INEEL/CON-01-00593
PREPRINT

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Chester G. Motloch
Jeffrey R. Belt
Jon P. Christophersen
Randy B. Wright
Gary L. Hunt

June 25, 2001

7th Workshop For Battery Development

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Chester G. Motloch, Jeffrey R. Belt, Jon P. Christophersen, Randy B. Wright, Gary L. Hunt
Idaho National Engineering & Environmental Laboratory
PO Box 1625, Idaho Falls, ID 83415-3830

ABSTRACT

The Idaho National Engineering and Environmental Laboratory has developed novel testing procedures and analytical methodologies to assess the performance of batteries for use in hybrid electric vehicles. Tests include both characterization and cycle life and/or calendar life. Tests have been designed for both Power Assist and Dual Mode applications. Analytical procedures include a battery scaling methodology, the calculation of pulse resistance, pulse power, available energy, and differential capacitance, and the modeling of calendar and cycle life data. At periodic intervals during life testing, a series of Reference Performance Tests are executed to determine changes in the baseline performance of the batteries.

INTRODUCTION

Lightweight, compact, high-power energy storage devices are critical enabling technologies for a viable hybrid electric vehicle (HEV) propulsion system. To this end, a cooperative research and development program called the Partnership for a New Generation of Vehicles (PNGV) was formed in 1994 between the Federal Government and the US Council for Automotive Research (USCAR), whose members are Daimler-Chrysler, General Motors, and Ford Motor Company (Ref. 1). Major objectives of the program are to develop technologies for a new generation of HEV's with fuel economies up to three times (80 miles per gallon) the average family sedan. At the same time, these vehicles should maintain performance, size, utility, and cost of ownership and meet federal safety and emissions requirements.

The investigation of energy storage devices for this application has focused in recent years on high-power lithium-ion, lithium polymer, and nickel metal hydride batteries, all of which are being tested at the Idaho National Engineering and Environmental Laboratory (INEEL). Prototypical batteries received at the INEEL may range from laboratory- and full-size cells, to modules consisting of an ensemble of cells, to full-size batteries including electronic and thermal control systems. To enable a consistent set of tests over the range of product sizes, a scaling methodology known as the Battery Size Factor has been developed.

Further, PNGV is evaluating both the Power Assist and Dual Mode applications. In general, the Dual Mode concept assumes that the battery supplies a larger fraction of the overall HEV power and energy needs than for the Power Assist concept. Hence, the Dual Mode power and energy goals are considerably higher than the Power Assist goals. To assess battery performance against these PNGV goals, a cadre of tests and analytical procedures has been developed, and are defined in detail in Ref. (2) and summarized below.

PNGV TESTING PROCEDURES

Following receipt inspection of test articles at the INEEL, a series of characterization tests are performed. These tests include static capacity, pulse power, available energy, self-discharge, cold cranking, thermal performance, energy efficiency, and electrochemical impedance spectroscopy (EIS).

Prior to starting any test sequence, all equipment is calibrated and all tests are closely controlled at prescribed states of charge (SOC), test profiles, and temperatures by using environmental chambers and programmable testers. A measurement and control study of the INEEL Energy Storage Laboratory testers has recently been completed, and has determined the uncertainty of both measured parameters (i.e., temperature, current, and voltage) and derived parameters (i.e., power, capacity, energy, impedance, efficiency, and self-discharge) (Ref. 3).

The static capacity test is a series of at least three complete C_1 discharges that are repeated until results agree within 2%. This demonstrates charge and discharge stability and helps condition the batteries for further testing. Next, discharge and regen pulse power is calculated utilizing the low-current Hybrid Pulse Power Characterization (L-HPPC) Test. The L-HPPC test consists of a series of discharge and regen pulses performed at every 10% depth of discharge (DOD) increment, with an hour rest at open circuit at each increment to ensure that the battery has electrochemically equilibrated. Each discharge pulse is performed at the larger of either a 5C current or 25% of the manufacturer's maximum rated current. Figure 1 shows a typical pulse power profile. Results from the first series of HPPC tests are used to calculate the Battery Size Factor, which is then used to scale the remainder of the PNGV power- and energy-based tests. The Battery Size Factor can also be utilized to calculate the unburdened cost, size, and weight of a full-size PNGV HEV battery.

The calculation of available energy for Power Assist applications is described below in the analytical methodologies section. However, the available energy for Dual Mode applications is simply the total energy during a constant 6 kW discharge over the DOD range where the PNGV Power goals can be met.

Self-discharge is calculated as the difference in capacity of a fully-charged battery compared to its capacity after sitting at open circuit for seven days. Cold cranking tests measure the battery's ability to provide three two-second 5 kW pulses at –30°C. Thermal performance is determined by repeating the static capacity and L-HPPC tests at various temperatures. Energy efficiency is determined using a charge-balanced pulse profile and calculating the ratio of watt-hours-output to watt-hours-input. EIS (i.e., full-spectrum complex impedance) measurements are made prior to the start of life testing, and then repeated when life testing is concluded.

Prior to commencing life testing, a series of Reference Performance Tests (RPT's) are executed at 30°C to establish the baseline performance and then are repeated every 25 days, thereafter. For Power Assist applications, the RPT's consist of a C_1 Constant-Current Discharge Test and a L-HPPC Test, and for Dual Mode applications the RPT's include these two tests plus a 6 kW Constant Power Available Energy Test.

End-of-Testing for all life tests occurs when the device has completed the required time interval or number of cycles, or when it can no longer simultaneously meet the PNGV power and energy goals. For Power Assist applications, the cycle, pulse discharge power, and available energy goals are 300,000 cycles, 25 kW, and 300 Wh, respectively; and for Dual Mode these are 3,750 cycles, 45 kW and 1500 Wh, respectively.

Calendar life testing is performed by bringing the battery to a prescribed SOC and temperature and holding at these conditions. A once-per-day single discharge and regen pulse is applied from which daily pulse resistances can be calculated.

Life cycling begins by bringing the device to the specified temperature and SOC conditions and performing an Operating Set Point Stability Test to ensure a stable cycling condition has been established. Figure 2 shows the 25-Wh Power Assist Efficiency and Cycle Life Profile, which is repeated continuously during testing. It consists of a discharge pulse and a regen pulse with interspersed rest periods. The cumulative length of a single profile is 72 seconds and constitutes once cycle.

Figure 3 shows the Dual Mode Cycle Life Power Profile and the corresponding Net Energy Profile. The power profile is composed of three Dynamic Stress Test (DST) pulse profiles followed by 45 recharge pulse profiles. The three DST profiles are scaled to 36 kW and have gross discharge of approximately 1500 Wh during this 18-minute sequence. The device under test is then returned to its initial charge condition using a 72-minute recharge profile sequence, for a total duration of 1.5 hours per complete cycle.

DATA ANALYSES

Power fade (which is directly related to resistance growth) has been identified as a limiting factor for PNGV HEV batteries. Thus, testing and analytical assessment is largely focused on this parameter.

Discharge and regen pulse resistance is calculated at each 10% DOD increment from the L-HPPC test data. It is the ratio of the change in the voltage divided by the change in current at specified times during selected pulses. Figure 4 shows typical discharge and regen resistance curves and the voltage curve versus DOD. This information is then used to calculate the discharge and regen pulse power capability. For example, the discharge pulse power, P_{dis}, at a given DOD is determined by:

$$P_{dis} = V_{min}\,(V_{OC} - V_{min})/R_{dis}$$

where V_{min} is the manufacturer's specified minimum allowable voltage, V_{OC} is the open-circuit voltage immediately before the pulse begins, and R_{dis} is the corresponding discharge resistance. Each DOD can be related to the corresponding amount of energy discharged to that point. Figure 5 shows typical discharge and regen pulse power curves versus energy. By calculating the difference in discharge energy between the discharge power curve and the regen power curve, the available energy is found as a function of power, as shown in Figure 6. The dotted-line in Figure 6 has a slope equal to the ratio of the PNGV Power Assist Energy Goal (i.e., 300 Wh) divided by the Power Goal plus a 30% Beginning-of-Life, BOL, power margin, (i.e., 25 kW x 1.3). The point where the dotted-line intersects the available energy curve is where the PNGV goals are optimally met for this battery technology example. This intersection point is used to calculate the Battery Size Factor by reading the device's energy at this point and dividing it into the PNGV Energy Goal (or alternatively dividing the device's power into the PNGV Power Goal).

LIFE MODELING

Cell degradation as a function of calendar time or cycle count and other test conditions is being investigated at the INEEL. From either the HPPC data collected during the RPT's or from the pulse data during calendar and cycle life testing, discharge and regen resistances can be calculated as a function of time and test conditions. This information is being utilized at the INEEL to develop predictive life models for PNGV. Two distinct modeling approaches are being developed and evaluated.

The first modeling approach is based upon the calculation of power fade over time as determined from the RPT's and associated available energy curves. Six Saft America, Inc. 12 Ah lithium ion HP-12 cells (1999 configuration) have been under test at INEEL for over 60 weeks using the PNGV calendar life test. Two cells each are being subjected to temperatures of 40°C, 50°C, or 60°C. First, power fade as a function of time is calculated for each pair of the cells at the three temperatures. This information can be used to construct an Arrhenius relation as shown in Figure 7, which enables extrapolation from the higher accelerated-aging temperatures back to 25°C. The graph plots the natural logarithm of the "Years to End of Life" versus the inverse temperature in degrees Kelvin. Two cases are presented. The first case linearly extrapolates life based on the average PNGV cell powers with their appropriate temperature-related power fades. The second case extrapolates calendar life based on the best (i.e., highest) PNGV cell power assuming that cell performance would be optimized in a commercial production environment. For case one, the model predicts a calendar life of 6.3 years, while the best case model predicts a calendar life of 12.4 years. Notably, the PNGV Calendar Life Goal is 15 years.

Through participation in the Advanced Technology Development (ATD) Program (Ref. 4), INEEL has also developed a second modeling approach for both calendar life and cycle life. For example, a calendar life model was developed to account for the time, temperature, and SOC of the batteries during testing (Ref. 5). The functional form of the model is given by:

$$R(t,T,SOC) = a\{\exp[b/T]\}t^{1/2} + c\{\exp[d/t]\}$$

Where a, b, c, and d are parameters that are a function of SOC, and where b and d are related to activation energies E_b and E_d such that $b = E_b/R$ and $d = E_d/R$, and where R is the universal gas constant. (A similar approach has also been used to develop ATD cycle life models (Ref. 6).)

The square-root-of-time dependence can be accounted for by either a one-dimensional diffusion type of mechanism, presumable of the lithium ions, or by a parabolic growth mechanism for the growth of a thin film solid electrolyte interface (SEI) layer on the anode and/or cathode. A diffusion type of mechanism would arise from the diffusion of lithium ions into/out of the electrodes, through the electrolyte, through the separator, or through the SEI that is present on the surface of the electrode materials. The growth of the thin film mechanism could be related to the growth of a SEI layer on the anode and/or cathode as a function of test time. The increased thickness of the SEI film would increase the resistance of the cell due to an increased hindrance of the transport of lithium ions through the SEI layer, where they are subsequently intercalated/de-intercalated into the active electrode material.

Figure 8 shows a representative comparison of ATD calendar life test results to the model at 80% SOC. The model fit is excellent at 40°C, 50°C and 60°C, but not at 70°C, where it is believed that at different physical mechanism is controlling.

Other tools and methodologies are being utilized at INEEL to investigate cell degradation, as well. For example, Figure 9 shows an EIS Nyquist plot for a representative ATD lithium-ion cell. Changes in the first semicircle with aging are related to growth in a thin film SEI layer on the anode and/or cathode. Lastly, a new measure of cell degradation under evaluation at the INEEL is differential capacitance, Q_{dif}. It is given by

$$Q_{dif} = [(1/Q)d(Ah)/dV]$$

where Q is the BOL capacity and d(Ah)/dV is the derivative of capacity with voltage. Figure 10 shows a typical plot of differential capacitance versus cell voltage for an ATD cell calculated from a $C_1/25$ discharge and charge test. Peaks are thought to be related to specific intercalation sites within the anode and/or cathode. It has been postulated that the degradation of cell performance with aging is related to the change in the amplitude and location of these peaks.

SUMMARY

Under the auspices of the PNGV, INEEL has developed new testing procedures and analytical methodologies. These enable the testing of various chemistries, technologies, and sizes of products and provide objective comparison of results. Also, calendar life and cycle life models are under development and evaluation that enable the extrapolation of accelerated-aging test data to normal operating conditions. Lastly, INEEL is constantly exploring new testing and analytical methodologies to further aid PNGV in the development of high-power cells for HEV applications.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude for the programmatic support provided by the US DOE Office of Advanced Automotive Technologies. This paper was prepared as an account of work sponsored by an agency of the United States Government under US DOE Contract DE-AC07-99ID13727.

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Figure 1. Pulse Power Characterization Profile

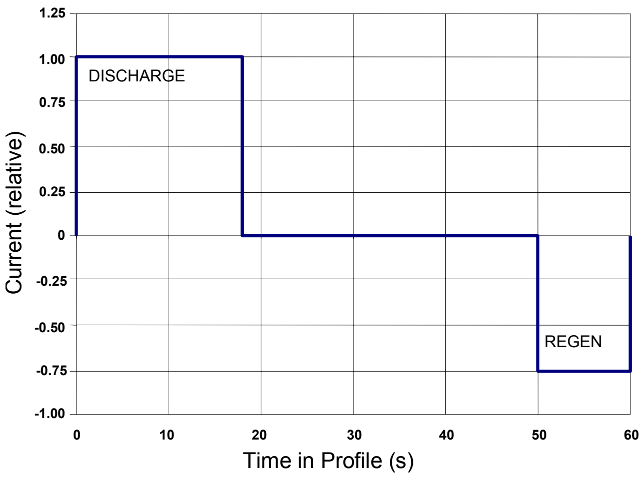

Figure 2. Power Assist Efficiency & Cycle Life Test Profile

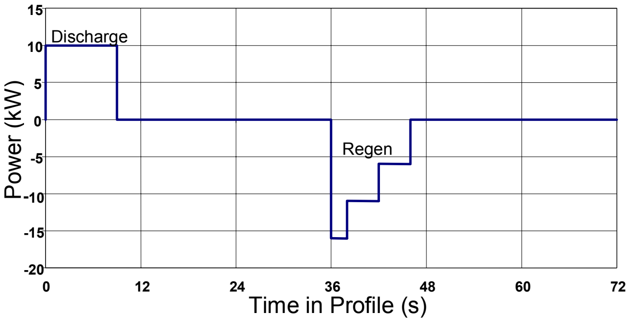

Figure 3. Dual Mode Cycle Life Total Test Profile

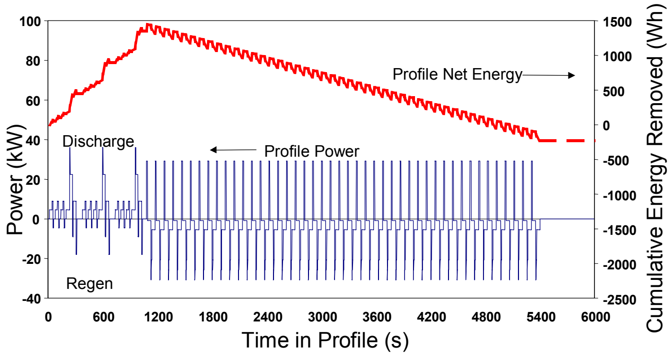

Figure 4. Pulse Resistance and Open Circuit Voltage

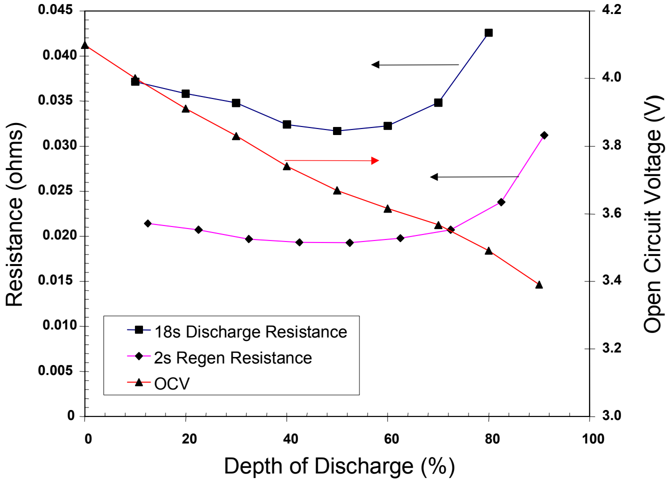

Figure 5. Pulse Power Capability vs Net Energy Removed

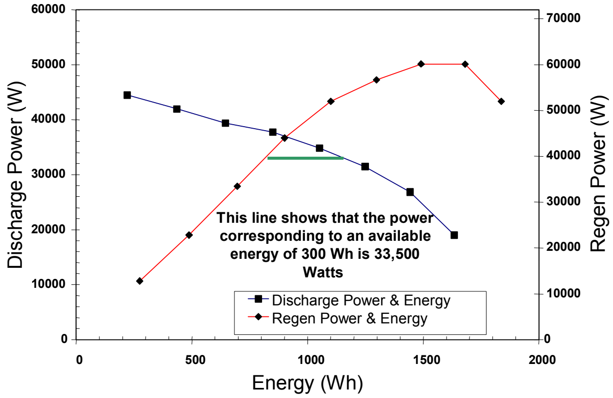

Figure 6. Available Energy as a Function of Peak Power Demand

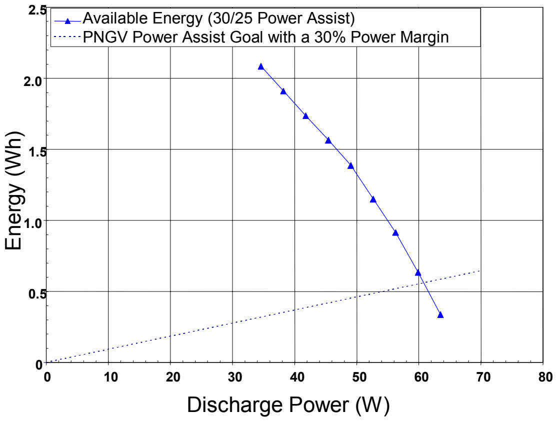

Figure 7. Arrhenius Plot of Calendar Life versus Temperature and Power Fade for Saft HP-12 Cells

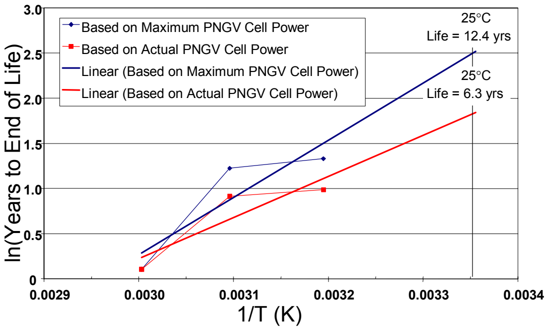

Figure 8. Calendar Life Discharge Resistance Data and Model Predictions for ATD Gen 1 Cells at 80% SOC

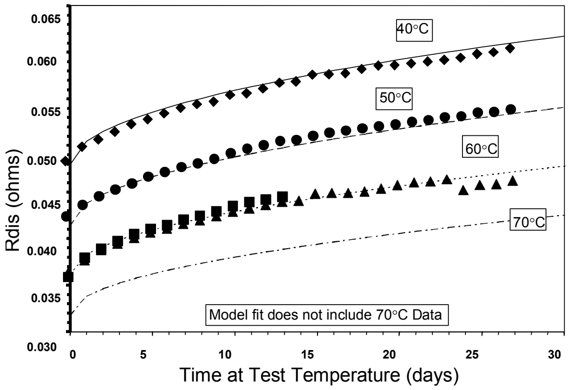

Figure 9. 60% SOC EIS Impedance

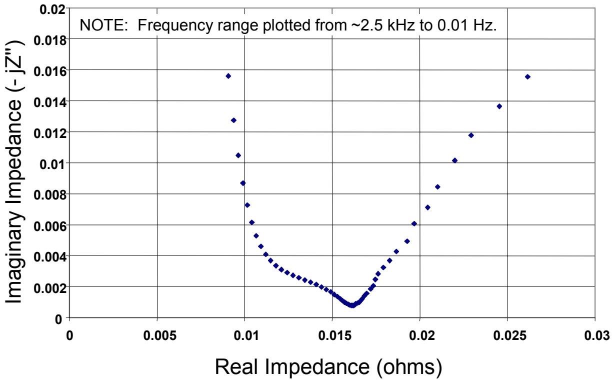

Figure 10. Characterization Differential Capacitance