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Post-Test Analyses of Aqueous Batteries Developed for Electric Propulsion

Summary Report for
January 1985–September 1986

by J. F. Miller, J. J. Marr,
and J. A. Smaga

Argonne National Laboratory, Argonne, Illinois 60439
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Summary Report for
January 1985 - September 1986

prepared for
Electric and Hybrid Propulsion Division
Office of Transportation Systems
U.S. Department of Energy

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	1
I. INTRODUCTION	3
II. PERFORMANCE DEGRADATION IN LEAD-ACID BATTERIES	4
A. Overview	4
B. Module Cycled at 30% Depth-of-Discharge	4
C. Modules Cycled at 80% Depth-of-Discharge	6
D. Modules Cycled at 120-A Discharge Rate	8
E. Module Operated in Electric-Vehicle Field Test	11
F. Flow-Through Lead-Acid Cell.....	12
III. PERFORMANCE DEGRADATION IN NICKEL/IRON BATTERIES	13
A. Overview	13
B. Module After 1100 Deep Discharge Cycles	13
C. Modules with Double-Pass Nickel Substrates	14
D. Module Tested on a Driving Profile	15
IV. INVESTIGATION OF THE EFFECT OF IRON ON NICKEL ELECTRODE PERFORMANCE	16
V. CONCLUSIONS	17
REFERENCES	18
APPENDICES	19
A. Post-Test Analysis Report for Lead-Acid Battery GU06IL37	19
B. Post-Test Analysis Report for Lead-Acid Battery GU06IL54	29
C. Post-Test Analysis Report for Lead-Acid Module GU06IL52	37

TABLE OF CONTENTS

	<u>Page</u>
D. Post-Test Analysis Report for Lead-Acid Module GU06IL51	45
E. Post-Test Analysis Report for Nickel/Iron Module EG10FN07	51

LIST OF FIGURES

	<u>Page</u>
1. Individual Cell Voltages of Module 4 During 3-h Discharge at Cycle 483	7
2. Individual Cell Voltages of Module 2 During 3-h Discharge at Cycle 577	7
3. Relationship Between Positive-Grid Corrosion and the Remaining Cell Capacity	11
4. Relationship Between Positive-Electrode Densification and the Remaining Cell Capacity	11
5. Effect of Iron and Lithium Hydroxide on Nickel Electrode Performance	16
A-1. Cell Voltage Curves for Module GU06IL37	20
A-2. Half-Cell Potential of Cell 3	21
A-3. Half-Cell Potential of Cell 4	21
A-4. SEM Image of the Active Material Found at the Core of the Positive Electrode	24
A-5. Coralloid Structure Found Near the Surface of the Positive Electrode	25
A-6. Positive Plate Cross Sections at the Top, Middle, and Bottom	26
A-7. Thick PbO ₂ Scale Found on the Corroded Grid Wire of a Positive Electrode	27
A-8. Poor Adhesion of the Negative Active Material to the Negative Grid	27
B-1. Half-Cell Potential of Cell 4	30
B-2. Blistered Area Beneath the Post on the Outer Negative Plate of Cell 6	31
B-3. Underpasted Side and Overpasted Side of Typical Negative Electrode	32
B-4. SEM Image of the Active Material from the Negative Electrode	34
B-5. Cross-Sectional View of the Negative Grid Wire	35

LIST OF FIGURES (contd)

	<u>Page</u>
B-6. Cross-Sectional View of the Positive Electrode	35
B-7. SEM Image of the Active Material from the Positive Electrode	36
B-8. Cross-Sectional View of the Positive Grid Wire	36
C-1. Individual Cell Voltages for Module GU06IL52	38
C-2. Half-Cell Potential for Cell 5	39
C-3. X-Ray Radiographs of Positive Plates from Cell 5 and Cell 4	41
C-4. Cross-Sectional View of Positive-Grid Wires from Cell 4 and Cell 5	42
C-5. SEM Image of Positive Active Material from the Core	43
C-6. SEM Image of Positive Active Material from the Surface	44
D-1. Reference Electrode Measurements of Cell 5	46
D-2. Comparison of Positive Grids from Cell 1 and Cell 5	47
D-3. Negative Active Materials of Cell 5	49
E-1. Half-Cell Potentials for Cell 3 at the 2-h Rate	52
E-2. Half-Cell Potentials for Cell 3 under the "Pontiac" Profile	52
E-3. Blistered Nickel Electrode	54
E-4. Blistered Iron Electrode	54
E-5. Typical Separator as Viewed from the Negative Electrode Side	55
E-6. Cross-Sectional View of a Positive Current Collector Wire	55
E-7. Cross-Sectional View of a Negative Current Collector Wire	56
E-8. SEM Image and Iron K_{α} Image of the Same Cross-Sectional Area of a Separator	57

LIST OF TABLES

	<u>Page</u>
1. Summary of Lead-Acid Battery Examinations	5
2. Analyses of Active Materials and Electrode Grids from Three JCI EV-2300 Modules	10
3. Summary of Nickel/Iron Battery Examinations.....	13
A-1. Lead Analysis for Positive Active Material	23
A-2. Lead Analysis for Negative Active Material	23
A-3. Antimony in Negative Active Material	23
B-1. Individual Cell Capacities for Module GU06IL54	30
B-2. BET Surface Area Measurement of the Active Material	33
B-3. Lead Analysis for Positive Active Material	33
B-4. Lead Analysis for Negative Active Material	33
B-5. Antimony in the Active Materials	33
C-1. Initial Performance of JCI EV-2300 Lead-Acid Module	37
C-2. Analysis of Positive Active Materials from Module 52	43
C-3. Analysis of Negative Active Materials from Module 52	44
D-1. Individual Cell Capacities for Module GU06IL51	45
D-2. Analysis of Active Materials of Module 51	48
E-1. Individual Voltages for the Cells of Module EG10FN07	53
E-2. Self-Discharge of Cells During Three Week Period and the Iron Content Found in Corresponding Separator Samples	58

POST-TEST ANALYSES OF AQUEOUS BATTERIES DEVELOPED FOR ELECTRIC PROPULSION

SUMMARY REPORT

January 1985 - September 1986

J. F. Miller, J. J. Marr, and J. A. Smaga

ABSTRACT

This document is a summary of the activities conducted at Argonne National Laboratory on post-test examination of aqueous electric-vehicle batteries from January 1985 to September 1986. The post-test analyses were conducted to determine the causes of performance degradation (e.g., capacity decline, power loss, self-discharge) in lead-acid and nickel/iron batteries. For the lead-acid batteries, the primary causes of capacity decline were generally found to be morphological changes in the positive active material, corrosion of the positive electrode grid, and loss of contact between the active material and grid in the positive electrode. For the nickel/iron batteries, the primary factors responsible for performance degradation were transport of iron through the separator to the nickel electrode and loss of contact between the active materials and current collector. These results have permitted more-accurate assessments of current technical progress in development of aqueous electric-vehicle batteries and have helped to direct future R&D efforts.

SUMMARY

Argonne National Laboratory (ANL) has been conducting post-test analyses of cells and multicell modules that have completed testing at ANL's National Battery Test Laboratory (recently renamed the Analysis and Diagnostics Laboratory) or elsewhere in the Department of Energy Battery Program. The objective of this activity is to support the R&D activities on lead-acid and nickel/iron systems through the identification of the degradation modes responsible for cell and module failures.

During this reporting period (January 1985 to September 1986), twelve lead-acid and nickel/iron modules were subjected to visual inspection, as well as chemical and physical analyses. In some cases, developers who had fabricated these cells were invited to participate in the disassembly phase of the post-test analyses. Occasionally, the analysis was performed at the developer's facility with the participation of ANL personnel. Reports of the complete post-test analyses findings were sent to the battery developers so that corrective action could be undertaken in the problem areas identified.

For the lead-acid modules investigated, one cause of capacity decline was attributed to deterioration of the positive electrodes. With increasing cycle life, the positive active material (lead dioxide) formed a coralloid structure. This type of microstructure generally decreased both the surface area of lead dioxide available for reaction and the electrolyte volume within the electrode. Both effects hinder electrochemical reactions occurring within the cell. In addition, corrosion of the positive electrode grid usually produced an oxidized layer on the grid wires, which developed cracks or gaps at the paste/grid interface. The loss of contact between the grid and the active materials caused by these cracks contributed to an increase in the electrical resistance and, as a consequence, reduced battery capacity.

The migration of iron to the nickel electrode was the primary mode of capacity decline in the nickel/iron modules. An iron-nickel oxide compound was observed on the surfaces of the nickel electrode. The formation of this compound might play an important role in the capacity loss observed for the nickel/iron battery.

An in-depth investigation of iron contamination of the nickel electrode was also carried out during 1985. The finding was that iron transferred from the iron electrode to the nickel electrode, and then formed an iron-nickel compound that may have lowered the oxygen evolution potential at the nickel electrode. This condition would reduce the charge acceptance of the nickel electrode and contribute to the decline of cell capacity. In addition, the transfer of iron particulate through the porous separator is suspected of forming electronically conductive paths that promote self-discharge of the cell. Recent tests of lithium hydroxide additions to the electrolyte have proven effective in restoring some of the capacity loss.

I. INTRODUCTION

Argonne National Laboratory (ANL) has been conducting post-test analyses of cells and modules that have completed testing at ANL's National Battery Test Laboratory (recently renamed the Analysis and Diagnostics Laboratory) or elsewhere in the Department of Energy Battery Program. The objective of this activity is to support the R&D activities for lead-acid and nickel/iron systems through the identification of the degradation modes responsible for cell and module failures. These examinations also allow assessment of the effects of design changes on battery performance. Efforts have also been directed toward elucidation of the causes and possible remedies for capacity loss in the nickel electrode. The knowledge gained from these activities has permitted greater accuracy in assessing current technical progress in development of these systems and has helped direct future R&D effort.

Post-test examinations employ a variety of techniques to identify and analyze the failure modes of cells and modules. Prior to disassembly, electrochemical measurements are made to determine individual cell capacities, voltages, and half-cell potentials. Visual inspection of the cells during disassembly identifies (1) mechanical defects that may have occurred during manufacturing and (2) changes in appearance or the physical nature of active materials that occurred during testing. Chemical analyses are performed to measure electrolyte concentration, to determine the composition of the electrodes, and to identify corrosion products and the active materials lost from the electrodes during testing. Physical analyses of electrode materials provide quantitative information on the changes in electrode structure that occur during cycling. The instrumentation used for the chemical and physical analysis includes scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), inductively coupled plasma/atomic emission spectroscopy (ICP-AES), gas chromatography (GC), X-ray radiography, and BET absorption analysis. The information derived from these techniques increases our comprehension of the factors that impair battery performance. During this report period (January 1985 to September 1986), seven lead-acid modules, a lead-acid cell, and four nickel/iron modules were subjected to post-test analysis. An in-depth investigation of iron contamination in the nickel electrode was also completed.

II. PERFORMANCE DEGRADATION IN LEAD-ACID BATTERIES

A. Overview

Seven lead-acid modules and a lead-acid cell fabricated for the electric-vehicle application were analyzed during the period covered by this report. Each one was terminated in the fully charged condition to establish a standardized basis of comparison. The highlights of the results are summarized in Table 1. One cause of capacity decline for the lead-acid modules was attributed to deterioration of the positive electrodes.¹ With increasing cycle life, the positive active material (lead dioxide) formed a coralloid structure. This type of microstructure generally decreased both the surface area of lead dioxide available for reaction and the electrolyte volume within the electrode. Both effects hinder electrochemical reactions occurring within the cell. Formation of this coralloid structure appears to be a common phenomenon.² In addition, corrosion of the positive electrode grid usually produced an oxidized layer on the grid wires, which developed cracks or gaps at the paste/grid interface. The loss of contact between the grid and the active materials caused by these cracks contributed to an increase in the electric resistance and, as a consequence, reduced battery capacity.

B. Module Cycled at 30% Depth-of-Discharge

Post-test examination was conducted on the EV-3000 module (GU06IL37) manufactured by Johnson Controls, Inc. (JCI). The module, which had six cells and a capacity of 240 Ah, was subjected to life-cycle testing exclusively at 30% depth-of-discharge at the 3-h (80 A) rate in tests conducted at ANL. This module achieved 1506 cycles before its capacity declined to less than 75% of its initial capacity; a companion module achieved 1648 cycles under identical test conditions.

Reference electrode measurements were conducted on the two weakest cells in the module, as determined by individual measurements of cell capacity. A sharp drop in the positive electrode potential with respect to a mercury/mercurous sulfate reference electrode at the end of discharge indicated that the positive electrode limited the capacity of the module.

A teardown examination revealed deterioration of both the positive and negative electrodes.

Examination of the positive active materials from three cells with a scanning electron microscope showed that the firm active materials at the core were in normal condition, with very few lead sulfate crystals present. The softened active materials at the surface, on the other hand, had a well-defined coralloid structure of lead dioxide. This region also contained a high concentration of lead sulfate.

All the positive grids were severely corroded. X-ray radiograph pictures showed broken wires throughout the grid frame. Metallographic examination of the positive-grid cross section determined that the outer corrosion layer averaged 200 μm in thickness. The corrosion layer was found to be adherent to the grid, with cracks that were perpendicular to the grid/paste interface. Johnson Controls has made similar observations.^{3,4}

Table 1. Summary of Lead-Acid Battery Examinations

Module Identification	Description and Test History	Major Findings
GU06IL37	A 240-Ah, 12-V module which completed 1506 cycles (30% DOD ^a) before capacity declined to 75%	<ul style="list-style-type: none"> o Coralloid structure in PbO₂ electrodes o Loss of adhesion to grids in both electrodes o Locally high Sb deposits on Pb electrodes
GE06IL02 and GE06IL04	183-Ah, 12-V modules cycled at the 3-h rate at 80% DOD until capacities declined to 80%	<ul style="list-style-type: none"> o Corrosion of positive grids o Softening and shedding of positive active material o Two fractured negative tabs in worst cell
GU06IL54 and GU06IL52	183-Ah, 12-V modules cycled at 120-A rate at 80% DOD until capacities declined to 95 and 85%, respectively	<ul style="list-style-type: none"> o Positive electrode limited o Corrosion of positive grids o Reduced pore volume of positive active material
GU06IL51	A 183-Ah, 12-V module cycled at 120-A rate at 80% DOD until capacity declined to 75%	<ul style="list-style-type: none"> o Voltage reversal of weakest cell during discharge o Corrosion of positive grids o Reduced pore volume of positive active material
Module #9	A 183-Ah, 12-V module which failed during field evaluation in an EV battery system	<ul style="list-style-type: none"> o Subsystem component failure o Loss of electrolyte circulation
GCD-9	A full-size cell based upon the flow-through concept	<ul style="list-style-type: none"> o Warping and cracking of positive electrodes o Loss of PbO₂ pellets o Densification of Pb plates

^aDOD is the depth-of-discharge.

Spectrochemical analysis of the negative active materials found high concentrations of antimony in these samples. This high concentration of antimony indicates that the antimony present in the positive electrode grids was anodically dissolved during operation and had plated onto the surface of the negative electrodes. The antimony contamination of the negative electrode might have caused a reduction of the negative charging efficiency.

In summary, the physical and chemical analyses of lead-acid module GU06IL37 revealed that positive active material deterioration, severe positive grid corrosion, and antimony "poisoning" of the negative electrode appear to be responsible for the capacity loss of this module. A detailed report on the results of this analysis is contained in Appendix A.

C. *Modules Cycled at 80% Depth-of-Discharge*

Life-cycle evaluation of two EV-2300 modules (12-V, 183 Ah) manufactured by JCI was conducted at the NBTL under sponsorship of the Electric Power Research Institute.⁵ Cycling of these modules (designated Nos. 2 and 4) was conducted at a 3-h discharge rate to 80% depth-of-discharge until each module could no longer deliver 80% of its initial capacity. Module 2 was operated for 538 cycles before reaching the end-of-life condition; Module 4 achieved a life of 425 cycles.

End-of-life tests were conducted by inserting individual cell voltage probes into both modules. The resulting individual cell voltages during a 3-h discharge are shown in Figs. 1 and 2. In Module 4, the capacity of one cell was significantly less than that of the other five cells; in Module 2, cell voltages were much more closely matched.

A post-test analysis was performed on Module 4. Two cells were examined: the bad cell (No. 1) and a representative good cell (No. 2). The examination of Cell 1 revealed that the two negative electrodes were broken at the tab; in the good cell, all of the negative plates had a metallic shine (indicating full charge) and were securely joined at the tabs. The breaks in the outer two negative plates of Cell 1 may have occurred early in the life of the module since a high degree of grid corrosion was found in the plates that were firmly attached to the terminals. There appeared to have been some electrical conductance through the negative plates with the damaged tabs because, although the plates were covered with lead sulfate crystals, metallic lead was also detected. In Cell 1, positive grid corrosion was severe, and the structure of the active material was extremely weak. In comparison, corrosion of the positive grid in Cell 2 was moderate, and its active material had not softened to the same extent. Partial clogging of the pump chamber hole in Cell 1 hindered electrolyte circulation, which may have accelerated the deterioration of the positive plates. Owing to the two broken negative plates in Cell 1, current distribution imbalances and charging inefficiencies also increased component corrosion.

In summary, the life of 538 cycles achieved by Module 2 is in good agreement with life data previously attained for this technology. The mechanically damaged plates found in Module 4 decreased both the capacity and lifetime of

Fig. 1. Individual Cell Voltages of Module 4 During 3-h Discharge at Cycle 483. Cells are numbered consecutively, beginning with the cell at the negative terminal of the module.

Fig. 2. Individual Cell Voltages of Module 2 During 3-h Discharge at Cycle 577

Cell 1 relative to the other cells in that module. As a result, Module 4 could not function as well as Module 2. Considering the cause and the magnitude of the cell imbalance in Module 4, an operational life of 425 cycles was a significant achievement.

The experience gained in this study indicates that the use of individual cell probes provides valuable additional information for evaluating the performance of cells and modules. Therefore, it was recommended that individual cell probes be used for module testing in the future.

D. *Modules Cycled at 120-A Discharge Rate*

A group of four EV-2300 lead-acid modules (12-V each) manufactured by Johnson Controls were cycled at the NBTL at a 120-A discharge rate to 80% depth-of-discharge. Comprehensive examinations were conducted on three of the four modules when performance declined to 95%, 85%, and 75% of original capacity. The purpose of these examinations was to study changes in electrode morphology and composition as a function of cycle life. The unexamined module served as a backup in case one of the other three modules failed by a mechanism other than capacity degradation.

The first module (Module 54) was removed from test on cycle 212 after its capacity dropped to 95% of its initial value. Operation of the second module (Module 52) was terminated at cycle 384, when its capacity fell to less than 85% of initial value. The third module (Module 51) achieved 482 cycles before available capacity declined to 75% of its initial capacity.

Individual cell voltage probes were inserted into each cell to measure the individual cell capacity. The measurements were used to select the cells with the highest and lowest capacities from each module for detailed analyses. Half-cell potential was then measured on the weakest (i.e., the lowest capacity) cell in each module. Results showed that the performances of Modules 54 and 52 were limited by the positive electrodes. For Module 51, capacity losses were observed in both sets of electrodes.

In addition to the visual inspection made during disassembly, the examined cells were studied in the following manner. X-ray radiography of representative electrodes determined the general condition (i.e., grid corrosion, electrode expansion, and active material loss) of the electrodes. Scanning electron microscopy characterized both the distribution of the active lead compounds within the electrodes and the interface region between the grid wire and the active material. Spectrochemical analysis of the negative active material measured the level of antimony transported to the electrode. A series of chemical analyses served to quantify the concentrations of the lead compounds within the electrodes. Mercury porosimetry and BET analysis were used to estimate electrode porosity and surface area, respectively. Finally, the active material shed from the electrodes was collected, dried, and weighed as an additional indicator of electrode deterioration. Detailed results of these examinations are presented in Appendices B, C, and D, and some salient findings are recounted below.

For Module 54, the measured cell capacities ranged from a low of 136 Ah in Cell 4 to a high of 145 Ah in Cell 6 at the 120-A discharge rate. Half-cell potential measurements of Cell 4 showed a gradual decline in positive-electrode potential during discharge. No evidence was found for the development of a coralloid structure in lead-dioxide plates, and the positive grid wires remained intact. The positive grids, however, did have an oxide layer ranging from 20 to 50 μm in thickness. One consequence of grid corrosion was reduced adhesion of the electrode pellets to the grid. In view of these findings, the 5% capacity loss was primarily attributed to resistive effects stemming from minor grid corrosion.

For Module 52, reference-electrode measurements of the weakest cell (No. 5) indicated that capacity was limited by the positive electrodes. Teardown examinations confirmed that the negative electrodes remained in good condition but the positive electrodes showed unmistakable signs of degradation. One form of degradation was severe corrosion of the positive electrode grids. The reduction in grid-wire diameters undoubtedly contributed to an overall resistance rise for the module. Grid corrosion was greatest in Cell 5, the weakest cell. Secondly, the positive active material developed a coralloidal structure of PbO_2 , which made the surfaces of the electrodes soft and susceptible to active material shedding. Shedding in Cell 5 was especially severe at the bottom of the plates and resulted in 5-mm bands of exposed grid wires. The active material that remained adherent to the grids was also mechanically weak.

For Module 51, which had the lowest capacity, the major factor for its performance decline was the failure of Cell 5. Apparently, this cell went into voltage reversal about 30 cycles before module performance declined to the 75% capacity criterion. All of the components in this cell were in severely degraded condition. A well-formed coralloidal structure of PbO_2 was found throughout the positive plates. Both extremely low pore volume of the positive active material and severe corrosion of the positive grid were observed in this cell. The concentration of antimony in the negative electrode (812 ppm) was also high. The antimony level found in this cell is much greater than that believed to be sufficient to cause antimony "poisoning," a condition that promotes charge inefficiency.

The quantitative information gained from examination of these three modules is summarized in Table 2. Comparisons were made across the modules to identify possible relationships between individual cell capacities and the post-test analytical findings. A strong correlation existed between the degree of positive-grid corrosion and the remaining cell capacity. As illustrated in Fig. 3, smaller remaining grid cross-sectional areas were found in cells with lower capacities. Porosimetry data for the positive electrodes showed that decreasing cell capacity was correlated with decreasing pore volume. The strength of this correlation is enhanced when combined with data for similar EV-2300 modules tested and examined at ANL under EPRI sponsorship.⁵ Figure 4 depicts the combined data graphically. This figure indicates that each 0.01 decline in pore volume accounts for a ~14% decline in cell capacity; however, it should be noted that nonlinear curves can also be fitted to these data.

These two correlations suggest two different underlying reasons for capacity degradation. Grid corrosion implies a loss in capacity brought about by increases in electrical resistance of the electrodes, i.e., IR losses due to thinner grid wires

Table 2. Analyses of Active Materials and Electrode Grids from Three JCI EV-2300 Modules

	Module 54		Module 52		Module 51	
	Cell 6	Cell 4	Cell 4	Cell 5	Cell 1	Cell 5
Cell Capacity, %	100.00	93.79	~85	35.10	83.45	16.55
Positive Electrode						
Grid Cross-Sectional Area, %	100	95	65	45	60	40
PbO ₂ , wt%	92.65	86.05	90.72	91.30	95.60	86.17
PbSO ₄ , wt%	6.06	10.06	7.48	5.88	3.79	7.01
Shed Mat'l, g	18.60	24.20	65.40	94.70	68.40	98.60
Pore Volume, cm ³ /g	-	-	0.172	0.148	0.185	0.133
Surface Area, m ² /g	1.81	1.34	1.51	2.22	-	-
Negative Electrode						
Grid Corrosion	minor	minor	minor	minor	minor	minor
Pb, wt%	93.37	92.58	91.79	94.31	96.45	93.72
PbSO ₄ , wt%	5.75	5.59	6.16	5.08	2.05	5.97
Antimony, ppm	137	85	400	350	417	812
Pore Volume, cm ³ /g	-	-	0.232	0.172	0.212	0.212
Surface Area, m ² /g	0.57	0.72	0.50	-	-	-

and fractures in the corrosion scale between the wires and the active material. Electrode densification implies a loss in capacity brought about by concentration polarization of the available electrolyte within the pores. These two mechanisms are not mutually exclusive and both presumably contribute to the overall decline in capacity.

Finally, two other correlations were discernible from the data in Table 2. Both the antimony concentrations of the negative electrodes and the quantity of active material shedding from the positive plates generally increased as cell capacity decreased. These inverse relationships probably reflect secondary effects of the primary degradation mechanisms. The source of antimony contamination is corrosion of the positive grids. Similarly, active material shedding is enhanced by the weakened mechanical strength of the morphologically altered positive electrodes. Compositional analyses and BET surface area measurements for the electrode materials proved to be inconsistent in comparisons among modules.

Fig. 3.

Relationship Between Positive-Grid Corrosion and Remaining Cell Capacity

Fig. 4.

Relationship Between Positive-Electrode Densification and the Remaining Cell Capacity. The open squares are for JCI EV-2300 modules from an EPRI-sponsored study.⁵

E. Module Operated in Electric-Vehicle Field Test

An EV-2300 module that was operated as part of a battery pack in an electric vehicle by the Detroit Edison Co. failed during the course of field operation. A post-test examination was subsequently conducted in January 1985 at Johnson Controls with participation by both ANL and JCI personnel. The physical operation of the post-test examination was recorded on video tape by JCI.

Disassembly of the module revealed no construction or material defects. However, bench testing of the air manifold system (which is used to provide air pulses to prevent electrolyte stratification) revealed a problem with the ball check valves, which were designed to prevent the transfer of electrolyte from one cell to another during vehicle acceleration or braking. It appeared, however, that the wetting of the plastic balls and changes in dimensions induced by temperature variations caused the balls to jam and, therefore, obstructed their intended operation. This defect would have caused shunt currents to develop due to electrolyte in the air manifolds and would also have interfered with the electrolyte destratification. Thus, this subsystem design problem accelerated or caused most of the failure modes observed.

As a result of this study, Johnson Controls has designed, developed, and tested a new system that employs an air-locking system for the air manifold line. This system prevents electrolyte transfer between cells without using check balls.

F. *Flow-Through Lead-Acid Cell*

A post-test examination was conducted on a proof-of-concept lead-acid cell which utilizes a forced flow of electrolyte through the porous lead and lead dioxide electrode to obtain significantly enhanced utilization of these materials.⁶ The examination was conducted jointly by ANL and JCI personnel at Johnson Controls.

This full-size cell, which contained nine electrodes, was operated for 32 cycles, 28 of which were at 100% depth-of-discharge. Cell capacity was stable during the first 14 cycles, but steadily declined thereafter. Utilization of positive active material was 101 Ah/kg, or 45% of its theoretical maximum, and 50% greater than that typically observed in EV-2300 cells at the same discharge rate.

The post-test examination found that the quality of cell construction was good; no case distortion or electrolyte leakage was observed. The electrolyte was cloudy, however, with suspended black solids. Although the positive active material was firm, all of the positive electrodes were warped and cracked, which resulted in the loss of pellets. Pellet loss created open channels for the flow of electrolyte, thus preventing the intended uniform flow of electrolyte through the porous plates and leading to the loss in capacity. These results indicate that the primary cause of failure was warpage and cracking of the positive plates.

All of the negative electrode had a dull, grainy appearance, with the presence of some small blisters. Most of the negative plates still exhibited some metallic luster when scraped, but the negative active material showed elevated levels of lead sulfate. This suggests a poor recharge efficiency, possibly due to densification of the negative active material resulting from a loss of expander material that may have been leached out of the negative electrode by the electrolyte flow. Varta⁷ has also proposed such an explanation as a secondary failure mode.

As a result of this investigation, Johnson Controls made several design changes in their flow-through cells. Attempts are being made to increase (1) the mechanical strength and support of the positive electrodes in order to prevent their warpage and cracking and (2) the amount of expander additives in the negative active material.

III. PERFORMANCE DEGRADATION IN NICKEL/IRON BATTERIES

A. Overview

Four nickel/iron electric-vehicle modules were examined during 1985. The major findings are indicated in Table 3. The migration of iron to the nickel electrode was the primary mode of capacity decline in the nickel/iron modules. High iron concentrations were observed on the surfaces of the nickel electrode. X-ray diffraction analysis of this layer revealed that the iron was in the form of an iron-nickel oxide compound. The formation of this compound might play a very important role in the capacity loss of the nickel/iron battery.

Table 3. Summary of Nickel/Iron Battery Examinations

Module Identification	Description and Test History	Major Findings
EP05FN06	Five-cell, 270-Ah module which completed 1101 cycles before failure	<ul style="list-style-type: none"> o Capacity limited by nickel electrode. o Iron contamination and $\text{Fe}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ formation on the Ni electrodes. o Hydrated FeO surface deposits on Fe electrodes.
EG10FN07	Ten-cell, 160-Ah module which completed 1050 cycles on the Pontiac driving profile	<ul style="list-style-type: none"> o Capacity limited by negative electrode, with loss of contact between active material and grid. o Blistering of both the Fe and Ni electrodes. o Iron contamination of the nickel electrodes.
EP05FN09 and EP05FN10	Two five-cell, 270-Ah modules; testing was terminated after 927 and 537 cycles, respectively, because of high self-discharge	<ul style="list-style-type: none"> o Iron contamination of nickel electrodes. o Loss of contact between positive current collector and positive active material. o Separator degradation and development of iron-particulate conductive bridges through the separators.

B. Module After 1100 Deep Discharge Cycles

A 270-Ah nickel/iron module (EP05FN06) constructed by Eagle-Picher Industries⁸ was examined upon completion of life-cycle testing at ANL. This five-cell module achieved 1101 cycles at 80% DOD before the capacity declined to less than 75% of its initial value. At that point, the testing was terminated.

Two cells from this module were disassembled and examined. The electrolyte in one cell was dried out, probably because leakage had occurred at the end of the test. The electrolyte in the other cell was cloudy, with suspended black solids. The separators in both cells were brittle and deteriorated somewhat, as was evident from their discoloration. However, no obvious short circuits were observed.

All the negative (iron) electrodes remained hard and rigid; there was, however, some shedding on the edges of the electrodes. Yellowish-green patches were also found on the surface of some of the negative electrodes. X-ray diffraction identified this material to be iron oxide hydroxide, i.e., $\text{FeO}(\text{OH})$.

The positive (nickel) electrodes in both cells were firm and hard. Although there was no appearance of any physical deterioration, a thin film of particles, which could be washed away by a stream of distilled water, was found on the surface of all the nickel electrodes. These fine particles were examined by X-ray diffraction and identified to be magnetite (Fe_3O_4) and elemental iron. Meanwhile, SEM examination of the cross section of the washed nickel electrode revealed that the iron content remained very high on the surface of the electrode. X-ray diffraction of this surface layer indicated the existence of an iron-nickel oxide compound with a spinel-type structure, namely, ferroan trevorite ($\text{Fe}_{0.43}\text{Ni}_{0.53}\text{Fe}_2\text{O}_4$). The iron appears to have migrated from the iron electrode to the surface of the nickel electrode and reacted with the positive active material to form this iron-nickel spinel. The formation of this compound on the surface of the nickel electrode might be a primary cause of the capacity decline of the module.

In summary, the performance degradation of this module was probably caused by the migration of iron to the nickel electrode and the subsequent chemical reaction with the electrode surface, which reduced the capacity of the nickel electrode. The finding of iron deposits on the surface and in the interior of the separators in nickel/iron cells suggests that the migration of iron-rich particulates through the separator could be the mechanism by which iron is transported from the iron electrode to the nickel electrode. The nickel electrode then becomes "poisoned" when the iron is incorporated into the active material as part of a mixed oxide compound. If this transport mechanism is correct, the lower-than-expected performance of the nickel electrode in nickel/iron batteries might be improved by using separators with smaller pores or greater thickness.

C. *Modules with Double-Pass Nickel Substrates*

Two 270-Ah nickel/iron modules (EP05FN09 and EP05F10) manufactured by Eagle-Picher Industries were examined after they had completed life-cycle testing at ANL. These five-cell modules contained nickel electrodes with substrates that were produced by the double-pass sintering process. Testing (at 80% DOD) was terminated after 927 cycles for module EP05FN09 and 537 cycles for module EP05F10, because both modules exhibited high self-discharge rates during open-circuit stand. Both modules were examined in the fully discharged state.

Cells from both modules were noticeably bulged. There had been considerable leakage of electrolyte from Module EP05F10. Upon disassembly, the positive electrodes were found to be mostly rigid and hard except for a layer of

soft, loose material that covered the electrode surface. The surface layer could be readily washed out by a stream of water. X-ray diffraction identified the loose material as a mixture of magnetite (Fe_3O_4), elemental iron, and the iron-nickel spinel. X-ray diffraction also detected some lithium carbonate on the surface of the positive electrode.

The separator was very brittle and could easily be broken by bending. Conductive paths through the separators had developed as a result of the migration of iron particulates within the pores of the separators. Translucent flakes were found adhered to the separator surface. Energy dispersive X-ray spectroscopic analysis indicated chlorine in the flakes, which were identified by X-ray diffraction to be composed of hydrated lithium chloride and potassium carbonate. Both chlorine and carbon are constituents of the separator material.

The negative electrodes were also rigid and hard but covered with a loose film that could be easily washed out with a stream of water. X-ray diffraction identified the loose material to be a mixture of magnetite and elemental iron.

In summary, it appears that migration of iron particulates from the negative electrode resulted in the buildup of conducting paths that were responsible for the high self-discharge rates observed.

D. *Module Tested on a Driving Profile*

Examination was conducted on a ten-cell nickel/iron module (160 Ah) that was originally part of a 170-V battery system fabricated by Eagle-Picher Industries for the electric-vehicle application. The battery was life cycled on the "Pontiac" driving profile at 85% DOD at ANL in testing sponsored by the General Motors Corp. (GMC), Truck and Bus Division.⁹ In total, 897 cycles were imposed on this battery before testing was suspended in accordance with the GMC direction. Approximately 15 months later, testing was resumed under DOE sponsorship on a representative ten-cell module removed from the battery. After 1019 cycles, the module was able to deliver 98% of its rated capacity at the 2-h discharge rate, but failed to deliver the desired power (82 W/kg) when discharged to 85% DOD under the driving profile. The module was removed from test after 1050 cycles for post-test analysis.

Additional diagnostic tests on the ten-cell module were conducted after the life-cycle testing was completed. Reference electrode measurements were conducted to determine the limiting electrode under 2-h constant current discharge and the "Pontiac" driving profile. In both cases, the performance data indicated that the negative electrode was the predominant factor responsible for the loss in capacity and power capability. A lack of good contact between the current collector and active material in the negative electrode was observed. Other factors that contributed to the performance decline observed for this module include iron contamination of nickel electrodes, the formation of conductive particulate paths through the separators, and blistering of both positive and negative electrodes. Additional details concerning the results of this investigation can be found in Appendix E.

IV. INVESTIGATION OF THE EFFECT OF IRON ON NICKEL ELECTRODE PERFORMANCE

An in-depth investigation of the effect of iron on nickel electrode performance was conducted during 1985. Figure 5 shows the experimental results for nickel electrodes cycled under various conditions. When a nickel electrode was cycled against nickel counter electrodes in an iron-free environment, the nickel electrode showed good capacity and satisfactory charge/discharge efficiency (curve A). On the other hand, when a nickel electrode was cycled against an iron electrode, the capacity of the nickel electrode dropped by up to 25% (curves B and C). Furthermore, it was found that a significant amount of iron had been incorporated into the nickel active material to form a iron-nickel spinel. Experimental results also indicated that the presence of LiOH in the electrolyte solution can prevent some of the capacity loss of the nickel electrode. A series of experiments is planned to study methods of preventing or minimizing the formation of the iron-nickel spinel.

Fig. 5.

Effect of Iron and Lithium Hydroxide on Nickel Electrode Performance

V. CONCLUSIONS

Post-test examinations of lead-acid cells and modules have provided needed information on the corrosion reactions and changes in electrode morphology that are associated with different degradation modes. These insights will aid in the interpretation of some of the failure modes that could develop in advanced cells which use the electrolyte flow-through principle.

Analyses of nickel/iron modules have shown that the predominant failure mode is loss in capacity of the nickel electrode caused by "iron poisoning." Work at ANL has identified the iron compounds that may deactivate the electrode surface. Recent tests of lithium hydroxide additions to the electrolyte have proven effective in restoring some of this capacity loss. Additional investigations are needed, however, to establish the iron transport mechanism and to develop viable solutions to overcome this degradation effect.

Post-test analyses of aqueous electric-vehicle batteries will be continued. The future efforts on the post-test analyses and investigations will focus on two areas: (1) the development of new techniques to measure the distribution and composition of the electrode phases and (2) the identification of mechanisms by which iron is transported to the nickel electrode, where it forms an inactive nickel-iron oxide compound. The latter information should permit identification of a method for preventing the iron contamination of the nickel electrode, thereby improving the nickel/iron battery performance.

REFERENCES

1. J. E. Battles, J. A. Smaga, and J. J. Marr, "Post-Test Analyses of Na/S Cells and Aqueous Batteries," Proc. of First Int. Workshop on Battery Testing, September 30-October 2, 1985, Heidelberg, Germany, pp. 136-138 (1985).
2. A. C. Simon, S. M. Caulder, and J. T. Stemmle, J. Electrochem. Soc. **122**, 461 (1975).
3. B. K. Mahato and J. L. Strebe, "Positive Grid Corrosion in a Deep-Discharge Cycled Lead-Acid Battery Part I: Cycling of Bare Antimonial Grid," Proc. of Symp. on Advances in Lead-Acid Batteries, K. Bullock and D. Pavlov, eds., Electrochemical Society, Vol. 84-14, pp. 154-165 (October 1984).
4. B. K. Mahato and J. L. Strebe, "Failure Characterization of Deep Cycled Lead-Acid Batteries: Part II, Positive Plate Grid Corrosion," Extended Abstracts, Electrochem. Soc. Fall Meeting, Las Vegas, NV, October 10-14, 1985, p. 67 (1985).
5. C. C. Christianson et al., *Testing and Development of Electric Vehicle Batteries for EPRI Electric Transportation Program, Technical Report for November 1982 through December 1984*, Argonne National Laboratory Report ANL/OEPM-85-4 (November 1985).
6. Johnson Controls, Inc. *Annual Report for 1985 on Research, Development and Demonstration of Lead-Acid Batteries for Electric Vehicle Propulsion*, Argonne National Laboratory Report ANL-86-12 (March 1986).
7. W. Borger and U. Hullmeine, "The Influence of Lampblack on Capacity Retention in Pb/PbSO₄ Electrodes with Forced Flow of Electrolyte," Proc. of Symp. on Advances in Lead-Acid Batteries, K. Bullock and D. Pavlov, eds., Electrochemical Society, Proceedings Vol. 84-14, pp. 302-313 (October 1984).
8. Eagle-Picher Industries, Inc., *Annual Report for 1984 on Research, Development, and Demonstration of Nickel/Iron Batteries for Electric Vehicle Propulsion*, Argonne National Laboratory Report ANL/OEPM-85-3 (August 1985).
9. M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1984*, Argonne National Laboratory Report ANL-85-9, pp. 38-39 (February 1985).

APPENDIX A

POST-TEST ANALYSIS REPORT FOR LEAD-ACID
BATTERY GU06IL37

At the National Battery Test Laboratory (NBTL), an EV-3000 lead-acid module manufactured by Globe Union (now part of Johnson Controls, Inc.) was subjected to charge/discharge cycling at 30% depth-of-discharge (DOD). Upon completion of the test, the module was sent to the ANL Post-Test Analysis Laboratory for failure analysis. Visual examination, physical analyses, and chemical analyses were performed on the module. In this appendix, quantitative data regarding grid corrosion, shedding, and softening of the positive active material, changes in negative electrode material, and electrode morphology changes are provided and discussed.

1. Battery History

This EV-3000 lead-acid module (six cells) was delivered to NBTL by Globe on January 18, 1983, and had the following characteristics:

<u>Wt</u> (kg)	<u>Rated Capacity</u>		<u>Demonstrated Capacity</u>		<u>Specific Energy</u>
	(Ah)	(Wh)	(Ah)	(Wh)	(Wh/kg)
76.6	240	2822	252	2946	38.4

The module was tested exclusively at 30% DOD to determine its cycle life. The testing was initiated in February of 1983. By December 20, 1984, the module achieved 1506 cycles, and the capacity declined to less than 75% of its initial value. The module had been placed on standby since then.

2. Electrical Testing

On May 16, 1985, testing was resumed on the module. Battery capacity and individual cell voltages were measured. The capacity was found to be only 69.5% of its rated value. Individual cell voltages are shown in Fig. A-1. As indicated by these curves, cell 3 had a relatively low voltage by the end of discharge; cell 4 not only discharged to a low voltage but also could not be recharged.

Half-cell potential measurements were conducted on cells 3 and 4. The discharge/charge curves for the positive and negative electrode of cell 3 are shown in Fig. A-2. The sharp drop in the positive electrode potential with respect to the $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode at the end of discharge indicates the limiting effect of the positive electrode. Reference electrode measurements for cell 4 are shown in Fig. A-3. These curves reveal that both positive and negative electrodes could not be charged. This was especially true with the positive electrode.

Fig. A-1.

Cell Voltage Curves for Module
GU06IL37

Fig. A-2. Half-Cell Potential of Cell 3 (with respect to $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode)

Fig. A-3. Half-Cell Potential of Cell 4 (with respect to $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode)

3. Teardown Analysis

The module was fully charged prior to post-test examination. The case of the module bulged slightly--about 1.3 cm on each end. The specific gravities of the electrolytes in all cells ranged from 1.292 to 1.300. The electrolyte circulation pumps were in good working condition. Four of the six cells (Nos. 3, 4, 5, and 6) were disassembled and carefully examined. General observations of the cells are as follows:

Cell 3

Some sediment was found suspended in the bulk electrolyte. The mud well on the bottom of the cell also contained shedded active material to a depth of 8 mm. The paste of active materials on both positive and negative electrodes was uneven. One side of the grid had a heavy application, and the other side had a light application. (This observation was also true for the other cells.)

The negative electrodes in the cell were in fairly good condition. Drawing a spatula across the electrode surface produced a lustrous metallic sheen. Mossy lead deposits had formed on the top of the plates and averaged 1 cm in height. Much smaller deposits were found on the side and the bottom of the plates. A light grayish-brown precipitate, which was later identified as PbSO_4 , was observed on the entire exterior as well as the inside edges of all the negative separators.

The positive grids were severely corroded. The grids had broken into pieces and adhered to the separators when the separator was lifted from the underpasted side of the positive electrode. Active material shedding occurred at the top and sides of the positive plates, leaving ~1.5 cm of exposed grid perimeter. Although the bulk of the active material remained hard and firm, it was easily separated from the grid. This observation indicated that the active material did not maintain adequate physical contact with the grid and, therefore, could not contribute totally to the capacity.

Cell 4

All of the positive electrodes were in deteriorated condition. The active material was weak, and the grids were badly corroded. Some separators were brittle, and small cracks could be seen throughout each separator. The positive active materials that had been shedded from the electrode stack covered the bottom of the cell to a height of 0.6 cm.

The top of the negative plates had mossy lead deposits that averaged 1 cm in height. White spots were also observed on the surface of the negative plates. The two end plates had black dimples present on the outer surface. The active material could be easily removed from the grid in these discolored areas.

Cells 5 and 6

Cells 5 and 6 were in better condition than the other two cells. Virtually all of the negative electrodes from cells 5 and 6 were in fairly good condition and had a bright metallic shine when scraped. The one exception was the outer electrode in cell 6. This negative plate had an 8 x 20 cm (semi-circular shape) blistered area near the post.

The active material on the positive plates was soft on the surface but hard and firm at the core. Approximately 1.3 cm of bare grid was exposed on the top of the plates. The corrosion of the grids was moderate in comparison with cells 3 and 4. However, all the grids were thin and brittle and could be broken by the slightest bend.

4. Physical and Chemical Analyses

Physical and chemical analyses were conducted on all the active material, grids, and shedded materials from cells 4 and 6. The results from the lead compound analyses for the positive and negative active materials and the antimony analyses for the negative electrodes are shown in Tables A1-A3.

Table A-1. Lead Analysis for Positive Active Material

Cell No.	Comp., wt %	
	PbO ₂	PbSO ₄
4	72.7	20.3
6	89.1	10.3

Table A-2. Lead Analysis for Negative Active Material

Cell No.	Comp., wt %	
	Pb	PbSO ₄
4	59.0	37.8
6	73.2	22.9

Table A-3. Antimony in Negative Active Material

Cell No.	Sb, ppm
4	550 (general area) 880 (black dimple area)
6	340

Scanning electron microscopy of the positive active materials from the three examined cells (cells 3-5) showed that the firm active materials at the core were in normal condition with very few PbSO_4 crystals present (Fig. A-4). The softened active materials at the surface, on the other hand, had a well-formed coralloid structure of PbO_2 (Fig. A-5).

Fig. A-4. SEM Image of the Active Material Found at the Core of the Positive Electrode ($\sim 3000\times$)

Examination of the porosity of the positive electrode required approximately 1 cm^2 portions of positive active material to be cut from the top, middle, and bottom of the plate. Figure A-C shows cross sections of the positive plate at these different locations. In the middle of the plate, the porosity was greater at the outer portion than at the core. In contrast, both the top and the bottom plates sections were more dense and uniform in active material across the full cross section. Both of the perimeter samples were also thinner in cross section. These findings suggest that the process of active material shedding begins at the perimeter and progresses toward the center of the plate.

The amount of shedded active material in the mud wells of cells 3-5 measured 133, 138 and 110 g, respectively. Analysis by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) revealed that the shedded material consisted of PbO_2 and PbSO_4 . No antimony or other elements could be found.

All of the positive grids were severely corroded. X-ray radiographs showed broken wires throughout the grid and the frame. Slight bulges were also found on the side and at the top of the grid frame. Metallographic examination of the

Fig. A-5. Coralloid Structure Found Near the Surface of the Positive Electrode (~3000X)

positive grid cross section showed the existence of an outer corrosion layer, averaging $200\text{ }\mu\text{m}$ in thickness. The corrosion layer was found to be adherent to the grid, with most of the cracks perpendicular to the grid/paste interface (Fig. A-7).

All the negative electrodes developed separations along the interface between the grid wire and the active material (Fig. A-8). Spectrochemical analysis of the negative active materials indicated that the antimony content was high. This was especially true in cell 4. The high concentration of antimony suggested that a recharging problem might have occurred.

5. Conclusions

The failure of this module was attributed to the deterioration of both the positive and negative electrode.

The high level of PbSO_4 in the positive active materials is indicative of incomplete recharging of the electrodes. The factors that contributed to charging problems for the positive electrodes were severe grid corrosion and active material degradation. Grid resistivity was increased by corrosion-induced thinning and fracture of the grid wires. The PbO_2 scale also increased the resistivity of the electrodes. The formation of a coralloid structure adjacent to the interface further impaired charge acceptance and promoted shedding of the active materials.

Fig. A-6. Positive Plate Cross Sections at the Top (A), Middle (B), and Bottom (C) (~27X)

Fig. A-7. Thick PbO_2 Scale Found on the Corroded Grid Wire of a Positive Electrode (60X)

Fig. A-8. Poor Adhesion of the Negative Active Material to the Negative Grid (60X)

Performance of the negative electrodes was affected by the presence of antimony and poor adhesion between the grids and active materials. The unusually high antimony concentration in the negative active materials indicates that the antimony present in the positive grids was anodically dissolved during operation and had plated onto the surface of the negative electrodes. The antimony "poisoning" of the negative electrode might have reduced the negative charging efficiency. Meanwhile, weak adhesion of the negative paste and grids also contributed to the increase of negative electrode resistance and reduced the charging efficiency. These observations would explain the extremely low content of free lead found in the negative active materials.

The deterioration of the positive separator in cell 4 was probably caused by excessive oxidation of the polyethylene. High levels of oxidizing compounds, such as PbO_4 , can form during charging. Low electrolyte levels or poor charge acceptance by the positive electrode promote the formation of these compounds. In the case of cell 4, separator embrittlement probably resulted because of the latter condition.

APPENDIX B

POST-TEST ANALYSIS REPORT FOR LEAD-ACID
BATTERY GU06IL54

One Globe Union (now part of Johnson Controls, Inc.) lead-acid module (EV-2300, improved state-of-the-art design) was tested in series with three other modules and cycled at NBTL until its capacity declined to 95% of the original capacity. The module was then removed from the testing pack and delivered to the ANL Post-Test Analysis Laboratory for teardown inspection. Visual examination, as well as physical and chemical analyses, was performed on the module. In this report, investigations of the structure, composition, and phase relationships of various components within the battery plates will be discussed.

1. Battery History

The module (six cells) was delivered to the NBTL by Globe on August 29, 1984, and had the following characteristics:

<u>Weight</u> (kg)	<u>Rated Capacity</u>		<u>Demonstrated Capacity</u>		<u>Specific Energy</u> (Wh/kg)
	(Ah)	(Wh)	(Ah)	(Wh)	
58	183	2156	184	2145 (C/3)	37.0
			145	1650 (120-A discharge rate)	28.4

This module was one of four tested at NBTL to study the changes in electrode morphology with cycle life. After 212 cycles at 120-A discharge rate to 80% DOD, the capacity of the module had dropped to 95% of its rated capacity. The module was then removed from the testing pack for post-test investigation.

2. Electrical Testing

Individual cell capacity and half-cell potentials were measured after the module was separated from the testing pack. Individual cell capacities are shown in Table B-1. Cell 4 had a relatively low capacity, and the capacity of cell 6 maintained 100% of its initial value. The half-cell potential measurements of cell 4 are shown in Fig. B-1. The potential of the negative electrode remains virtually constant, whereas the potential of the positive electrode shows a large decrease toward the end of the discharge. The capacity decline of the cell, therefore, might be associated with the electrochemical processes occurring at the positive electrode.

3. Teardown Analysis

The module was fully charged prior to the post-test examination. After delivery to the Post Test Analysis Laboratory, cells 4 and 6 were disassembled and carefully examined. Similar results were observed for both cells during the teardown. The specific gravity of the electrolyte was found to be around

Table B-1. Individual Cell Capacities for
Module GU06IL54^a

Cell No.	Cell Capacity, ^b Ah
1	138
2	141
3	142
4	136
5	140
6	145

^aOriginal module capacity was 145 Ah.

^bAt 120-A discharge rate.

Fig. B-1. Half-Cell Potential of Cell 4 (with respect to Hg/Hg₂SO₄ reference electrode)

1.250, which was slightly lower than normal. The electrolyte circulation insert pumps were in perfect working condition, and the amount of shedded active materials in the pump chambers was negligible. In addition, the quality of the cell assembly was excellent. No mechanical defect or interelectrode short circuiting was detected.

All of the negative electrodes appeared to be in excellent condition, except for the first negative electrode in cell 6. This electrode had a semicircular blister area (15 x 4 cm) near the lug (Fig. B-2). The lead exhibited a bright, metallic shine when it was scraped, a sign that usually indicates a good electrode. However, the pasting process produced uneven negative electrodes. Figure B-3 represents the two sides of a negative electrode. It can be seen that one side is underpasted, leaving grid wires visible, while the reverse side is overpasted.

Fig. B-2. Blistered Area Beneath the Post on the Outer Negative Plate of Cell 6

All of the positive electrodes were found to be in relatively good physical condition as well. The positive active materials were rigid and hard. No appreciable softening of the positive active material was found. Distribution of the active material on the positive grids was again nonuniform because of the pasting process used. The positive active materials collected from the mud wells of cells 4 and 6 were 18.6 and 24.2 g, respectively. Although all of the grid wires were intact, the paste-to-grid adhesion was not of the desired strength. More than 60% of the pellets broke loose from the grid wire when the electrodes were subjected to a slight shake. This is probably due to both the minor grid corrosion, which is discussed below, and the uneven pasting of the positive active materials.

Fig. B-3. Underpasted Side (top) and Overpasted Side (bottom) of Typical Negative Electrode

4. Physical and Chemical Analyses

Both physical and chemical analyses were performed on all of the active materials. The results of the BET surface area measurement, the lead compound analyses for the positive and the negative active materials, and the antimony analyses are shown in Tables B-2 to B-5.

Table B-2. BET Surface Area Measurement of the Active Material

Cell No.	Surface Area, m ² /g	
	Negative	Positive
4	0.72 ± 0.07	1.37 ± 0.14
6	0.57 ± 0.06	1.81 ± 0.18

Table B-3. Lead Analysis for Positive Active Material

Cell No.	Comp., wt %	
	PbO ₂	PbSO ₄
4	86.05	10.06
6	92.65	6.06

Table B-4. Lead Analysis for Negative Active Material

Cell No.	Comp., wt %	
	Pb	PbSO ₄
4	92.58	5.59
6	93.37	5.75

Table B-5. Antimony in the Active Material

Cell No.	Antimony, ppm	
	Negative	Positive
4	77	85
6	168	137

The results of the morphology studies were similar for the negative electrodes in both cells. Scanning electron microscopy of the negative active material revealed no noticeable change in particle morphology (Fig. B-4). Metallographic examination of the negative-electrode cross section indicated that the interface between the grid and the active material was generally good. Neither corrosion layer nor gaps could be found (Fig. B-5).

Fig. B-4. SEM Image of the Active Material from a Negative Electrode (6000X)

Electron micrographs of polished cross sections of specimens collected from top, middle, and bottom parts of the positive plate showed that greater porosity developed at the outer layer than at the core (Fig. B-6). However, the morphology of the active material at all locations was normal (Fig. B-7). No evidence was found for the development of a coralloid structure in the PbO_2 .

Although X-ray radiography of the positive electrode revealed that all of the positive grids were intact, metallographic examination of the grid cross section indicated that a layer of oxide, ranging from 20 to 50 μm in thickness, had developed around the grid (Fig. B-8). This finding suggests that grid corrosion had begun.

5. Conclusion

The results of the post-test investigation indicated that all of the components in this module were in relatively good condition. The 5% capacity loss of the module was probably due to the minor positive grid corrosion and the "less than desirable" adhesion between the positive active material paste and the positive grid wires.

Fig. B-5. Cross-Sectional View of the Negative Grid Wire (65X)

Fig. B-6. Cross-Sectional View of the Positive Electrode (22X)

Fig. B-7. SEM Image of the Active Material from the Positive Electrode (3000X)

Fig. B-8. Cross-Sectional View of the Positive Grid Wire (75X)

APPENDIX C

POST-TEST ANALYSIS REPORT FOR LEAD-ACID
MODULE GU06IL521. Battery History

The EV-2300 lead-acid module (six cells) was one of a group of four modules delivered to NBTL by Johnson Controls (JCI) on August 29, 1984, to study changes in electrode morphology with cycle life. The initial performance of the module is summarized in Table C-1. The module was tested at a 120-A discharge rate to 80% DOD. After 384 cycles, the capacity of the module declined to 81% of its initial value, and tests of the module were terminated. The module then received occasional boost charges and capacity checks at the 3-h rate during the next two months. Five additional cycles at the 120-A discharge rate determined that the capacity of the module at that point had further declined to 68% of its original value.

Table C-1. Initial Performance of JCI EV-2300 Lead-Acid Module (GU06IL52)

<u>Rated Capacity</u>		<u>Discharge Rate</u>	<u>Demonstrated Capacity</u>		<u>Specific Energy, Wh/kg</u>
Ah	Wh		Ah	Wh	
183	2156	C/3 (61 A)	184	2145	36.9
		120 A	145	1650	28.4

2. Electrical Testing

During the final five cycles, voltage measurements were also made for the individual cells, and the voltage traces are shown in Fig. C-1. The trace for cell 5 shows that this cell went into voltage reversal during discharge. Reference electrode measurements of cell 5 indicated that its capacity was limited primarily by the positive electrode (Fig. C-2). The module was then given a final charge and sent to the Post-Test Analysis Laboratory for examination.

3. Teardown Observations

The external condition of the module was good. No case distortion or electrolyte leakage was observed. The specific gravity measurements of the electrolyte from the six cells ranged between 1.265 and 1.286. Cells 4-6 of the module were disassembled and examined. Visual inspection upon their disassembly revealed the following:

Fig. C-1

Individual Cell Voltages for Module
GU06IL52

Fig. C-2. Half-Cell Potential for Cell 5

Cell 4

The electrolyte circulating pump was in good working condition. All of the negative electrodes were in excellent condition. The lead exhibited a bright metallic shine when it was scraped. The positive electrodes were in fair-to-good condition. The grids were intact. The positive active materials were soft on the surface but hard and firm at the core. Very small quantities of loose active materials were observed on the bottom edge of the plates. The mud well at the bottom of the cell contained shed active materials to a depth of 5 mm.

Cell 5

The negative electrodes in this cell were discolored. Both white and black spots were observed on the surface of the electrodes. Small holes and cracks were also noticed on the electrode at the grid intersection. The lead, however, still exhibited a metallic luster when a spatula was drawn across the electrode. This was especially true for the upper half of the negative electrode.

The positive electrodes in this cell were in deteriorated condition. The grids were severely corroded. Active material shedding was especially severe at the bottom of the plates and resulted in 5-mm bands of exposed grid wires. Except for the first positive plate, which had a thin and firm layer of active material near the grid, the rest of the positive active material in this cell had little mechanical strength.

Cell 6

The observations for this cell were similar to those for cell 4. The only difference was that the positive grid corrosion was somewhat more extensive in cell 6. The grid network readily broke into several pieces when it was lifted.

4. Physical and Chemical Analyses

Samples of the active materials and grids from cells 4 and 5 were collected and subjected to physical and chemical analyses. X-ray radiography of the positive grids showed that the grid from cell 4 was in reasonably good condition. For the grid from cell 5, on the other hand, broken wires were found throughout the grid structure (Fig. C-3). Comparisons were made to a previously examined positive grid from cell 6 in module 54. (The capacity of this cell was still 100% of rated capacity when testing of the module was halted after 212 cycles.) The positive grid wires from cells 4 and 5 had cross-sectional areas that were reduced to 65 and 45%, respectively. Cross sections through typical grid wires are shown in Fig. C-4.

The results of tests to characterize the positive active materials from both cells are listed in Table C-2. The lead compound analyses performed on representative samples indicate that both cells have relatively low PbSO_4 levels in the positive electrodes and are roughly equivalent in overall composition. Morphological investigations of the active materials found that the firm active materials at the core retained a normal structure (Fig. C-5), but the softened active materials on the surface had developed a well-formed coralloid structure of PbO_2 (Fig. C-6). The development of the coralloidal structure was more extensive for the positive electrodes of cell 5. The degree of active material shedding is related to this structural conversion, and the quantity of PbO_2 and PbSO_4 found in the mud well of cell 5 was 45% greater than the amount found in the mud well of cell 4.

Both BET and mercury porosimetry measurements were made to further characterize the structure of the positive electrodes. As shown in Table C-2, the positive active material in the weaker cell, No. 5, had a much higher BET value than that from cell 4. However, the positive active material for cell 5 had a smaller pore volume than the material from cell 4. Our experience with these analytical techniques indicates that the values for pore volume provide better correlations with individual cell capacity. Specifically, lower pore volumes are found for cells with lower capacities.

The chemical and physical analyses conducted on the negative active materials are summarized in Table C-3. The lead compound analyses indicate that only minor sulfation of the negative electrodes occurred in both cells. The surface area and pore volume measurements yielded values that are within the

Fig. C-3. X-Ray Radiographs of Positive Plates from Cell 5 (left) and Cell 4 (right).
(Notice the distorted and broken grid wires in the plate from cell 5.)

Fig. C-4. Cross-Sectional View of Positive-Grid Wires
from Cell 4 (top) and Cell 5 (bottom) (75X)

Table C-2. Analysis of Positive Active Materials from Module 52

	Cell	
	4	5
PbO ₂ , wt %	90.72	91.30
PbSO ₄ , wt %	7.48	5.88
Shed Mat'l, g	65.4	94.7
BET Surface Area, m ² /g	1.51±0.15	2.04±0.20
Pore Volume, cm ³ /g	0.172	0.148

Fig. C-5. SEM Image of Positive Active Material from the Core (3000X)

ranges observed for electrodes in good condition. Scanning electron microscopy provided visual confirmation of these analyses. Spectrochemical analyses of the negative active materials did show antimony concentrations of 350-400 ppm, a level at which charging inefficiency is believed to occur; however, the negative electrodes for both cells showed no evidence that this condition existed.

5. Conclusions

The capacity of this module was limited by the positive electrodes. In both of the examined cells, the negative electrodes remained in good condition, but the positive electrodes showed unmistakable signs of advanced degradation. One form

Fig. C-6. SEM Image of Positive Active Material from the Surface (3000X)

Table C-3. Analysis of Negative Active Materials from Module 52

	Cell	
	4	5
Pb, wt %	91.79	94.31
PbSO ₂ , wt %	6.16	5.08
Antimony, ppm	400±40	350±35
BET Surface Area, m ² /g	0.50±.05	0.47±.05
Pore Volume, cm ³ /g	0.232	0.172

of degradation was severe corrosion of the positive electrode grids. The reduction in grid-wire diameters undoubtedly contributed to an overall resistance rise for the module. In addition, the positive active material developed an extensive coral-loidal network that extended from the interface to the central core of the electrode. This type of structure was more pronounced for the electrodes of cell 5, the weaker cell. Surface area and pore volume measurements indicate that cell capacity is more closely associated with the latter measurement. This finding suggests that the loss in electrolyte volume within the positive plates is a critical factor that limits cell capacity.

APPENDIX D

POST-TEST ANALYSIS REPORT FOR LEAD-ACID
MODULE GU06IL511. Battery Test History

This EV-2300 lead-acid module (six cells) from Johnson Controls, Inc., was the third and the last module removed from a group of four modules tested at 120-A discharge rate. The purpose of this test was to study the change of electrode morphology with cycle life. The module had achieved 482 cycles before its capacity had fallen below 75% of its initial value, which was the termination criterion for this module. Measurements of individual cell capacities indicated that cells 1 and 5 were the strongest and weakest cells, respectively, in terms of Ah capacity (Table D-1). As shown in Fig. D-1, reference electrode measurements of cell 5 showed severe capacity losses for both sets of electrodes. In addition, it is apparent from this figure that cell voltage reversal was occurring during discharge. A review of the average discharge voltage for this module indicated that this condition began around the 450th cycle and eventually lowered the average discharge voltage by more than 20%. Normal operation continued, however, because the module voltage still remained above the preset discharge cut-off voltage.

Table D-1. Individual Cell Capacities for
Module GU06IL51

Cell No.	Cell Capacity, Ah	Capacity Decline, ^a %
1	121.00	16.55
2	79.14	45.42
3	101.90	29.72
4	119.90	17.31
5	24.00	83.45
6	68.34	52.87

^aBased on 80% of the rated capacity (155 Ah).

2. Teardown Observations

The module was fully charged prior to the post-test examinations. The external condition of the module was good. The specific gravities of the cells were slightly low, ranging from 1.217 to 1.244. Visual examination of cell 1, the strongest cell, revealed that both positive and negative electrodes were in reasonably good condition. As shown in Fig. D-2, the positive grid corrosion was moderate for cell 1. The positive active materials were soft on the surface but

Fig. D-1. Reference Electrode Measurements of Cell 5

hard and firm at the core. Loose active material was only found near the tab of the plates. Upon visual observation, all of the negative electrodes also appeared to be in good condition, except for the outermost negative electrode, which had nearly 1 cm of mossy lead present on the top of the plate. The lead exhibited a bright metallic shine when scratched.

The examination of cell 5, on the other hand, showed that all of the electrodes (both positive and negative) were heavily degraded. In addition to one positive plate that was partially broken at the tab, the positive grids were severely corroded (Fig. D-2) and the positive active materials were soft throughout the plate. Loss of active materials occurred along the edges of all the positive plates, leaving 0.6 to 1.3 cm of exposed grid perimeter. The negative electrodes had a coarse and a dull appearance, with white spots due to sulfation present on the surface of the electrodes. Approximately 0.6 cm of mossy lead was found on the top of every negative plate in this cell.

3. Physical and Chemical Analyses

The results of the physical and chemical analyses of the two examined cells are summarized in Table D-2. Lower cell capacity could be correlated with a number of the analytical findings, including increased PbSO_4 concentrations in the electrodes, higher antimony concentration for the negative active material, and reduced pore volume of the positive active material.

Fig. D-2. Comparison of Positive Grids from Cell 1 (top) and Cell 5 (bottom) (75X)

The lead compound analyses showed that the sulfation of the active materials (both positive and negative) was moderate for both cells. Morphological studies, however, indicated a noticeable amount of PbSO_4 crystal present on the surface and in the interior of the negative electrodes of cell 5 (Fig. D-3). X-ray diffraction analysis also supports this observation

Table D-2. Analysis of Active Materials of Module 51

	Cell ^a	
	1	5
Pos. Electrode		
PbO ₂ , wt%	95.60	86.17
PbSO ₄ , wt%	3.79	7.10
Pore Volume, cm ³ /g	0.185	0.133
Shed Mat'l, g	68.40	98.60
Neg. Electrode		
Pb, wt%	96.45	93.72
PbSO ₄ , wt%	2.05	5.97
Antimony, ppm	417	812
Pore Volume, cm ³ /g	0.212	0.212

^aCapacity was 121.0 Ah for cell 1 and 24.0 Ah for cell 5. See Table D-1.

The concentrations of antimony in the negative electrode were high in both cells, especially for cell 5. The 812 ppm level found in this cell is much greater than the value believed to be sufficient to cause antimony "poisoning," a condition that promotes charging inefficiency.

4. Conclusions

Post-test examinations revealed that the performance decline of the module could be traced to the failure of cell 5. The performance degradation of this cell was primarily attributed to the condition of the negative electrodes. Extremely high content of antimony was observed in the negative active material of cell 5. This antimony "poisoning" is believed to reduce the charging efficiency of the cell.

Other forms of degradation were also observed for cell 5, including low pore volume of the positive active material and severe corrosion of the positive grids. Both of these factors are known to limit the performance and lifetime of lead-acid batteries.

(A)

(B)

Fig. D-3. Negative Active Materials of Cell 5
(A) Surface (1000X)
(B) Inside (3000X)

APPENDIX E

POST-TEST ANALYSIS REPORT FOR NICKEL/IRON
MODULE EG10FN071. Battery History

A nickel/iron battery of 140 cells was delivered to NBTL on October 7, 1981, and had the following characteristics:

Weight	Rated Capacity*		Demonstrated Capacity*		Specific Energy
	(kg)	(Ah) (Wh)	(Ah) (Wh)	(Wh)	(Wh/kg)
47.6	160	1980	165	2012	42.3

*At 2-h discharge rate.

The GM/Eagle-Picher battery accumulated 987 cycles in life-cycle tests with the "Pontiac" driving profile before operation was discontinued in December 1983. Subsequently, a decision was made to test a 10-cell module composed of well-matched cells from this battery. Fifteen months elapsed from the time that battery operation was halted to the time that module testing began. Cells 5, 6, and 1 in the module were electrically bypassed at cycles 936, 960, and 1004, respectively, because of unacceptable losses in capacity. The remaining seven cells had a measured capacity at the 2-h rate of 156 Ah after 1019 cycles. The module, however, failed to deliver the desired power when discharged to 85% of its rated Ah capacity under the driving profile discharge. Diagnostic tests indicated that the module was peak-power limited. In an attempt to improve the power capacity of the module, all of the cell interconnectors were cleaned, and LiOH was added to the electrolyte to bring the concentration up to 1.0 molar from a minimum of 0.79 molar. However, only slight improvement was realized, and the module was removed from the test program after 1050 cycles for failure analysis at the Post-Test Analysis Laboratory.

2. Diagnostic Tests

Additional diagnostic tests on the module were conducted by NBTL staff after the life-cycle testing was completed. A reference electrode was inserted in Cell 3 to determine the limiting electrode under the 2-h constant current and the "Pontiac" profile conditions. The results of these tests are shown in Figs. E-1 and -2, respectively. In both cases, the performance data suggested that the negative electrode was the predominant factor responsible for the loss in Wh capacity of the cell.

3. Teardown Observations

The module was fully charged before it was delivered for post-test analysis. The individual cell voltages were measured, and the results are shown in Table E-1. Cells 1, 6, and 7 were disassembled and examined. Visual examination showed no distortion or expansion for any of the three cell cases. The

Fig. E-1. Half-Cell Potentials for Cell 3 at the 2-h Rate

Fig. E-2. Half-Cell Potentials for Cell 3 under the "Pontiac" Profile

Table E-1. Individual Voltages for the Cells of Module EG10FN07

Cell No.	Voltage, V
1	1.2708
2	1.4830
3	1.4791
4	1.4832
5	1.2822
6	1.2637
7	1.4845
8	1.4880
9	1.4597
10	1.4623

electrolyte level was low, and less than 100 mL of free electrolyte could be collected from each cell instead of the expected 400 mL. The mud wells on the bottom of the cells contained some sludge, but there was no evidence of short-circuit paths through the sludge.

Visually, the positive electrodes in Cell 7 appeared to be in fairly good condition. The positive electrodes in Cells 1 and 6, on the other hand, had developed large blisters on one side of each electrode (Fig. E-3). The blistered area ranged from 10-20% of the total surface area in Cell 1 to 30-40% in Cell 6.

All of the negative electrodes were blistered severely, ranging from 20% to 40% of the total surface area. In some instances, more blistering was noticed on the center plate of the cell, which might be related to the heat generation. Figure E-4 shows the appearance of a blistered negative electrode.

All of the separators remained in good mechanical condition; however, large areas of the separators were discolored, as shown in Fig. E-5. The discoloration ranged from light brown to varying degrees of gray-brown to black. The pattern of discoloration tended to reproduce the blistered appearance of the corresponding electrodes. This was especially true for the central region of a separator. Toward the perimeter, the degree of separator discoloration was often greater than the degree of blistering found for the corresponding regions of the electrodes.

4. Physical and Chemical Analyses

Samples of the active materials, current collectors, and separators from all three cells were collected and subjected to physical and chemical analyses. Metallographic examination of the electrodes indicated that the positive current collectors were in excellent condition (Fig. E-6). No corrosion layers or gaps could be found around the current-collector samples. The negative current collectors also showed no evidence of corrosion. However, gaps had developed between the current collector and the active materials, as shown in Fig. E-7. This was especially true in Cell 7.

Fig. E-3. Blistered Nickel Electrode

Fig. E-4. Blistered Iron Electrode

Fig. E-5. Typical Separator as Viewed from the Negative Electrode Side

Fig. E-6. Cross-Sectional View of a Positive Current Collector Wire (390X)

Fig. E-7. Cross-Sectional View of a Negative Current Collector Wire (50X)

Analysis of the active materials by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) found that a significant amount of iron was incorporated into the active material of the nickel electrode. Much of the iron was present as a subsurface layer. The iron content in this zone or layer was ~40 wt % in Cells 1 and 7 and 30% in Cell 6. X-ray diffraction analysis of this layer suggested that an oxide solid solution of the type $\text{Fe}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ had formed. This compound had a lattice constant of 0.836 ± 0.001 nm. Particles of $\alpha\text{-Fe}$ and Fe_3O_4 were also found on the surface of the nickel electrodes.

Iron-rich particulate was also found on surfaces and in the interior of the separator. The localized concentration of particulate was higher in areas of severe separator discoloration. In addition, Fig. E-8 shows that the quantity of particulate within a cross section of the separator decreases from the iron interface to the nickel-oxide interface. The separator particulate was also identified as a mixture of $\alpha\text{-Fe}$ and Fe_3O_4 . Cells 2, 8, and 10 of this module were disassembled and examined after standing for three weeks to better understand the effect of the above-mentioned deposits on self-discharge. The voltage declines of the cells are shown in Table E-2. A reasonably high-charged state was maintained in Cell 8. Cell 2, on the other hand, was near the fully discharged state. Table E-2 also includes the results of analyses conducted to determine the weight percent of iron found in these separators. Representative samples were examined by SEM-EDS, and the sizes of the iron and chlorine peaks in the spectrum were compared. The values listed in Table E-2 assume that the polyvinyl chloride material used

Fig. E-8. SEM Image (top) and Iron K_{α} Image (bottom) of the Same Cross-Sectional Area of a Separator. (The iron electrode was to the left) 360X

Table E-2. Self-Discharge of Cells During Three Week Period and the Iron Content Found in Corresponding Separator Samples

Cell No.	Voltage Decline, mV	Iron Content, wt %
8	82.4	10.7
10	151.4	10.8
2	227.0	15.7

for these separators is 56.7 wt % Cl. The data show that the iron content for the sample from Cell 2 is more than 45% greater than found for the samples from Cells 8 and 10. This finding indicates that a correlation existed between the degree of self-discharge and the quantity of the iron deposits in the separator.

5. Conclusion

The condition of the negative electrodes was the primary cause for the loss of power capacity in the ten-cell module. The negative electrodes showed a loss of contact between the current collectors and the active material mass. In addition, the negative electrodes developed severe blisters during operation, a condition which further increased electrical resistance within the electrodes. Other forms of degradation were also observed for module EG10FN07, including iron contamination of nickel electrodes, the formation of conductive particulate "bridges" through the separators, and blistering of the positive electrodes.

The finding of iron deposits on the surface and in the interior of the separator suggests that the migration of iron-rich particulate through the separator could be the mechanism by which iron is transported from the iron electrode to the nickel electrode. The nickel electrode then becomes "poisoned" when the iron is incorporated into the active material as part of a mixed oxide compound. If this transport mechanism is correct, the lower-than-expected performance of the nickel electrode in nickel/iron batteries can be improved by using separators with smaller pores or greater thickness.

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