ANL/OEPM-80-5

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DEVELOPMENT OF NEAR-TERM BATTERIES FOR ELECTRIC VEHICLES

Summary Report

October 1977—September 1979

ARGONNE NATIONAL LABORATORY

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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October 1977—September 1979

by

The Office of Electrochemical Project Management

June 1980

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FOREWORD

This work is done by the Argonne National Laboratory under contract W-31-109-Eng-38 to the Department of Energy. The work is part of DOE's Electric and Hybrid Vehicle (EHV) Research, Development and Demonstration Program in response to Public Law 94-413, mandated by the Congress in September 1976 and amended later by Public Law 95-238 in March 1978. The overall objective of the DOE's EHV program is commercialization and widespread use of EHV's beginning in the late 1980's, thus resulting in reduction of petroleum use in the transportation sector. Toward these objectives, five projects have been established. They are the (1) Market Demonstration Project, (2) Vehicle Evaluation and Improvement Project, (3) Electric Vehicle Commercialization Project (4) Hybrid Vehicle Commercialization Project and (5) Advanced Vehicle Development Project. The current near-term battery development effort is in support of the Electric Vehicle Commercialization Project.

The Office for Electrochemical Project Management (OEPM) is the Project Field Office responsible for the development of major near-term batteries amenable to commercialization in the late 1980's. The battery candidates are improved lead-acid, nickel/iron and nickel/zinc systems. The ANL/OEPM battery project is an industry-based approach whereby industry carries out a major part in the battery technology development and ANL/OEPM provides technical management and in-house support for battery verification testing and relevant support research.

ANL/OEPM initiated eight major industrial contracts for the battery technology development early in 1978: three in lead-acid, two in nickel/iron and three in nickel/zinc. Each contractor pursues a parallel, but differing technical approach offering promise of meeting the project objectives. The technical progress and the approaches will be critically assessed and a selection of the most promising technologies will be made in 1981. ANL/OEPM's National Battery Test Laboratory (NBTL) provides technology verification testing of the full-size cells, modules, and batteries delivered by the industrial contractors on a scheduled basis. ANL/OEPM also provides timely research support on those topics that are critical or generally applicable to the advancement of the technologies.

This summary report represents an interim progress report for the period of October 1977 through September 1979. The report summarizes the approach and results of the industrial contractor research and development, the verification testing at NBTL, the support research activities, the research and development in battery components, and the battery/vehicle system integration activities.

The Near-Term EV Battery Project is implemented at ANL through a team composed of management technical staff, and support personnel. Each team member provides a focused and expert contribution to the project. Members of the ANL/OEPM Battery Project Team responsible for specific management and task leadership areas are:

Dr. N. P. Yao, Project Manager and Director, OEPM
Mr. C. C. Christianson, Deputy Project Manager
Mr. F. Hornstra, Manager, NBTL
Mr. R. Elliott, Technical Monitor, Nickel/Iron Contracts
Dr. T. Lee, Technical Monitor, Lead-Acid Contracts
Dr. J. Miller, Technical Monitor, Nickel/Zinc Contracts
Dr. G. Cook, Group Leader, Battery Support Research
Mr. W. DeLuca, Group Leader, Battery Components
Mr. F. Foster, Contract Administrator
Mr. J. Geller, Quality Assurance Engineer

ACKNOWLEDGEMENTS

Support of this work was provided by DOE's Electric and Hybrid Vehicle (EHV) and Electrochemical Energy Storage Systems (EES) Divisions within the Office of Deputy Assistant Secretary for Conservation and Solar Energy. The DOE Headquarters Program Manager is Mr. W. H. Webster, with Mr. J. Purcell as the Field Manager at DOE/CORO.

Major technical contributions were made by ANL's industrial contractors, namely ESB, Globe-Union, Eltra, Westinghouse, Eagle-Picher, Gould, Energy Research Corporation, and Yardney Electric.

Members of the OEPM team who contributed sections of this report are N. P. Yao, J. B. Rajan, T. S. Lee, R. C. Elliott, J. F. Miller, F. Hornstra, G. M. Cook, W. DeLuca, K. W. Choi, V. J. Kremesec and J. J. Barghusen.

This report was compiled by J. B. Rajan under direction of and with input from C. C. Christianson. This report was edited by J. Harmon of the editorial group of the Chemical Engineering Division at ANL.

ABSTRACT

The status and results through FY 1979 on the Near-Term Electric Vehicle Battery Project of the Argonne National Laboratory are summarized. This project, under ANL's Office for Electrochemical Project Management (OEPM), conducts R&D on lead-acid, nickel/iron and nickel/zinc batteries with the objective of achieving commercialization in electric vehicles in the 1980's. The bulk of the R&D is performed by eight industrial contractors with support research in areas of critical need supplied by ANL. Other important project activities include performance verification testing of contractor supplied cells, modules, and batteries at ANL's National Battery Test Laboratory (NBTL), battery separator development, development of techniques for battery charging and state-of-charge determination, battery test in vehicles, and definition of battery application models.

Key results of the R&D indicate major technology advancements and achievement of most of FY 1979 performance goals. In the lead-acid system the specific energy was increased from less than 30 Wh/kg to over 40 Wh/kg at the C/3 rate; the peak power density improved from 70 W/kg to over 110 W/kg at the 50% state of charge; and over 200 deep-discharge cycle life demonstrated. In the nickel/ iron system a specific energy of 48 Wh/kg was achieved; a peak power of about 100 W/kg demonstrated and a life of 36 cycles obtained. In the nickel/zinc system, specific energies of up to 64 Wh/kg were shown; peak powers of 133 W/kg obtained; and a life of up to 120 cycles measured. Future R&D will emphasize increased cycle life for nickel/zinc batteries and increased cycle life and specific energy for lead-acid and nickel/iron batteries. Testing of 145 cells was completed by NBTL. Cell evaluation included a full set of performance tests plus the application of a simulated power profile equivalent to the power demands of an electric vehicle in stop-start urban driving. Simplified test profiles which approximate electric vehicle demands are also described.

EXECUTIVE SUMMARY

The Electric and Hybrid Vehicle Research, Development and Demonstration Act of 1976 (PL 94-413), later amended in March 1978 by PL 95-238, provides for the development of improved batteries for electric vehicle propulsion. This activity is performed as part of the Department of Energy's Electric Vehicle Commercialization (EVC) Project. The EVC Project consists of two main elements. The primary element is aimed at inducing electric car mass production through a business relationship with a major automobile manufacturer. The secondary element involves the commercialization of components and subsystems for use by the general EV industry. The development and commercialization of improved near-term batteries is a major part of the second element of the EVC Project. The Office for Electrochemical Project Management (OEPM) at Argonne National Laboratory (ANL) was given project management responsibility by DOE for the development of those improved battery systems considered to be suitable for near-term application in electric vehicles. Three battery systems were identified by OEPM as likely candidates for improvement and commercialization in electric vehicles by the mid 1980's. These were designated near-term batteries and are the lead-acid, nickel/iron and nickel/zinc types. The bulk of the R&D efforts on these batteries is carried out on a cost sharing basis by industrial organizations who were competitively selected by OEPM in 1977-1978. These contractors follow a pre-established statement-of-work and submit regular progress reports to OEPM. They also send cells, modules and batteries to the National Battery Test Laboratory (NBTL) at Argonne for test verification of their technical progress.

Associated project activities by OEPM include several interactive tasks collectively aimed at the development and commercialization of near-term battery technology. These technical activities include:

- -Verification testing of contractor fabricated cells and batteries at the NBTL
- -Battery analysis and optimization studies
- -Support research in areas of critical need
- -Post test analysis of cells and batteries
- -Development of supporting technologies such as separators, techniques for charging and state of charge monitoring
- -Preparation of battery application information for vehicle/system developer use
- -Monitoring of performance of improved near-term batteries in engineering test vehicles
- -Battery/vehicle system integration studies to ensure compatibility of R&D goals with vehicle needs

Both ANL and contractor tasks are well underway. Progress from project initiation to the end of FY 1979 are summarized in the following paragraphs:

Each of the three lead-acid battery contractors is pursuing a different technical approach which is aimed at developing batteries having improved specific energy, specific power, and life at an acceptable cost. For example, Eltra is emphasizing low cost and minimum maintenance through use of expanded lead-calcium metal alloy grids which lower self discharge and have a high corrosion resistance. They have developed a pilot line for continuous manufacture of electrodes utilizing these grids. ESB is pursuing definition of the optimum cell construction through use of factorial experiments which evaluate several construction combinations and design parameter variations. These include both flat plate and tubular plate positive electrodes. Globe-Union's approach emphasizes cell design optimization by means of a sophisticated computer model, and the use of an unique intracell electrolyte circulation system.

Lead-acid R&D objectives for FY 1979 were a specific energy of 39 Wh/kg, a specific power of 90 W/kg, and a cycle life of 300 cycles. A specific energy improvement from precontract values of less than 30 Wh/kg to over 40 Wh/kg at the 3-hour rate was demonstrated at NBTL. Peak specific power was increased from pre-contract values of 70 W/kg to 110 W/kg for a 30 second pulse with the battery at 50% state of charge. Cycle life at an 80% depth of discharge was demonstrated to be greater than 200 cycles.

The two nickel/iron battery contractors are also pursuing differing technical approaches. Westinghouse is emphasizing low initial cost through minimization in the amount of nickel used while still maintaining good performance. They use pressed, sintered steel wool electrode substrates in both electrodes thereby limiting the nickel to that required as the active material. They also utilize a central electrolyte circulation system for accomplishing thermal management, gas management, and easy electrolyte maintenance. Eagle-Picher is stressing high performance through use of a nickel electrode having a nickel substrate and a proprietary iron electrode developed by the Swedish National Development Company.

Nickel/iron R&D objectives for FY 1979 were a specific energy of 58 Wh/kg, a specific power of 110 W/kg, and a cycle life of 800 cycles. Both contractors achieved a specific energy of about 48 Wh/kg and a specific power of about 100 W/kg. Life cycle tests are underway with about 36 cycles having been demonstrated.

In the case of the nickel/zinc batteries, each of the three contractors is also pursuing a different technical approach. The Energy Research Corporation (ERC) is emphasizing low initial cost through use of plastic bonded electrodes which reduce the quantity of nickel needed. ESB is developing a battery with an unique vibrating zinc electrode in order to overcome the life limiting dendritic growth and shape change problems. Gould is developing a high performance battery based on the use of sintered nickel electrodes.

The nickel/zinc R&D objectives for FY 1979 were a specific energy of 65 Wh/kg, a specific power of 130 W/kg, and a cycle life of 200 cycles. Those objectives were essentially achieved except for cycle life where the best life demonstrated in NBTL was 120 cycles with most cells displaying a much lower life. However, no modules from ESB were evaluated in FY 1979 since the ESB nickel/zinc R&D contract was only initiated in April 1979.

A key part of the project is the performance verification testing at NBTL of contractor supplied cells, modules, and batteries. Standard test procedures have been defined for measuring specific energy, specific power, self-discharge rate, performance with a simulated power profile (based on an electric passenger car driven on the SAE J227a/D urban cycle), effects of partial depths of discharge, and battery cycle life. Contractor modules are submitted to these standard tests providing a common evaluation basis. As of the end of FY 1979, 145 cells from eight battery contractors had been tested. Specific energies measured varied from 35 to 41 Wh/kg for improved lead-acid batteries, 45 to 48 Wh/kg for nickel/iron batteries, and 35 to 64 Wh/kg for nickel/zinc batteries. Corresponding vehicle ranges based on simulated urban driving (J227a/D cycle) in a GE/Chrysler type electric car with regenerative braking are 74-79 miles for improved lead-acid batteries, and up to 96 miles for the nickel/iron battery. As of the end of FY 1979, simulated vehicle range tests were not yet completed on the nickel/zinc batteries. By comparison, the pre-contract state-of-the-art lead-acid battery (ESB EV-106) gives a simulated range of 60 miles. Comparative simulated vehicle range testing with and without regenerative braking indicate range increases of 18 to 31% with regenerative braking. All batteries tested show excellent charge acceptance of the regenerative braking current. Another significant finding by NBTL was that the temperature rise exhibited by nickel/zinc modules during discharge was proportional to the specific energy. Thus, as higher specific energies are achieved more attention must be devoted to thermal management. Present modules having a specific energy of 60 Wh/kg exhibit a 22°C temperature rise during a 3-hour discharge.

As of the end of FY 1979, 15 test stations were operational in NBTL with work underway to expand to 40 test stations. A typical cell/module test station has current capability of ± 500 amps and a voltage range of 0-12 volts. Capability of a battery test station is +350 amps, -500 amps and 10-120 volts.

The support research activities are directed at conducting basic and applied research in specific areas of critical need and complementing the research activities of the contractors. These activities include research efforts on improving performance and predicting failure modes by experimental studies and mathematical modeling related to electrode and cell design, determining the details of the electrode chemistry, and analyzing electrode behavior and cell operation.

Experimental and mathematical modeling has been carried out to provide design criteria describing the electrochemical and thermal behavior of electrodes and cells. In-situ measurements of reaction zone thickness demonstrate the design limitations on the electrode thickness. Mathematical modeling has provided design criteria relating electrode and electrolyte characteristics to the uniformity of reaction over the electrode surface. Thermal modeling has predicted the impact of cell dimensions on internal temperatures and has resulted in design changes in some contractor cells. Studies of new separator materials for nickel/zinc batteries have demonstrated materials capable of reducing zinc/zinc oxide electrode shape change and of increasing cell cycle life.

Studies of fundamental electrode chemistry are being carried out on the three battery systems. In lead-acid batteries the primary concern is active material utilization. Measurements are underway to define the physical-chemical nature of anodic films on lead and to identify the factors leading to loss of capacity and non-reversibility of active materials. Laser-Raman spectroscopy has been used for the in-situ identification of active materials and to monitor the direct oxidation of tetrabasic lead sulfate to PbO_2. In alkaline batteries electrode kinetics and thermodynamics are being surveyed to define the fundamental operating limitations of cells composed of various couples. Experimental studies of convection-limited porous zinc/zinc oxide electrodes have failed to verify the suggestion that OH^- depletion is a primary failure mode for that electrode.

The analysis of electrode behavior and cell operation is being carried out to obtain data needed to specify optimum operating conditions. Direct in-situ viewing of nickel/nickel oxide and zinc/zinc oxide electrodes has permitted observation of the initiation and growth of zinc dendrites and of the loss of electrical contact of active materials with the substrate as a function of operating conditions. Prompt post-test analysis of "failed" contractors batteries has been initiated to obtain quantitative measurements of the degree of cell failure and to identify possible future failure modes. Finally, methods developed for stibine measurement in 1978 led to the development of monitoring equipment and studies of stibine emissions from EV lead-acid batteries. These measurements indicated that only nominal precautions are required to maintain emissions in a safe range.

An important task in the area of Battery Components Research and Development is the definition of techniques for proper charging and also for monitoring the state-of-charge of the various near-term batteries. A knowledge of the acceptable and proper charging techniques is vital to achieving good battery life and efficiency, minimizing battery servicing needs, attaining acceptable recharge times, and meeting the AC power limitations and restrictions imposed by the electric utility service. Methods for monitoring battery state-of-charge are needed to provide information to the electric vehicle operator on the remaining distance that may be driven before battery charge depletion.

This task was initiated in FY 1979 and is now well underway. Two special purpose test stations were assembled which have the flexible charge and discharge features needed for this study. Preliminary studies are underway to evaluate rapid charging of lead-acid batteries, to assess the merits of individual cell equalization, and to determine the impact on battery performance of charging pulses produced by conventional SCR type chargers. In addition, the capabilities and limitations of various available state-of-charge monitoring approaches are being evaluated.

Another task in the Battery Components and Development area is devoted to the development of improved separators for nickel/zinc batteries. The proper separator properties are key to obtaining good cycle life and performance in the case of the nickel/zinc battery. Many separator materials and combinations are being evaluated by the Ni/Zn battery contractors with only limited success. This task, initiated by FY 1979, is directed at defining quantitatively the desired separator characteristics, assessing the suitability of available separators in meeting those characteristics, and enlisting through contract the expertise of a separator manufacturer to develop a separator with the required properties. This task effort is underway with contracting scheduled for FY 1980.

The Vehicle Integration and Engineering task in FY 1979 emphasized the testing of selected full-size nickel/iron and nickel/zinc batteries in vehicles in order to uncover any unexpected battery/vehicle interface problems. The Jet Propulsion Laboratory (JPL) performed the vehicle testing using batteries provided by ANL. The batteries selected included a nickel/ iron battery from Westinghouse and nickel/ zinc batteries from ERC and Yardney. No serious unexpected battery/vehicle interface problems occurred in the JPL testing and the vehicle test results correlated well with those projected on the basis of module tests at NBTL. Since the batteries utilized pre-1979 technology, reliability and life were short (as expected). Vehicle performance varied with the different batteries under the various driving modes. The range obtained at a constant 35 MPH, for example, was about 50% greater with the three nickel batteries than that obtained with the baseline state-of-the-art lead-acid battery. However, due to the early battery technology used, any vehicle performance data should be treated cautiously since it does not represent the capability of present day battery technology.

One of the battery/vehicle system integration tasks involved the definition of a simplified load profile for use in laboratory testing of batteries. The objective is a simple load profile composed of no more than four fixed current steps which subject the battery to load conditions equivalent to that imposed by an electric car being driven on schedule "D" stop/start cycle specified by the SAE J227a Test Procedure. Equivalency requires that the battery deliver the same watt-hours and amp-hours in the same total discharge time when exposed to either the exact vehicle power profile or the simplified profile. A methodology for defining a simplified profile having four current steps was derived and verified. Most battery manufacturers will be able to test batteries using this simplified profile with their present test equipment.

The development of a battery application model is another important task in the battery/vehicle system integration area. This effort, initiated in FY 1979, is emphasizing the development of simplified application models which portray the dynamic electric behavior of each of the near-term batteries. These models can be used by vehicle developers to simulate the behavior of the battery for purposes of designing or developing motors, controllers, and total vehicle systems. The models are in the form of equivalent electrical circuits and the electrical component values are determined as a function of the state-of-charge of the battery. The models use a semi-empirical approach where the equivalent circuit component values are selected such that the electrical output behavior of the model is the same as that measured on the battery for any specified state-of-charge. Preliminary results indicate that a simple electrical circuit model consisting of two resistors, a capacitor, and voltage source can simulate the electrical behavior of the various near-term batteries with acceptable accuracy. The results also show that the internal resistance of the nickel/iron and nickel/zinc and lead-acid batteries stays approximately constant for states-of-charge between 20 and 80%. As of the end of FY 1979, this modeling work was well underway and will be continued in FY 1980.

An important ingredient of the project is the dissemination of the knowledge gained from the R&D effort. To that end, a total of 65 publications consisting of reports, papers, and extended abstracts had been issued through FY 1979. A list of the publications is included at the end of the report.

I. INTRODUCTION

The increasing reliance on foreign import oil, the interruption of gasoline supply in the United States and the increasing levels of pollutants in urban areas due to automobiles resulted in the enactment by Congress of the Electric and Hybrid Vehicle Research, Development and Demonstration Act of 1976 (PL 94-413) and its amendment, PL 95-238, in March 1978. The Office for Electrochemical Project Manangement (OEPM) at Argonne National Laboratory (ANL) is assisting the Department of Energy (DOE)* in the research and development of near-term batteries for use in electric and hybrid vehicles being developed under this act. Overall objectives of the ANL project are to accelerate the development of the near-term battery technology, make available batteries of improved performance and lower cost for demonstration, and encourage industry to prepare for battery manufacture and commercialization.

In 1977, design and cost studies(1-9) were conducted by ANL on the specific energy, specific power, lifetime and cost capabilities of various batteries. The lead-acid, nickel/iron and nickel/zinc systems were identified as having potential for near-term electric vehicle application and commercialization. The R&D of these three systems is being conducted primarily by industrial firms under cost-sharing contracts with ANL/OEPM. OEPM provides the technical and project management of the contracts. In addition, OEPM provides the following: verification testing of contractor fabricated cells and batteries by the National Battery Test Laboratory (NBTL); post-test analyses of cells and batteries; support research in critical problem areas encountered by the industrial contractors; battery analyses and optimization studies; and development of supporting technologies such as separators and techniques for charging and state-of-charge monitoring.

Other efforts at OEPM include battery/vehicle integration tasks directed at ensuring compatibility of battery R&D goals with vehicle needs. OEPM also develops battery application information for use by vehicle system developers and monitors the application performance of these near-term batteries in engineering test vehicles.

The project strategy is to emphasize technology development by industry through cost shared contracts. This ensures a sharp focus by industry on those technical approaches which offer the greatest probability of success. In addition it provides incentive to industry for rapid application and commercialization of the technology developed.

The initial project effort concentrates on R&D exploring promising technical approaches in the three near-term battery systems. Late in FY 1981 the number of contractors in each battery type will be reduced, retaining only those contractors having the most promising approaches. Manufacturing process development will also be initiated in the 1981-84 period directed at the availability of quantity production capability in 1986.

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*Sponsored by the Division of Electrochemical Energy Storage Systems and the Division of Electric and Hybrid Vehicles.

The purpose of this report is to present a description of the project activities and associated key results from project initiation through FY 1979. The report contains a summary of the battery contractor research and development efforts, results of the battery verification testing at ANL/NBTL, status and results of the support research activities at ANL, results to date in the battery components research and development efforts at ANL, and a summary of the major results in the battery/vehicle system integration area. The report stresses brevity and conciseness at the expense of completeness in the details presented. A reader desiring additional data or information in a particular area should contact the ANL/OEPM project office.

II. BATTERY CONTRACTOR RESEARCH AND DEVELOPMENT

A. Summary

The major contractors participating in the program of Near-Term Electric Vehicle Battery project are listed in Table II-1. Table II-1 also shows the contract period and contract value including the contractors cost share. The industrial contractors within each battery type are pursuing different technical approaches following their specific areas of expertise.

The electrochemical and thermodynamic characteristics of the three systems are given in Table II-2. Characteristics of major importance in electric vehicle batteries are a high specific energy and specific power, low cost, long cycle life, low maintenance requirements and safety in operation. Battery R&D must be directed at achieving the best combination of all of these characteristics. Each of the three near-term battery types has its own merits and shortcomings.

For example, the state-of-the-art (SOA) lead-acid battery has low cost and acceptable cycle life but low specific energy. The SOA nickel/iron battery however, has good cycle life, medium specific energy, but high cost. High specific energy is the virtue of the nickel/zinc battery, but a major improvement in cycle life is needed while maintaining an acceptable cost.

The R&D approaches taken by the contractors are varied as mentioned earlier. For example in the lead-acid area Eltra is using grids for both the positive and negative plates made from an expanded lead-calcium metal alloy. These alloys have lower self discharge and corrosion rates than the conventional lead-antimonial alloys. They have also developed a pilot line for continuous manufacture of expanded metal pasted electrodes. ESB is using their golf cart battery EV-106 as baseline technology. By means of factorial experiments, they are evaluating several construction combinations directed at increasing the specific energy of the battery to over 40 Wh/kg. Their evaluation includes both flat plate and tubular plate positive electrodes. Globe-Union's approach emphasizes optimization of the cell design, and use of an unique electrolyte circulating system.

In the nickel/iron system Westinghouse is emphasizing development of a battery of good performance with low initial costs. They use sintered steel wool current collectors for the electrodes. Westinghouse has also designed an active gas and electrolyte management system for their battery.

Table II-1. Industrial Contractors for Near-Term Battery Project

Battery	Contractors	Contract Period	Contract Value,[a] $
Lead-Acid	Eltra Corporation	04/78-05/81	2,576,969
	ESB Technology Co.	02/78-01/82	3,385,544
	Globe-Union, Inc.	03/78-04/81	3,042,783
Nickel/Iron	Eagle-Picher Ind., Inc.	03/78-02/81	2,074,725
	Westinghouse Electric Corporation	12/77-11/80	2,005,306
Nickel/Zinc	ESB Technology Co.	04/79-03/82	1,096,634
	Energy Research Corp.	03/78-02/81	2,920,764
	Gould Inc.	03/78-09/80	5,736,121
	Yardney Electric Corp.	07/77-09/80[b]	1,000,000

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[a] Includes contractors' share

[b] Contract terminated by mutual agreement in May 1979

Table II-2

LEAD-ACID, NICKEL/IRON AND NICKEL/ZINC SYSTEM CHARACTERISTICS

	Lead-Acid	Nickel/Iron	Nickel/Zinc
Cathode Reaction	$PbO_2 + SO_4^{=} + 4H^+ + 2e^- \xrightleftharpoons{D} PbSO_4 + 2H_2O$	$2NiOOH + 2H_2O + 2e^- \xrightleftharpoons{D} 2Ni(OH)_2 + 2OH^-$	$2NiOOH + 2H_2O + 2e^- \xrightleftharpoons{D} 2Ni(OH)_2 + 2OH^-$
Anode Reaction	$Pb + SO_4^{=} \xrightleftharpoons{D} PbSO_4 + 2e^-$	$Fe + 2OH^- \xrightleftharpoons{D} Fe(OH)_2 + 2e^-$	$Zn + 2OH^- \xrightleftharpoons{D} ZnO + H_2O + 2e^-$
Overall Cell Reaction	$PbO_2 + Pb + 2H_2SO_4 \xrightleftharpoons{D} 2PbSO_4 + 2H_2O$	$2NiOOH + Fe + H_2O \xrightleftharpoons{D} 2Ni(OH)_2 + Fe(OH)_2$	$2NiOOH + Zn + H_2O \xrightleftharpoons{D} 2Ni(OH)_2 + ZnO$
Theoretical Cell Voltage	2.09 volts	1.36 volts	1.73 volts
Nominal Cell Voltage	2.1 volts	1.2 volts	1.6 volts
Theoretical Capacity			
$Ni(OH)_2$, or PbO_2	0.224 Ah/g	0.289 Ah/g	0.289 Ah/g
$Fe(OH)_2$, ZnO, or Pb	0.259 Ah/g	0.588 Ah/g	0.645 Ah/g
Theoretical Energy Density	175 Wh/kg	263 Wh/kg	345 Wh/kg
Parasitic Reactions			
at positive electrode	$2H_2O \xrightarrow{C} O_2 + 4H^+ + 4e^-$	$2OH^- \xrightarrow{C} 1/2\ O_2 + H_2O + 2e^-$	$2OH^- \xrightarrow{C} 1/2\ O_2 + H_2O + 2e^-$
at negative electrode	$2H^+ + 2e^- \xrightarrow{C} H_2$	$2H_2O + 2e^- \xrightarrow{C} H_2 + 2OH^-$	$2H_2O + 2e^- \xrightarrow{C} H_2 + 2\ OH^-$
Thermodynamic			
ΔG (for cell reaction)	-93.5 Kcal/mole	-63.0 Kcal/mole	-80.0 Kcal/mole
ΔH (for cell reaction)	-90.4 Kcal/mole	-68.5 Kcal/mole	-85.8 Kcal/mole
$T\Delta S$ (at 298K)	+3.1 Kcal/mole	5.5 Kcal/mole	5.8 Kcal/mole

The Eagle-Picher nickel/iron approach favors high performance using a proprietary nickel positive electrode and an iron electrode from the Swedish National Development Company.

In the nickel/zinc system ESB is developing a battery with a unique vibrating zinc electrode, which overcomes dendritic growth and shape change problems. Gould is developing a high performance battery utilizing sintered nickel electrodes. Much attention is also given to separators and thermal management techniques. Energy Research Corporation (ERC) is emphasizing low initial cost through use of plastic bonded electrodes and thus reduction in the amount of nickel required.

The precontract status, FY 1979 development objectives, FY 1979 accomplishments and the present program goals for 1986 are shown in Figures II-1 to II-3. At the end of FY 1979 DOE established performance and cost objectives for the electric passenger cars to be available in 1986. Characteristics required of these vehicles were a 100 mile urban range, an acceleration comparable to presently available diesel engine subcompact cars, and a cost to own and operate competitive with ICE vehicles. Studies are underway to define the associated battery capabilities required to achieve these vehicle performance and cost objectives. Thus, the 1986 program goals for the batteries are subject to revision contingent upon the results of these studies. Preliminary study results indicate the present battery program goals are adequate to allow the vehicle mission objectives to be met.

The details of the varied approaches and accomplishments are provided in the following sections.

B. Lead-Acid Batteries

In the past, electric vehicle lead-acid batteries available on the market were mainly limited to those applied to golf-cart type vehicles. These batteries have low specific energy, 25 to 30 Wh/kg, and low cycle life, estimated to range from 125 to 200 cycles, and were never tested under the ANL testing regime.* Since the initiation of the near-term electric vehicle project, the three industrial contractors for lead-acid batteries (ESB, Globe-Union, and Eltra) have concentrated on the development of both improved state-of-the-art (ISOA) batteries and batteries of advanced designs. The principal emphasis during 1979 was on the component improvements, and on the construction of ISOA cells and modules to be delivered to National Battery Test Laboratory (NBTL) for testing. The FY 1979 objectives and accomplishments as measured by NBTL for ISOA cells and modules are listed in Table II-3. As shown, the performance objectives for FY 1979 have been exceeded, but the cycle life was less than desired, ranging from 52 to 203 cycles depending upon the contractor. Cycle life measured by one contractor has exceeded 250 cycles.

During 1979, ESB began a comprehensive factorial experiment, with ninety-six lead-acid ISOA modules of a flat plate design directed at characterizing key design parameters, such as paste density and composition,

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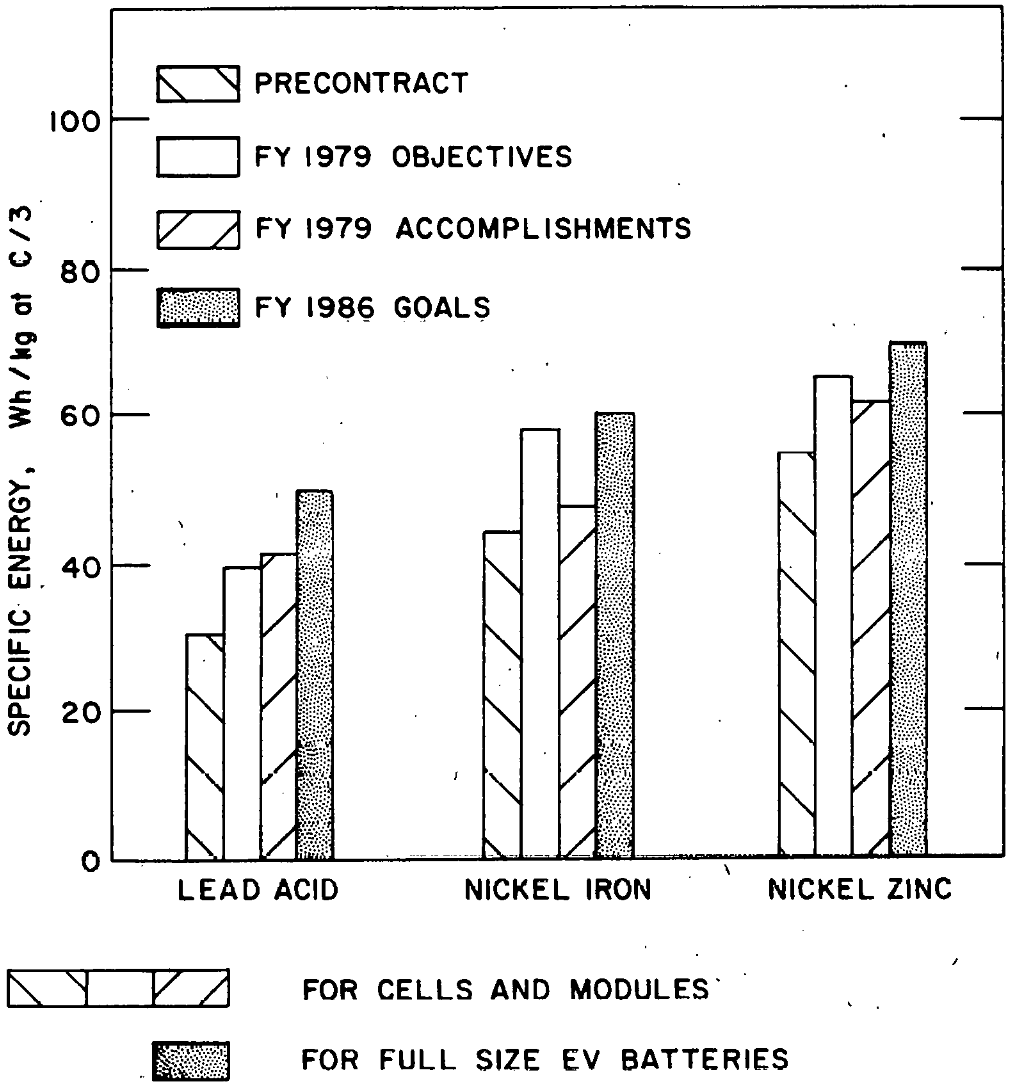
*ANL testing regime is to discharge the battery to 80% of the rated capacity each cycle at room temperature.



Note: Several cells (usually 3-6) are combined to form a module; a full-size EV battery is composed of several modules.

FIGURE II-1: SPECIFIC ENERGY: GOALS AND ACCOMPLISHMENTS FOR THE NEAR-TERM BATTERIES

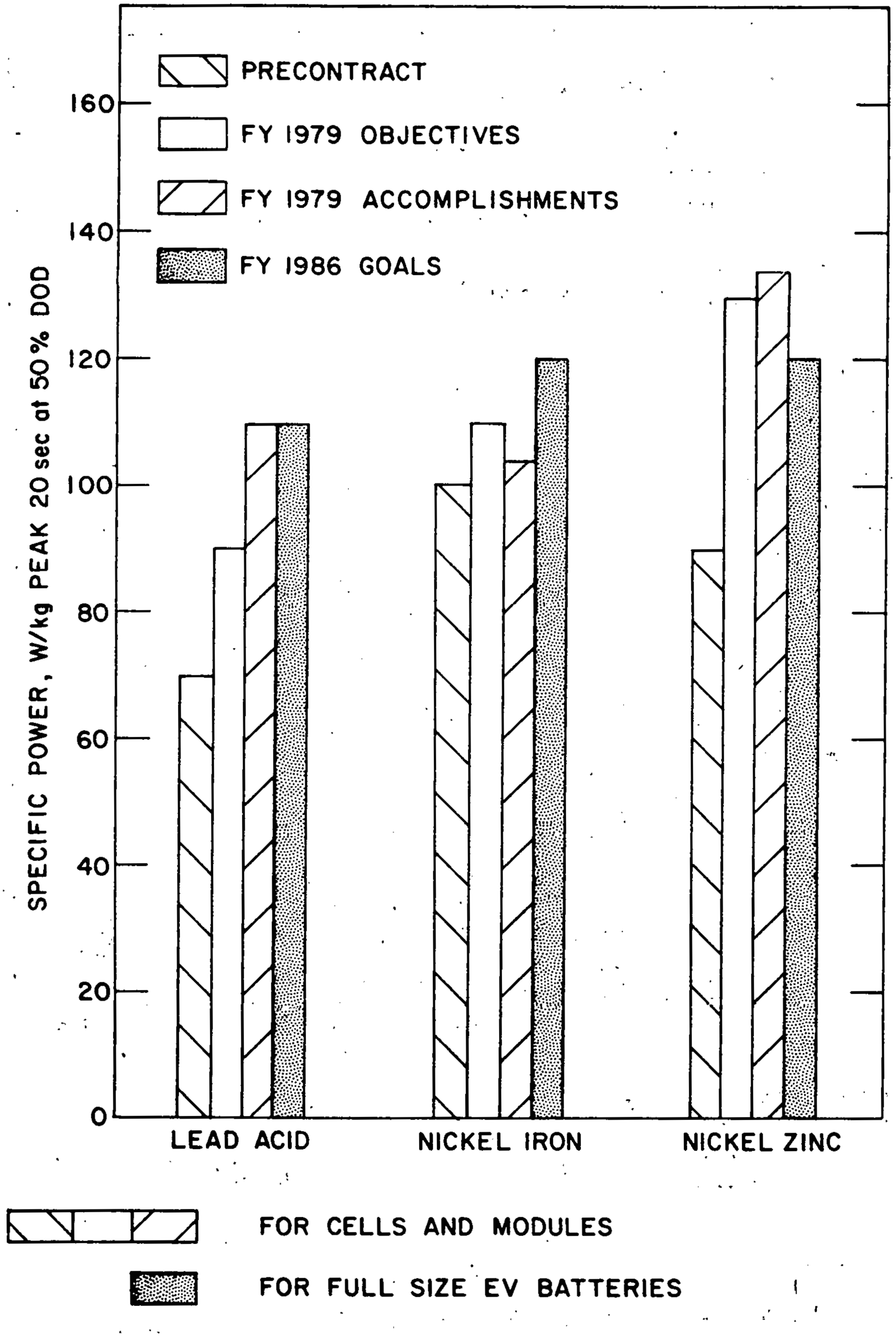


FIGURE II-2: SPECIFIC POWER: GOALS AND ACCOMPLISHMENTS FOR THE NEAR-TERM BATTERIES

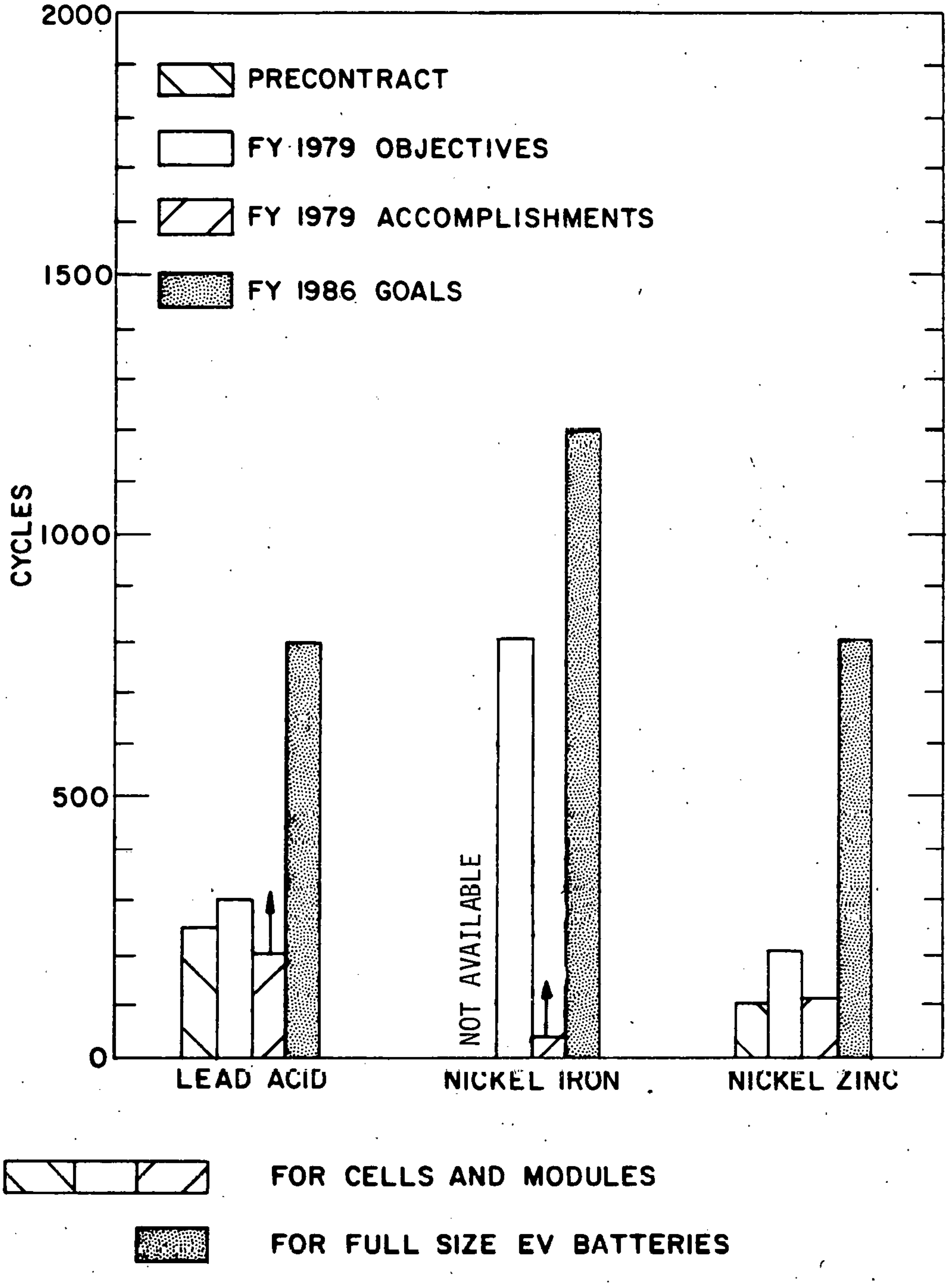


FIGURE II-3: CYCLE LIFE: GOALS AND ACCOMPLISHMENTS FOR THE NEAR-TERM BATTERIES separator type, and acid density(10,11). In the course of this experiment, some modules attained specific energies of up to 40.7 Wh/kg at the 3-hour discharge rate, thus exceeding the FY 1979 objective of 39 Wh/kg. Two 3-cell ISOA modules tested at NBTL operated for 116 and 105 cycles before the capacity declined below 75% of the manufacturer's rated capacity. Research on advanced batteries at ESB has focused on comparing the performance of three types of cells using pasted flat-plate, tubular, and bipolar electrodes. Of the three types, cells constructed with pasted flat plates showed the best overall performance, particularly with respect to load voltage and cell capacity; cells with tubular and bipolar electrode construction never achieved specific energy as high as that obtained by the ISOA battery. Accordingly, ESB suspended work on the tubular and bipolar design for the advanced battery in preference to the flat-plate design. To improve grid design, ESB is utilizing Battelle Columbus Laboratory to develop a computer model for grid design optimization. A computerized machining program for cutting the grid mold is in the process of being formulated.

Table II-3

Performance Data on Lead-Acid Cells/Modules Tested at NBTL

	FY 1979 Objectives	Eltra	ESB	Globe-Union
Specific Energy[a] Wh/kg	39	37	35	41
Specific Peak Power[b] W/kg	90	75	85	118
Cycle Life[c]	300	52[d]	116[e]	203[e]
Energy Efficiency, %	70	77	78	85

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[a] C/3 rate

[b] 30 sec. average at 50% DOD

[c] Each cycle should deliver 80% or more of the rated capacity at 25°C.

[d] Characterization and cycle life tests were carried out on same module.

[e] Tests in progress

Globe-Union(13,14,15) is investigating an optimized electrode design and an unique electrolyte circulation device. With the aid of a proprietary computer program, Globe-Union was able to determine the optimum electrode dimensions and the dimensions of the grid ribs which extend radially from the terminal tabs to the edges of the grid. The result is a grid with a minimum weight and more uniform distribution of current density to achieve the power capability needed. Globe-Union's electrolyte circulation device maintains uniform acid concentration within the cell, thus minimizing grid corrosion and increasing battery life. In experimental work at Globe-Union the addition of lignosulfonate to the negative electrode was found to improve charge acceptance, increase electrode capacity, and improve cycle life. These benefits were attributed to the presence of distinct molecular weight fractions of the lignosulfonate, which were found to specifically influence the initial capacity and maintenance of capacity during cycling of the negative electrode. During FY 1979, Globe-Union delivered five 250 Ah ISOA cells to NBTL for testing. Three cells were put through the characterization cycle (defined in Section III). The remaining two cells delivered 176 and 156 cycles on life test at ANL/NBTL before the capacity declined below 75% of the manufacturer's rated capacity. It should be noted that Globe-Union cells received 27 full cycles prior to delivery to the ANL/NBTL. The same type cell was tested at Globe-Union and attained 247 to 260 cycles at 80% depth of discharge. For the advanced battery, Globe-Union is employing the concept of reducing the battery weight by using composite metal-plastic grids.

Eltra(16,17) is developing an electrode fabricated from expanded lead-calcium metal mesh instead of the conventional cast grid. Lead-antimony alloys are conventionally used in cast grids to assure high-quality castings and to enhance cycle life. Eltra's expanded mesh is constructed from a lead-calcium alloy containing no antimony, thus promising to reduce battery self-discharge and grid corrosion. In addition, the expanded mesh grid contains less lead, and the energy consumed in fabrication of the mesh material is less than that consumed in the casting process. Eltra has constructed a pilot-line facility for producing expanded mesh stock and pasted plates. Initially, the ISOA cells fabricated by Eltra consisted of 10 positive and 10 negative plates (165 Ahr size)per cell, but these were found to have insufficient acid and insufficient positive active material. Therefore, one of the negative plates has been eliminated, thereby increasing the acid volume and reducing the weight of the negative plates in the cell. The design change is expected to proportion the reactants in a more electrochemically efficient manner. Tests of this new design showed a specific energy density of 37 Wh/kg at the 3-hr rate, which is 10% less than predicted, but an improvement over the 35 Wh/kg on the best previous ISOA cell delivered by Eltra. Eltra has delivered three 3-cell modules to NBTL for test. Similar cells tested at Eltra operated for 125 cycles. For the advanced design, Eltra is experimenting with different formulations of the positive active material to improve cycle life. One of these formulations, tetrabasic lead sulfate, has resulted in an increase of the cycle life from 125 to 183 cycles.

C. Nickel/Iron Batteries

Nickel/iron batteries were invented in 1901 by Edison of United States and Jungner of Sweden. The cell electrolyte is typically 30% KOH in water and also contains approximately 10 g/l LiOH to improve the capacity retention (or cycle life) of the nickel electrode. The reactants, β-NiOOH and Fe, and products, $Ni(OH)_2$ and $Fe(OH)_2$, are extremely insoluble in this electrolyte thereby leading to a high stability of the electrochemically active materials. Containers and electrode separators in modern Ni/Fe cells are generally made from plastics such as polyphenylene oxide (PPO), polypropylene, poly-vinyl chloride (PVC), or polyamides. Current collectors, which hold the positive and negative active materials in position and transport electrical current to the cell terminals, are typically made from steel, nickel-plated steel, or nickel metal. Steel-clad copper or nickel metal is typically used for the battery terminals.

The two Ni/Fe battery contractors are Westinghouse and Eagle-Picher. In their cell designs, Westinghouse is emphasizing the use of low-cost materials and Eagle-Picher is concentrating on high performance. The cycle life potential for the Ni/Fe cell is high, and about equal for the cell designs of both contractors. For their cells, Westinghouse(18,19) uses sintered steel-wool current collectors for both the positive and the negative electrodes. For the positive electrode, the steel wool is nickel plated in order to avoid undesirable, irreversible side reactions within the cells. The nickel hydroxide active material for the positive electrode is applied by either an electrochemical process or a pasting process. The electrochemical process is at a more advanced stage of development than the pasting process. However, the latter process has the potential for lower ultimate production costs. The iron electrode is prepared by pasting a slurry of Fe_2O_3 into the sintered steel-wool substrate.

Eagle-Picher(20,21) uses an electrochemically prepared nickel positive electrode with a current collector of powder metallurgically prepared porous sintered nickel plaque. This traditional nickel electrode approach permits projections of high performance and long life. The iron electrode consists of a central mesh of iron surrounded by a sintered iron-powder current collector and active material. This iron electrode has a high capacity density (>0.9 Ah/cc), and can be efficiently recharged (67% whr efficiency compared to 50% for the conventional). Eagle-Picher has subcontracted certain separator and negative electrode development work to the Swedish National Development Company.

The known major problems with the nickel/iron system are as follows: poor utilization of the iron-electrode active material (presently ∿25% of theoretical); poor current efficiency (66% in the worst case) leading to excessive gassing during charging from both electrodes, especially from the negative electrode; degraded (∿25%) performance at temperatures of 5°C and below (attributable to the iron electrode); and a high cost per kilowatt-hour of $120/Kwh in 10,000 unit/year quantities caused by the inherently low nominal cell potential, (1.2V). Both contractors are actively pursuing improved technologies in both electrodes to combat these problems. For example, the poor low temperature performance is being improved by battery operational techniques which maintain battery temperature or by careful engineering design in which electrode capacities are tailored for lower temperature performance. Westinghouse has designed an active gas and electrolyte management system for their battery which controls and minimizes the safety hazard associated with the gas generated during battery charging.

Each contractor delivered Ni/Fe modules during 1979 to the NBTL. In addition, Westinghouse delivered a full-size (23 KWh) battery pack to the Jet Propulsion Laboratory (JPL) for electric vehicle testing.

The performance resulting from the modules delivered to the NBTL is shown in Table II-4.

While demonstrated specific energy fell short of the 1979 objective, much was learned while fabricating and testing these first electric vehicle Ni/Fe modules that indicates the goal of 60 Wh/kg can be achieved by applying recent developments in electrode performance improvements. In fact, specific energies of greater than 60 Wh/kg have already been demonstrated by experimental cells tested in the contractors' laboratories. These latest full-sized cell designs contain improvements such as lower hardware weights and increased electrode capacities which were not used in the first delivered designs. These higher performance cell designs will be introduced into future test modules to be delivered to NBTL.

Table II-4. Performance Data on Ni/Fe Modules Tested at NBTL

	FY 1979 Objectives	Westinghouse	Eagle-Picher
Specific Energy, Whr/kg[a]	58	48	45
Specific Power, W/kg[b]	100	102	98
Cycle Life[c]	800	36[d]	-
Energy Efficiency, %	50	49	65

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[a] C/3 rate

[b] 30 second average at 50% DOD

[c] Each cycle should deliver 80% or more of the rated capacity at 25°C.

[d] Tests in progress

The cycle life of the Ni/Fe modules also was less than 1979 goals, although life tests of the Eagle-Picher modules are not yet complete. Post test analyses remain to be completed on the modules after the tests are completed; however, it is anticipated that engineering modifications will permit attainment of the required life.

As shown in Table II-4, Eagle-Picher and their subcontractor, Swedish National, have made notable progress in the energy efficiency of this system due to improvements in their iron electrode. Further improvements are expected as battery charging techniques are refined, and electrode and cell designs are optimized to lower cell internal resistance.

In summary, the years 1978 and 1979 have resulted in the applications of new technology to an old, previously established battery system. This effort has resulted in improved performance of nickel/iron batteries. Additional improvements can be expected with the further development planned for the coming years.

D. Nickel/Zinc Batteries

The four contractors who performed research and development on Ni/Zn batteries are Gould, ERC, Yardney, and ESB. All contractors are concentrating on reducing battery life-cycle costs (i.e., the amortized battery cost plus cost of operation during lifetime) while maintaining or improving performance, but each has taken a different approach to achieve that end. Table II-5 summarizes the performance of various contractor modules along with the FY 1979 project objectives.

Gould(22,23) is developing improved separator systems to extend cycle life. Both microporous as well as membrane-type separators have been investigated. Microporous separators, such as Celgard (polypropylene) and inorganic/organic composites, have been de-emphasized because they are susceptible to accumulation of zinc within the pores of the separator, leading to cell failure. Gould has developed membrane-type separators based upon cross-linked polymeric films, which are zinc-free, stable in KOH, have low ionic resistivity, and are capable of low-cost production. In addition, a new synthetic wicker material has been utilized to replace the commonly used nylon-based interseparator (Pellon) which degrades in the cell environment. A number of proprietary additives, both to the zinc electrode and to the electrolyte, have also been investigated for extending cycle life. The role of the additives is to alter the characteristics of zinc dissolution and deposition in such a way as to suppress dendrite formation and shape change in the zinc electrode. Small (5 Ah) cells with such additives have operated for 250 deep cycles, whereas control cells containing no additives only operated for 60 cycles. In the area of thermal management, Gould has developed a model(24) that accurately portrays heat generation and rejection rates during actual battery operation. This has led to the redesign of cells reducing the capacity from 400 to 225 Ah (thinner cell) and a redesign of modules to include cooling channels between cells in order to provide better thermal control.

A developmental pilot line, which utilizes scaled-up processes, has been developed and produces all components, cells, and modules for the project testing activities. Gould believes that the development of advanced fabrication techniques for sintered nickel electrodes, coupled with their superior performance, will reduce the life-cycle costs sufficiently to make the sintered electrode as economically attractive as the non-sintered plastic-bonded nickel electrode.

Gould has delivered five 400 Ah modules (4 cells each) to NBTL for testing. The first module displayed an energy density of 63.5 Wh/kg and a life of 120 cycles. Tests conducted at Gould indicated this module has a peak power capability of 101 W/kg at 80% depth of discharge (15 sec. pulses). The four other modules delivered to NBTL, containing high conductivity bi-metallic composite current collector in the electrodes, demonstrated a specific power of 154 W/kg at 80% depth of discharge and a specific energy of 62 Wh/kg. However, these modules all failed at 26 cycles or less due to embrittlement or corrosion of the current-collector assembly.

Energy Research Corporation (ERC)(25,26,27) is emphasizing the development of a Ni/Zn battery with a low initial cost. Efforts are focused on the nickel electrode, which is the most expensive component in the battery. The technical approach is based upon the development of a low-cost, plastic-bonded electrode fabricated from chemically precipitated nickel hydroxide. This electrode contains about 30% graphite as a conductive diluent in place of the conventional sintered nickel-powder plaque. The cost of the plastic bonded electrode is projected to be half that of a comparable sintered nickel electrode. In 20-Ah Ni/Cd test cells, ERC demonstrated a lifetime of over 1000 cycles and a positive active-material utilization of 80% of theoretical for their plastic-bonded nickel electrode. Early tests with full-size electrodes indicated poor utilization (55%) of the positive active material, but this problem was overcome by increasing the electrode porosity. Full-size cells (rated at 250 Ah) containing increased porosity nickel electrodes exhibited capacities of 239-266 Ah; and utilization of 76-84%.

To achieve longer lifetimes in their Ni/Zn cells, ERC is investigating cast-film separators. Two separator materials, cross-linked polyvinyl alcohol and a thermoplastic-based composite, have been developed with low ionic resistivities and are currently undergoing life-cycle evaluation in 20-Ah test cells. An additional approach to achieve the same objective is through additives to the zinc electrode to reduce shape change. The development of sealed cells is also being pursued by ERC as a means to reduce or eliminate maintenance (addition of water) and possibly to extend life. To keep low hydrogen and oxygen pressures in sealed cells, auxiliary electrodes or pocket catalysts are being employed to promote recombination of these two gases. Early results are favorable, but much additional work will be required before cell capacities, which have been found to be limited during charge by gas pressure build-up, are equal to those of standard vented cells.

ERC delivered four modules (250 Ahr, 6.4V module) to NBTL and a full-size (25 KWh, 108 V) battery to JPL for in-vehicle testing. The best specific energy for the ERC modules delivered to NBTL was 35 Wh/kg, with a life of 76 cycles.

ESB(28) is pursuing a unique cell design approach based upon vibrating zinc electrodes. When the zinc electrode is vibrated during charging, the lifetime limiting problems of zinc dendrite formation and electrode shape change are surmounted. Since vibration is required only during charging most of the added weight required for vibration could be incorporated into an off-vehicle charger. The vibrating zinc electrode also results in high utilization of negative active material. Consequently, much less zinc is required. Thus, the ratio of negative-to-positive theoretical capacity is only 1.2 for the vibrating anode cell, compared to a ratio of 2 to 4 for conventional Ni/Zn cells.

In prior work at ESB's Swedish Tudor subsidiary, the long lifetime capability (over 1200 cycles) of the Ni/Zn system with the vibrating electrode had been demonstrated in a six-cell, 145-Ah module. However, the specific energy of this module was limited to 40 Wh/kg at the 3-hr rate. The emphasis of the present work at ESB, therefore, is to increase the gravimetric and volumetric specific energy of the system, while retaining the long cycle-life capability. To this end, the following design changes are being examined in Ni/Zn cells: higher specific capacity nickel electrode, thinner zinc electrodes, and smaller inter-electrode spacing. The nickel electrode improvements consist of replacing the pocket-type electrode (75-90 Ah/kg) used in the past by a suitable high capacity electrode (110-140 Ah/kg). Several types are being evaluated, including electrochemically impregnated sintered nickel (Matsushita), pasted metal wool (D.A.U.G Mercedes), and layered nickel foil (INCO's CMG electrode). The plastic-bonded nickel electrode of ESB was found to have excessive swelling in the unrestrained structure of the vibrating anode cell. Current efforts are underway to reduce this swelling. A reduction in thickness of the zinc electrode at constant capacity per plate has been made possible as a result of special charging techniques that create much denser zinc deposits on the negative substrate without the loss of high-rate discharge capability. In addition, the denser zinc deposits are more adherent; and, as a result, slumping of active material from the vibrating electrode has been largely eliminated. Studies are under way to evaluate the effect of inter electrode spacing and to determine its optimal value. A reduction in spacing from the 2.5 mm used in previous cells to 1.5 mm, if feasible, would result in a 20% improvement in volumetric energy, concomitant with a yet to be determined increase in specific energy. Other studies are aimed at selecting a negative electrode substrate material that will reduce the present self-discharge rate of 7-9% loss in capacity on a five-day charged stand. Since the contract with ESB was only recently initiated (April 1979) no cell deliveries have yet been made to NBTL.

The Ni/Zn battery R&D contract with Yardney was terminated by mutual agreement on May 31, 1979 at the end of phase I of their development program because Yardney decided the business risk was too great to continue further cost-sharing with DOE. The phase I program had focused on reducing the initial battery cost and improving component lifetime. Early in the program, failure-modes analysis established that the negative electrode was responsible for capacity degradation during cycling. The use of additives and binder in the zinc electrode, improvements in the separator system, and an alternative charging technique were employed to mitigate this problem. Subsequent attempts to increase cell life emphasized combining the strengths of both membrane-type and microporous-type separator materials. Initial efforts to reduce cost dealt primarily with the development of a plastic-bonded nickel electrode. However, the poor performance (reduced capacity at high discharge rates and low volumetric specific energy per plate) led to the abandonment of this approach in favor of the sintered electrode. The cost of the sintered electrode was reduced by fabricating a thicker, more porous plaque as well as streamlining the manufacturing process. Collectively, these steps reduced the amount of nickel, labor, and processing required for this electrode. The specific energy of 30-Ah cells tested at Yardney has been about 70 Wh/kg, with greater than 130 cycles to 80% depth of discharge. The performance of the six, four-cell, 250-Ah modules delivered to NBTL by Yardney has been disappointing. Although a specific energy of 62 Wh/kg has been demonstrated, cycle life has been limited to 38 cycles. It appears that the failure mechanisms of zinc penetration and imbalanced electrolyte distribution are accelerated in large cells. In addition, Yardney delivered a full-size Ni/Zn battery to JPL for in-vehicle testing.

One aspect of the program is to maintain an ongoing effort to ensure that any promising Ni/Zn technology is further investigated. Accordingly, five 4-cell Ni/Zn modules (225 Ah) were procured from Eagle-Picher Industries for testing at NBTL. These modules displayed a specific energy of 50 Wh/kg; cycle life testing is continuing.

Table II-5

Performance Data on Nickel/Zinc Modules Tested at NBTL

	FY 1979 Objectives	Gould	ERC	Yardney	ESB[d]
Specific Energy[a] Wh/kg	65	64	35	62	-
Specific Power[b] W/kg	130	133	-	-	-
Cycle Life[c]	200	120	76	14	-
Energy Efficiency, %	>60	72	73	80	-

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[a] C/3 rate

[b] 30 second average at 50% DOD

[c] Each cycle should deliver 80% or more of the rated capacity at 25°C

[d] Delivery of modules from ESB expected in February 1980

III. BATTERY VERIFICATION TESTING AT NBTL

The National Battery Test Laboratory (NBTL)[29] was established to provide a facility for the independent testing and evaluation of various batteries as they are developed. Cells and batteries developed within DOE-sponsored programs and those developed by private funds are tested at the NBTL. The laboratory is capable of the simultaneous testing of about 40 to 50 cells and six to eight full-size (30-40 kWh) batteries under simulated driving conditions as well as under normal test conditions. Graphical displays and tabulations of battery performance are directly available through a computer.

A. Standard Test Procedures

Upon arrival at the NBTL, the test battery is labeled, physically inspected, weighed and dimensioned, the cell voltages measured, and the electrolyte level determined and, if necessary, adjusted. In some cases, a sample of the electrolyte may be obtained and analyzed for future reference.

The battery is then installed in a test station and, if necessary, undergoes a conditioning cycle in accordance with the manufacturer's instructions. Finally, the battery is submitted to a capacity measurement at a 3-hr (C/3) constant current discharge rate to verify the manufacturer's specifications, establish a baseline capacity for future reference, and qualify it for comparison purposes in further testing in the NBTL. As a part of establishing a baseline of performance the coulombic (Ah) and energetic (Wh) capacities and efficiencies are also measured. Once these steps are completed, the battery is ready for either characterization testing or life cycle testing as described below.

The purposes of characterization testing are as follows:

1. To assess the functional capabilities of a battery over a range of test conditions. The test results permit evaluation of the battery performance in specific vehicle applications.

2. To measure the performance of a battery on a specified simulated load profile (for example, a power profile of a given electric vehicle operated under the "D" driving schedule of the SAE J227a Test Procedure(30)).

3. To provide data for battery analyses and modeling.

The sequence of tests is arranged in the general order of increasing stress on the battery. The tests are performed at ambient temperatures and are as follows:

1. Self-Discharge Test. The purpose of this test is to determine the capacity loss as a measure of the self-discharge of a battery after seven-days stand on open circuit following a full charge.

2. Partial Depth of Discharge Test. The response of a battery to a series of shallow (~50%) discharges is used to uncover any so called memory effects wherein the battery may not exhibit maximum capacity for several cycles following a series of shallow discharges.

3. Energy Density Versus Power Density. This test is to provide information over a range of test conditions such that the performance for various applications can be interpolated and information for battery modeling may be provided. The battery is discharged at 10, 20, and 30 W/kg and the corresponding energy density is measured at each of the following temperatures: -20, 0, 25, and 50°C. In addition, efficiencies and the temperature rise of the battery is measured for each discharge and charge.

4. Simulated Load Profile Test. The purpose of this test is to measure the performance of a battery discharged under a simulated load driving profile for a specific application. The simulated load profile used in the NBTL is the "D" driving cycle of the SAE J227a Test Procedure applied to the newly developed DOE/GE/Chrysler Electric Test Vehicle (ETV-1), with and without regenerative braking. Batteries are subjected to this profile with the power levels

scaled according to the weight of the battery under test. In this manner, a cell, a multicell module, or batteries of any arbitrary fraction of a full-size battery can be tested under simulated driving conditions with the power density remaining the same in all cases. During this test, the number of driving cycles completed during a discharge are counted, the coulombic and energetic capacities and efficiencies recorded and the temperature rise measured.

5. Peak Power for Sustained Duration. The purpose of this test is to measure the capability of a battery for up to 30 seconds of sustained peak power at three states of charge: 80%, 50%, and 20%. Two steps comprise this test: the first step involves a procedure to determine the instantaneous peak power at the designated state of charge and the next step involves the measurement of the sustained power for 30 seconds duration at the three states of charge. The values obtained of the peak sustained power are reported for the 8, 16, 24, and 30 second points. This test concludes the characterization of the battery.

The purpose of life-cycle testing is to determine the number of charge/discharge cycles that a battery can achieve before the capacity declines to a given value. In the NBTL tests, the battery is discharged at the 3-hr rate to 80% of its rated capacity. The number of cycles achieved before the battery capacity declines to 75% of rated capacity is the measure of cycle life.

B. Summary of Test Results

Since the National Battery Test Laboratory became operational in 1978 over 145 cells from the eight near-term battery contractors have been tested. Table III-1 lists the number, type, and capacity of the cells delivered to NBTL from the contractors. Figures III-1 to III-5 represent some of these units. Table III-2 shows the ranges of specific energy, efficiency, and cycle life demonstrated in the testing at the NBTL. Notable achievements in specific energy (up to 41 Wh/kg) of lead-acid cells have been verified. Higher specific energies (up to 63 Wh/kg) have been exhibited by some Ni/Zn modules, but Ni/Zn cycle life has never exceeded 120 cycles in the best case and has been considerably less in most cases. Testing of Ni/Fe modules was started just prior to the end of FY 1979 so that cycle life data are still being accumulated; however, specific energies of up to 48 Wh/kg have been demonstrated. Although some overlapping exists, energetic efficiencies were generally best for the lead-acid and least for nickel/iron batteries.

Tests were conducted with simplified, simulated driving profiles derived from the application of the SAE J227 a/D driving schedule to the newly constructed DOE/GE/Chrysler electric vehicle, operated with and without regenerative braking. Figure III-6 is a bargraph showing the results obtained from these tests. The longest range obtained was with the nickel/zinc module from Eagle-Picher and the nickel/iron module from Westinghouse, 102 and 101 driving cycles, respectively; [each cycle represents 0.95 miles (1.5 km)]. At the other end of the spectrum, the state-of-the-art lead-acid EV106 battery fabricated by ESB achieved only 63 driving cycles. Ranges manifested by other batteries are interspersed between these two extremes. As well as showing the comparative ranges, these results show that, in all cases, worthy

Table III-1. Testing of Cells at NBTL for June 1978 to October 1979

Contractor	System	Number of Cells[a]	Nominal Rated Cell Capacity Ah
Eltra, C&D	Lead-Acid	9	165
ESB	Lead-Acid	15	180
Globe-Union/GE	Lead-Acid	6	174
Globe-Union	Lead-Acid	5	250
Eagle-Picher	Ni/Fe	6	280
Westinghouse	Ni/Fe	6	220
Eagle-Picher	Ni/Zn	20	225
ERC	Ni/Zn	34	240
Gould	Ni/Zn	20	400
Yardney	Ni/Zn	24	250

[a] These cells have been tested or are under test at the NBTL.

Table III-2

Performance Data Obtained from Cells/Modules Tested at NBTL

	Specific Energy (Wh/kg)	Energy Efficiency (%)	Cycle Life
ISOA Lead-Acid			
Eltra	37	77	52
ESB	35	76	116
Globe-Union	41	85	203
Nickel/Iron			
Eagle-Picher	45	65	-
Westinghouse	48	49	36[a]
Nickel/Zinc			
Eagle-Picher[b]	50	70	38
ERC	35	73	76
Gould	64	72	120
Yardney	62	80	14

[a] Tests in Progress.

[b] Direct Purchase

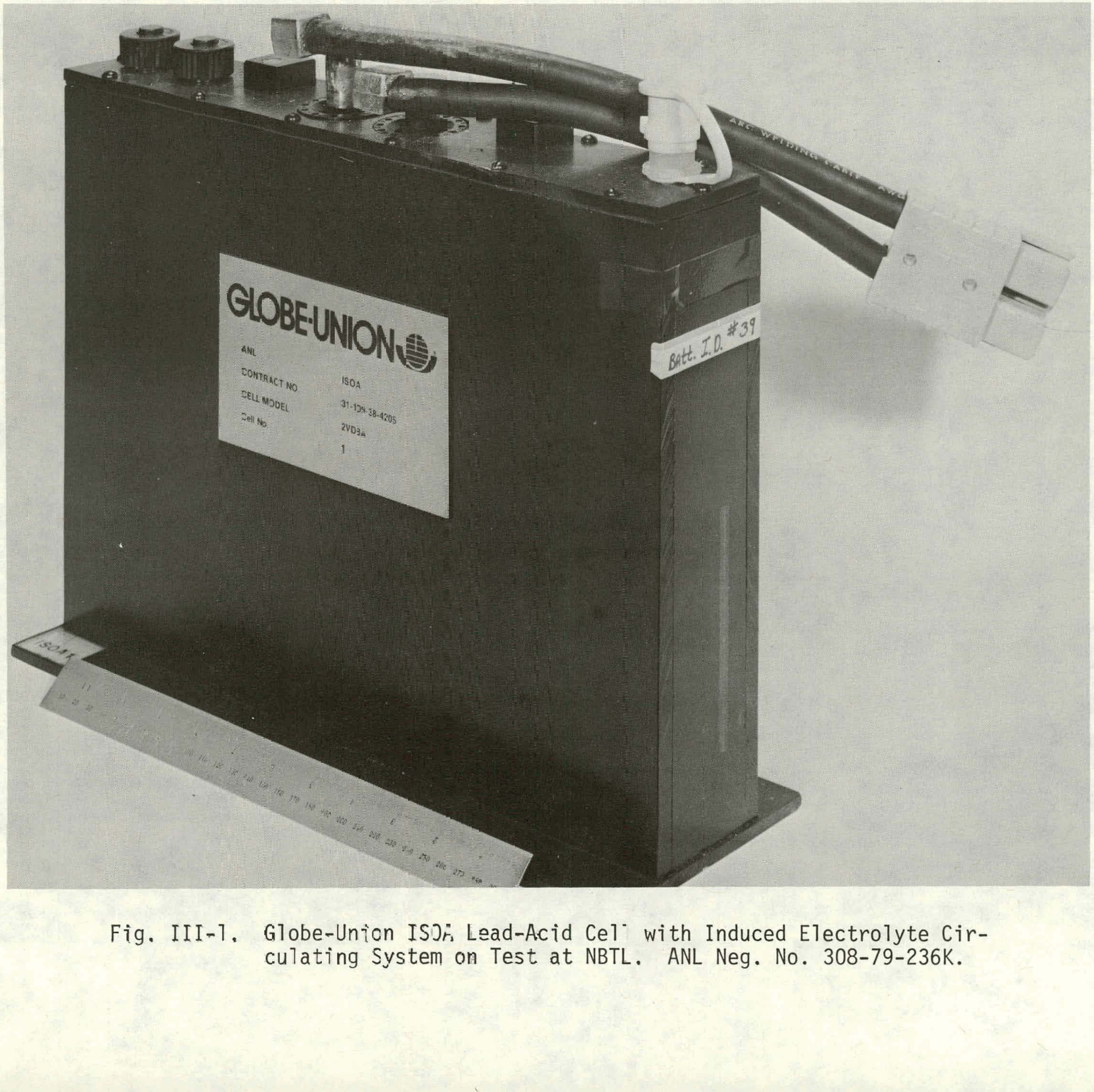

Fig. III-1. Globe-Union ISOA Lead-Acid Cell with Induced Electrolyte Circulating System on Test at NBTL. ANL Neg. No. 308-79-236K.

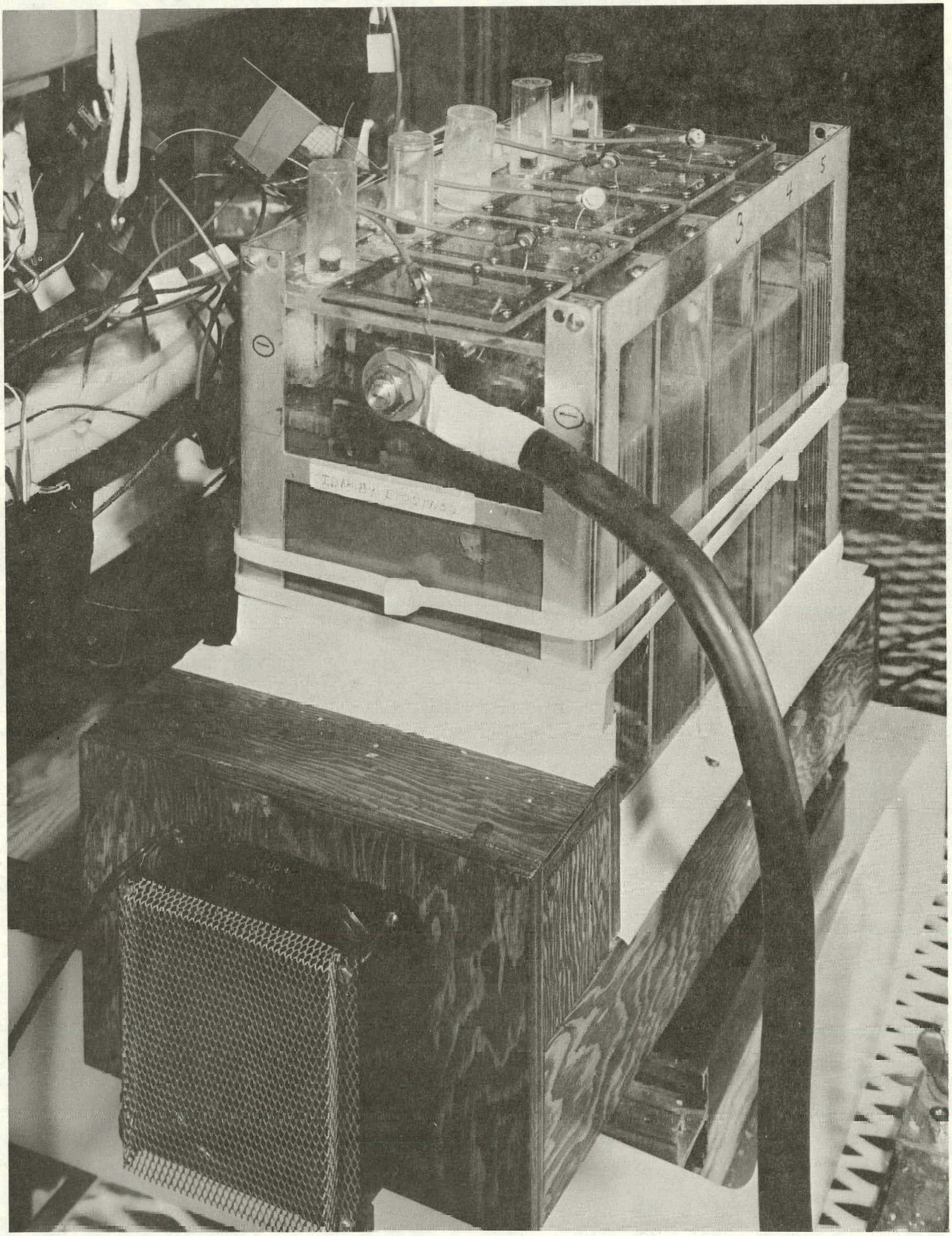

Fig. III-2. An Eagle-Picher Nickel/Iron Module with Forced Air Cooling Under Test at NBTL. ANL Neg. No. 308-80-29K.

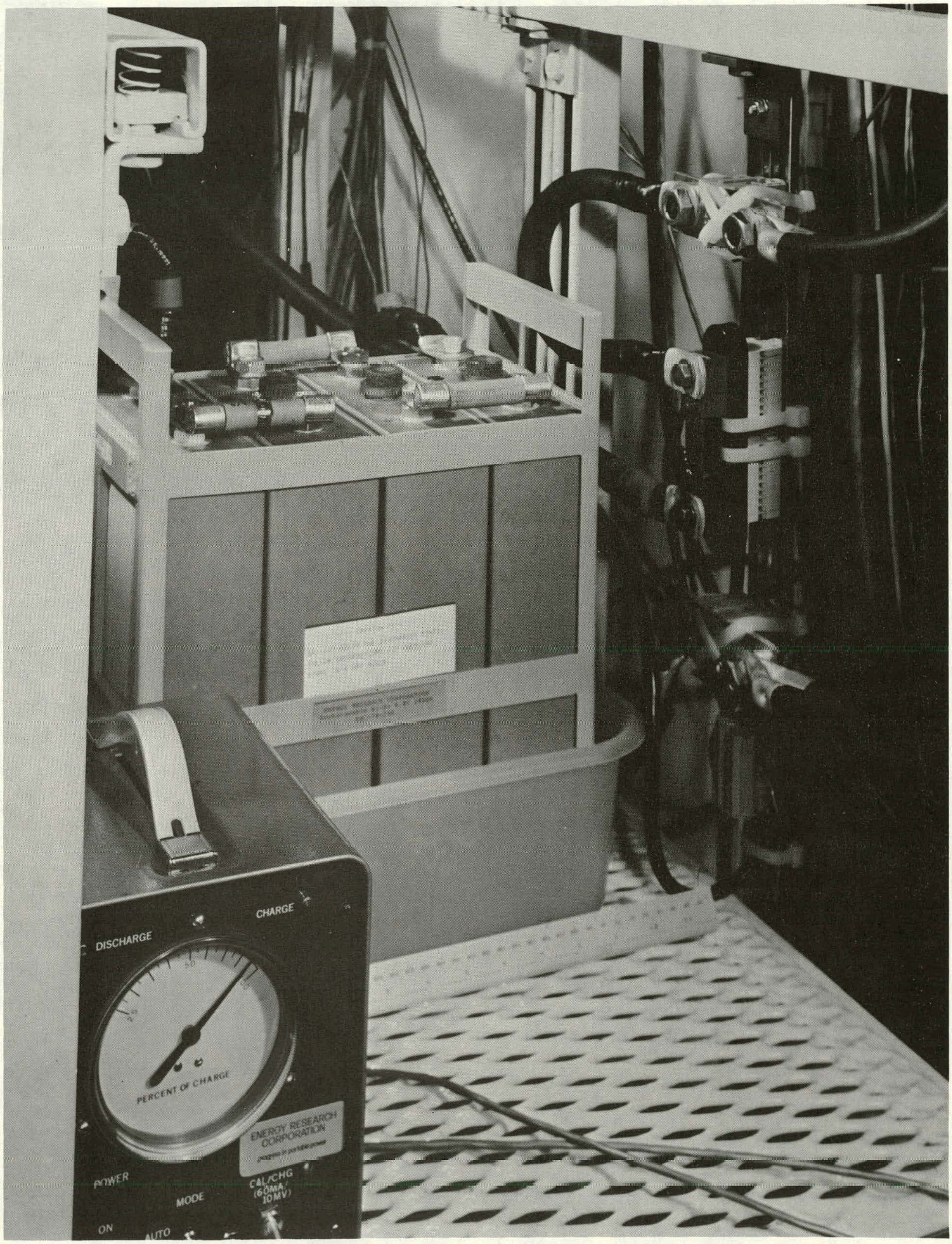

Fig. III-3. An Energy Research Corporation Nickel/Zinc Four-Cell Module with Charge Controller Under Test at NBTL. ANL Neg. No. 308-78-753K.

Fig. III-4. Two Gould Nickel/Zinc Modules Under Test in the NBTL. ANL Neg. No. 308-78-754K.

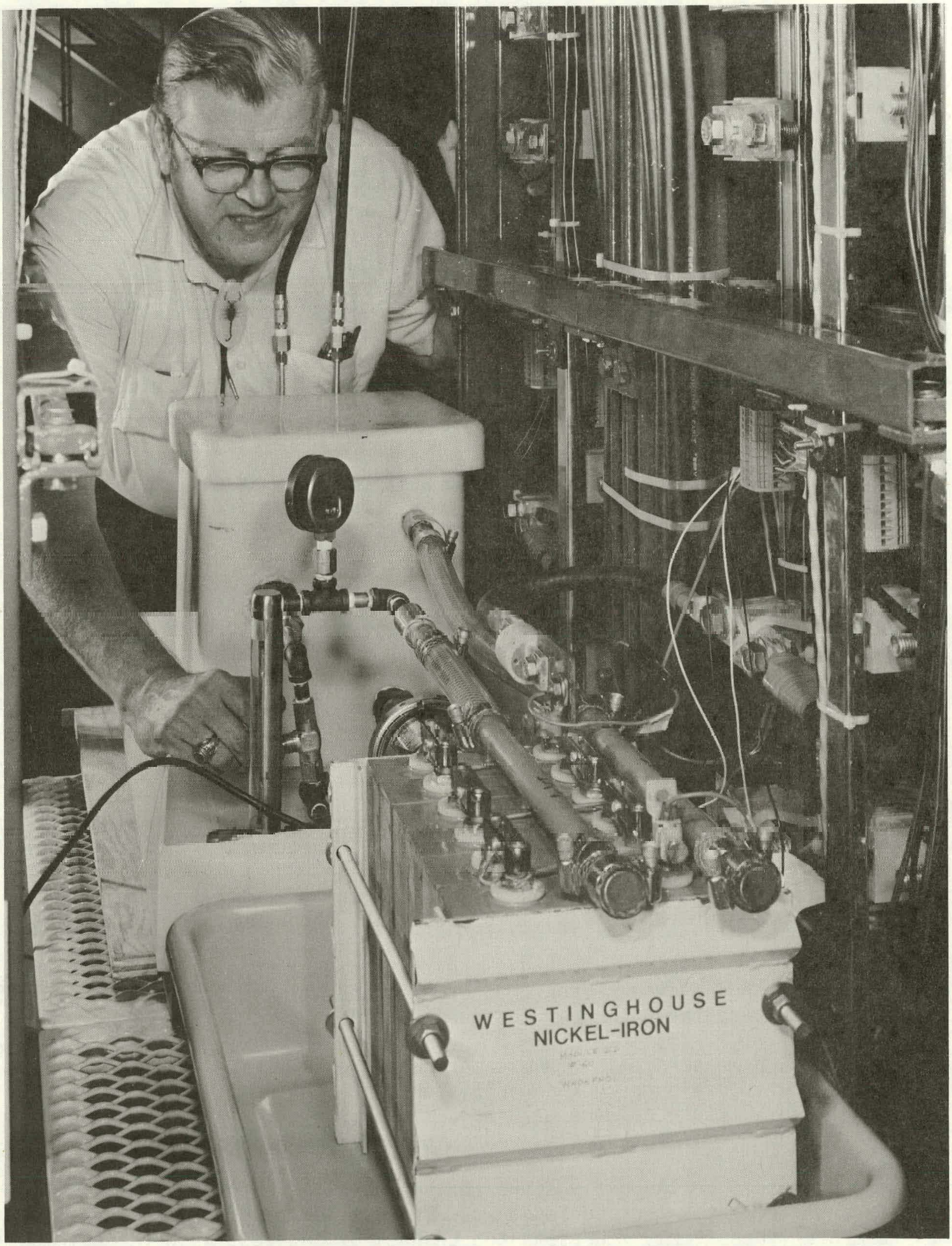

Fig. III-5. An Engineer Adjusts the Flow on a Westinghouse Nickel/Iron Module with Electrolyte Circulating System Under Test in the NBTL. ANL Neg. No. 308-79-628K.

increases in range (18% to 31%) are exhibited with regenerative braking. Other evidence also suggests that charge acceptance by batteries seems particularly good during the regenerative braking phase of the driving cycle.

A significant phenomenon discovered in the NBTL is that, during testing at room temperature, the Ni/Zn modules exhibited during discharge a temperature rise which was found to be proportional to the specific energy of the module. Table III-3 lists the temperature rise (ΔT) measured for Ni/Zn modules from four separate contractors, the corresponding energy manifested during the discharge, the respective weight of each of the modules, and finally the resultant specific ΔT. As noted, ΔT ranges from 12 to 22°C and the specific ΔT ranges from 0.31 to 0.36 °C-kg/Wh. These results indicate that, as batteries of higher specific energy are achieved, more attention must be devoted to thermal management. Presently, a module exhibiting a specific energy of 60 Wh/kg manifests a temperature rise of 22°C during a 3-hr discharge initially. Further evidence indicates that as the battery ages, the temperature rise may increase by 50% or more before the end of useful life of the module.

C. Advances in Testing Capability. The advances made in the testing capability of the NBTL over the past year are listed below:

Test Station Development. The testing capability of the NBTL increased from 2 to 15 test stations during the past year, and work is currently underway to expand to 40 test stations. A typical cell/module test station has current and voltage capability of ±500A and 0-12V, respectively. A full-sized battery test station has +350A, -500A and 10-120V capability.

Simulated Driving Profiles. As indicated earlier in the report, a method was developed to apply simplified driving profiles to batteries. In addition, a system was developed and made operational to apply precision power profiles to simulate any electric vehicle driving schedule.

Peak Power Measurements. A system was designed and constructed for determining and measuring peak power for a sustained duration from a battery.

Environmental Chambers. Three walk-in chambers were ordered to provide controlled temperature and humidity for batteries under test.

NBTL Annex. A building to house the environmental chambers, vibration test equipment, and a dynamometer was ordered and will be constructed early in 1980 adjacent to the Chemical Engineering Building.

Temperature Measurements. A microprocessor based temperature measurements system was developed by Kinetic Systems International Inc. and was installed in the NBTL control and data acquisition system. An interesting feature of this device is that residing in its memory is a look-up table containing Bureau of Standards conversions from thermocouple voltages to temperatures. The microprocessor continuously scans 16 thermocouples, converts the voltage read to a temperature, and updates an addressable channel for each one. The main computer then simply addresses the channel of interest whenever a temperature reading is required and obtains the value directly in engineering units. This system saves the main computer a significant amount of processing time and reduces software effort also.

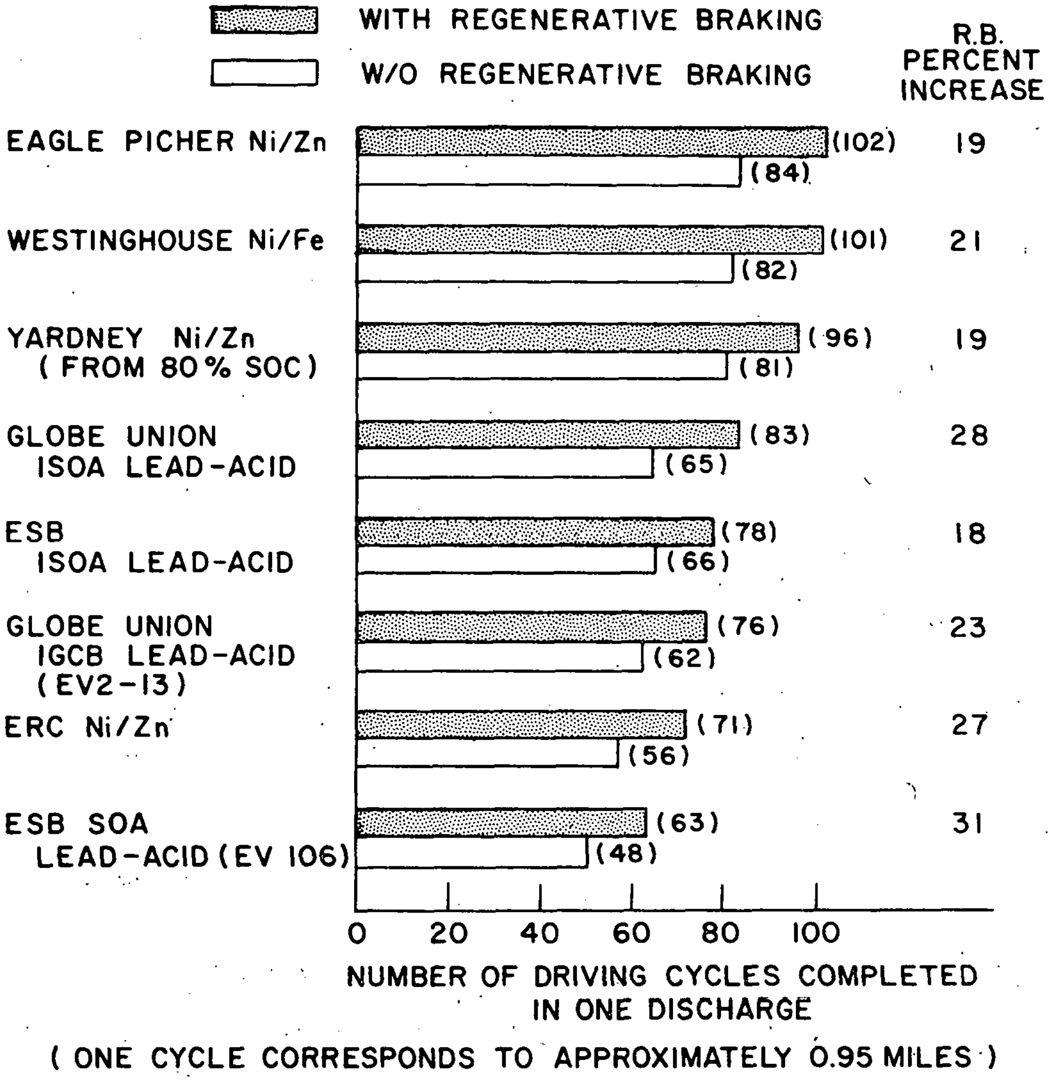

FIGURE III-6: TEST RESULTS OF SIMPLIFIED DRIVING CYCLES WITH AND WITHOUT REGENERATIVE BRAKING FOR THE NEAR-TERM BATTERIES (SAE J227aD, GE CHRYSLER VEHICLE)

Table III-3

Temperature Rise in Relation to Specific Energy of Ni/Zn Modules

	Gould	ERC	Yardney	Eagle-Picher
ΔT,[a] °C	22	12	22	14.3
Manifested Capcity, Wh	2675	1260	1750	1340
Weight of Module, kg	42.5	36.2	28.3	29.1
Specific ΔT,[b] (°C-kg/Wh)	0.35	0.34	0.36	0.31

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[a] Temperature change for battery discharged at 3-hr rate.

[b] Obtained by multiplying ΔT by the module weight and dividing by the capacity.

The following activities were completed in software development for the NBTL:

1. Interactive Control Console. The interactive control console has been enhanced to provide easier and broader access to test data. In particular, the graphics page makes the obtaining of graphs more automatic and efficient.

2. Special Software Tasks. A number of programs were written to accomodate special charging requirements of certain batteries, such as temperature compensated and stepped current charging.

3. Data Management. The graphics portion of data management was improved by adding grid lines and efficiency computations. The operator also now has the option to specify that the computer system automatically provide plots of specified tests in the morning before the workday starts. In that way, graphical data may be reviewed immediately to assess the status of the ongoing tests. Programs were developed to provide tabular data for every test. Work is currently in progress to extend these programs to automatically feed Datatrieve, a data base management system from Digital Equipment Corporation.

IV. ANL SUPPORT RESEARCH

Basic and applied research is performed at ANL in support of the near-term battery contractors for electric vehicle and load-leveling applications. The effort is in parallel, but complimentary to the research activities being conducted by ANL contractors. The particular topics are selected because of significant interest and importance to the progress of the technologies.

A. Fundamental Electrode Studies

1. Current Profiles in Zinc Electrodes(31)

During the past year, an experimental study was carried out to determine the current density profiles in a simulated porous zinc/zinc oxide electrode. During 1977, a simulated porous electrode consisting of a hundred or more cylindrical pores was developed. It is fabricated from multiple layers of thin metal, with well-defined porous characteristics, to permit the continuous determination of current as a function of depth within the pore, and is a valuable tool for investigating time-dependent performance parameters occurring within operating porous electrodes. The simulated electrode was used to determine the initial current distributions (t=0) at three applied currents : 10, 25, and 100 mA. These data are shown in Figure IV-1 along with the predicted current distribution curve based upon a constant species concentration and linear polarization kinetics. The observed poor fit at high current (100 ma) indicates that this assumption is not valid under that condition. In addition these experiments show an effective reaction depth of only 0.2 mm, i.e., 70-90% of the current is within this thickness. Therefore, zinc electrodes thicker than about 0.5 mm (thickness of battery electrodes is 0.8-1.2 mm) will not be fully utilized until the reaction is forced into the center of the electrode by a lack of active material at the surface.

This non-uniformity of the current distribution as a function of electrode depth is found to be more pronounced as the time of discharge increases, except in the case of passivation. However, passivation is undesirable since it reduces the useful energy output of the electrode altogether. Mathematical modeling of the time-dependent behavior of the current distribution indicates that electrolyte conductance is a critical parameter. Figure IV-2 shows the experimental and predicted current distributions for two conditions: 1) constant electrolyte conductance, 2) conductance which varies with time. This second condition more closely approximates the expected experimental condition. The conductance decreases as zincate concentration in electrolyte increases due to the anodic reaction. Improvements in the results predicted by the model requires information on the ionic conductance of supersaturated zincate solutions. Therefore, a small effort is being made to obtain the conductance of these solutions.

2. Three-Dimensional Electrode Modeling

A three-dimensional model(32) has been developed to predict potential distribution and reaction uniformity in porous electrodes as functions of electrode dimensions, kinetics, component conductivities, and operating current. This model is useful in the design of nickel and zinc electrodes because one can, for example, determine the effect of various design parameters on electrode performance. By using the information in Figure IV-3, one can, for example, determine the effect of varying the grid conductivity (σ_g) on the potential distribution and on the maximum/ minimum current density ratio over the electrode plate, while keeping other battery properties constant. The curves 1, 2 and 3 show the effect of three different grid conductivities.

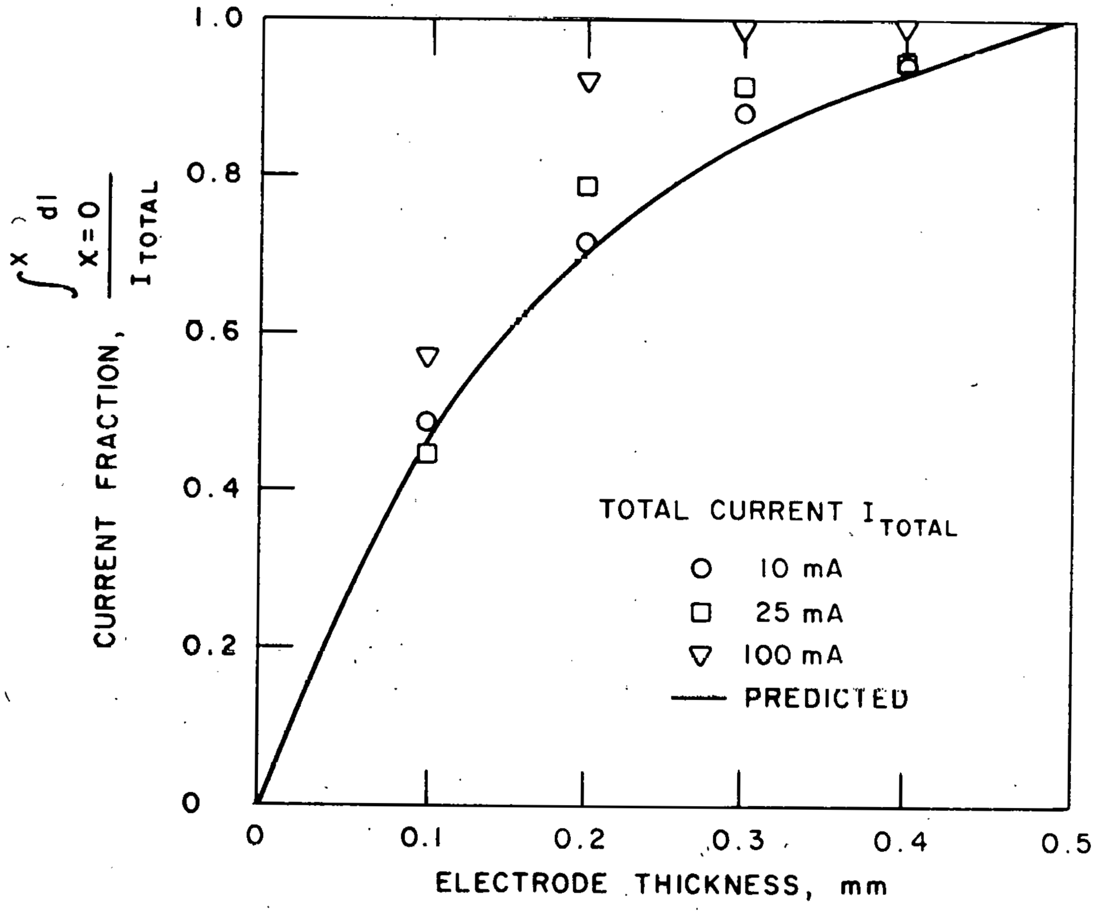

FIGURE IV-1: COMPARISON OF INITIAL AND PREDICTED CURRENT DISTRIBUTION IN SIMULATED POROUS ZINC ELECTRODES

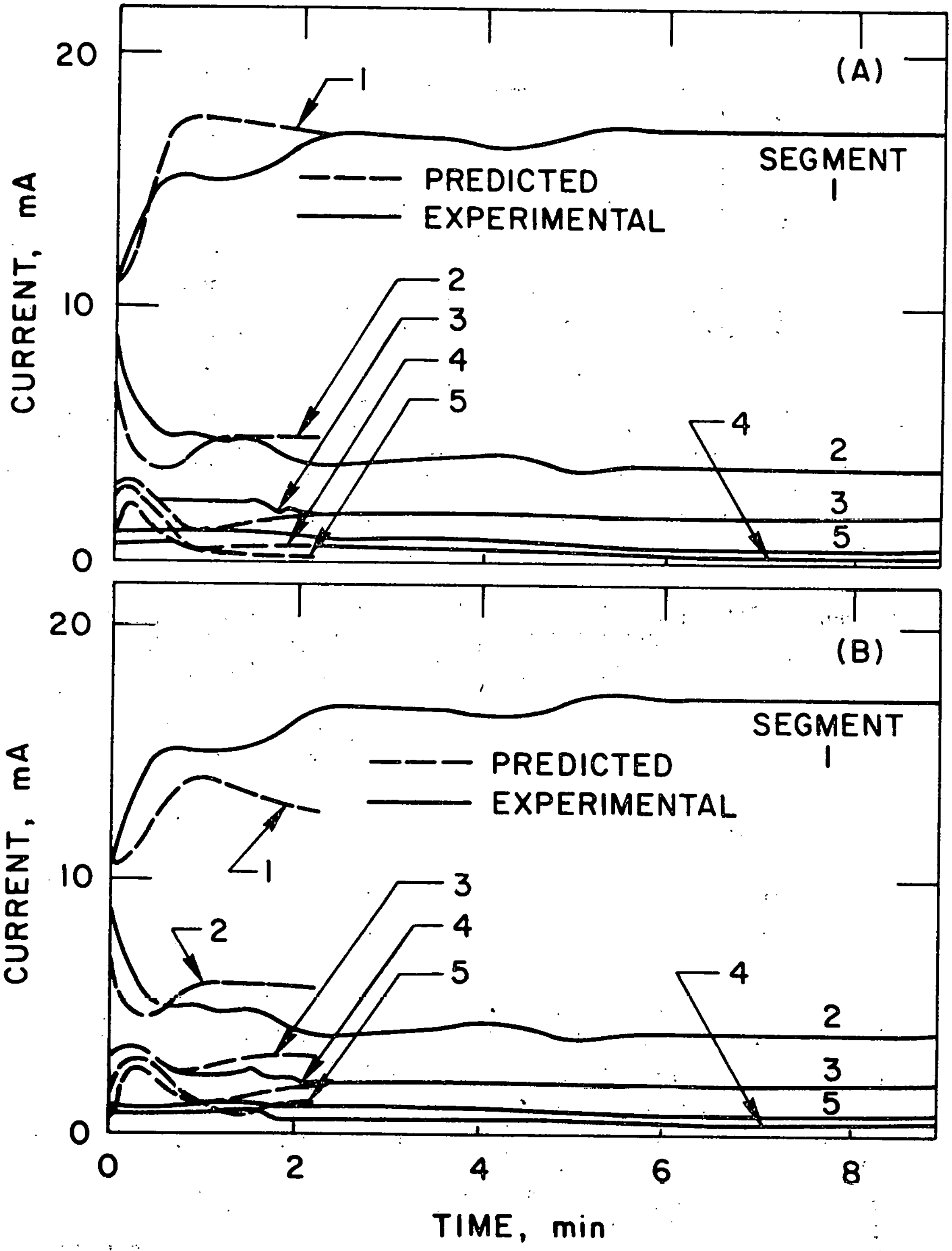

FIGURE IV-2: EXPERIMENTAL AND PREDICTED CURRENT DISTRIBUTIONS OF THE SIMULATED ZINC/ZINC OXIDE ELECTRODE IN KOH ELECTROLYTE
A. VARIABLE SPECIFIC CONDUCTIVITY OF ELECTROLYTE
B. CONSTANT SPECIFIC CONDUCTIVITY OF ELECTROLYTE

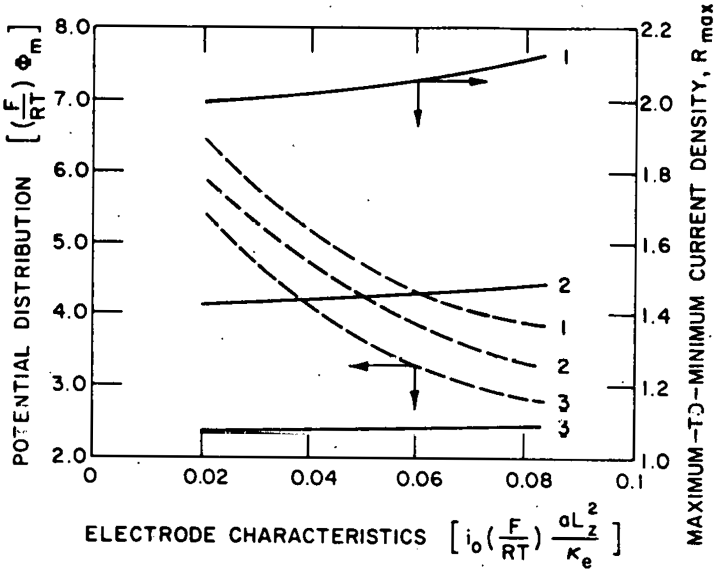

FIGURE IV-3: VARIATION IN ELECTRODE POTENTIAL AND REACTION NON-UNIFORMITY AS A FUNCTION OF ELECTRODE PROPERTIES (ALL UNITS ARE DIMENSIONLESS)

Curves	$\sigma_g \cdot \left(\frac{L_z^2}{L_x L_y}\right)\left(\frac{1}{\kappa_e}\right)$
1	0.15
2	0.30
3	1.5

The nomenclature for terms used in the figure is as follows:

F, R, T	Usual electrochemical definitions
i_o	Exchange current density
L_x, L_y, L_z	Electrode length, width, and thickness, respectively.
a	Specific surface area of the electrode
I	Total electrode current
R_{max}	Ratio of the maximum-to-minimum current density at a fixed total current (a measure of non-uniformity of reaction)
Φ_m	Electrode/electrolyte potential
κ_e, σ_g	Conductivities of electrolyte and grid, respectively.

3. Laser Raman Scattering Studies

Laser Raman spectroscopy has been used for the in-situ identification of electrochemically active compounds and crystalline phases of electrode materials. An experimental cell was designed to permit the spectroscopic measurements to be made while the electrode was under potentiostatic or galvanostatic control. Typical spectra for in-situ and ex-situ $PbSO_4$(33) are given in Figure IV-4. Both cases provide essentially the same spectra. However, in the case of the in-situ spectrum the signal is somewhat less intense causing a loss of the weaker bands. With anodic oxidation of tetrabasic lead sulfate (TBLS), which is used commercially by some manufacturers to fabricate the lead/lead dioxide positive electrode, laser Raman spectra indicated the direct oxidation to PbO_2 when TBLS was potentiostatically oxidized. The work is being continued.

B. Thermal Modeling of Ni/Zn Batteries

In previous work at ANL(34-36), a thermal model was developed for predicting thermal excursion in lead-acid electric vehicle and utility batteries. The same techniques were recently applied to Ni/Zn electric vehicle batteries to determine the time dependency of thermal excursion during cycling. The results obtained were in excellent agreement with data obtained from tests of Ni/Zn batteries at the NBTL.

Based on this model, the effects of cell height and electrode thermal conductance on the cell temperature rise were predicted for Ni/Zn cells. The impact of these parameters on cell temperature is shown in Table IV-1. The height of electric vehicle battery cells generally varies between 26 cm and 40 cm.

Table IV-1

Predicted Effect of Cell Design Parameters in the Maximum Temperature Rise on Ni/Zn Cells

Parameters		
Height cm	Dimensionless[a] Thermal Conductivity	Maximum Temperature Rise °C
34.4	1	22.7
24.2	1	18.2
34.4	1.5	16.2

[a] An arbitrary parameter used to fit typical experimental data to provide a baseline.

As a result of the insight gained in this study, a subcontracted effort has been initiated with the University of Illinois to investigate the possibility for design modification to permit passive cooling of Ni/Zn cells.

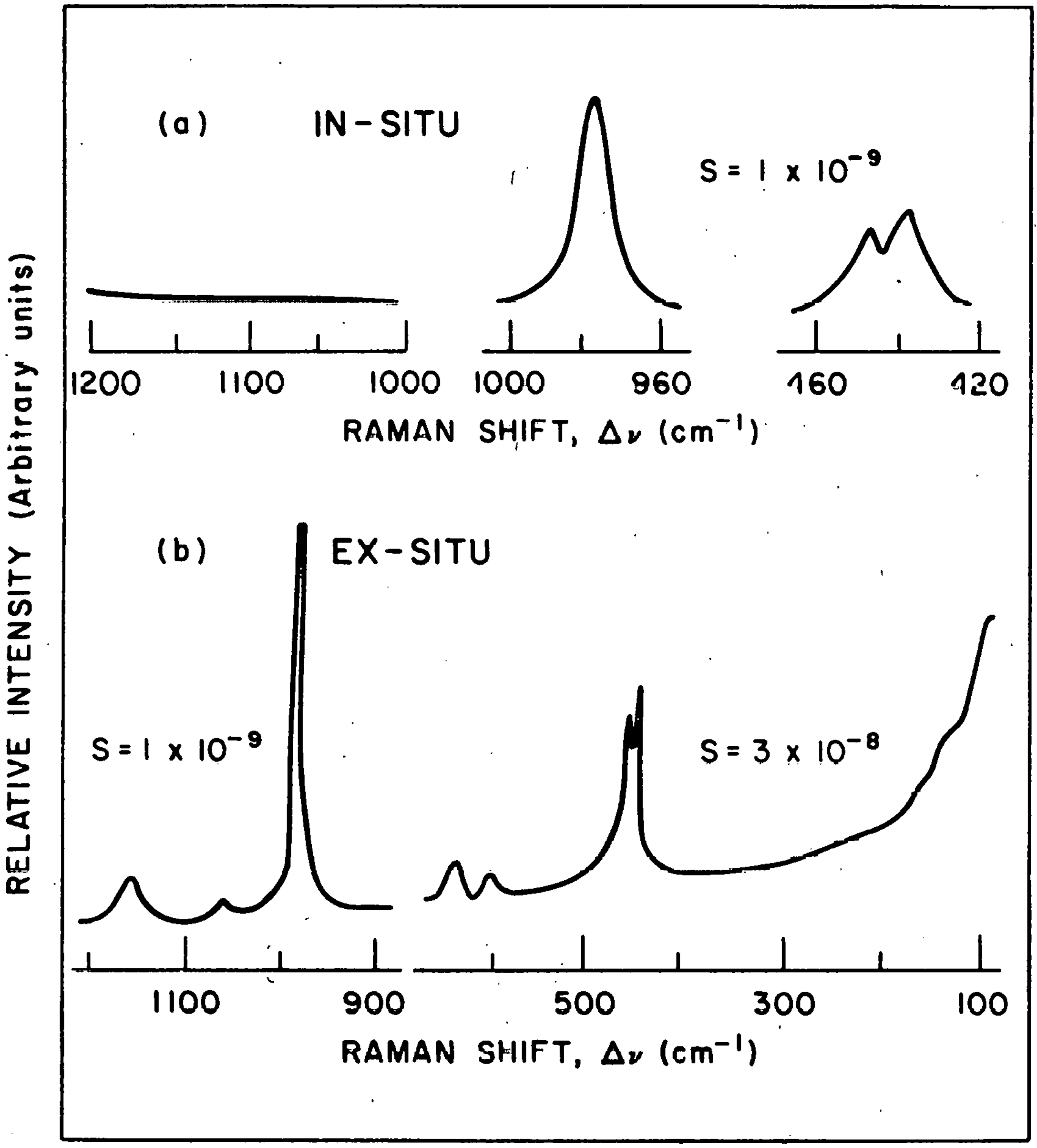

FIGURE IV-4: RAMAN SPECTRA FOR $PbSO_4$

RAMAN SCATTERING

Argon Blue Laser, λ = 4879.9 A°

(a) Lead Electrode Anodized in 0.1 N H_2SO_4 at -0.451 V vs. Hg/Hg_2SO_4 Reference

(b) Compressed $PbSO_4$ Pellet

C. Temporary Loss of Capacity in Ni/Zn Cells

Electrochemical studies carried out during the past year have provided information on the declining cell capacity observed in Ni/Zn cells. At times, charged Ni/Zn cells under test at the NBTL have been observed to temporarily lose usable capacity. The capacity however can be recovered by gradual return of cycling to normal deep discharge levels. During post-test analysis of these batteries, several techniques have been used to verify this. The results of these tests are being analyzed. However, bench-scale studies seem to indicate that the zinc reacts with the electrolyte at a rate comparable with the observed decline in cell capacity. This would seem to indicate that the zinc electrode is the cause of the temporary loss in capacity. Further work is underway in order to understand and to minimize this undesirable effect.

D. Stibine and Arsine Investigations in Lead-Acid Batteries

In 1978, an experimental field kit(37) was developed to estimate the amounts of SbH_3 and AsH_3 produced in lead-acid batteries during normal charging and equalization charging. SbH_3 and AsH_3 generation is expected when antimonial grid lead-acid batteries are charged above 2.4V. During this past year, this kit was used to sample air in and around electric vehicles undergoing testing at U.S. Army MERADCOM, Fort Belvoir, VA. This study has indicated that, in general, the levels of these gases are below the OSHA* TLV** limits of 0.1 ppm v for SbH_3 and 0.05 ppm v for AsH_3. Typical results are given in Table IV-2. However, since the OSHA limits are approached under some conditions such as during equalization charging of the battery, proper handling and ventilation of electric vehicle batteries being tested is required. An alternative approach is to modify the charging conditions such as to reduce the maximum charging voltage to the minimum level required to fully charge the battery, thus minimizing the quantities of SbH_3 and AsH_3 produced. Work is continuing to test additional lead-acid battery vehicles under variable operating conditions.

E. Post Test Analysis

The purpose of this effort is to supplement the contractor efforts by providing prompt analysis of failed units. In this way, the observations are not confused by reactions which take place after failure, such as chemical attack of electrode active materials. Other aspects of this task include:

a. The development of quantitative measure of failure or degree of failure.

b. Identification of not only the actual failure mode, but also possible future failure modes.

c. Identification of failure modes which are common to each battery system, regardless of manufacturer.

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*Occupational Safety and Health Administration

**Threshold Limiting Value

Table IV-2. Stibine and Arsine Generated During
Electric Vehicle Tests at MERADCOM
(Sample taken 5 inches above cell top)

Batteries Tested: Models XPV-23 and EV-106 from ESB Inc.,
Model P-20 from Varta A.G.

Normalized Condition		SbH_3, ppmv	AsH_3, ppmv
8 hour equalization	Average:	0.044	0.007
	Range:	(0.010-0.097)	(0.001-0.020)
1 hour on-board vehicle with regenerative braking	Average:	0.020	<.001
	Range:	(0.007-0.037)	(<.001)
8 hour OSHA TLV		0.1	0.05
15 minute OSHA TLV		0.3	0.15

V. RELEVANT NON-ANL SUPPORT RESEARCH

In addition to the battery research and development activities carried out under the direction of ANL, DOE supports other research efforts on electric vehicle batteries. Of particular interest are a number of basic research topics grouped under the Applied Battery and Electrochemical Research Program managed by The Lawrence Berkeley Laboratory. The pertinent topics are described briefly in the following paragraphs.

Research on Lead-Acid Battery Electrodes(38)

Caulder and Simon of the Naval Research Laboratory are investigating the basis for the improvement of life, capacity, and specific energy of the lead-acid battery by increasing utilization of the electrode active material, and by determining the factors that ultimately lead to nonreversibility of the electrode reactions and loss of battery capacity, such as changes in the active material composition and structure. Nuclear magnetic resonance spectroscopy, x-ray diffraction, and neutron diffraction have been employed to characterize the PbO_2 species formed on the positive plate as the battery is charged and discharged. These studies have shown that electrochemically active PbO_2 contains a small concentration of a proton species, perhaps as OH^- occupying O^{2-} sites in the ionic lattice, and that loss of electrochemical activity is apparently associated with loss of this proton species from the PbO_2 structure.

Development of Electrochemical Synthesis and Energy Storage-Anodic Surface Layers on Battery Materials (39)

Muller of Lawrence Berkeley Laboratory is obtaining direct experimental evidence about properties and modes of formation of anodic surface layers on materials of interest for battery applications in order to define the physical condition of surface layers with desirable electrochemical properties and find means for their consistent generation. The growth of $PbSO_4$ films on planar Pb electrodes has been studied using fast in-situ automatic ellipsometry. Transport of dissolved reaction products has been shown to be an important factor in determining the porosity of the sulfate film.

Research on Alkaline Zinc Secondary Electrodes(40)

Hamby at Linfield Research Institute is performing studies to provide information which will aid in the production of a reproducibly long-lived zinc secondary battery. This battery will be designed and constructed in such a manner as to retain the high energy density and power density capabilities of the porous zinc electrode. Recent work has emphasized evaluation of failure modes of electrodes operated under conditions of severely limited convection as predicted by Sunu(41) The failure mode which has been investigated experimentally is that of short-term failure due to OH^- concentration decreases in small electrodes, operated under the stated restrictions. Results to date fail to support OH^- depletion as a primary failure mode under the given circumstances.

Temperature Limitation of Primary and Secondary Alkaline Battery Electrodes

McKubre and McDonald(42) of SRI International studied the limitations imposed on the operation of alkaline batteries containing nickel, iron, or zinc electrodes in the temperature range of -20° to 120°C. The principal accomplishment has been comprehensive surveys of the kinetics and thermodynamics of these electrodes in aqueous NaOH systems; a number of specific features that relate to the use of these metals for battery electrodes were observed.

Basic Development of Nickel/Zinc Batteries

The goals of this work by Katan(43) at Lockheed Missiles and Space Co. Inc. is to gain insight into the operation of nickel oxide and zinc electrodes from a study of a model single-pore system containing two planar electrodes. In-situ viewing of the working electrodes with a stereozoom microscope has led to these principal findings:

1. Short circuiting at open circuit due to dendrite growth was observed in the presence of concentration gradients which resulted in zinc deposition at frontal locations.

2. Migration of metallic zinc particles by means of electrochemical displacement was demonstrated (this process may contribute to shape change and slumping).

3. Evidence was obtained that indicates hydrogen formation precedes zinc dendrite growth and that hydrogen formation occurs when zincate ions are depleted at local sites.

4. Nickel oxide electrode deterioration was found to be associated with exfoliation or detachment of the nickel oxides from the nickel substrate.

Other R&D efforts on near-term electric vehicle batteries directed by the Navy and funded by DOE through ANL are described below:

High Cycle Life, High Energy Density Ni/Zn Batteries

Otto Wagner(44) of U.S. Army ERADCOM has developed a 5-Ah rated Ni/Zn cell which has provided a life of over 300 cycles at the C/5 rate with capacities ranging from 4.1 to 4.3 Ah at cycle 300. An important component of this cell is a nickelized Celgard 2500 plus cellophane separator sandwiched between two layers of Celgard 3500. This separator combination has also minimized shape change of the zinc electrode on cycling. Reduced hydrogen evolution and zinc penetration rates have been achieved by additives and modified charging rates respectively.

Separators for Zinc Systems

Isaac Angres(45) of Naval Surface and Weapons Center (NSWC) is evaluating separators based on polyphenylquinoxaline (PPQ) heterocyclic polymer in combination with cellulose acetate (CA) in 2-Ah Ni/Zn and Ag/Zn cells. Preliminary cycling results indicate that this combination of separators outperforms the commonly used cellulosic separators.

VI. BATTERY COMPONENTS RESEARCH AND DEVELOPMENT

A. Techniques for Charging and State-of-Charge Monitoring

Two 200-A test stations which provide a variety of charge and discharge test conditions, were assembled to initiate battery charging studies at ANL. Selectable features include programmable current or power discharges with constant or pulsed levels of operation; variable individual cell discharge rates to establish known deviations in cell depths of discharge for equalization studies, and bulk, taper, and equalization charging. Cell equalization can be performed either electronically by limiting the voltage and bypassing the current of individual cells or chemically by limiting battery voltage only. Using these test stations, studies of cell and battery characteristics have been initiated.

Electronic cell-charge equalization tests were performed on a 4-cell, 240 Ah Ni/Zn module. This module exhibited a capacity of only 94 Ah during cycling at NBTL due to the limiting behavior of a single cell. Electronic equalization was performed using various cell voltage limits in an attempt to improve capacity. These tests showed that the poor performance of the capacity limiting cell was due to active material loss, rather than due to increased self-discharge. With an equalization current of 6 A, a rise in cell temperature and a decrease in cell voltage occurred during the equalization period. These test data are being reviewed and additional tests will be performed.

Charging studies are in progress to quantify cell and battery characteristics of an EV-106 lead-acid battery as a function of charging rate. A LSI-11 computer system is temporarily being used to control and monitor test conditions and acquire performance data. Bulk charge currents of 25 to 200 A (in 25 A increments) followed by taper and equalization charge will be used. The test data are presently being acquired and reviewed, and results will be reported in the future.

Charging studies were initiated to quantify battery performance and charge current characteristics using an SCR current controlled scheme directly off the AC line without the use of a transformer. Initial test data showed that the high frequency structure of the charge current waveform yields a high ratio ($\sim$3) of root-mean-square (RMS) current to average current. This leads to increased battery temperatures and power losses during the charging period. Various levels of current filtering can be used to reduce this ratio thereby improving performance and energy efficiencies. To provide wideband power and RMS current measurements, a detector and signal conditioning module was designed. Two such units are being fabricated, and testing will be resumed when their construction is completed.

To facilitate the simultaneous testing of multiple battery components and acquisition of test data, a multi-user test control and monitoring system is being procurred. Laboratory space to accommodate the additional equipment and the multiple testing stations is being prepared at ANL. The expanded test system and laboratory, which is to be operational in June 1980, will provide the required test and data acquisition capabilities for battery charging studies, state-of-charge monitor development, and Ni/Zn battery separator testing.

Commercially available state-of-charge monitors of the battery voltage sensing type have been evaluated. Several design proposals for other state-of-charge monitoring equipment of the battery impedance and/or electrolyte specific gravity sensing type have been reviewed. A state-of-charge indicator manufactured by Perfection Electronic Products Corp. was tested and analyzed; other devices are also being assessed.

B. Nickel/Zinc Battery Separator

The separator is one of the key elements in sustaining cell performance and cycle life in Ni/Zn batteries. Separators commonly used in alkaline cells are made from commercially available organic or inorganic films, generally composed of one of the following materials: 1) Cellulosic material such as DuPont cellophane, Union Carbide fibrous sausage casings, grafted cellophane, etc., 2) nylon-type materials such as Pellon 2505 and 2506, Cerex and other non-woven nylon fabrics, etc. 3) polypropylene-type materials such as Pellon FT-214, GAFWEX-1242, Kendall XM-1249, Hercules 2615-15, W. R. Grace

3073-22, RAI/GAF 4215-5, Celanese Celgard and other nonwoven polypropylene fabrics; 4) polyethylene-type materials such as RAI permion 2291; and 5) other separator materials such as nonwoven polyvinyl alcohol (PVA), PVA films, PVA felt, polyvinyl chloride (PVC) films, and asbestos papers.

The cellulosic materials have the desired pore structure, but have low permeability to electrolyte and water and tend to deteriorate in the alkaline environment. Nylon-type separators have a fine pore structure, low electrical resistance, and are of low cost, but are unstable in the cell environment and subject to degradation by oxidation. The porous polypropylene materials have pores too large to prevent dendrite growth of the zinc electrode, whereas separators of grafted polyethylene have small pores which retard dendrites growth, but tend to accelerate shape change in the zinc electrode. In addition, the latter material is relatively expensive.

A contract to conduct a survey of separator material has been awarded to Brigham Young University and will become effective January, 1980.

Other separator development studies have also been carried out by NASA-Lewis Research Center; U.S. Navy contractor at Naval Surface and Weapons Center (NSWC) at White Oak Lab, Silver Spring, Maryland; US Army Electronic Technology and Devices Laboratory (ERADCOM) at Fort Monmouth, NJ; and DOE/ANL Ni/Zn battery contractors. Related efforts at General Motors Research Lab have also been reported.(46,47)

VII. BATTERY/VEHICLE SYSTEM INTEGRATION

A. Vehicle Integration and Engineering Activities

Vehicle integration and engineering activities during this period consisted of providing technical support for the testing of batteries in vehicles. A few vehicles were built for the purpose of testing new technologies such as those from the near-term battery research and development efforts discussed earlier. These vehicles are tested primarily at JPL under closely controlled conditions. During 1979 this task was initiated to give direct battery support to in-vehicle testing activities.

In 1977, DOE contracted with four manufacturers to fabricate two vehicles each (sometimes called the "2x4" program) with "off-the-shelf" components and using selected product improvements where possible. These vehicles used various lead-acid batteries which generally represented the state-of-the-art. These vehicles were delivered during 1979 to MERADCOM for acceptance testing, and also to JPL for use as test vehicles in evaluating improved batteries and propulsion components. Argonne and JPL jointly selected (in early 1979) three near-term battery contractors to supply one Ni/Fe battery and two Ni/Zn batteries for system compatibility testing in these vehicles. Figures VII-1 to VII-3 are photographs of these batteries. Identical battery modules were also delivered to NBTL for performance verification testing and data correlation with JPL in-vehicle test results.

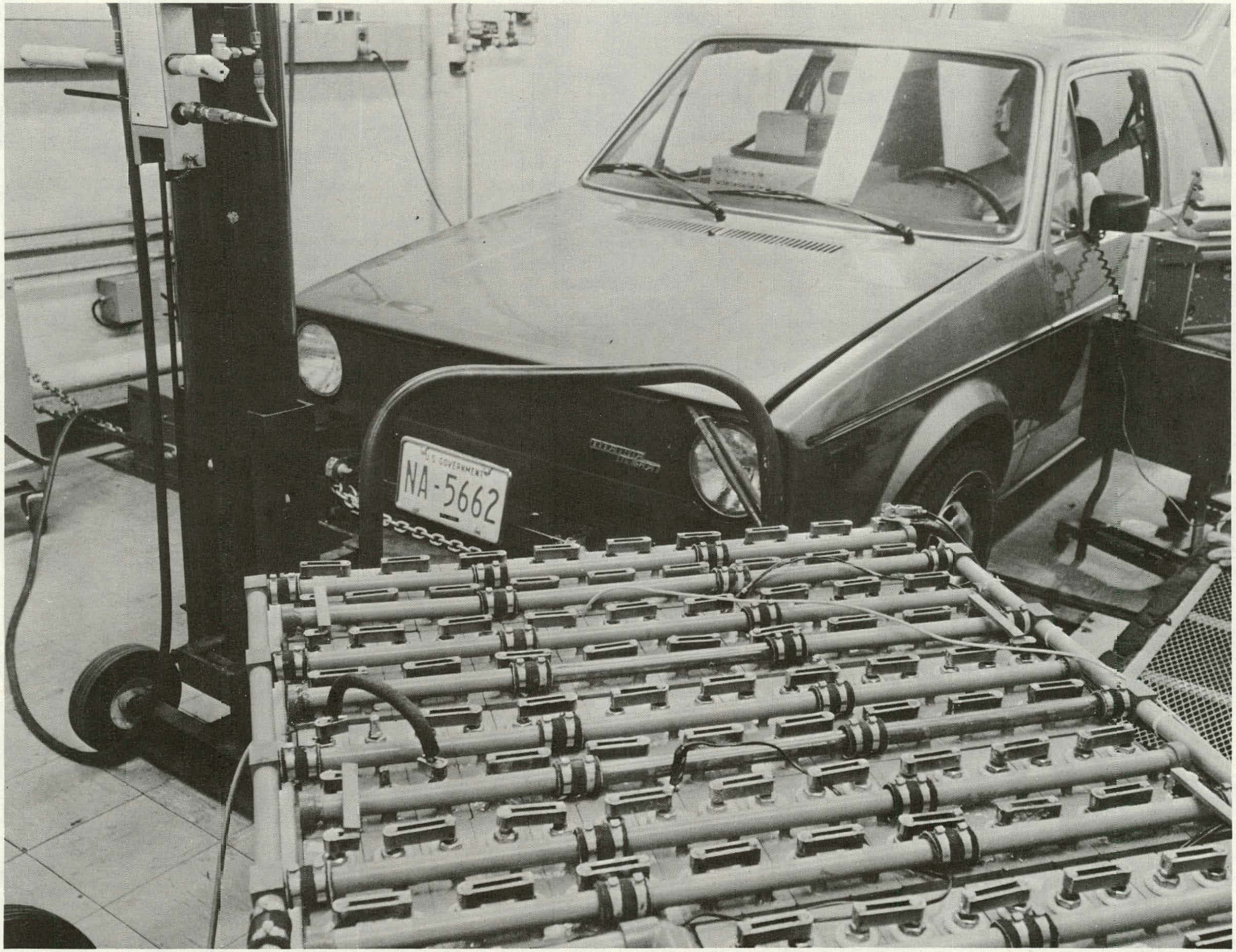

Fig. VII-1. Westinghouse Nickel/Iron Battery, 122 V, 210 Ah, Total Weight - 1194 lbs. ANL Neg. No. 308-80-182K.

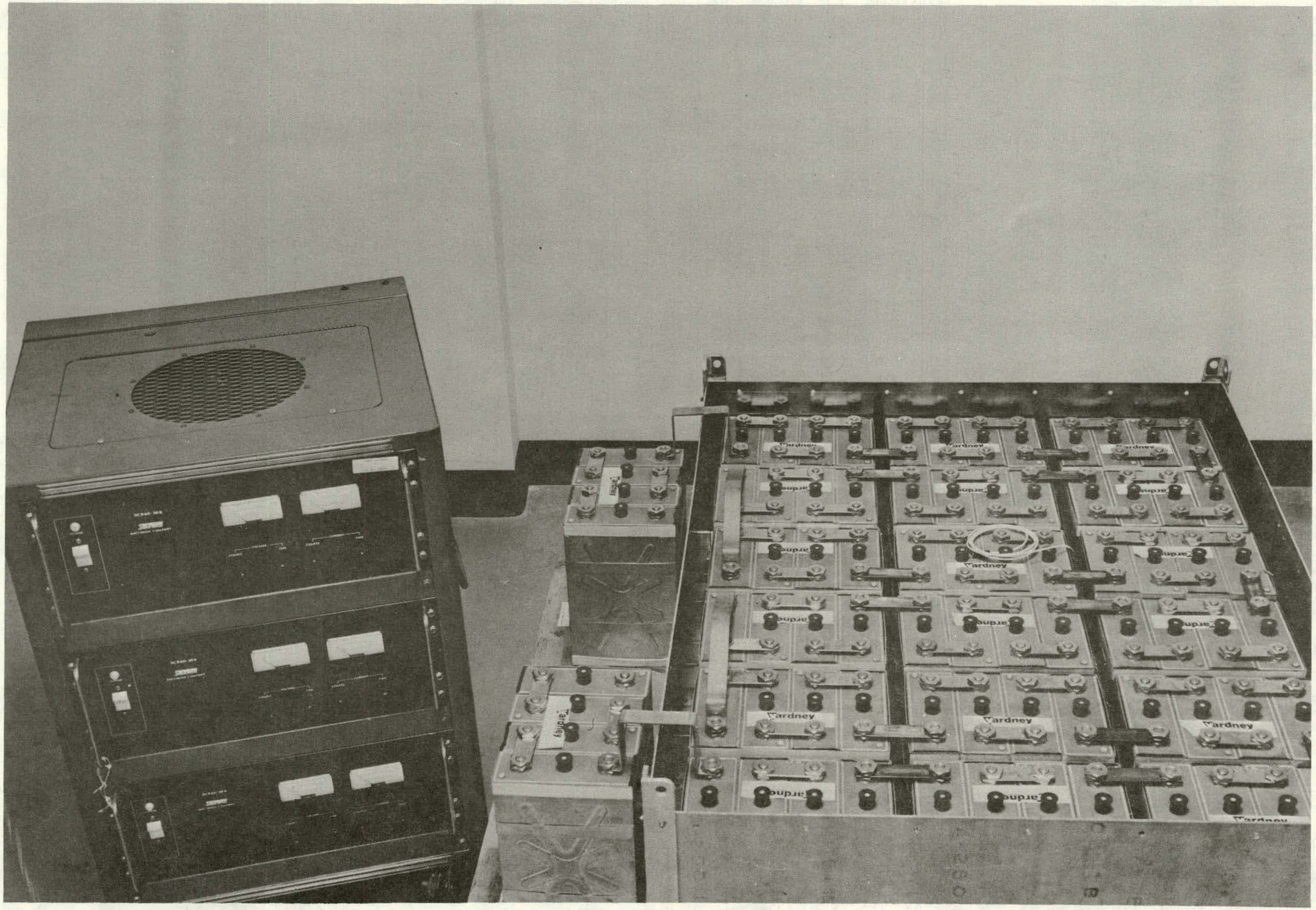

Fig. VII-2. Yardney Nickel/Zinc Battery, 180 V, 250 Ah, Total Weight - 1152 lbs. ANL Neg. No. 308-40-184K.

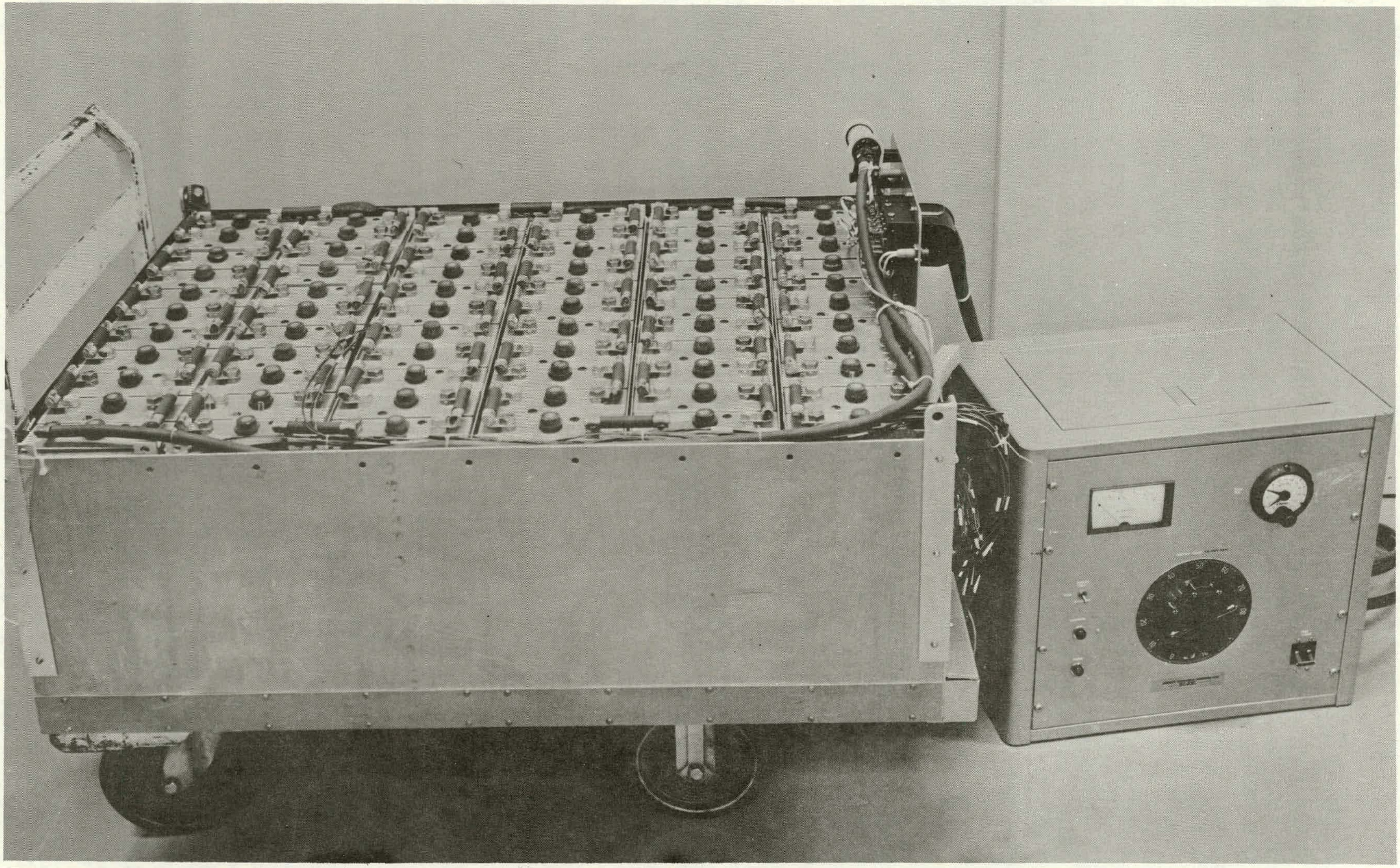

Fig. VII-3. ERC Nickel/Zinc Battery, 108 V, 250 Ah, Total Weight - 1210 lbs. ANL Neg. No. 308-80-183K.

The object of the JPL testing was to uncover any unexpected battery/vehicle interface problems associated with these batteries. Of course, the relative performance of these battery types would also be determined from these tests. However, the batteries represented early contractor designs and were expected to require close maintenance and to exhibit premature cell failure since the cell designs and manufacturing techniques were untested. Even with this handicap the 1979 program objective was reached. No serious unexpected battery/vehicle interface problems occurred with the Ni/Fe and Ni/Zn batteries.

JPL will report separately, in detail, on the performance results achieved in these in-vehicle battery tests(48). However, preliminary performance results from NBTL and JPL can be reported and are shown in the following table VII-1. The ESB lead-acid battery (EV-130) represents the baseline battery incorporated in the vehicle as delivered.

Table VII-1
Battery Data From JPL Tests in South Coast
Technology Inc. Electric Rabbit and Tests in NBTL

Battery Characteristics	ESB	Westinghouse	ERC	Yardney
Type (108V)	Lead-Acid (EV-130)	Nickel/Iron	Nickel/Zinc	Nickel/Zinc
Weight, kg	507	542	564	524
Capacity, kwh rated	19	23	27	29
Performance				
Specific Energy, Wh/kg				
Module, NBTL	32[a]	48	32	46[b]
Battery, JPL	31[c]	44	40	46[b]
Range Tests, JPL, miles				
35 mph (constant)	82	120	121	126
55 mph (constant)	44	74	48	84
Variable[d]	26	48	27	49

a. Manufacturers data, battery modules not yet tested in NBTL.
b. Based on manufacturer's recommended operation at 80% state of charge.
c. Estimate based on test data obtained for constant vehicle speeds of 35 and 55 mph.
d. Based on SAE J227a/D driving cycle.

The cycle life capability of the three near-term batteries used in these tests was determined to be too low to justify a previously planned 200 vehicle technology demonstration in FY 1980. Instead, the FY 1980 program was redefined along the lines of the FY 1979 program, including additional vehicle and battery deliveries to JPL for testing and further battery module deliveries to NBTL for support testing. Limited field and dynamomater testing of no more than 10 new vehicles using various near-term battery technologies is planned during 1980.

This FY 80 program, as structured, will show a clearer technical picture of the various near-term battery capabilities, and provide further manufacturing and test experience prior to the broader scale demonstrations planned for the following years.

B. Simplified Battery-Test Profile Definition

The capacity of a battery is normally determined by withdrawing a constant current until the voltage of the battery decreases to a specified value (the cutoff voltage). However, this is not representative of the battery discharge conditions during vehicle operation. Vehicle acceleration requires high power. The resulting drop in voltage requires a large discharge current from the battery to maintain the power level. During vehicle coast, battery power requirements are low, and so are the discharge currents. Further, some vehicles are capable of charging the battery during braking. This is termed "regenerative braking". Thus, an electric vehicle battery is subjected to varying discharge currents, and possibly charging during normal operation of the vehicle. To properly design or choose a battery for the electric vehicle application, the effects of these variable operating conditions upon battery capacity and life should be known.

The laboratory equipment necessary to simulate the battery power profile during vehicle operation is expensive as the voltage and current must be varied approximately every tenth of a second in order to track the vehicle power demand profile. Therefore, a simplified battery power profile is desirable. Step changes in battery current can be implemented with a minimum of difficulty and equipment complexity. Thus, a current profile incorporating three or four different current levels can be readily implemented. This section of the report describes the procedure and rationale used to arrive at such a simplified profile.

It was first necessary to select a representative battery power output profile. Then, a calculational procedure was defined for converting the power profile to a stepped current discharge. A schematic of a standard driving profile based on the schedule "D" cycle of the SAE J227a Test Procedure is shown by the dashed line of Figure VII-4. A vehicle would be subjected to repetitions of this cycle involving acceleration, constant velocity, coasting, and braking simulating operation in an urban/surburban environment. The battery power profile associated with this driving profile is shown by the solid line in Figure VII-4 and represents that of the GE/Chrysler vehicle (ETV-1) based on computer simulations by General Electric. The negative portion of the power curve represents the power available from regenerative braking. The required battery power output during each portion of the driving cycle is dependent upon vehicle weight, vehicle road load characteristics, and efficiencies of the vehicle drive-train components.

The GE/Chrysler electric vehicle is generally assumed to be representative of the type of electric passenger vehicle which may be commercially available in the mid 1980's. Thus, its battery output power profile is assumed to be representative of what any battery of the same weight must supply in a well-designed commuter car transversing the SAE J227a/D cycle. Implicit in this asusumption is the requirement that the total battery weight in this vehicle is 488 kg regardless of the battery type and characteristics. This necessitates that the motor, controller, and charging sys-

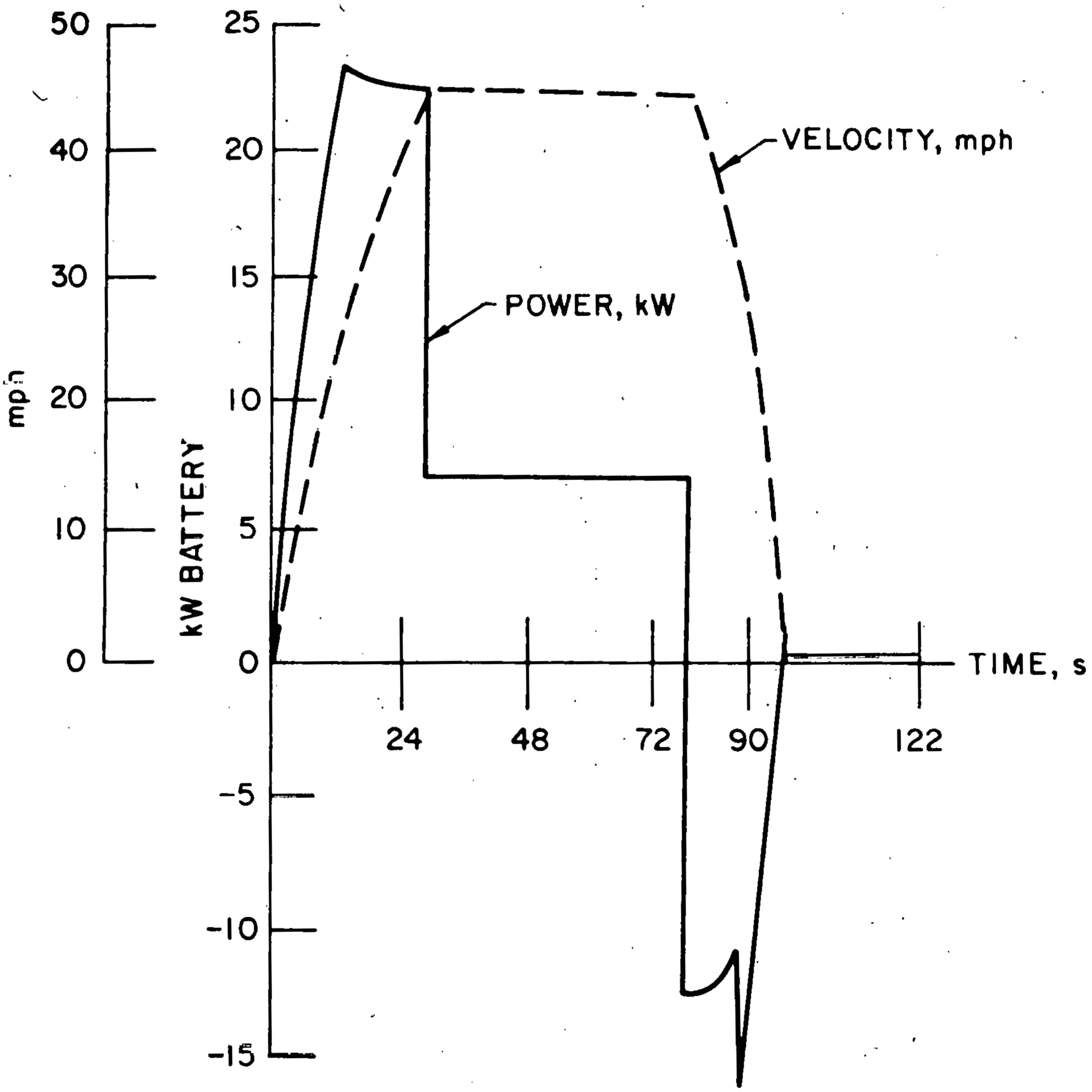

FIGURE VII-4: SIMULATED BATTERY POWER PROFILE AND VELOCITY PROFILE FOR SAE J227a/D GE-CHRYSLER VEHICLE tems be matched to the battery voltage level and that other vehicle characteristics (performance specifications, gross weight, and drive-train efficiencies) are not greatly altered. A first step in arriving at a simplified profile is to square up the profile of Figure VII-4 so as to yield the profile shown in Figure VII-5 having the same discharge and recharge energy, and very nearly the same cycle time.

Based on the above assumptions, determination of the battery power output profile for any particular battery is simple. The power levels shown in Figures VII-4 and VII-5 are multiplied by the weight of the cell, module or battery pack divided by the weight of the vehicle battery (488 kg) in order to obtain the applicable discharge profile.

The second step in arriving at a simplified battery test profile is to convert the power output profile to a stepped current discharge. As a battery is discharged using the power profile given in Figures VII-5, the voltage of the battery will decrease and thus, the current must increase to maintain the required power. Therefore, a representative average current must be determined. For example, the voltage-current characteristics of a Ni/Zn battery as a function of the depth of discharge would be as depicted in Figure VII-6. These lines illustrate the variation of voltage and current as a function of the depth of discharge. The nearly vertical dashed lines in this figure are lines of constant power illustrative of that needed for the acceleration and constant velocity portions of the driving cycle. The average currents to be used for the simplified profile are approximately those corresponding to the intersection of the two constant power lines with the voltage-current characteristics for a 50% depth of discharge.

The criteria for a choice of voltage-current characteristics to be used in determining the average currents can be quantified. The objectives to be met in choosing the average currents for the stepped-current battery discharge are that the ampere hours and watt hours delivered by the battery and the total discharge time of the battery be the same in both the simplified and actual profiles. It appears that all three objectives can be met but confirmation testing remains to be performed. Several computational schemes have been formulated for a prior estimate of current levels and appear to give good results, but comparison with the actual power profile discharge data awaits the installation of the necessary experimental equipment.

Experimental results for lead-acid, Ni/Zn and Ni/Fe batteries subjected to simplified discharge profiles with and without regenerative braking are reported in Figure III-6 of a preceding section.

C. Battery Application Model Development

The primary emphasis of the battery modeling effort has been the development of simplified application models which portray the dynamic electrical behavior of the battery in vehicle use. Such models are important for determining vehicle range, for studies of motor and controller design parameters and efficiencies, and for the development of state-of-charge meters. When coupled with thermal models, temperature effects under various loads and with different battery configurations can be studied.

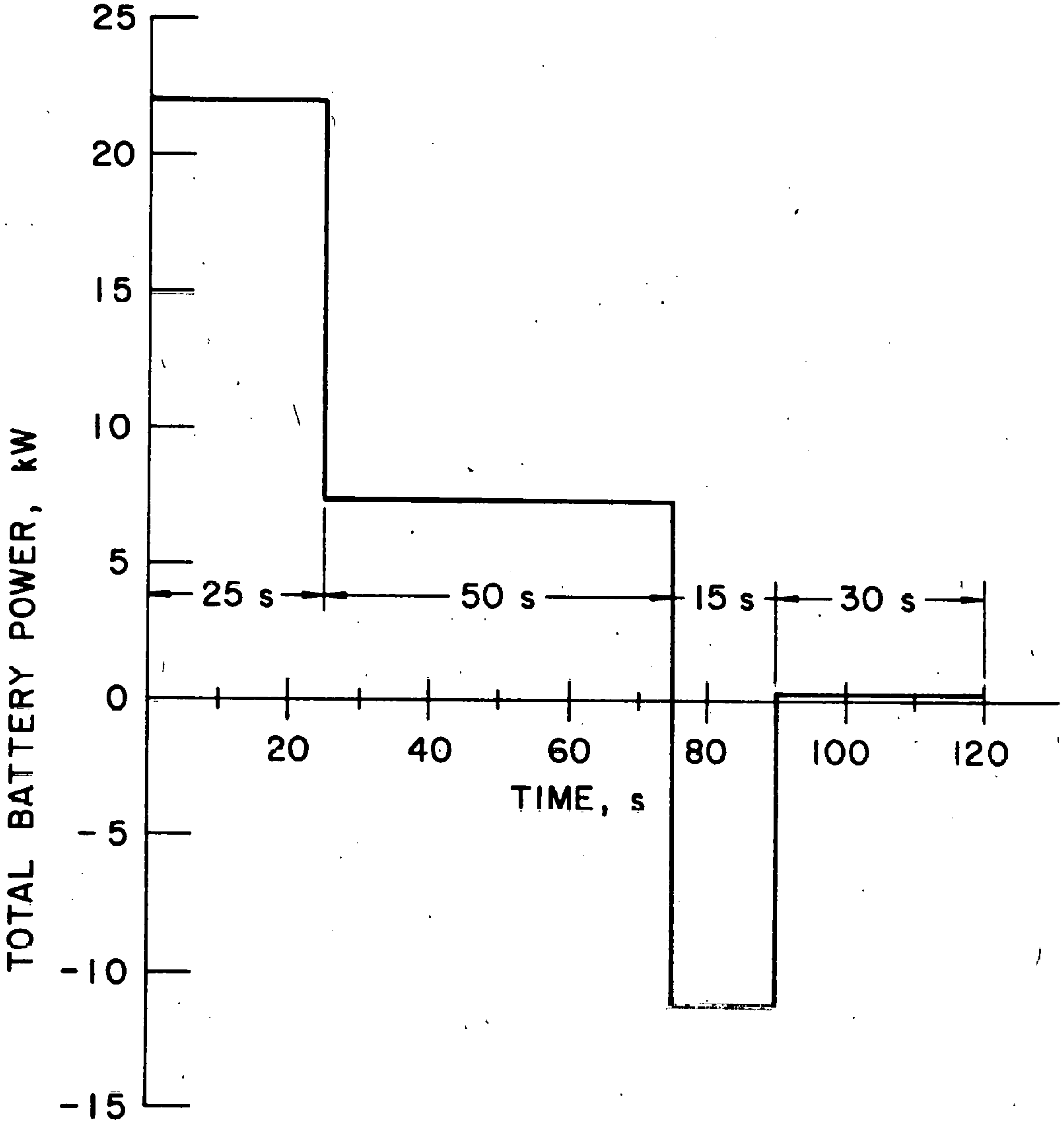

FIGURE VII-5: SQUARED UP BATTERY POWER SPECIFICATION FOR THE GE/CHRYSLER CAR (ETV-1) UNDERGOING THE SIMULATED J227a/D DRIVING PROFILE

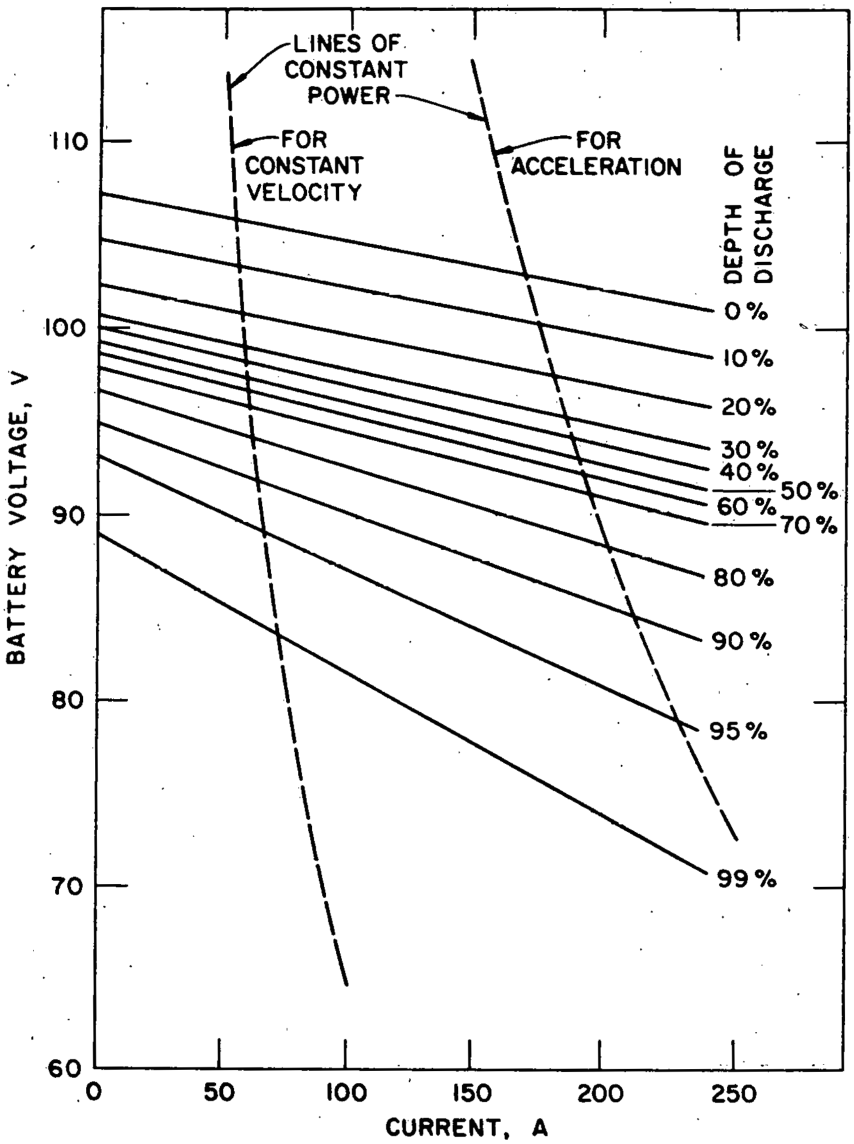

FIGURE VII-6: SCHEMATIC OF VOLTAGE - CURRENT CHARACTERISTICS AS A FUNCTION OF THE DEPTH OF DISCHARGE FOR A NICKEL/ZINC BATTERY

This initial modeling effort is based on a semi-empirical approach utilizing equivalent electrical circuits consisting of various combinations of resistors, capacitors, etc. to simulate the battery voltage-time behavior under various cycling conditions. The resistor, capacitors, etc. can be thought of as representing various aspects of the chemical kinetics and mass transfer which occur within the battery cells during operation of the battery. This type of approach has been previously used in the literature by Shepard(50) and is termed an equivalent electrical circuit (EEC) model.

Several EEC models of varying complexity have been developed. One of the simpler circuits is depicted in Figure VII-7. All of the EEC models are capable of simulating the most important features of the voltage-time behavior exhibited under an applied driving profile.

For example, the voltage-time behavior of a typical cell is depicted in Figure VII-8 along with an imposed stepped current discharge which simulates a driving cycle of about 120 seconds in duration. Assuming that the voltage source, resistances, and capacitance are constant, the battery voltage as a function of time and current is given by the following equations:

$$E_B = E_i - b_1R_2 - R_1b_1 \left[1-e^{-t/R_1C}\right]; \qquad \text{for } 0 \leq t \leq t_1$$

$$E_B = E_i - b_2 (R_1 + R_2) - R_1 \left[(b_1-b_2)e^{t_1/R_1C} - b_1\right]e^{-t/R_1C} \qquad \text{for } t_1 \leq t \leq t_2$$

$$E_B = E_i - R_1\left[b_2e^{t_2/R_1C} + (b_1-b_2)e^{t_1/RC} - b_1\right]e^{-t/R_1C} \qquad \text{for } t_2 \leq t \leq t_3$$

where the notation is defined in Figures VII-7 and VII-8. The voltage source, resistances, and capacitance are assumed not to vary for one stop/start driving cycle of 120 seconds duration. From data obtained at NBTL, values for the voltage source and resistances can be estimated. If it is assumed that the value of the capacitance is small, and hence that voltage transients die out quickly, a plot of battery voltage versus current as a function of the depth of discharge can be made. Figure VII-9 illustrates such a plot for the Yardney Ni/Zn cell. From this plot, the open-circuit voltage and total resistance for each depth of discharge can be obtained. These are shown in Figure VII-10. Similar plots are shown in Figures VII-11 and 12 for the Ni/Zn cell of ERC. For the EV-106 lead-acid and the Westinghouse Ni/Fe batteries, the voltage-current plots are non-linear and are depicted in Figures VII-13 and 15, respectively. Figures VII-14 and 16 provide the corresponding open circuit voltage versus resistance plots for the EV-106 lead-acid and the Westinghouse Ni/Fe batteries.

From these and other data on battery performance under driving profile loads, the following general observations were made: (1) The lead-acid and Ni/Fe batteries exhibit a similar non-linear voltage-current behavior; the Ni/Zn battery exhibits a nearly linear voltage-current relationship until approximately 80% depth of discharge, after which the relationship is non-linear. (2) As the batteries are discharged above 60% depth of discharge the internal resistance increases rapidly. The data analysis has also been used to define the experiments necessary to obtain the data accuracy required to fit the model coefficients. The determination of these coefficients (resistances, etc.) and tests to establish their validity will be performed in FY 1980.

A general or physicochemical type of model is also planned for development in FY 1980. In its simplified forms it will be more complex than the EEC model, but have a wider range of application. In its more complex form, it will be used to help understand the effects of the physicochemical interactions upon battery performance during electric vehicle operation.

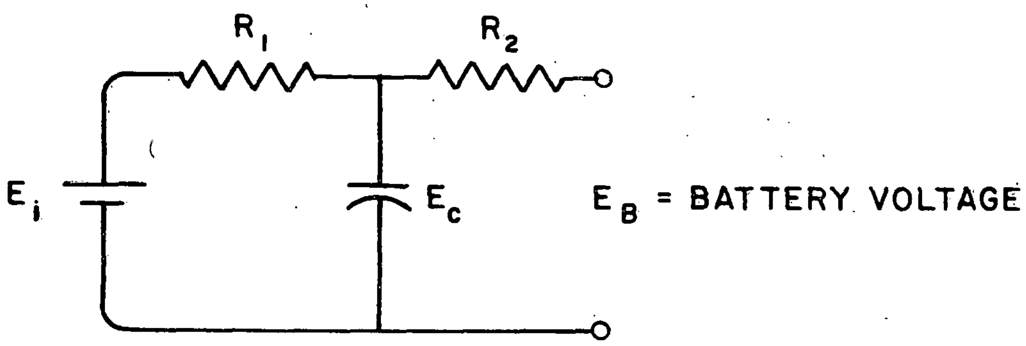

FIGURE VII-7: SIMPLE EQUIVALENT ELECTRICAL CIRCUIT FOR A BATTERY

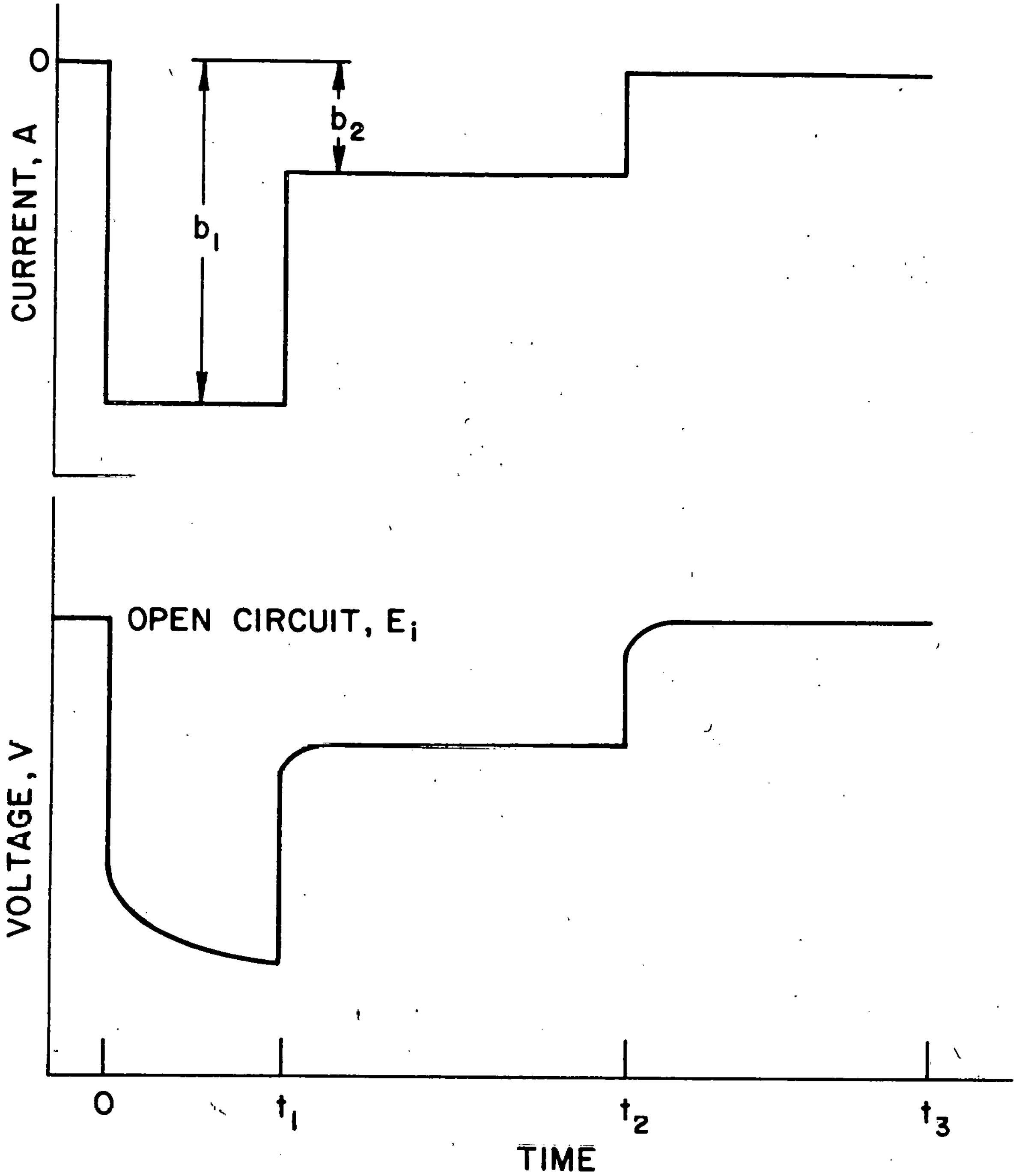

FIGURE VII-8: VOLTAGE-TIME BEHAVIOR OF A TYPICAL CELL AS A RESULT OF AN IMPOSED STEPPED CURRENT DISCHARGE

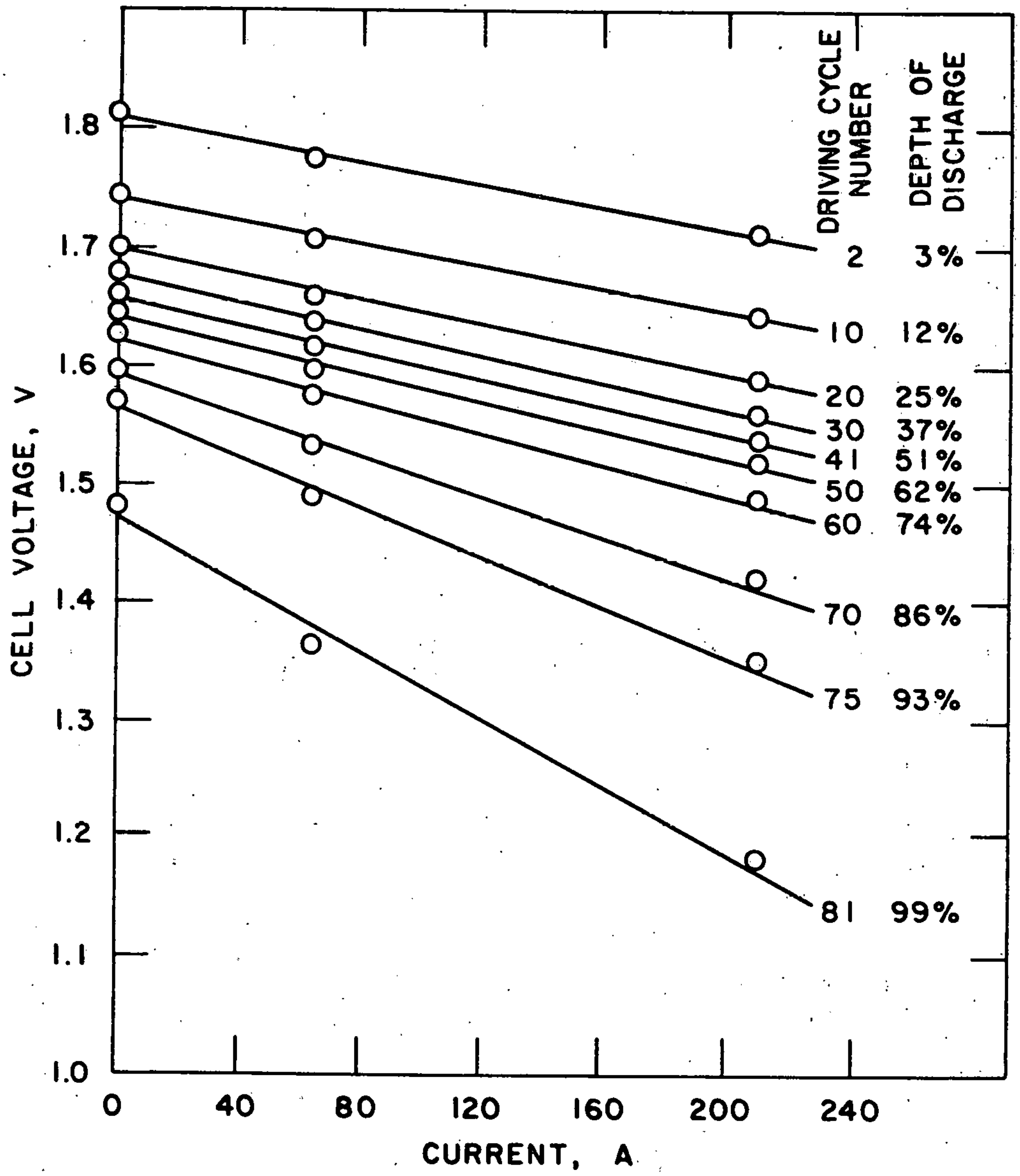

FIGURE VII-9: CELL VOLTAGE VERSUS CURRENT FOR A YARDNEY NICKEL/ZINC CELL

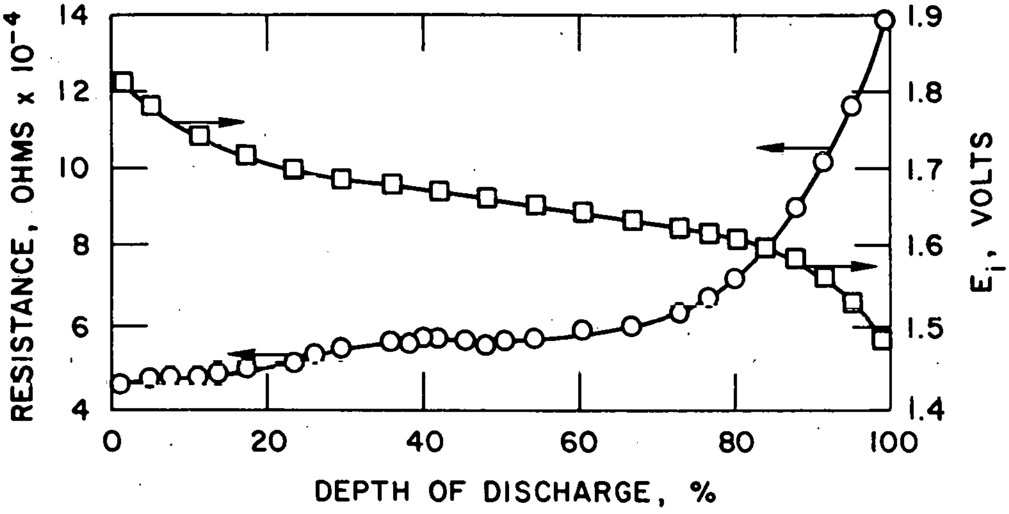

Figure VII-10: RESISTANCE AND OPEN CIRCUIT VOLTAGE AS A FUNCTION OF DEPTH OF DISCHARGE FOR A YARDNEY NI/ZN CELL

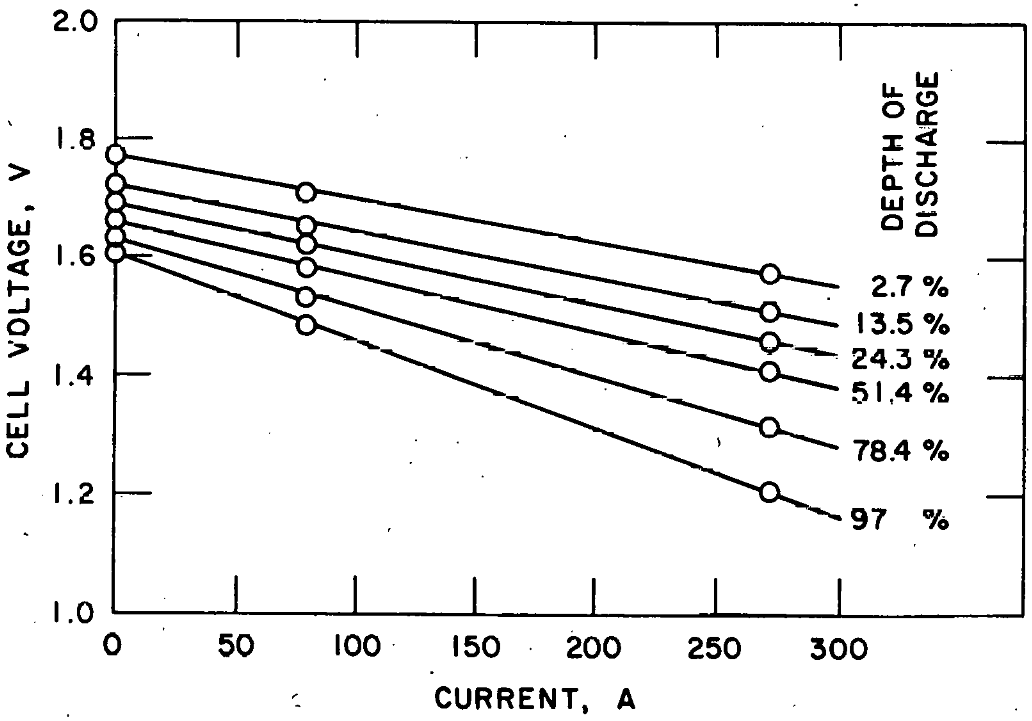

FIGURE VII-11: CELL VOLTAGE VERSUS CURRENT FOR AN ERC NI/ZN CELL

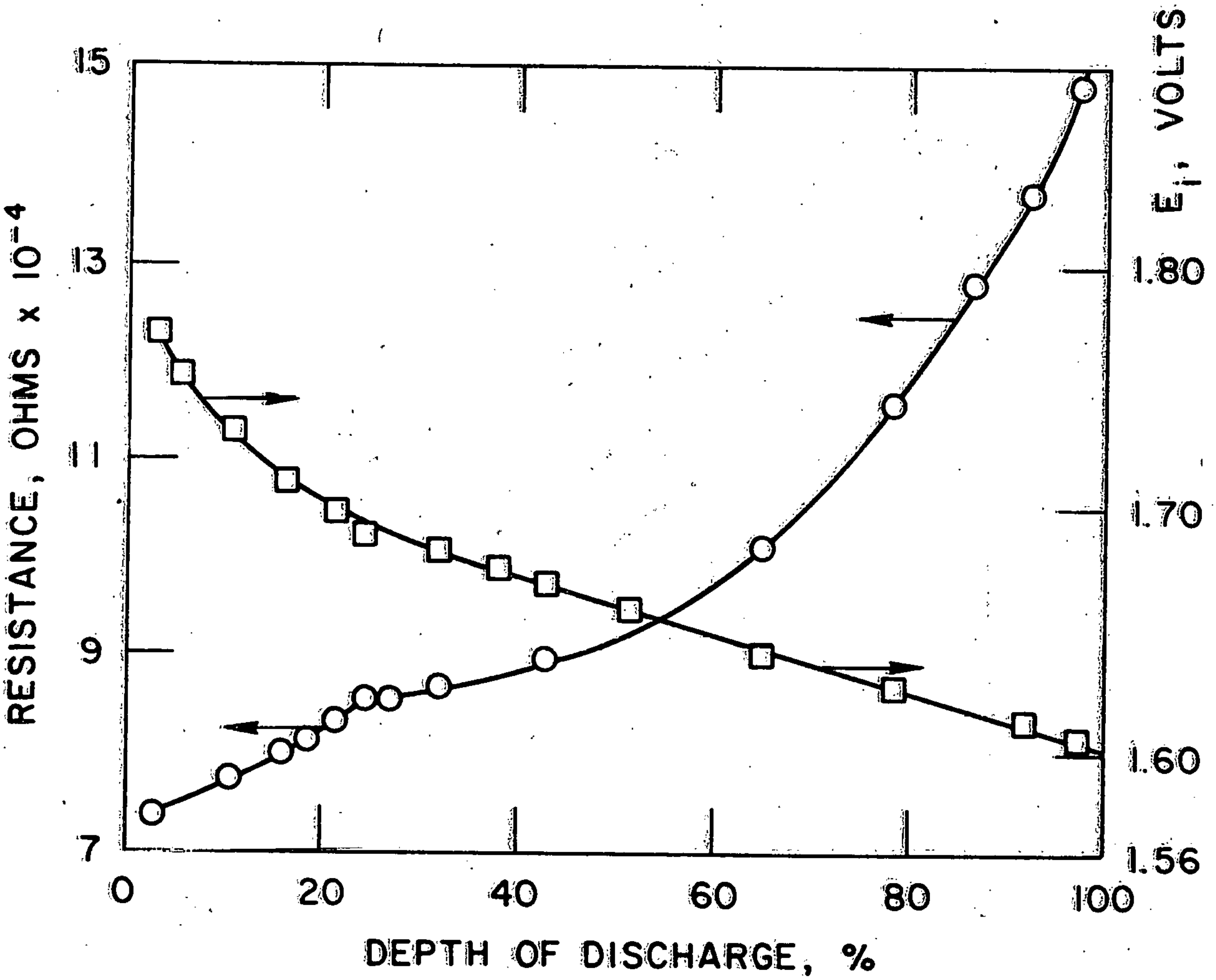

FIGURE VII-12: RESISTANCE AND OPEN CIRCUIT VOLTAGE AS A FUNCTION OF DEPTH OF DISCHARGE FOR AN ERC NICKEL/ZINC CELL

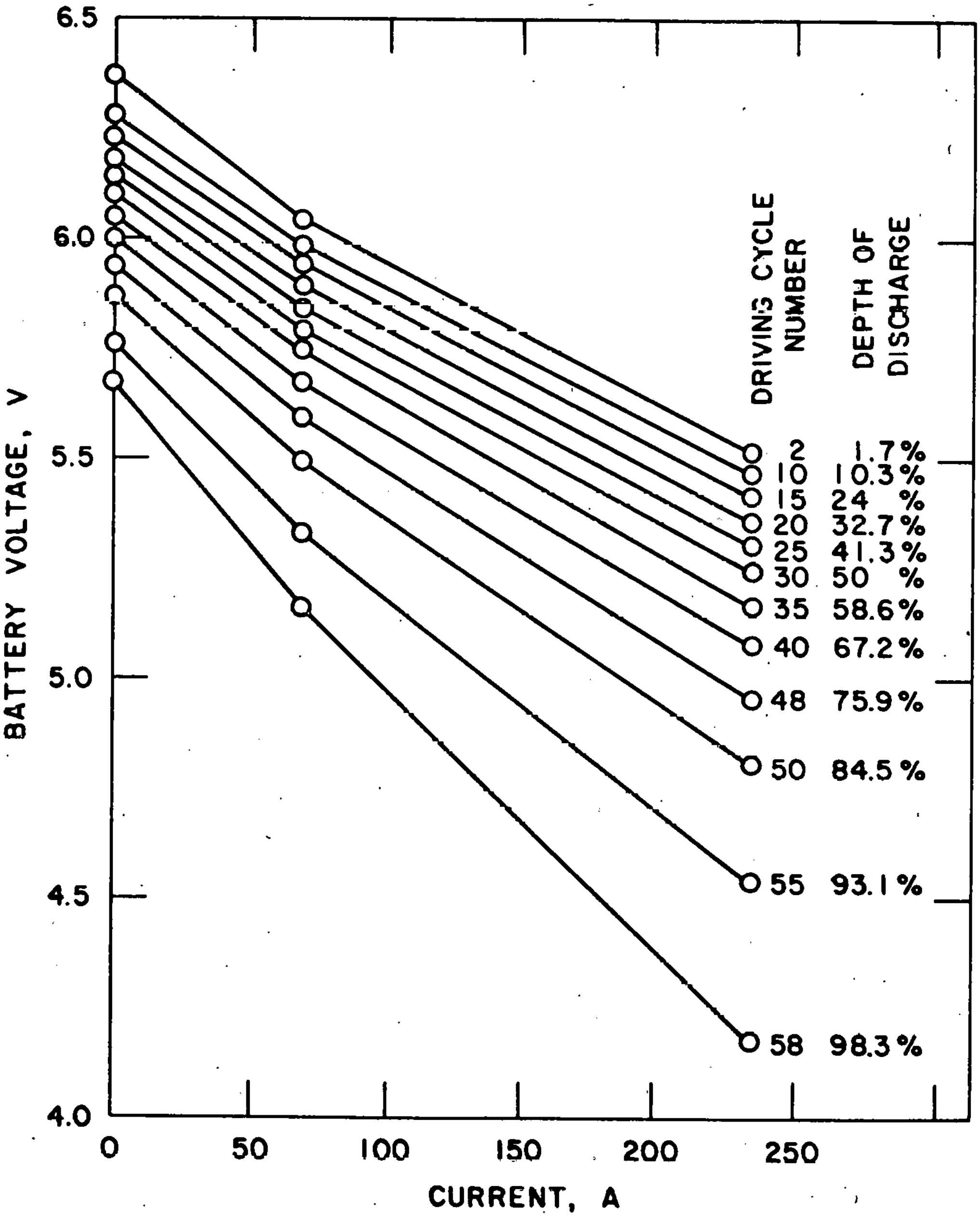

FIGURE VII-13: BATTERY VOLTAGE VERSUS CURRENT FOR THE EV-106 LEAD-ACID BATTERY

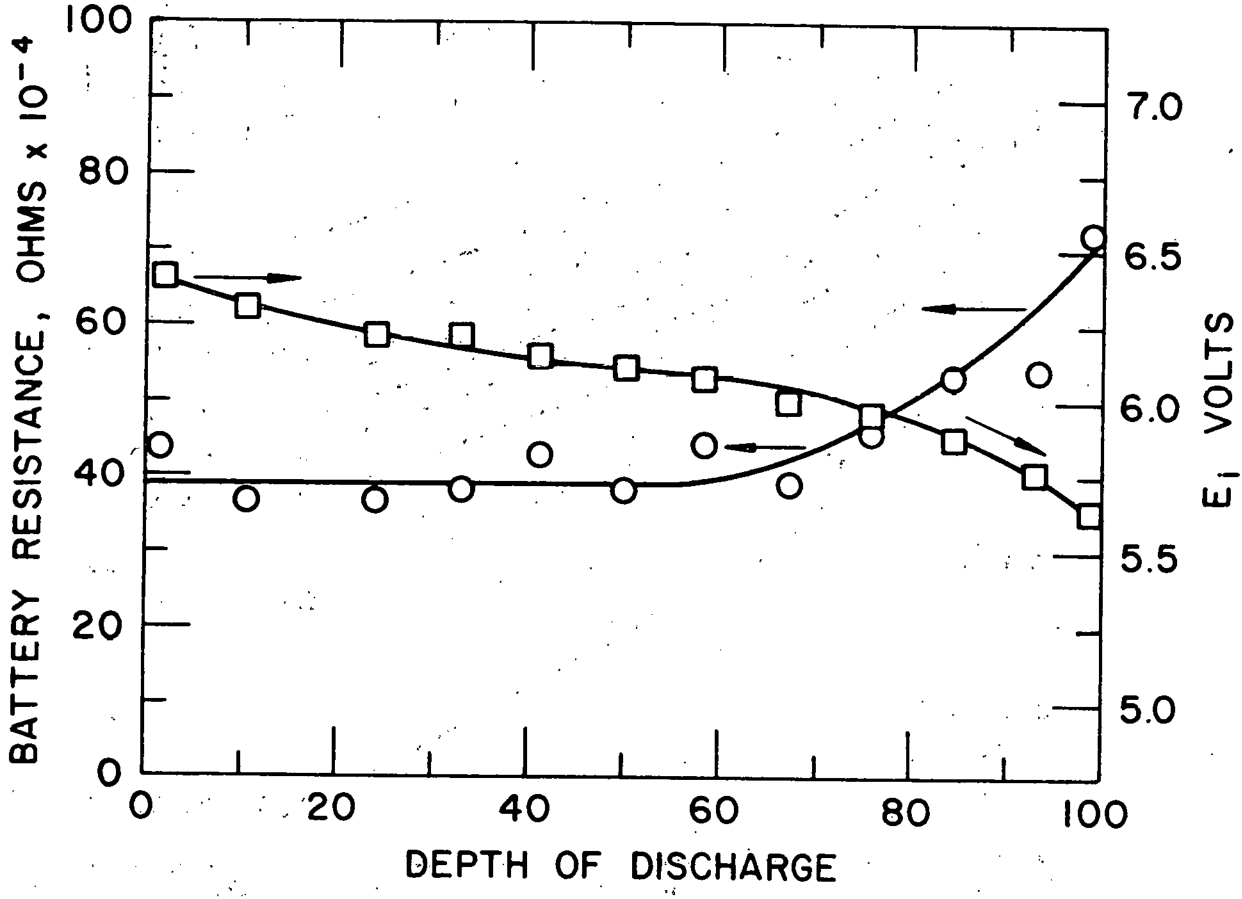

FIGURE VII-14: RESISTANCE AND OPEN CIRCUIT VOLTAGE AS A FUNCTION OF DEPTH OF DISCHARGE FOR AN EV-106 LEAD-ACID BATTERY

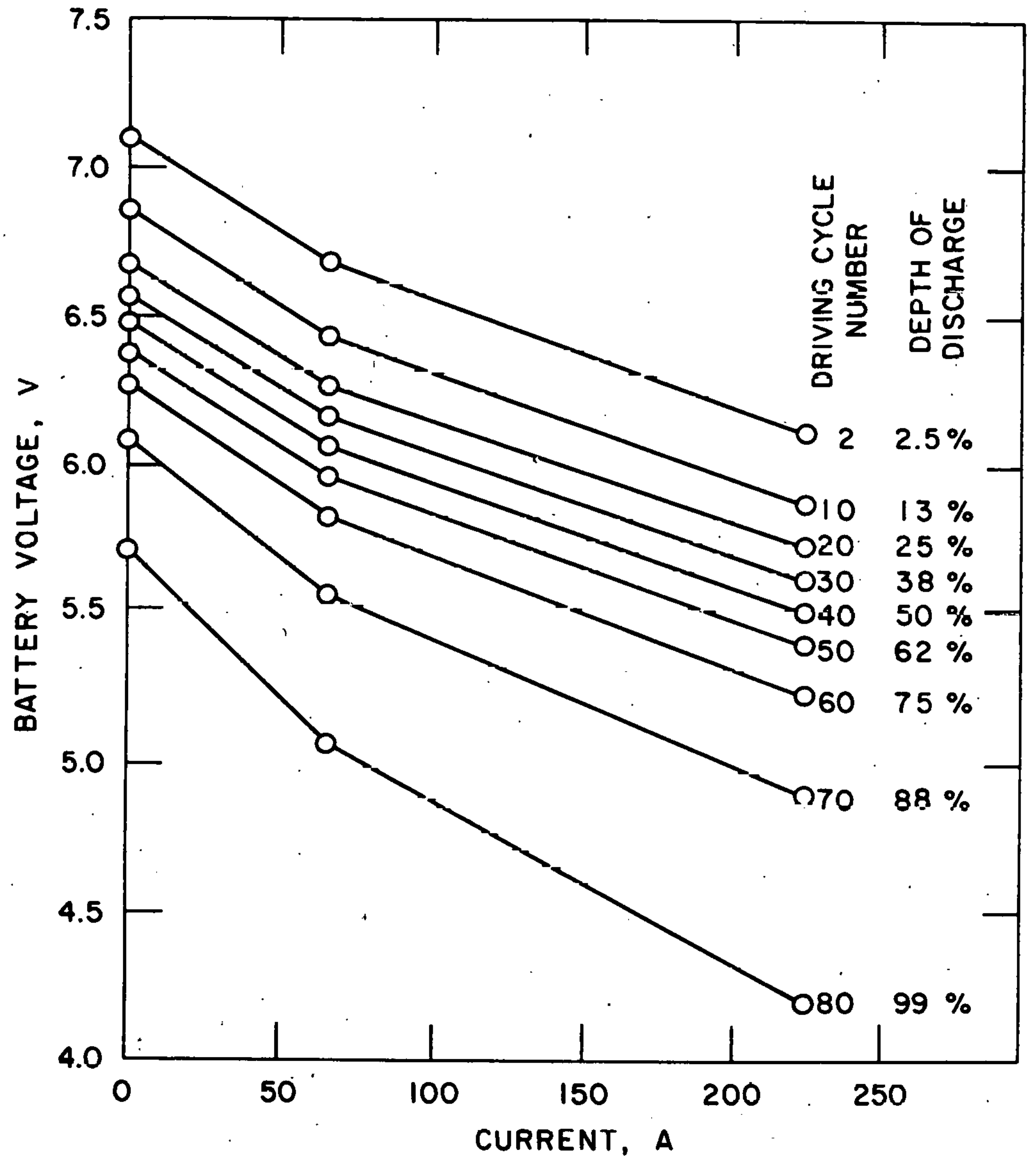

FIGURE VII-15: BATTERY VOLTAGE VERSUS CURRENT FOR THE WESTINGHOUSE NICKEL/IRON 5-CELL BATTERY

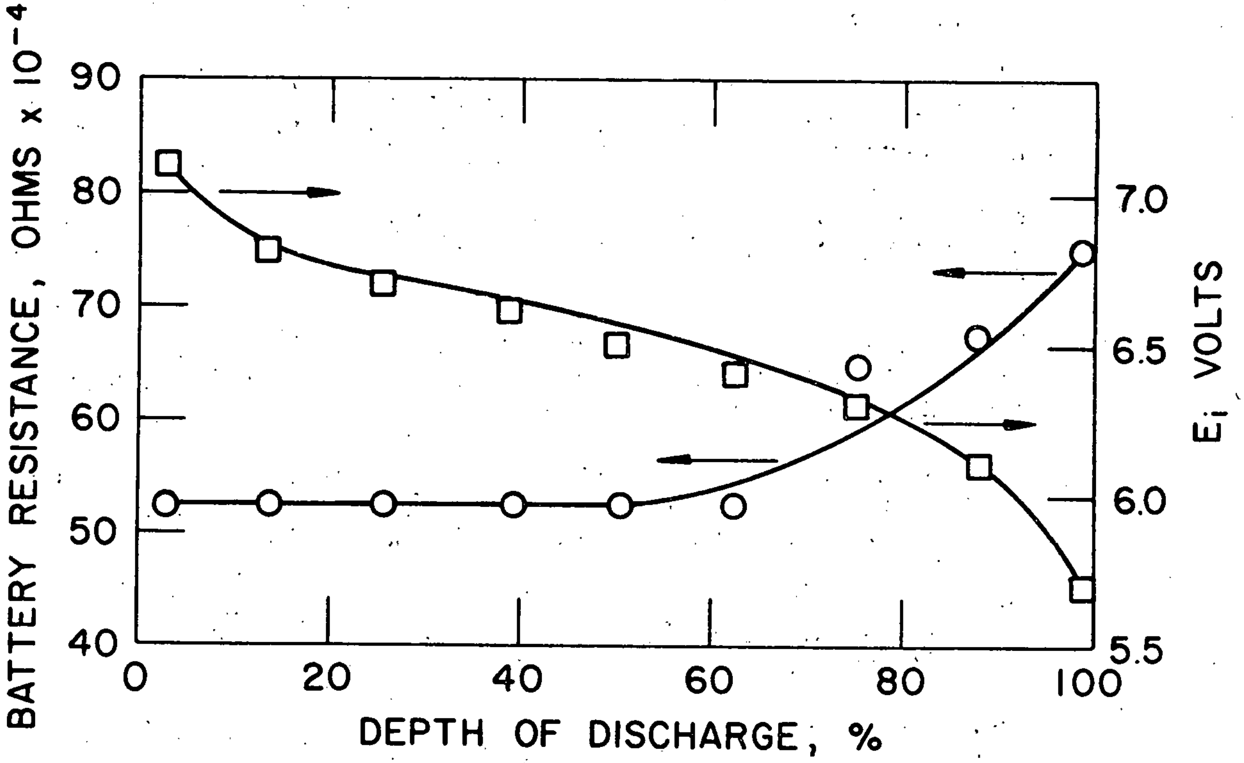

FIGURE VII-16: RESISTANCE AND OPEN CIRCUIT VOLTAGE AS A FUNCTION OF DEPTH OF DISCHARGE FOR A WESTINGHOUSE NICKEL/IRON BATTERY

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