LONG LIFE NICKEL ELECTRODES FOR A NICKEL-HYDROGEN CELL: CYCLE LIFE TESTS

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ABSTRACT

In order to develop a long life nickel electrode for a Ni/H_2 cell, cycle life tests of nickel electrodes were carried out in Ni/H_2 boiler plate cells. A 19 test cell matrix was made of various nickel electrode designs including three levels each of plaque mechanical strength, median pore size of the plaque, and active material loading. Test cells were cycled to the end of their life (0.5v) in a 45-minute low earth orbit (LEO) cycle regime at 80% depth-of-discharge (DOD). This is an interim report of this cycle life test. The results to date show that the active material loading level affects the cycle life the most with the optimum loading at 1.6 g/cc void. Mechanical strength did not affect the cycle life noticeably in the bend strenth range of 400 to 700 psi. The best plaque type appears to be one which is made of INCO nickel powder type 287 and has a median pore size of 13 μm.

INTRODUCTION

Nickel electrodes have been recognized as the life limiting components of nickel-hydrogen cells. In order to develop a long life nickel electrode for a nickel-hydrogen cell, we are engaged in a study program under a contract for NASA-Lewis Research Center. In this study we investigated the effects of various electrode parameters on the cycle life of the electrodes. These parameters include plaque pore size, plaque mechanical strength, and active material loading level which were varied in three levels for each parameter. The overall program effort is outlined in Fig. 1. Various fabrication parameters of nickel plaques including nickel powder type, powder density, and sintering time were studied in order to fabricate plaques with desired parametric variations.[1] Selected plaques (7 types) were impregnated in three levels of active material loading using the standard Air Force/Hughes electrochemical deposition process in an alcoholic bath. Subsequently these electrodes were tested by a Hughes standard stress test procedure (200 cycles) as a part of their evaluation. For a cycle life evaluation of these electrodes, 19 different nickel-hydrogen boiler plate test cells were fabricated and tested for initial cell performance. These results have been published earlier[1]. The present report describes interim results of the cycle life tests which are still in progress.

TEST CELL MATRIX AND DESIGNATION OF ELECTRODES

The nickel-hydrogen boiler plate test cells matrix includes 19 out of 21 various designs of electrodes as shown in Table 1. Each electrode was designated as follows for convenience of later discussions: The first two digits represent the nickel powder type and the median pore size, i.e. 55 for INCO nickel powder type 255 and 10 μm pore size, 25 for 255 powder type and 16 μm pore size, and 87 for 287 powder type and 13 μm pore size, respectively. The last two digits represent mechanical strength (bend strength): 40 for 400 psi, 55 for 550 psi, and 70 for 700 psi. For example, an 8755 plaque is made of 287 type powder with the bend strength of 550 psi and the median pore size of 13 μm.

TEST CELLS AND CYCLE LIFE TEST

All test cells contained three standard flight type nickel electrodes in a recirculation stack design[2] and 31% KOH electrolyte. The capacity of the cells were rated into three groups, i.e., 2.7, 3.0 and 3.3 AH, based on capacities measured by charging the cells for 80 minutes at C rate and then discharge to 1.00V at 2.74 C rate. The measured capacities ranged from 2.8 to 3.1 AH, from 3.1 to 3.5 AH, and 3.5 to 3.9 AH for 2.7, 3.0, and 3.3 AH ratings, respectively.

The cycle life test of all the 19 boiler plate test cells were carried out at 23°C by a continuous cycling to 80% depth-of-discharge (DOD) of their rated capacities using a 45-minute cycle regimes except for interruptions for periodic capacity measurements after approximately every 1500 cycles. The cycling regime included a 2.74C rate discharge for 17.5 minutes and a 27.5 minute charge at 1.92C rate for 110% recharge. End-of-charge voltages (EOCV), end-of-discharge voltages (EODV), end-of-charge pressures (DOCP), and end-of-discharge pressures (EODP) of the cells were monitored daily (every 32 cycles).

CYCLE LIFE TEST RESULTS

Plots of EODV and EODP of various cells vs. number of the life cycles are shown in Fig. 2A and 2B. The group of electrodes made of 2540 plaques showed the lowest cycle life, as shown by the EODV curves, regardless of the active material loading level. The next lowest cycle life group included all electrodes with the lowest active material loadings (L-series; 1.4 g/cc void), regardless of the plaque type. The comparison of the cycle life of the remaining electrodes was not as clear cut as the other electrodes. However, the general trend showed that the medium loading level (M-series; 1.55 g/cc void) gave better cycle life than the high loading level

(H-series; 1.7 g/cc void). No noticeable trend was observed with the variation of plaque mechanical strength. In regard to the effects of pore size, the best plaque appears to be the 87XX series which are made of 287 type nickel powder with 13 μm median pore size. These series of plaques with M or H level loading showed slightly higher cycle life on the average than the 55XX series with comparable loadings. The 55XX are made of 255 type nickel powder with 10 μm median pores. The 2540 plaques with 16 μm pores were the worst plaques as discussed above.

The EOCV's of the cells showed neither any appreciable variations with various electrode types nor any appreciable change during the cycle life test.

The EOCP's and EODP's of a given cell changed parallel to each other as expected by the fixed quantity of charge and discharge. The cells with short cycle life showed overall lower pressure than the other cells. These short life cells, which include the 2540 types and all L-series, also showed a pressure peak. The pressure of these cells were initially increased with cycling along with other cells up to about 1000 cycles and then started to decrease while the pressure of the other cells on the average either remains constant or increases with cycling.

The cycle life of various cells to 0.5 and 0.9 v of EODV are plotted against active material loading level in Figs. 3 and 4, respectively. Both curves show that the loading level for the optimum cycle life is about 1.6 g/cc void. These figures also show the effects of plaque type on the cycle life. The 87XX plaques on the average give better cycle life than the other types with comparable active material loading as discussed above.

CELL PRESSURE AND ACTIVE MATERIAL UTILIZATION

A normalized cell pressure after full charge and discharge, $(P-P_o)/C_o$, where P is cell pressure, P_o is precharge pressure, and C_o is theoretical capacity of nickel electrode, is plotted against active material utilization of the cells after 1700 life cycles in Fig. 5. The term $(P-P_o)/C_o$ is a measure of the average oxidation state of nickel active material. The plots after full charge and full discharge of the cell gave straight lines, respectively. The values of $(P-P_o)/C_o$ at charged state were increased while the values at discharged state were decreased as the utilization increased. The values at charged state increased more rapidly than those at discharged state decreased when the utilization increased. This result appears to indicate that an increased active material utilization is more dependent on reaching a high average oxidation state than on discharge to a low average oxidation state. This observation after 1700 cycles is quite contrary to an earlier observation at the beginning of life on the relationship between $(P-P_o)/C_o$ and the active material utilization[1] as shown in Fig. 6. The earlier observation showed that the average oxidation state in the charge state was independent of the utilization. The utilization was entirely dependent on the oxidation state in the discharged state. This change of the relationship between the utilization and $(P-P_o)/C_o$ with cycling may indicate the change of the mechanism of the active material utilization.

The plots of $(P-P_o)/C_o$ vs. the utilization at various life cycles are shown in Fig. 6. An additional trend observed in this figure is that the overall value of $(P-P_o)/C_o$ is increased with increased number of cycles. This increase appears to be due to either an increase in the average oxidation state of active material or a gradual corrosion of the nickel sinter to be converted to nickel oxides or hydroxides, or both.

CONCLUDING REMARKS

This report is an interim report of our studies on various parametric effects on the cycle life of a long life nickel electrode for nickel-hydrogen cells. The following remarks are based on the combination of the results of present cycle life test and the initial performance reported earlier[1].

- Among all parameters studied presently, the active material loading level affected cycle life of the nickel electrodes the most. The optimum loading level was about 1.6 g/cc void.

- No noticeable effect of the plaque mechanical strength on the cycle life was found in the bend strength range of 400 to 700 psi.

- Type 87XX plaques with 13 μm median pore size showed the longest cycle life on the average and slightly were better than type 55XX plaques which have 10 μm pore size. However, the active material utilization at the beginning of life was slightly higher with 55XX than 87XX. Type 2540 plaques with 16 μm median pore size showed the poorest life performance of all types.

- Values of $(P-P_o)/C_o$ gradually increased with the cycling.

- The relationship between active material utilization and $(P-P_o)/C_o$ indicated that the mechanism of maximum utilization of the active material may be changing with cycling.

REFERENCES

1. H. S. Lim, S. A. Verzwyvelt, C. Bleser, and K. M. Keener, "Long Life Nickel Electrodes for a Nickel-Hydrogen Cell: I. Initial Performance", Proc. 18th IECEC, Orlando, Florida 1983. P. 1543.

2. G. Holleck, "Failure Mechanisms in Nickel-Hydrogen Cells", the 1976 Goddard Space Flight Center Battery Workshop Proceedings, NASA Publication X-711-77-28, P. 297.

Table 1

Boiler Plate Test Cell Matrix and Designation of Cell Types

BEND STRENGTH	400 psi			550 psi		700 psi	
PORE SIZE, μm / ACTIVE MATERIAL LOADING LEVEL	10	13	16	10	13	10	13
1.4 g/cc VOID	* 5540L	* 8740L	* 2540L	* 5555L	* 8755L	5570L	* 8770L
1.55 g/cc VOID	* 5440M	* 8740M	* 2540M	* 5555M	* 8755M	* 5570M	* 8770M
1.7 g/cc VOID	* 5540H	* 8740H	* 2540H	* 5555H	* 8755H	5570H	* 8770H

*INCLUDED IN 19 TEST CELLS

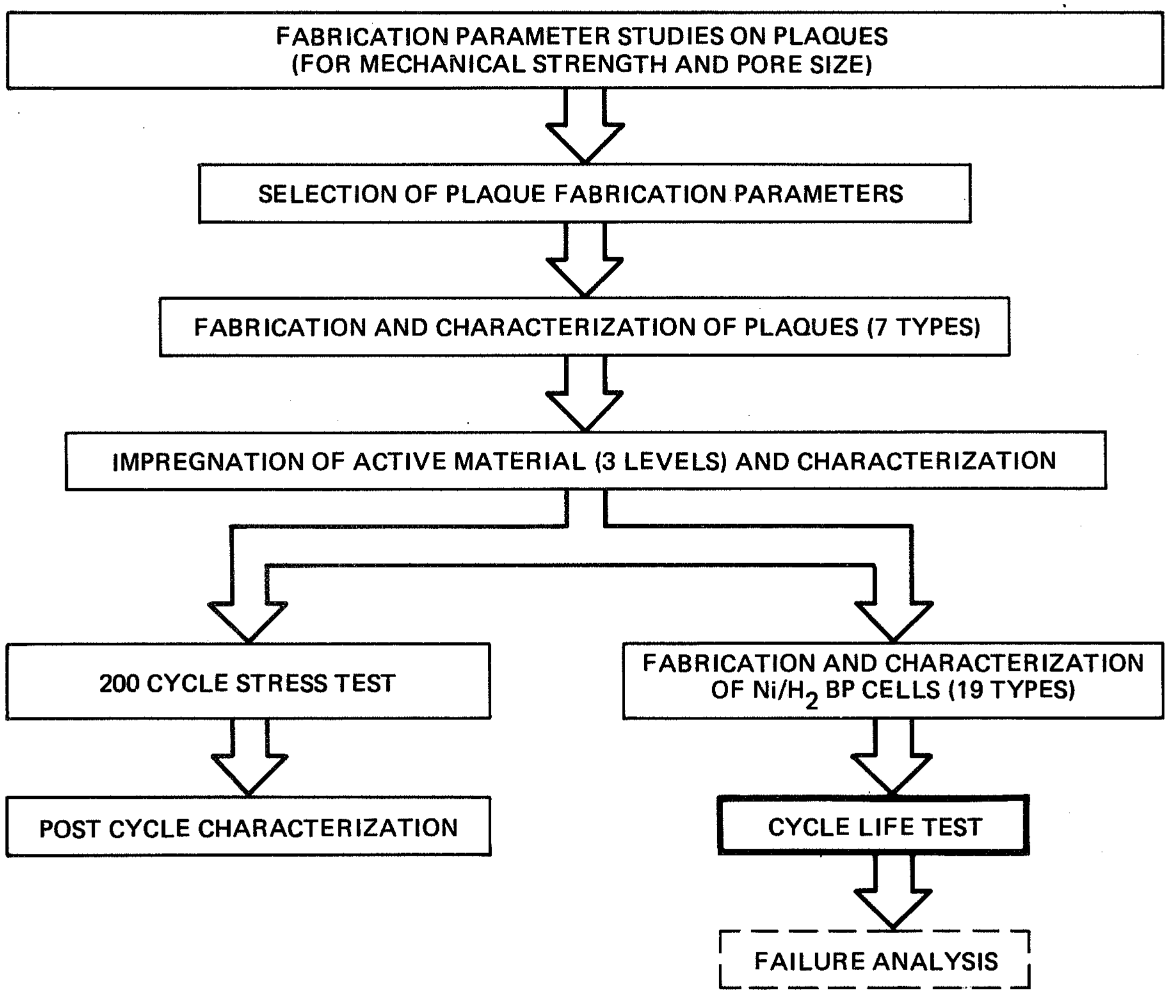

Figure 1. Outline of program.

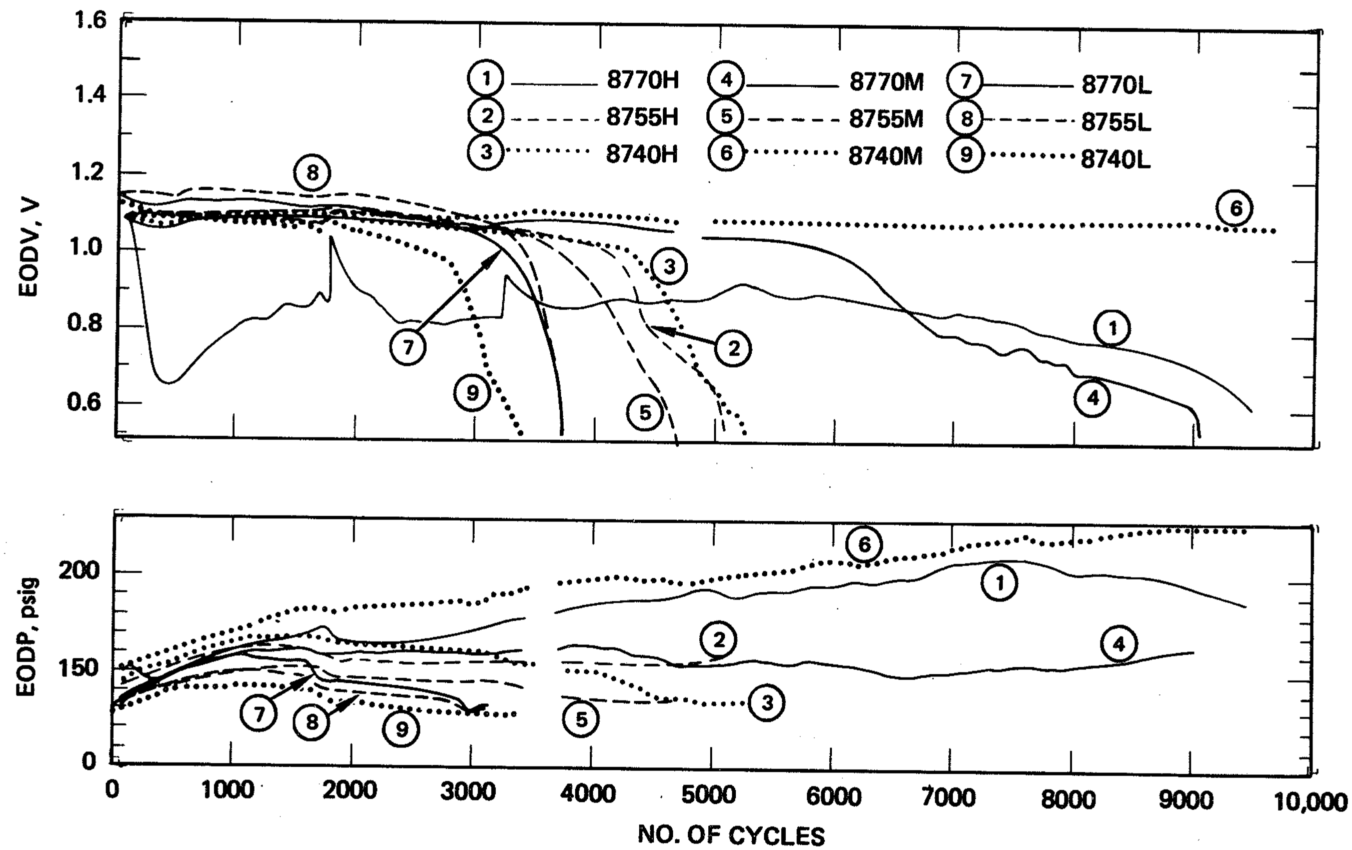

Figure 2A. Plots of EODV and EODP vs. number of cycles for 87XX electrodes.

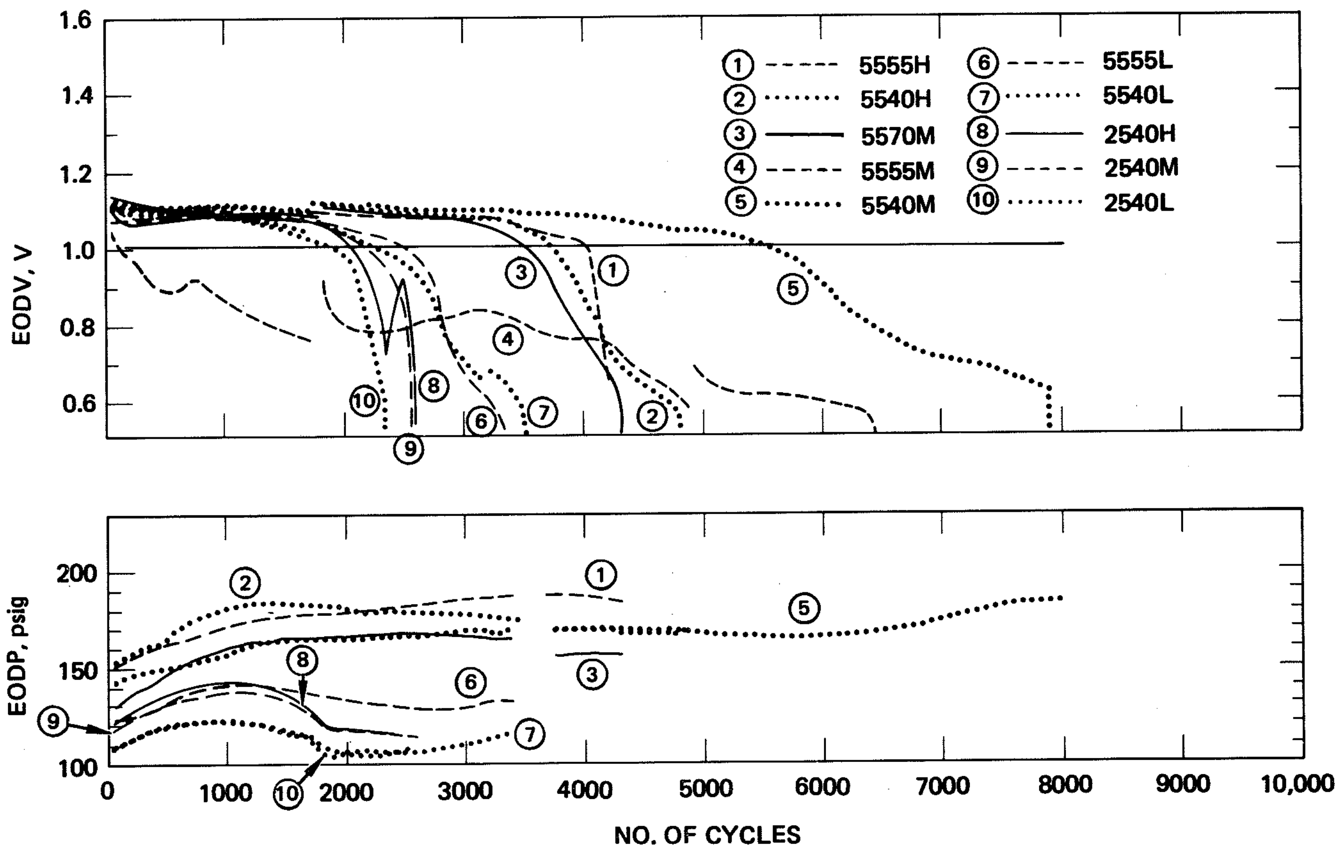

Figure 2B. Plots of EODV and EODP vs. number of cycles for 55XX and 2540 electrodes.

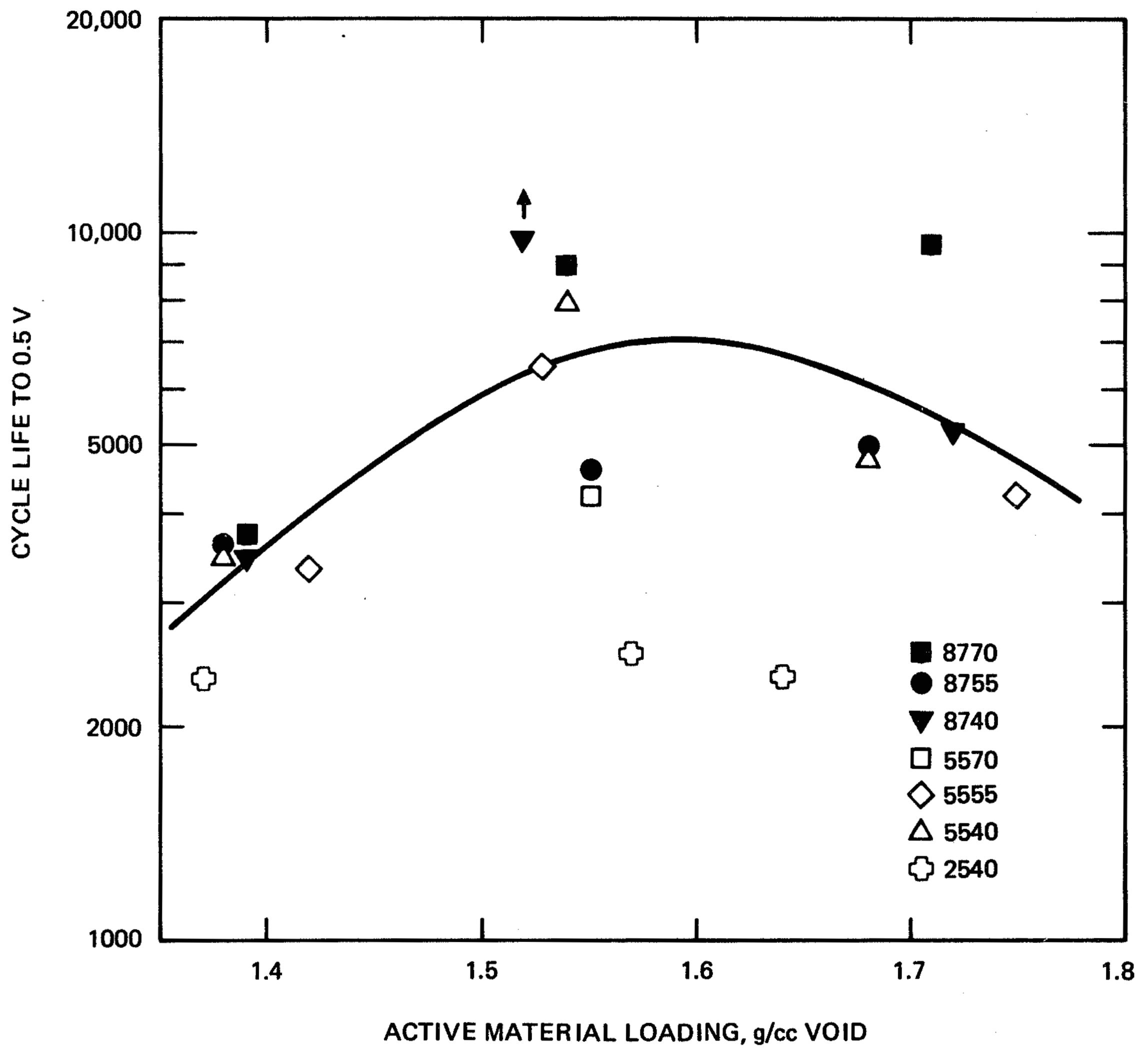

Figure 3. A plot of cycle life to 0.5V of EODV vs. active material loading level.

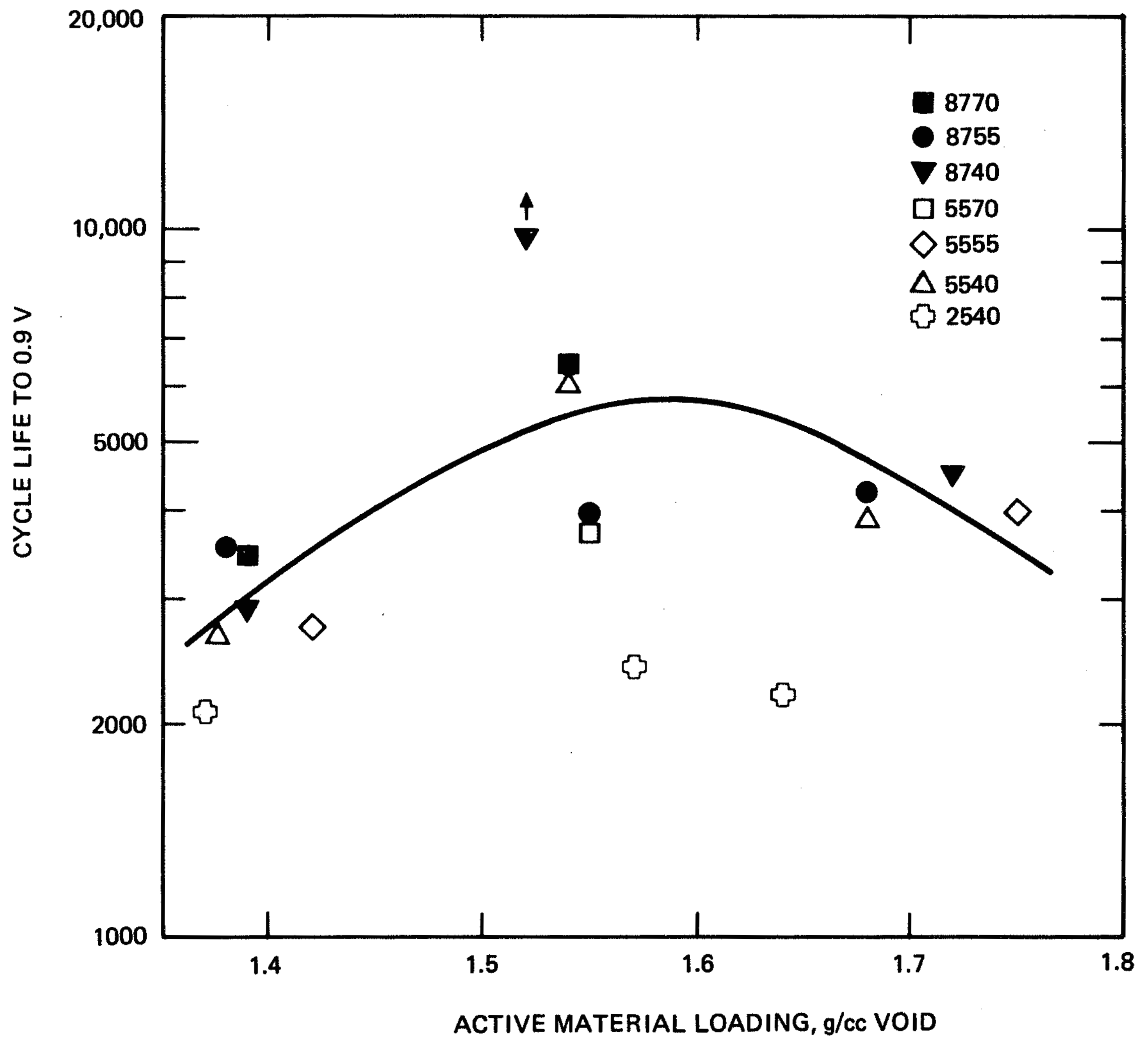

Figure 4. A plot of cycle life to 0.9V of EDOV vs. active material loading level.

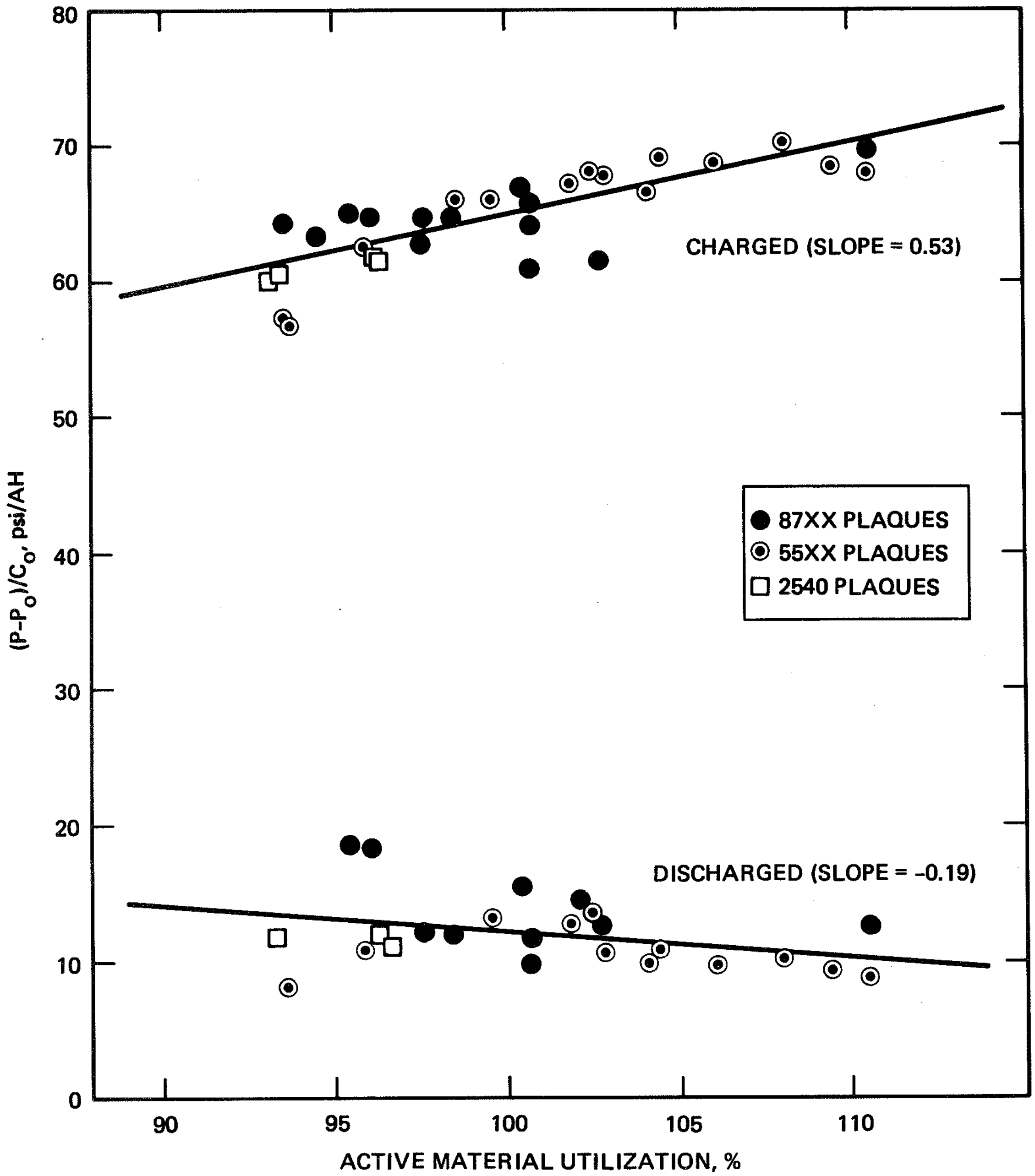

Figure 5. $(P-P_O)/C$ vs. active material utilization after 1700 cycles. Charged for 16 hours at 0.1C rate and discharged to 0.5V at 0.5C rate.

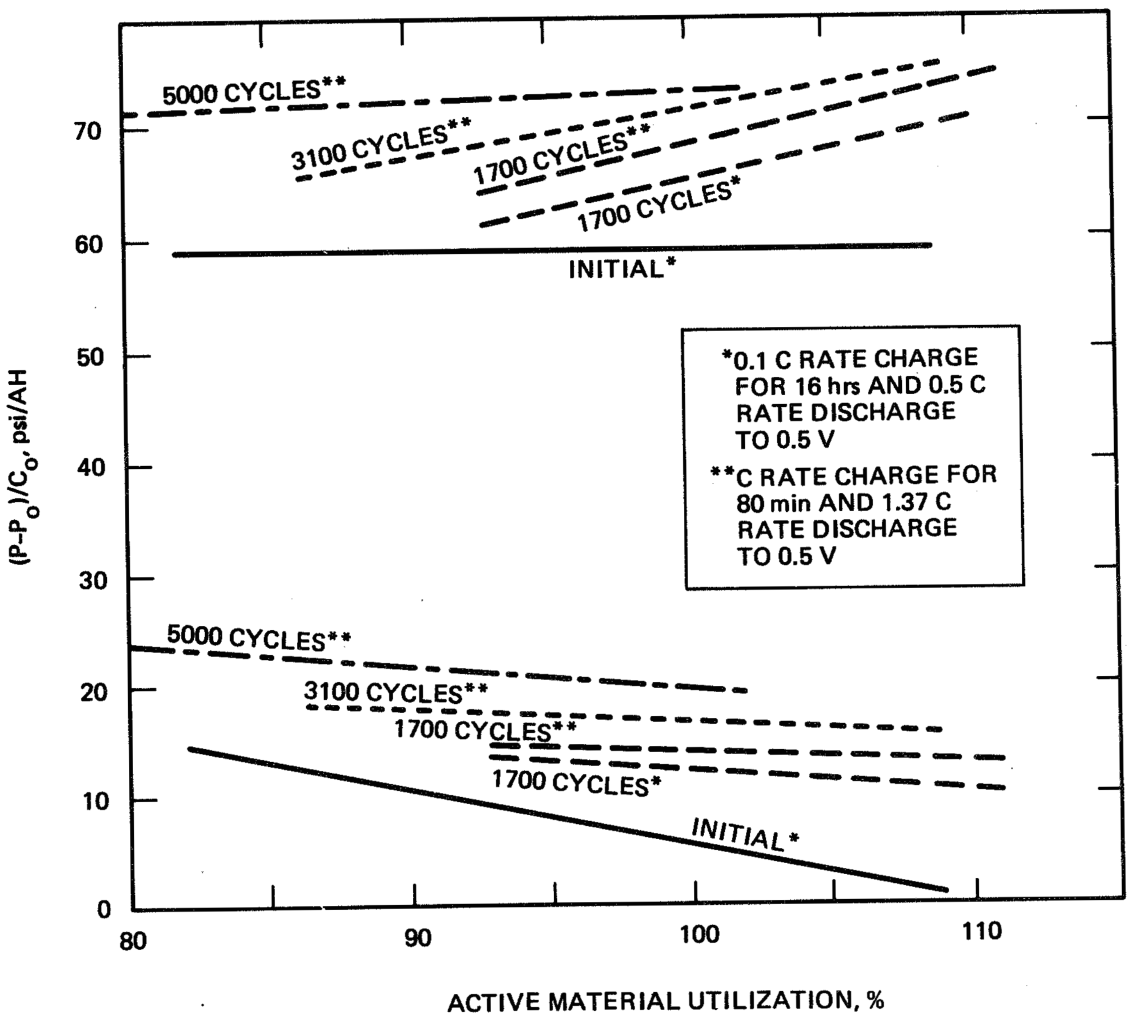

Figure 6. $(P-P_O)/C_O$ vs. active material utilization at various life cycles.

Q. Gross, Boeing: Based on the data you have taken so far how would you compare the best of your combinations with the performance of the existing nickel electrodes used for nickel hydrogen cells.

Q. Lim, Hughes Research Lab: The best combination appears to be the 87 excess plaques here which is 287 powder. We didn't see any strong effect of the mechanical trends so the mechanical trends in the range of 400 to 700 PSI didn't make that much of a difference.

Q. Gross, Boeing: Well how does that material compare in other respects with the existing nickel electrodes commercial.

A. Lim, Hughes Research Lab: I cannot speak it's all different types of nickel electrode presently available but this is very close to the Hughes Air Force standard electrode which is made of 287 nickel powder and the average pressure is around 550 PSI and the loading level is I understand close to 1.55 to 1.6 which is very close to the optimum.

Q. Edgar, Eagle Picher: Could you comment briefly on active material loss from these electrodes at the different cell sizes you investigated.

A. Lim, Hughes Research Lab: The active material loss we have reported earlier after the 200 cycle stress test the loss was I think it was around 2% overall except 25 to 40 plaque which has a medium size of 16 microns. The plaque I think it's loss was about twice as the other average and after this test we didn't measure the loss yet.

Q. Mallory, AT&T Bell Labs: Could you remind me what impregnation method you were using for these?

A. Lim, Hughes Research Lab: This was Dr. Pickett's method.

Q. Mallory, AT&T Bell Labs: And do you know what level the carbonate was in the cells?

A. Lim, Hughes Research Lab: We didn't analyze the carbonate level of this cell yet but I think we have a low initial carbonate content of the stock solution. I don't have the number with me. Maybe my co-worker Scott has it.

Q. Lim, Hughes Research Lab: Scott, do you remember? We had a very low value initially but after the test we didn't measure that yet.