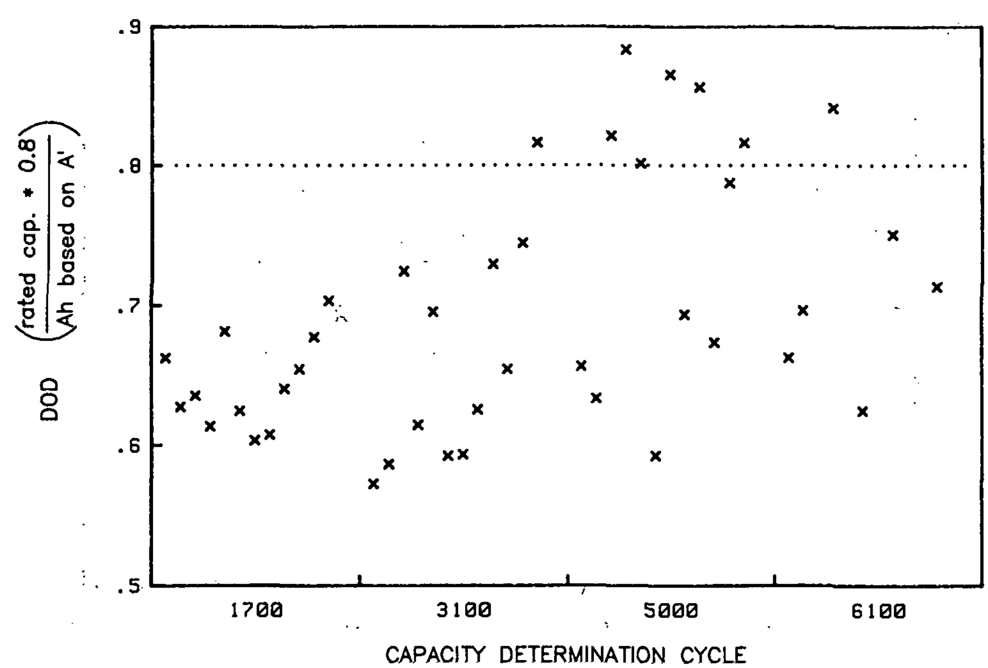

FIG. 4 Cell actual cycling DOD. Design DOD = 0.8

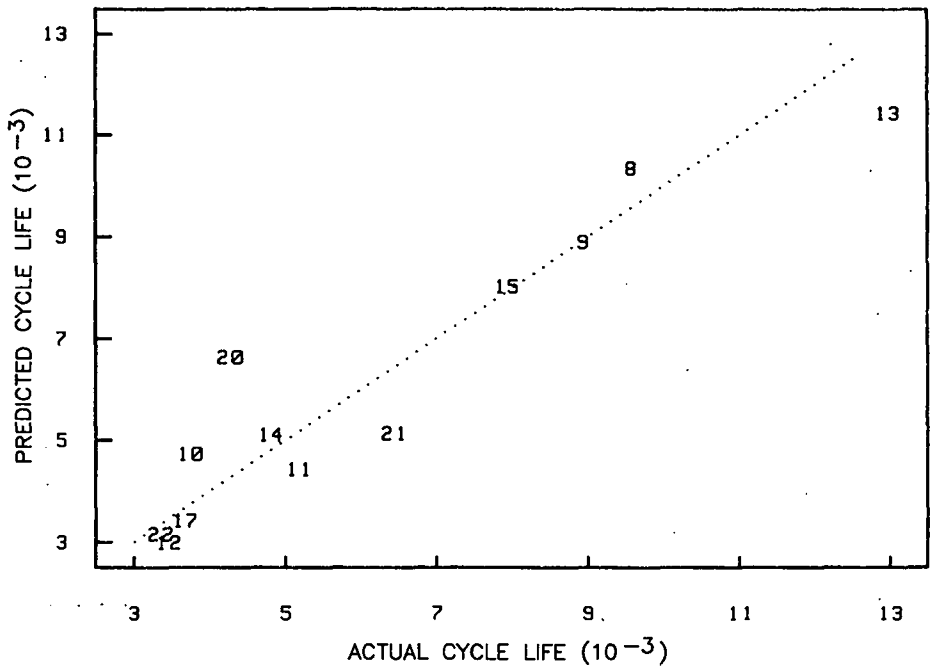

FIG. 5a Predicted cycle life from 1700 cycle capacity determination data.

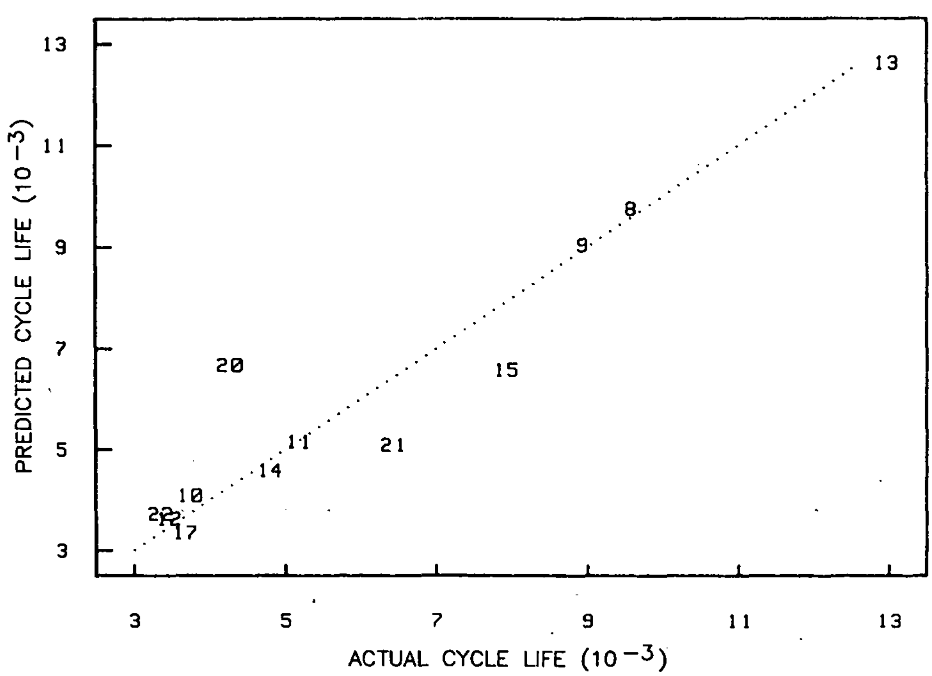

FIG. 5b Predicted cycle life from 3100 cycle capacity determination data.

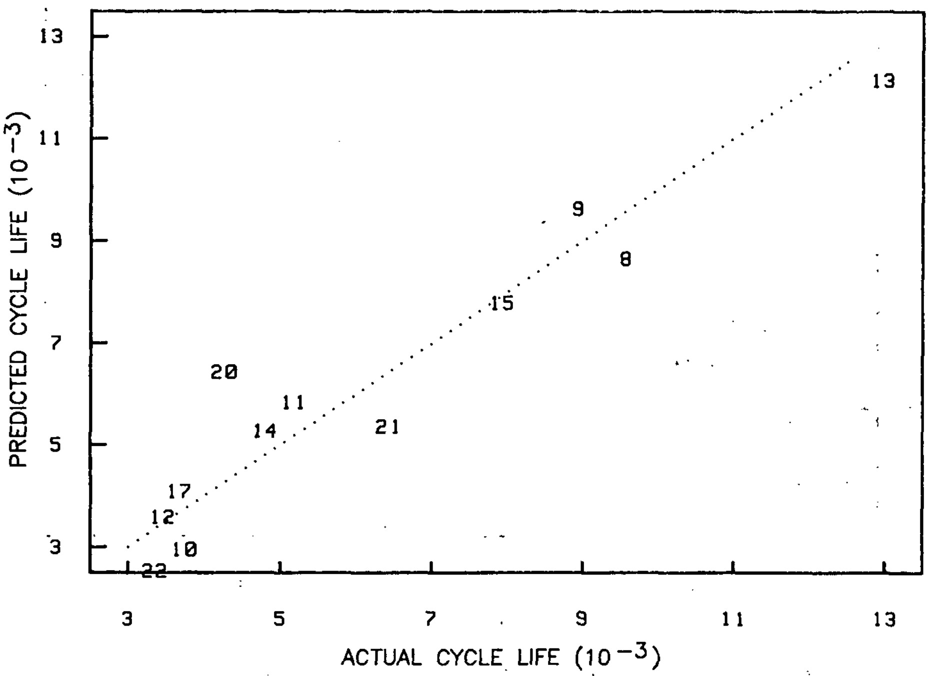

FIG. 5c Predicted cycle life from 5000 cycle capacity determination data.

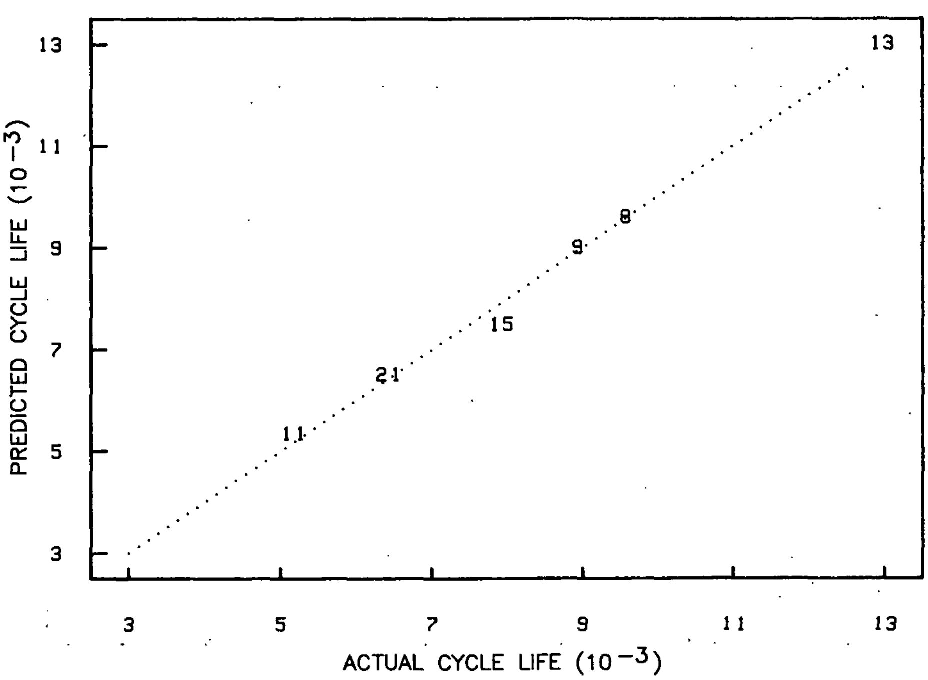

FIG. 5d Predicted cycle life from 6100 cycle capacity determination data.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-88803		

4. Title and Subtitle	5. Report Date
A Mathematical Approach for Evaluating Nickel-Hydrogen Cells	
	6. Performing Organization Code 506-41-21
7. Author(s) Harold F. Leibecki	8. Performing Organization Report No. E-3114
	10. Work Unit No.
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135	11. Contract or Grant No.
	13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

Prepared for the 1986 Fall Annual Meeting of the AIChE, Miami, Florida, November 2-7, 1986.

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17. Key Words (Suggested by Author(s))	18. Distribution Statement
Batteries Fuel cells	Unclassified - unlimited STAR Category 25

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price*
Unclassified	Unclassified		

*For sale by the National Technical Information Service, Springfield, Virginia 22161

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