

SANDIA REPORT

SAND2008-5583

Unlimited Release

Printed September 2008

Selected Test Results from the LiFeBatt Iron Phosphate Li-ion Battery

Thomas D. Hund and David Ingersoll

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of Energy's
National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.



Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.osti.gov/bridge>

Available to the public from

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: <http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online>



Selected Test Results from the LiFeBatt Iron Phosphate Li-ion Battery

Thomas D. Hund and David Ingersoll
Power Sources Component Development Department 02547 and
Advanced Power Sources R&D Department 02546.
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185

Abstract

In this paper the performance of the LiFeBatt Li-ion cell was measured using a number of tests including capacity measurements, capacity as a function of temperature, ohmic resistance, spectral impedance, high power partial state of charge (PSOC) pulsed cycling, pulse power measurements, and an over-charge/voltage abuse test. The goal of this work was to evaluate the performance of the iron phosphate Li-ion battery technology for utility applications requiring frequent charges and discharges, such as voltage support, frequency regulation, and wind farm energy smoothing. Test results have indicated that the LiFeBatt battery technology can function up to a $10C_1$ discharge rate with minimal energy loss compared to the 1 h discharge rate ($1C$). The utility PSOC cycle test at up to the $4C_1$ pulse rate completed 8,394 PSOC pulsed cycles with a gradual loss in capacity of 10 to 15% depending on how the capacity loss is calculated. The majority of the capacity loss occurred during the initial 2,000 cycles, so it is projected that the LiFeBatt should PSOC cycle well beyond 8,394 cycles with less than 20% capacity loss. The DC ohmic resistance and AC spectral impedance measurements also indicate that there were only very small changes after cycling. Finally, at a $1C$ charge rate, the over charge/voltage abuse test resulted in the cell venting electrolyte at $110\text{ }^{\circ}\text{C}$ after 30 minutes and then open-circuiting at $120\text{ }^{\circ}\text{C}$ with no sparks, fire, or voltage across the cell.

ACKNOWLEDGMENTS

The author gratefully acknowledges the assistance of Michelle Robinson and Don Harmon of LiFeBatt, Inc. USA, and in addition Alan Hsu and Dr. Jerry Yao (Dr. Yao owns the license from ITRI Taiwan) of LiFeBatt Taiwan for providing the Li-ion Iron phosphate cells. Also, the assistance of David Johnson at Sandia National Labs for providing the over charge/voltage abuse testing measurements and Wes Baca at Sandia National labs for test setup and configuration is greatly appreciated.

CONTENTS

Acknowledgments.....	4
Contents	5
Figures.....	6
Nomenclature.....	7
1. Introduction.....	9
2. Test procedures	11
2.1 Capacity Test	11
2.2 DC Ohmic Resistance.....	12
2.3 AC Spectral Impedance	12
2.4 Cell Power Density And Specific Energy.....	13
2.5 Cell Capacity And Recharge As A Function Of Temperature	13
2.6 Utility PSOC Pulsed Cycle Test	13
2.7 Hybrid Pulse Power Test	15
2.8 Over Voltage/Charge Abuse Test.....	17
3. Test Results.....	19
3.1 Initial and Final Capacity.....	19
3.2 DC Ohmic Resistance.....	19
3.3 AC Spectral Impedance	20
3.4 Cell Power and Specific Energy Density.....	21
3.5 Cell Capacity and Recharge as a Function of Temperature.....	23
3.6 Hybrid Pulse Power Test	24
3.7 Utility PSOC Pulse Cycle-Life Test	26
3.8 Over Voltage/Charge Abuse Test.....	27
4. Summary.....	31
5. References.....	33
Distribution	34

FIGURES

Figure 1.	LiFeBatt Li-FePO ₄ Cell Under Test.	10
Figure 2.	Typical Utility Energy Pulses (Charles Koontz, WPS).	14
Figure 3.	Utility PSOC Pulsed Cycle Test with 1C 6 min. (10% DOD) Charge/Discharge Pulses.	15
Figure 4.	Hybrid Pulse Power Test.	16
Figure 5.	Initial and Final Capacity of Cell #1 (5A Chr/Dch).	19
Figure 6.	Ohmic Resistance Measurement On Cell #1 (100% SOC).	20
Figure 7.	Impedance behavior of cell before and after PSOC cycling.	21
Figure 8.	Specific Energy And Power Performance	22
Figure 9.	Energy Density And Power Density.	22
Figure 10.	Capacity vs. Temperature at 10A.	23
Figure 11.	Recharge vs. Temperature at 10A.	24
Figure 12.	Hybrid Pulse Power Capability As A Function Of %SOC.	25
Figure 13.	Hybrid Pulse Power Capability As A Function Of Capacity In Wh.	25
Figure 14.	Utility PSOC Pulse Cycle-Life Test Results At $\pm 40A$ for 1.5 min.	26
Figure 15.	Utility PSOC Pulse Cycle Test Results.	27
Figure 16.	Over Voltage/Charge Abuse Test.	28

Tables

Table 1.	LiFeBatt Cell Specifications.	10
Table 2.	LiFeBatt Summary Test Results.	29

NOMENCLATURE

AC	alternating current
Ah	Amp-hour
C_1	battery capacity in Ah at the 1 h rate
DC	direct current
ESR	equivalent series resistance
FePO_4	iron phosphate
ΔI_{chr}	change in current on charge
ΔI_{dch}	change in current on discharge
kg	Kilogram
LiFePO_4	lithium iron phosphate
OCV_{chr}	open-circuit voltage before charge
OCV_{dch}	open-circuit voltage before discharge
PSOC	partial state of charge
R_{chr}	charging resistance
R_{dch}	discharging resistance
SNL	Sandia National Laboratories
SOC	state of charge
V_{min}	minimum operational voltage
V_{max}	maximum operational voltage
ΔV_{chr}	change in voltage on charge
ΔV_{dch}	change in voltage on discharge
Wh	Watt-hour
W	Watt

1. INTRODUCTION

This work was supported by the U.S. Department of Energy (DOE) Office of Electricity Delivery & Energy Reliability. The DOE program goals are directed at supporting industry and utilities in the areas of:

- Development and evaluation of integrated electrical energy storage systems;
- Development of batteries, superconducting magnetic electrical energy storage (SMES), flywheels, super capacitors and other advanced energy storage devices;
- Improvement in multi-use power electronics, controls, and communications components;
- Analysis and comparison of technologies and applications; and
- Encouraging program participation by industry, academia, research organizations and regulatory agencies.

The work reported in this paper is part of our effort to characterize the performance parameters of advanced batteries. The iron phosphate Li-ion battery technology has recently entered the battery market with a number of manufacturers from the United States (*A123 and Valence*), Taiwan (*LiFeBatt*), and China (*AA Portable Power and K2 Energy*). This technology was originally developed and patented by Dr. John Goodenough and his team at the University of Texas in 1996, additional work by Université de Montreal (UDM) and Hydro-Quebec resulted in the addition of carbon to the Li-FePO_4 in a process called carbon Nano-painting. This process improves energy density and power performance. In 2002, UDM and Hydro-Quebec, as owner or co-owner of many patents on LiFePO_4 technology, established Phostech Lithium Inc. to commercialize the product. Phostech Lithium produces material to replace the LiCoO_2 and other cathode materials typically used in Li-ion batteries. The LiFeBatt battery uses iron phosphate cathode material because it has a number of advantages over conventional Li-ion cathode materials. These advantages include lower cost, improved safety, and high power performance. The most significant limitation to the iron phosphate cathode material is the lower energy density at approximately 80 Wh/Kg vs. 165-180 Wh/Kg for LiCoO_2 and other oxide cathodes[1]. However, as a result of the safety and power performance improvements, the iron phosphate Li-ion battery technology is being evaluated for new market areas including hybrid electric vehicles, utility energy storage, and other large energy storage applications. In this paper the performance of the LiFeBatt cell was evaluated using high rate capacity tests, low temperature capacity, ohmic resistance, spectral impedance, partial state of charge (PSOC) pulse power cycling, pulse power performance, and an over-charge/voltage abuse test.

In Figure 1 is a photograph of one of the LiFeBatt 10 Ah cells. This cell has dimensions of 40 mm in dia by 139 mm long, weighs 360 g, and has a nominal rated capacity of 30 Wh. Table 1 summarizes the LiFeBatt cell specifications.

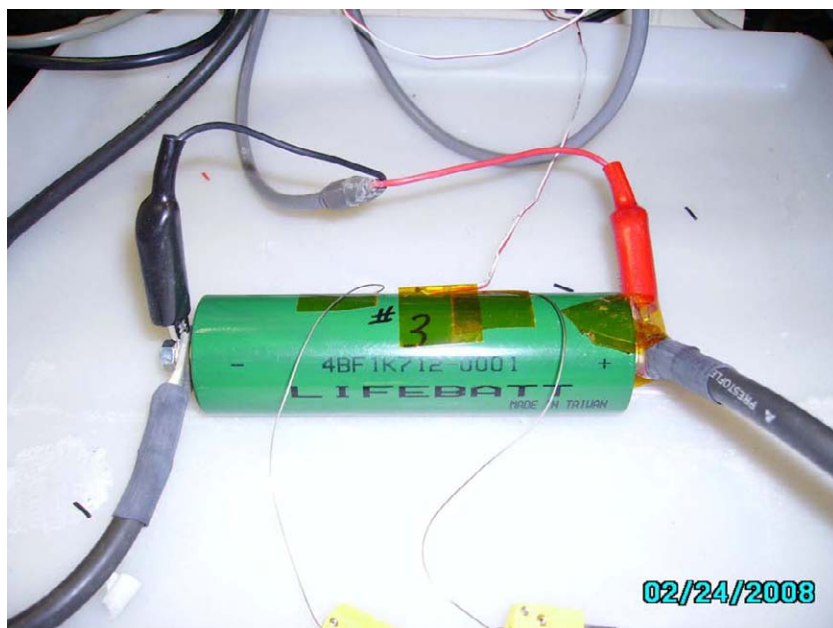


Figure 1. LiFeBatt Li-FePO₄ Cell Under Test.

Table 1. LiFeBatt Cell Specifications.

Model #PC40138F1W Cell	
Operating voltage window	2.10 – 3.65 V
Max voltage	3.65 V
Discharge end voltage (1C rate)	2.10 V
Charge Regulation Voltage	3.65 V
Full Charge Termination (V, I, Time)	3.65 V and 0.2 A or 60 min @ 3.65 V
Maximum Charge Current	30 A
Maximum Pulse Current, I	140 A
Maximum Constant Current, I	120 A
Internal Ohmic resistance, mOhm +25 °C	<6 mohm
Ah Capacity (0.25C and 1C rate)	10,000 mAh, 9,000 mAh
Energy stored in operating voltage window, Wh or kJ	80 Wh/kg 170 Wh/L
Overall dimensions, mm	171.1 x 40.6
Weight, kg	0.360
Operating temperature, °C	0 to 45 Chr -10 to 55 Dch
Storage temperature, °C	-10 to 45
Cycle life, cycles	1,500

2. TEST PROCEDURES

The cell test procedures used in this effort were initially developed as part of a plan to test batteries for partial state of charge (PSOC) pulsed cycling in utility applications, and the eight characterization tests used are itemized below.

- 1) **Capacity Test** – Establishes a capacity on each cell.
- 2) **DC Ohmic Resistance** – Establishes a resistance of the cell.
- 3) **AC Spectral Impedance** - Establishes the AC impedance of the cell.
- 4) **Cell Power Density and Specific Energy Density** – Measures the cell power and energy density.
- 5) **Cell Capacity and Recharge As A Function Of Temperature** – Capacity measurements at the 1C rate were conducted at 35°, 22°, 0°, -20°, -40 °C.
- 6) **Cell Utility PSOC Pulsed Cycle Test** – Measures the ability of the cell to PSOC cycle at high power for utility voltage support, frequency stabilization, and wind farm energy smoothing applications.
- 7) **Hybrid Pulse Power Test** – Measures the 10 second pulse power performance from 90% to 10% state of charge (SOC).
- 8) **Over Voltage/Charge Abuse Test** – Measures the effects of an uncontrolled continuous 10 A charge.

2.1 Capacity Test

The capacity test is used to determine the cell capacity and this test is done prior to testing to establish a baseline as well as being repeated at the end of PSOC cycle testing. This will help identify how the various tests in this plan affect the cell capacity.

The cell shall be tested for its capacity, as follows:

1. Each cell shall be charged at 0.5C (5.0 A) up to Charge Voltage (3.65V). On reaching the Charge Voltage, the current shall be allowed to taper while maintaining the Charge Voltage until the current tapers to 0.2 A. The ampere-hour input into the cell shall be measured.
2. The cell shall rest at open circuit for 30 minutes.
3. The cell shall be discharged at 0.5C (5.0 A) until the end voltage (2.1 V) is reached. The ampere-hour capacity of the cell shall be measured.
4. The cell shall rest at open circuit for 30 minutes.
5. Steps 1 to 5 shall be repeated 3 times. The third capacity measurement will be the recorded capacity.

2.2 DC Ohmic Resistance

The DC resistance shall be measured with a high current discharge pulse of at least $2C_1$ at the 100% SOC point. An oscilloscope will be used to measure the ohmic voltage drop and current ramp using the following steps:

1. Charge cell at 1C rate to the Charge Voltage (3.65V) and hold at voltage until the current tapers to 0.2 A.
2. Allow the cell to sit open-circuit for 30 min.
3. Measure the dynamic DC ohmic resistance of the cell using an oscilloscope by discharging at $2C_1$ for 2 seconds.

2.3 AC Spectral Impedance

AC spectral impedance measurements of the as-received and after PSOC pulsed cycling were also made. These measurements shall be made in the following manner:

1. Each cell shall be charged at 1C up to the Charge Voltage (3.65V) until the current tapers to 0.2A.
2. The cell shall rest at open circuit for 30 minutes.
3. The cell shall be discharged at the 1C rate to 50% SOC.
4. The cell shall rest at open circuit for at least one day prior to measurement.
5. Each terminal on the cell shall be fitted with two gold plated interconnects (to minimize contact impedance).
6. The cell shall be placed into an environmental chamber regulated at 25 °C for at least 12 h prior to initiating measurements.
7. All measurements shall be made with the cell in a controlled temperature maintained at 25 °C.
8. The cell shall be connected to the instrumentation in a four-wire configuration.
9. The peak-to-peak AC voltage shall be in a range to allow 1% accuracy of the impedance of the cell being measured, and in this case 3 mV was used.
10. The frequency range shall be large enough to encompass the anticipated network response, and in this case corresponds to a range of 100 kHz to 10^{-4} Hz. At least six different frequencies per decade shall be measured.
11. All measurements shall be made at 0 V vs. the open circuit voltage corresponding to 50% SOC.

2.4 Cell Power Density And Specific Energy

Measure cell capacity as close as possible to the following rates:

1	0.1C,	10 h
2	0.2C,	5 h
3	1C,	1 h
4	2C,	0.5 h
5	4C,	0.25 h
6	10C,	0.1 h

The cell capacity shall be measured as follows:

- 1 Each cell shall be charged at 1C up to Charge Voltage (3.65V). On reaching the Charge Voltage, the current shall be allowed to taper while maintaining the Charge Voltage until the current tapers to 0.2 A. The ampere-hour input into the cell shall be measured.
- 2 The cell shall rest at open circuit for 30 minutes.
- 3 The cell shall be discharged at specified rate until the end voltage (2.1 V) is reached. The ampere-hour and Watt-hour capacity of the cell shall be measured.
4. Steps 1 to 4 shall be repeated 3 times.

Using the data above, calculate the power and energy density with respect to volume and weight and display using the Ragone plot.

2.5 Cell Capacity And Recharge As A Function Of Temperature

Cell capacity and charge and discharge characteristics at the 1C rate (10 A) were measured at 35, 22, 0, -20, and -40 °C. The capacity test procedure was the same as that described in the capacity measurement.

2.6 Utility PSOC Pulsed Cycle Test

The utility PSOC pulsed cycle test is designed to evaluate battery performance under short high power charge and discharge environments. In many utility applications the battery is required to both sink and source power for voltage support, frequency stabilization, and wind farm energy smoothing. In Figure 2 are actual utility data obtained from Charles Koontz of WPS Energy Services, Inc. showing the magnitude and duration of the power pulses required to support a utility application. In general, the pulse durations are minutes in length. The utility PSOC charge and discharge pulses chosen for this test are between 1.5 and 6 minutes in length at discharge rates between $1C_1$ (10 A) and $4C_1$ (40A). The goal of this testing is to evaluate PSOC pulsed cycling, cell stability, efficiency, power performance, thermal management, and charge management strategies.

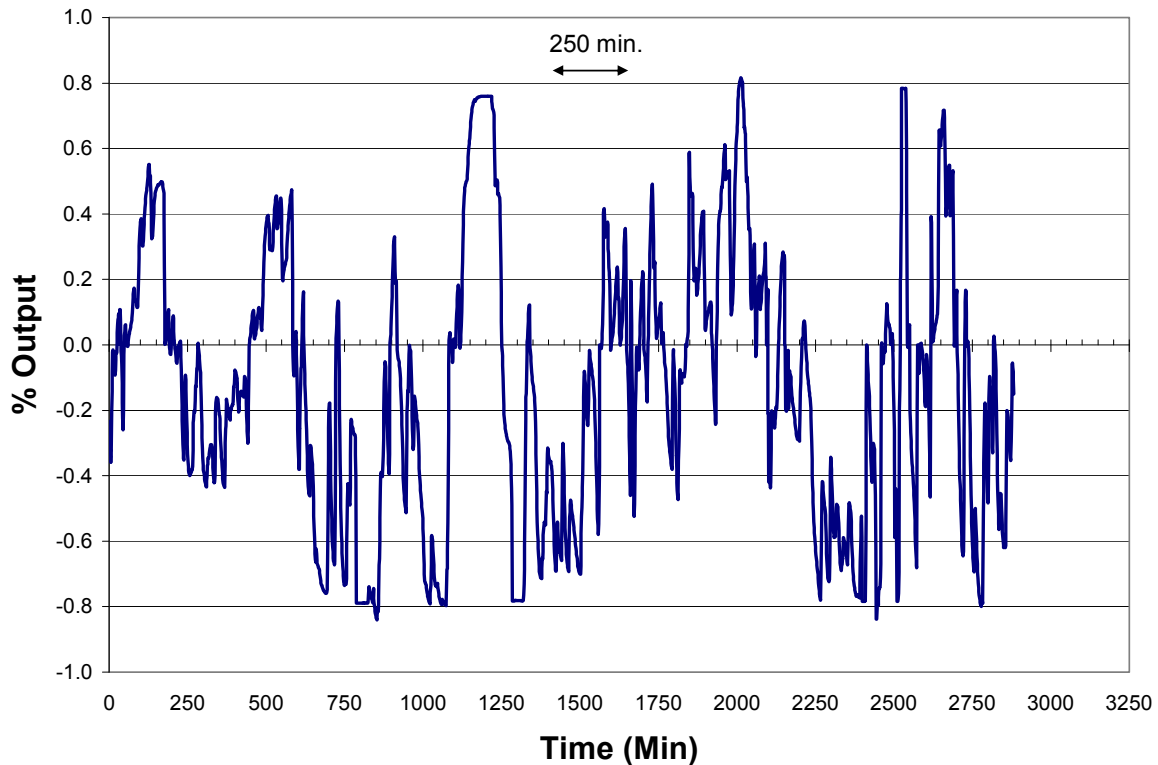


Figure 2. Typical Utility Energy Pulses (Charles Koontz, WPS).

The cycle profile in this test is illustrated in Figure 3 and consists of the following steps:

- 1 Charge cell at 1C rate until voltage reaches Charge voltage (3.65V).
- 2 Keep voltage at Charge voltage until current tapers to 0.2 A.
- 3 Rest for 30 min.
- 4 Discharge at 1C rate to end voltage (2.1 V).
- 5 Rest for 30 min.
- 6 Recharge cell as in step 2.
- 7 Discharge at 1C rate to 50% Ah capacity.
- 8 Rest for 5 min.
- 9 Discharge at 1C rate for 6 min. (10% DOD).
- 10 Rest for 5 min.
- 11 Charge at 1C rate for 6 min.
- 12 Rest for 5 min.
- 13 Repeat steps 9 through 12 for 100 cycles.
- 14 Measure available capacity as specified in steps 3 through 5.
- 15 Repeat 100 cycle profile five times per test sequence.
- 16 Evaluate battery performance and determine if higher power levels are possible and if the PSOC cycle interval can be extended to 500 or 1,000 cycles.
- 17 Additional testing may be conducted at the 2C, 3 min. or 4C, 1.5 min. rates and times (10% DOD).

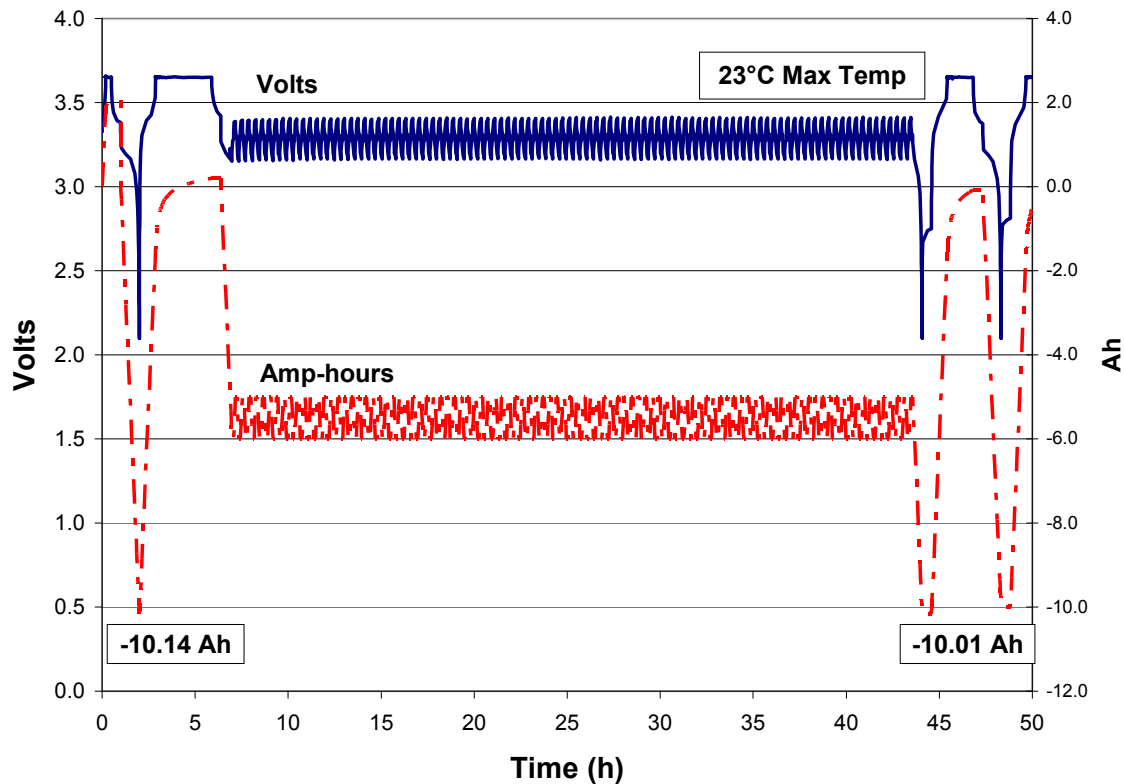


Figure 3. Utility PSOC Pulsed Cycle Test with 1C 6 min. (10% DOD) Charge/Discharge Pulses.

2.7 Hybrid Pulse Power Test

The Hybrid Pulse Power Test is extracted from the [FreedomCAR Battery Test Manual For Power-Assist Hybrid Electric Vehicles](#). This test procedure uses a 10 second $5C_1$ discharge pulse and a $3.75C_1$ charge pulse 40 seconds apart (see Fig. 4). The test sequence is listed below:

- 1) Measure capacity at the 1C rate.
- 2) Fully recharge cell.
- 3) Allow cell to rest open-circuit for 1 h.
- 4) Discharge cell 10% at the 1C rate,
- 5) Allow the cell to rest for 1 h rest open-circuit (measure Voc).
- 6) Discharge cell at the $5C_1$ rate for 10 seconds (measure end of discharge V).
- 7) Allow the cell to rest open-circuit for 40 seconds (measure Voc).
- 8) Charge at the $3.75C_1$ rate for 10 seconds (measure end of charge V).
- 9) Discharge at the 1C rate 10% of the cell capacity.
- 10) Repeat steps 4 through 8 until battery is at 10% SOC.
- 11) Record open-circuit voltage after the 1 h rest before the discharge pulse, record voltage at 10 second point in charge and discharge pulse and record open-circuit voltage at end of 40 second rest for each SOC.

- 12) Calculate discharge resistance using the 1 h open-circuit voltage and charge resistance using the 40 second open-circuit voltage for each SOC.

$$R_{Dch} = \frac{\Delta V_{Dch}}{\Delta I_{Dch}}$$

$$R_{Chr} = \frac{\Delta V_{Chr}}{\Delta I_{Chr}}$$

- 13) Calculate the Discharge Pulse Power Capability for each SOC using the minimum operational voltage.

$$Watts = V_{Min} \cdot (OCV_{Dch} - V_{Min}) \div R_{Dch}$$

- 14) Calculate the Charge Pulse Power Capability for each SOC using the maximum operational voltage.

$$Watts = V_{Max} \cdot (V_{Max} - OCV_{Chr}) \div R_{Chr}$$

- 15) Plot the discharge and charge power as a function of % SOC and discharged energy (Wh) at the 1 h rate.

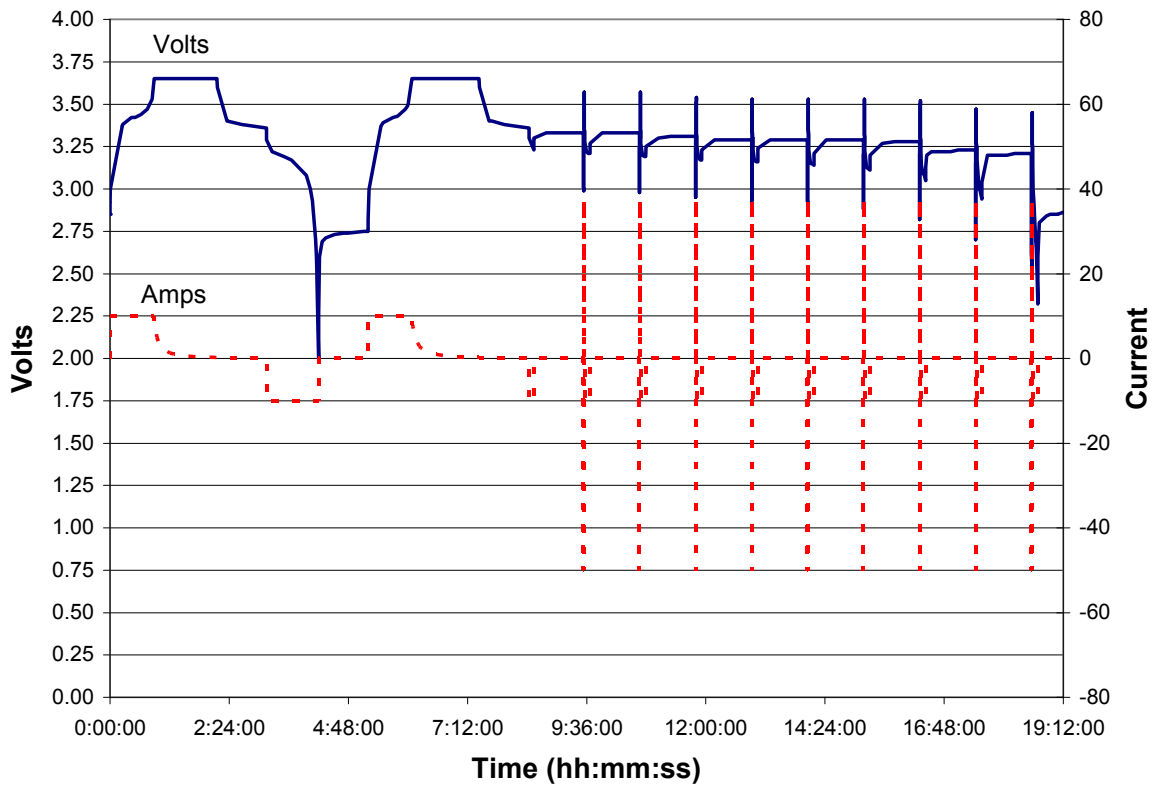


Figure 4. Hybrid Pulse Power Test.

Max power was calculated from the recorded data and using the equations shown in steps 13 and 14 above. Using ohms law, current is calculated by dividing the voltage by resistance. The voltage difference between the cell open-circuit and cell max and min voltages divided by resistance is assumed to be a measure of maximum current. In the second half of the two equations, the min and max voltages are multiplied by the calculated current to yield max 10 second power ($\text{Watts} = V \times I$). Once the max charge and discharge power is calculated, then the power data can be plotted as a function of % SOC and battery energy level in Wh. The power vs. energy plot can then be used to scale an energy storage system for any power and energy requirement at specified pulse durations.

2.8 Over Voltage/Charge Abuse Test

The Over Voltage/Charge Abuse Test was duplicated from the LiFeBatt battery Product Specifications. In the Product Specifications the cell/battery is charged at the 1C rate (10 A) up to 12 V and 7 h. The test conducted for this report was modified slightly because of a number of unforeseen events. The charge and data acquisition was terminated when the cell under test lost all voltage and caused the data acquisition system and battery cycle test equipment to stop due to the loss in cell voltage.

3. TEST RESULTS

3.1 Initial and Final Capacity

Figure 5 shows the voltage and capacity (Ah) data for a discharge and charge on cell #1 as received and after 8,394 PSOC pulse cycles. At an initial capacity of 9.61 Ah this cell is within the capacity specifications of between 9 and 10 Ah. After 8,394 PSOC pulse cycles the capacity dropped to 8.91 Ah a loss of 7%. The final capacity test was able to recover capacity from end of PSOC cycling measured at the 1C rate (8.61 Ah) to 8.91 Ah measured at the $0.5C_1$ rate. This recovery is attributed to the deep-cycle, lower rate, and full charges using an end of charge current of 0.2 A. In addition, the initial capacity measured at the 1C rate during the PSOC pulse cycling was 10.14 Ah. This increase from the initial value was attributed to an apparent “break-in” or formation period for the cell resulting from a number of deep-cycles before the PSOC pulse cycling.

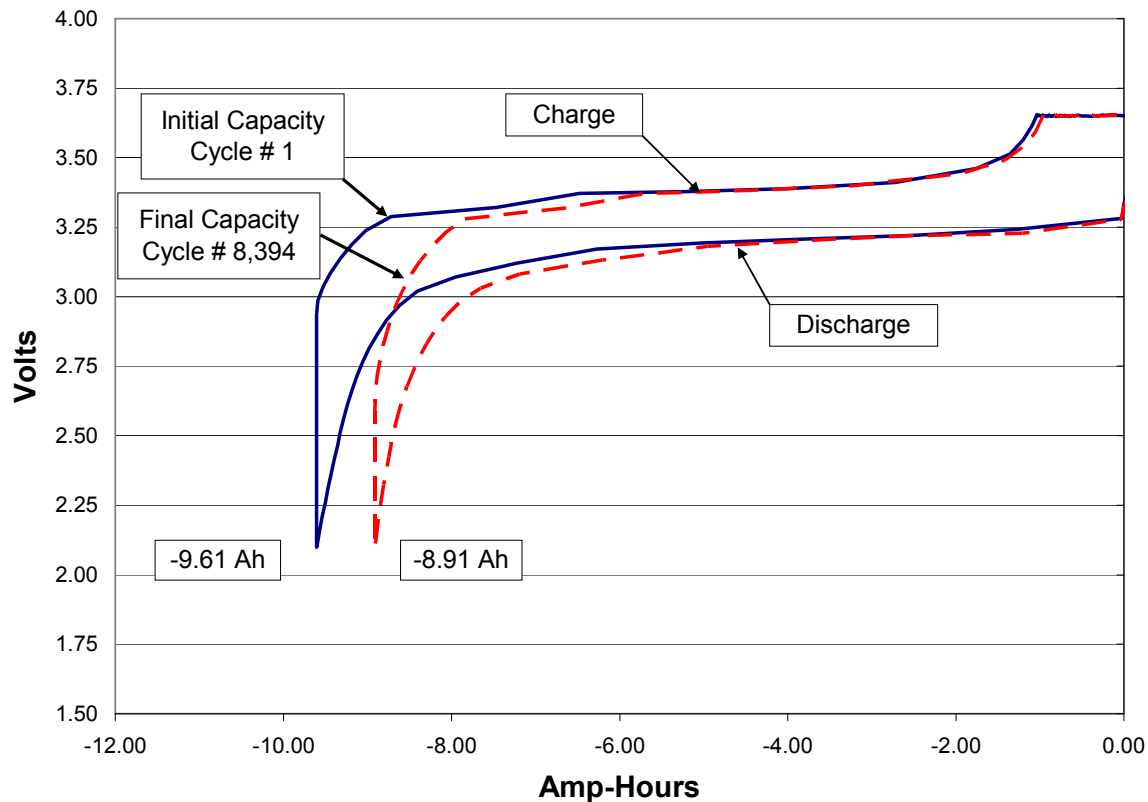


Figure 5. Initial and Final Capacity of Cell #1 (5A Chr/Dch).

3.2 DC Ohmic Resistance

Figure 6 shows the initial ohmic resistance measurement for cell #1 at 0.0036 ohms ($\Delta V/\Delta I$) and after 8,394 PSOC pulsed cycles at 0.0042 ohms. The measurement is made using a

linear regression to obtain the average slope of the line. In this case the regression is a good fit to data. The slope of the current and voltage measurement is the average resistance value for a discharge between 0 and -20 A. This battery chemistry has a slope that is consistent throughout the discharge. In some battery technologies there can be a significant difference from beginning to end of the discharge pulse. The data in this measurement is significantly less than the manufacturer's specification of less than 0.006 ohms impedance. It is not clear how the manufacturer has measured the impedance. The final ohmic resistance measurement is also lower in voltage, but it is not clear why there was a drop in voltage at 100% SOC.

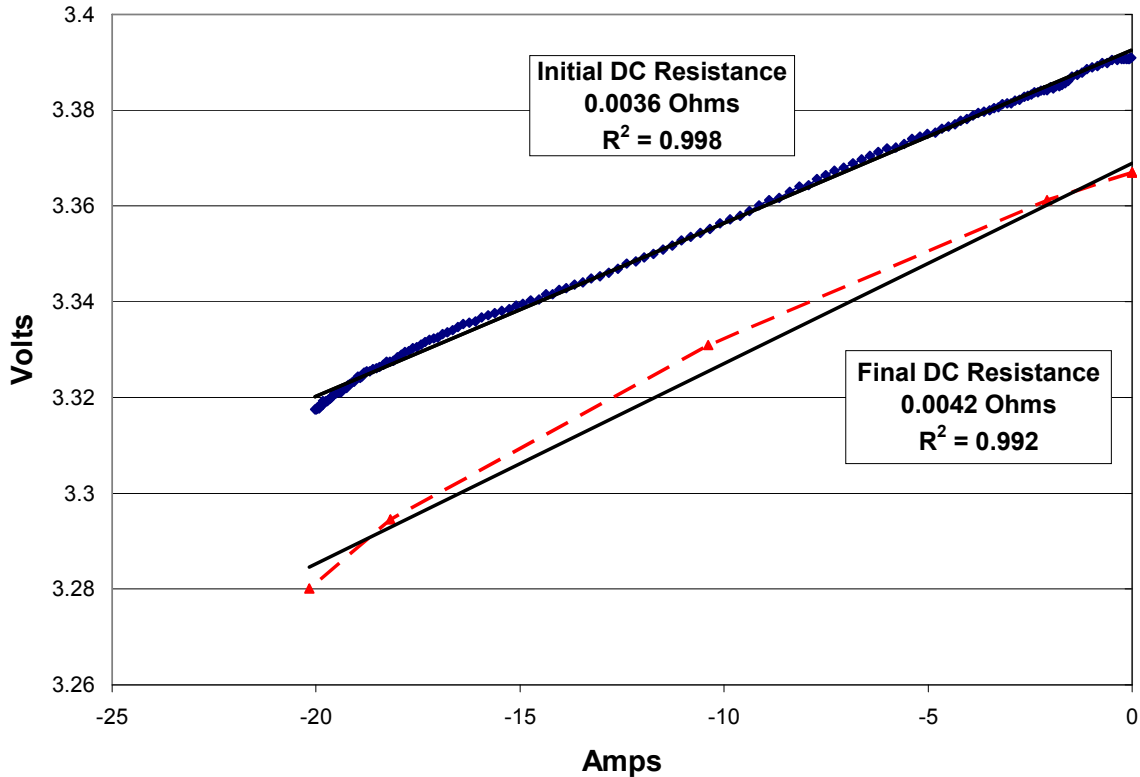


Figure 6. Ohmic Resistance Measurement On Cell #1 (100% SOC).

3.3 AC Spectral Impedance

A Nyquist plot of the impedance data before and after PSOC pulsed cycling is shown in Figure 7, and as seen there is very little difference in behavior. In fact, differences in the before and after PSOC pulsed cycling behavior cannot be observed when all of the data is displayed, and differences only become apparent after expanding the scale. The expanded scale high frequency response is also shown in Figure 7. The high frequency impedance of the cell is essentially the same before and after PSOC pulsed cycling. The small decrease in impedance from 4.01 m Ω to 3.74 m Ω after cycling may in fact be a reflection of the slight differences in SOC, as seen by the lower OCV of the cell at the time the measurements were made. Although we attempted to minimize this difference as described previously, the loss in cell capacity on

cycling may result in different SOC's for the electrodes when the impedance measurements are made, and in the two electrode configuration we do not have a means for determining the relative contribution of each to the impedance measured. Also seen in the high frequency data is what is presumably a single passive layer having a total resistance of 1.52 m Ω before cycling. As in the case of the cell impedance, there is little or no change in the resistance of this film after cycling, and its resistance is estimated to be 1.6 m Ω after cycling. Again, because of the uncertainty in the measurements, this value is essentially unchanged.

These behaviors are significantly different from the more typical lithium-ion chemistries that operate at higher voltages, (eg LiCoO₂-based materials [2]). In these other cell chemistries we generally observe increases in all of the impedances measured, and in some cases the formation of another passive film. In the case of the LiFeBatt cell, we see essentially no change of impedance as a result of PSOC cycling. Based on this behavior, it would be very useful to complete an in depth study of the impedance behavior of these materials in order to identify the processes occurring and limiting conditions.

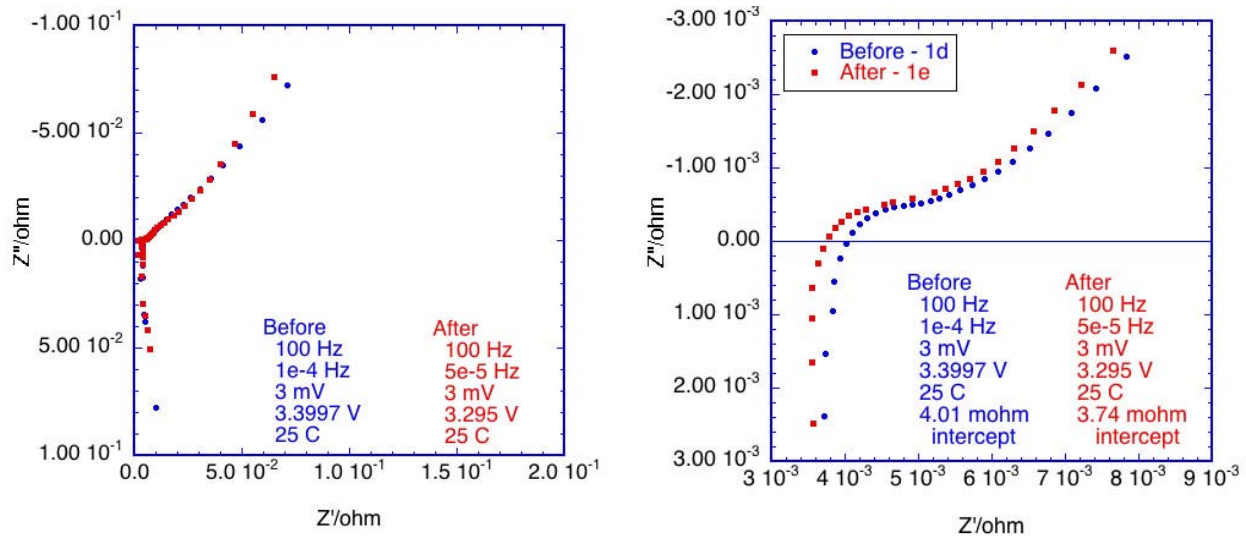


Figure 7. Impedance behavior of cell before and after PSOC cycling.

On the left is shown the full range of data collected, and on the right is an expanded scale version of the high frequency response near the intercept. The OCV of the cell at the time of the measurements was 3.3997 V and 3.295 V for the cell before and after PSOC cycling respectively.

3.4 Cell Power and Specific Energy Density

In Figure 8 is a plot of the cell specific energy and power performance and in Figure 9 is the energy and power density using the Ragone plot. The results show a steep curve as the power level increased indicating minimal energy losses and a sharp rollover at high power as the cell discharge is terminated due to excessive temperatures over 60°C.

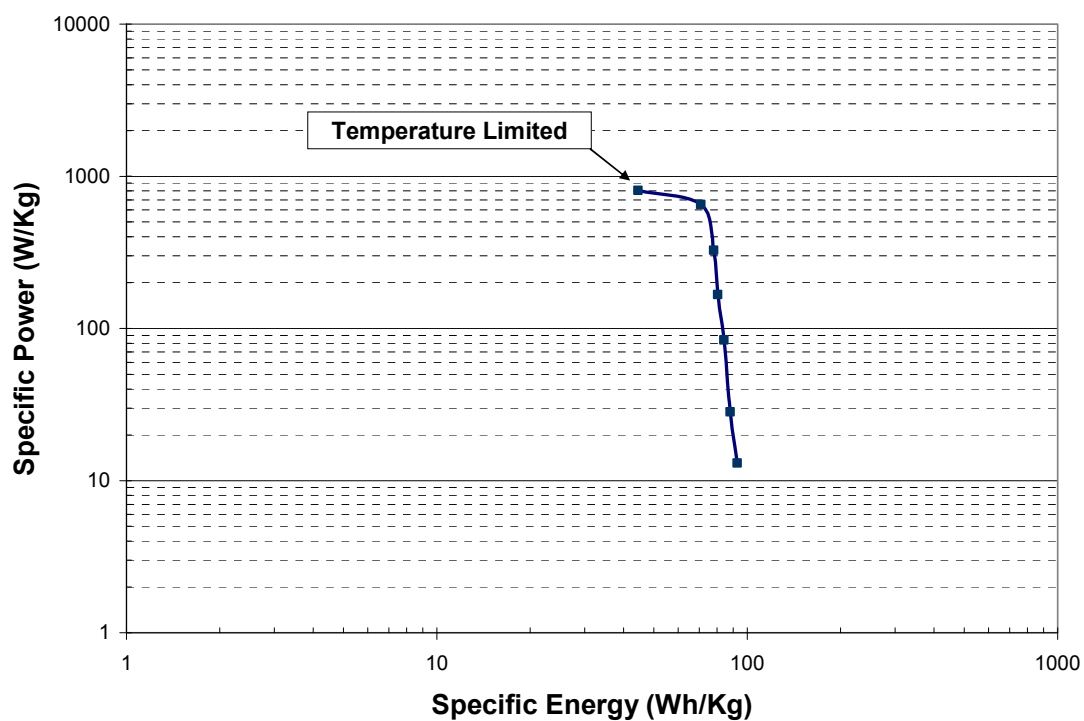


Figure 8. Specific Energy And Power Performance.

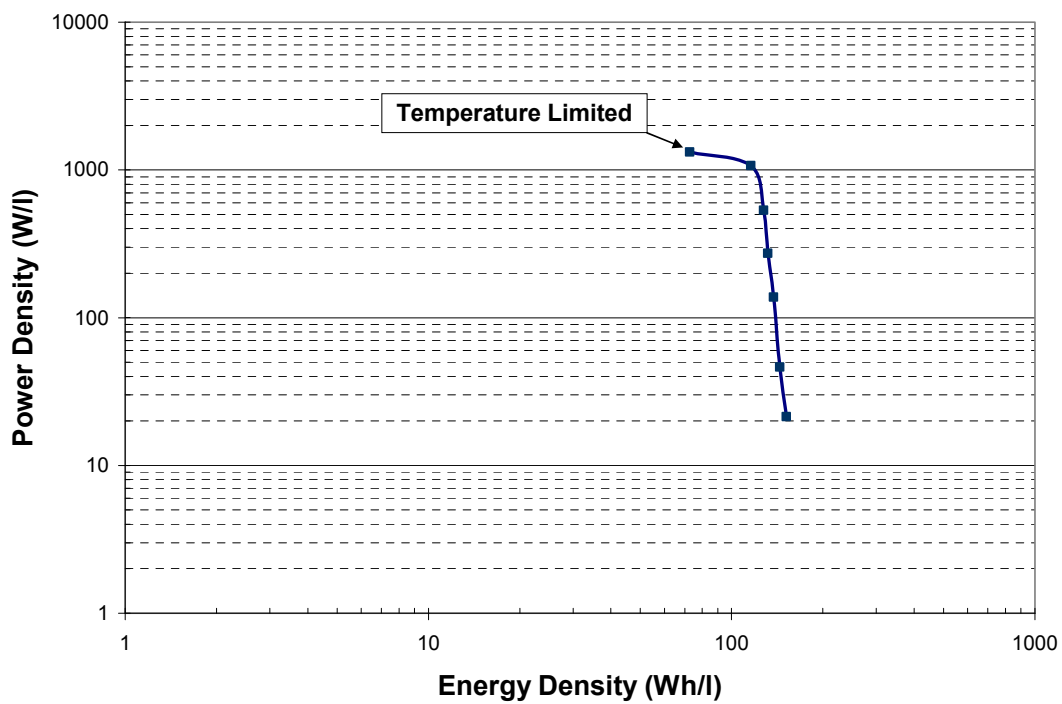


Figure 9. Energy Density And Power Density.

3.5 Cell Capacity and Recharge as a Function of Temperature

In Figure 10 are the 1C capacity measurements at 35, 25, 0, -20, -30, and -40 °C. The results show a rapid drop in capacity at -20 °C and below, and at -40 °C there is virtually no usable capacity. In Figure 11 are the recharge voltage profiles at the 1C rate. At -20 °C and below, the recharge is dramatically slowed due to the rapid increase in cell voltage up to the regulation voltage. At these low temperatures the charge currents are very low requiring long recharge times.

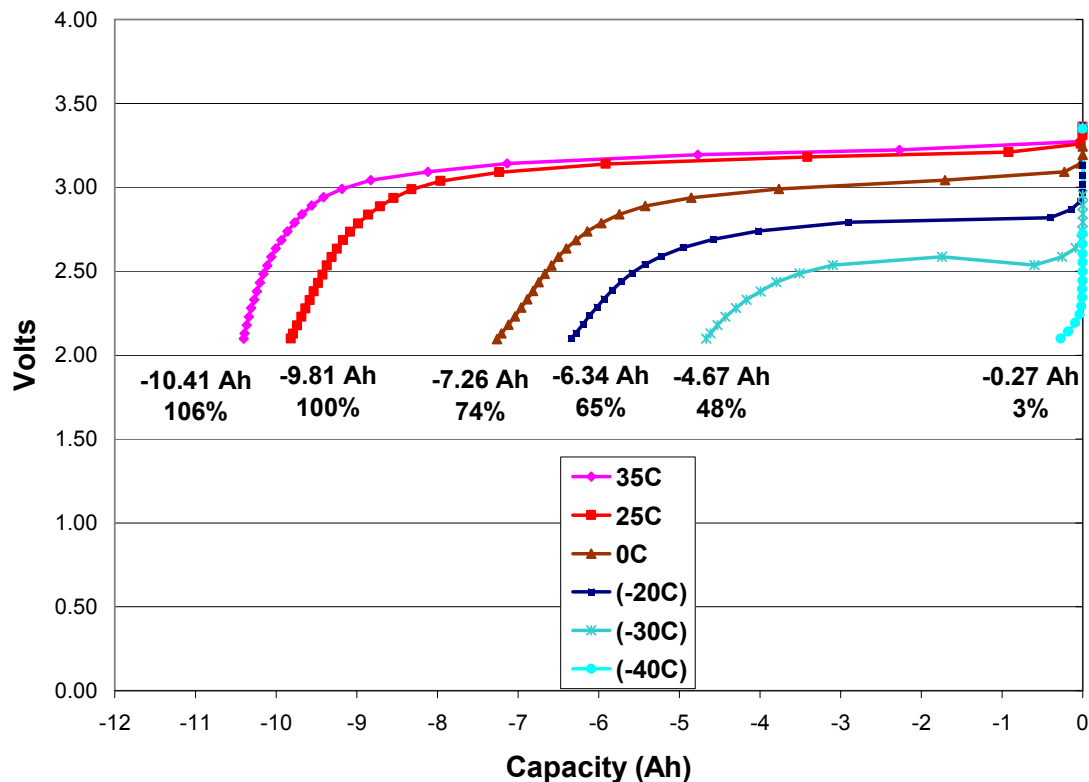


Figure 10. Capacity vs. Temperature at 10A.

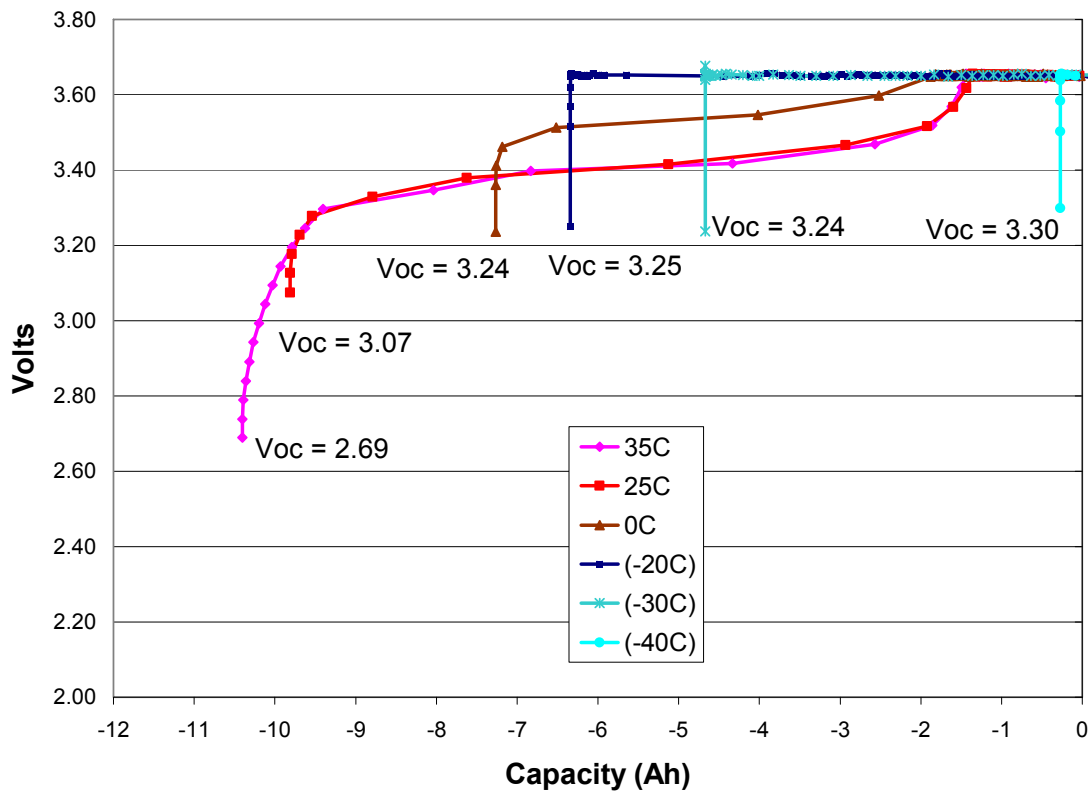


Figure 11. Recharge vs. Temperature at 10A.

3.6 Hybrid Pulse Power Test

The hybrid pulse power test results are shown in Figure 12 and 13. As expected, the maximum discharge pulse at a low state of charge is significantly reduced and as the SOC increases so does the pulse power, from 164 W (10% SOC) to 380 W (90% SOC). Usually the charge pulse has a similar decrease in power as the SOC increases, but in this case it remains fairly constant at about 200 W between 30 and 60% SOC. In addition, at 80 and 90% SOC the charge pulse is also constant at about 180 W. This behavior was replicated several times and might possibly reflect a functional dependence of cell impedance on SOC. In Figure 13 the available battery energy is plotted on the abscissa (X-axis) providing an operational range with available energy. This can be useful for scaling up to the necessary power and energy levels needed to meet the 10 second pulse power requirements of the desired system.

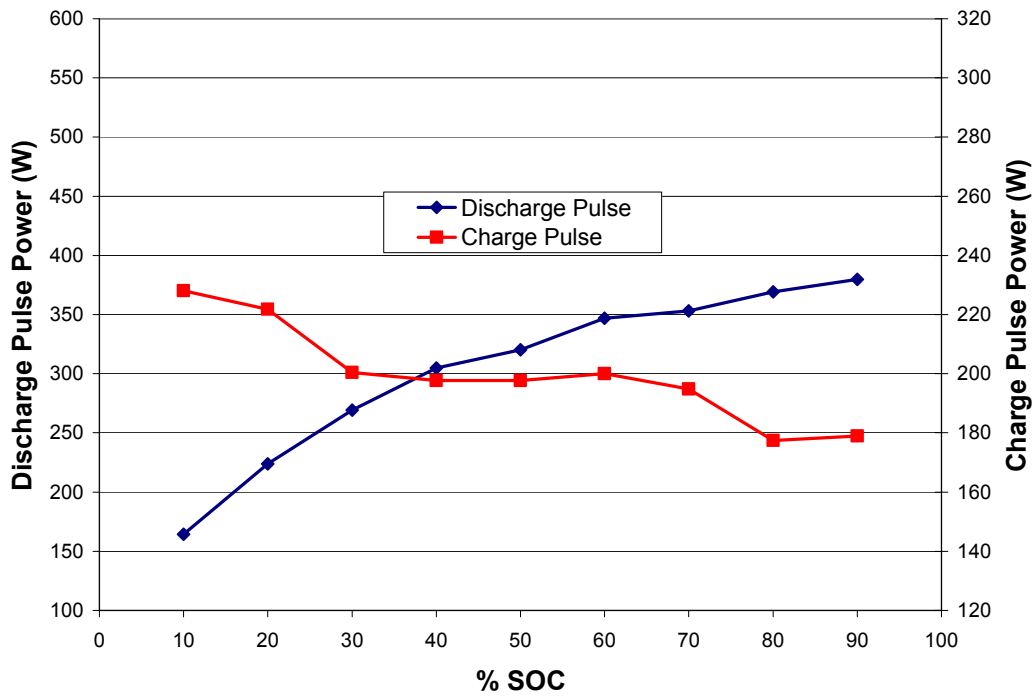


Figure 12. Hybrid Pulse Power Capability As A Function Of %SOC.

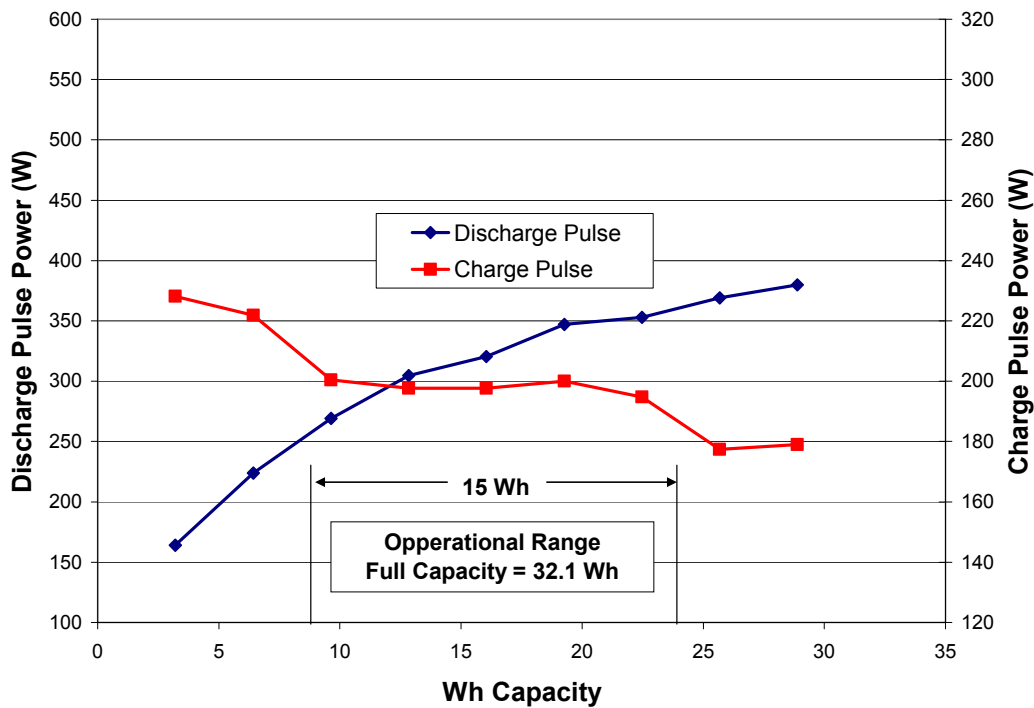


Figure 13. Hybrid Pulse Power Capability As A Function Of Capacity In Wh.

3.7 Utility PSOC Pulse Cycle-Life Test

In Figure 14 and 15 are the last Utility PSOC test results at $4C_1$ (± 40 A) and the summary capacity plot of the $1C$, $4C_1$, and $2C_1$ PSOC pulse cycling results.

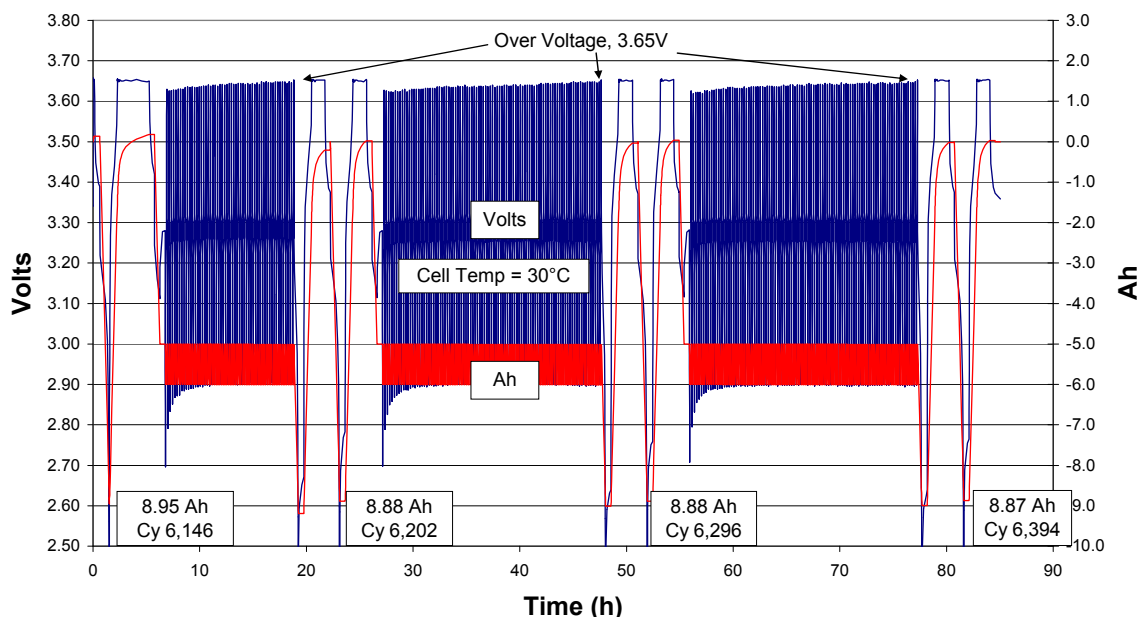


Figure 14. Utility PSOC Pulse Cycle-Life Test Results At $\pm 40A$ for 1.5 min.

Figure 14 is a plot showing the steady increase in end of charge voltage at the $4C_1$ (± 40 A) rate. In this plot, the cell voltage steps up to 3.65 V from 3.63 V in 56, 94, and 98 cycles, while at the same time the cell temperature increases from 22° to 30°C . Initially at cycle 500, the step up in voltage began at 3.58 V and required 917, 745, and 1,000 pulse cycles to reach the maximum end of charge voltage. As a result of the pulsed cycling, the ability of the cell to accept the 40 A pulse charge has degraded. Additional testing at 20 A starting at cycle 6,394 has also shown the same steady increase in end of charge voltage. Since the end of charge voltage at 20 A is well below the maximum limit, the cell could cycle well beyond 1,000 PSOC cycles without limiting current or implementing a recovery cycle to recover the voltage back to its initial value. In an actual application, this step up in voltage would limit the number and rate of the pulse charges available before a recovery cycle was implemented.

Figure 15 is made up of three different regions where the charge/discharge current and time was changed from 10 A for 6 min, to 40 A for 1.5 min, to 20 A for 3 min. These changes were the result of the initial characterization at 10 A, then high power testing at 40 A, and finally reduced power testing at 20 A. The plot shows that the capacity drops to about 88% of its initial value of 10.14 Ah after about 2,000 cycles. After 2,000 cycles, the capacity slowly fades down to 85% (8.61 Ah) of the initial value out past 8,394 cycles. At five points along the curve are 0.25 Ah increases in capacity at the same cycle number. This jump is the result of a second full charge after finishing a test sequence. The data shows that the recovery is short lived and the

capacity quickly returns to the original trend line. It is difficult to know how many cycles are possible to the 80% capacity value, but based on a linear trend line, the cell may cycle for 18,000 cycles before reaching 80% of its initial capacity. Also, the spacing between capacity measurements at the high power 40 A rate is a function of how quickly the cell reaches the maximum voltage at 3.65 V. When the cell reaches 3.65 V, the PSOC cycling is stopped and a capacity measurement is initiated. In the 40 A test region, the curve shows that this is happening initially at about 1,000 cycle intervals but has decreased to near 100 cycles after the 6,000 cycle point. After 6,000 cycles, the cell is cycled at medium power (± 20 A) and returns to the predetermined 1,000 cycle interval between capacity measurements. Thus, the cell is aging as seen by the accelerated increase in end of charge voltage and walk down in capacity.

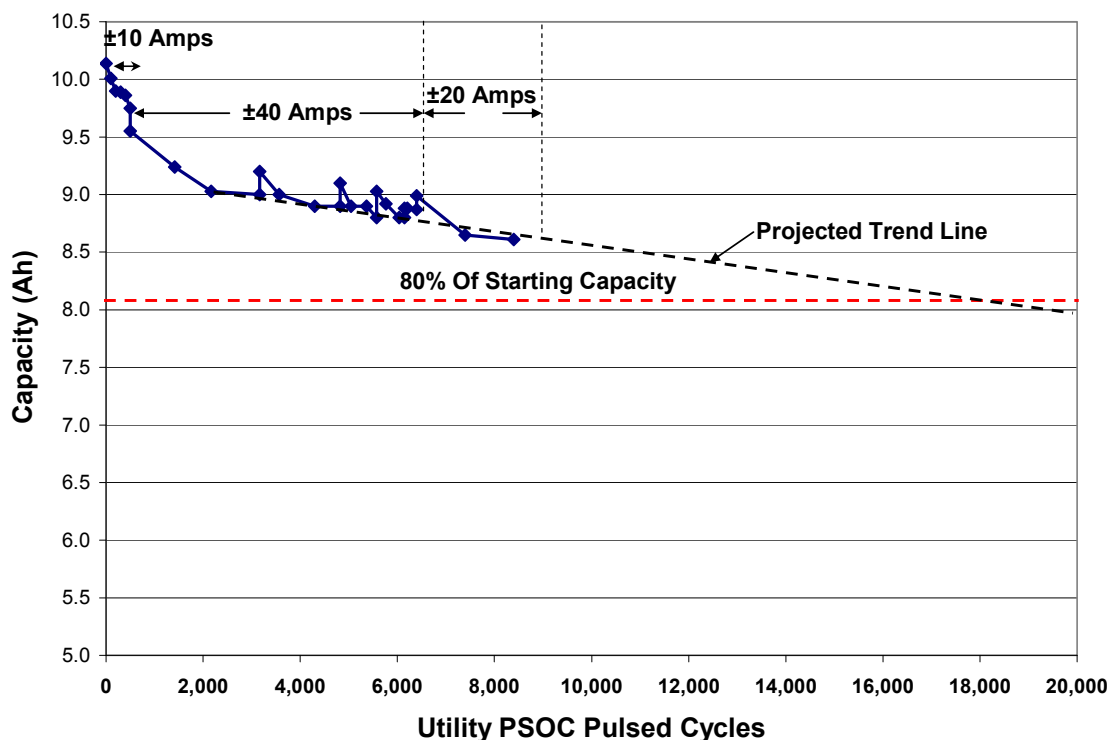


Figure 15. Utility PSOC Pulse Cycle Test Results.

3.8 Over Voltage/Charge Abuse Test

In Figure 16 the events in an over charge/voltage abuse test are documented. Initially, as expected, the cell voltage increases quickly while being charged at 10 A, but then slowly increases after 4.7 V. The cell voltage slowly increases for about 30 minutes while the cell temperature continues to slowly rise to about 100 °C at which time cell voltage spikes to the maximum value of 12 V. At about 110 °C the cell vents liquid electrolyte without any fire or sparks and then open-circuits at 116 °C. After open-circuiting and a loss of electrolyte, the cell loses all voltage at 120 °C. The data acquisition shuts down due to a no voltage condition, but temperature is manually monitored until the cell reaches its maximum value at 160 °C about 20 minutes after the cell open-circuited.

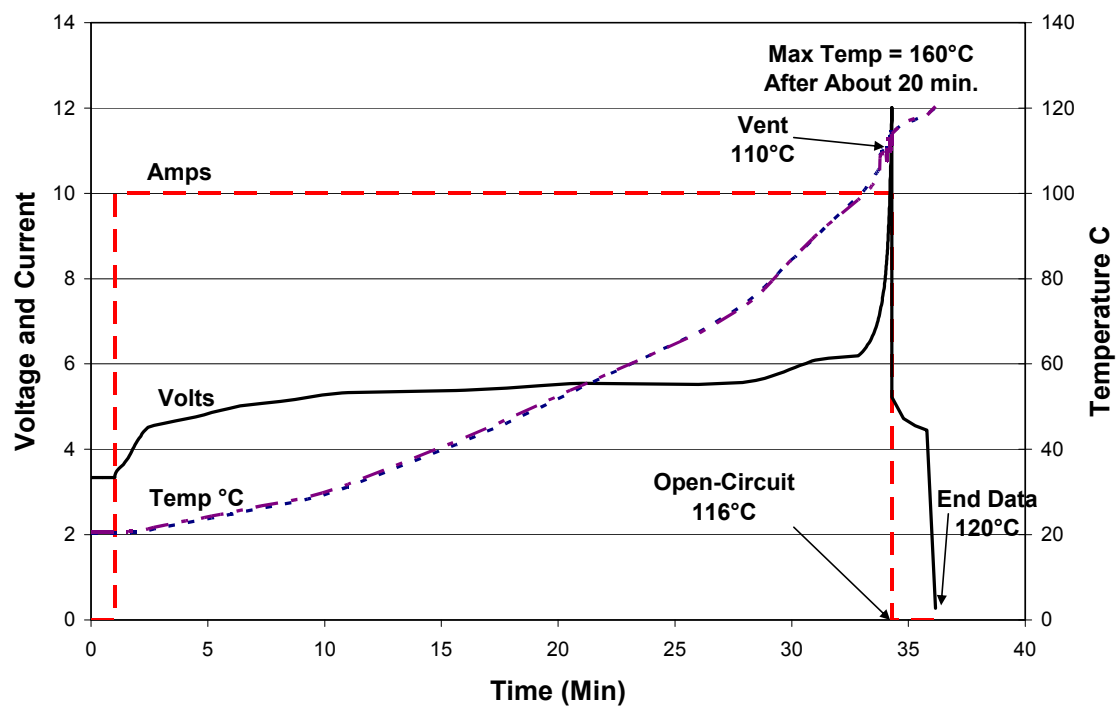


Figure 16. Over Voltage/Charge Abuse Test.

Table 2. LiFeBatt Summary Test Results.

Test	Cell #1	Cell #2	Cell #3
Initial Capacity C/2 (Ah)	9.61	9.88	9.81
Initial DC Ohmic Resistance (Ohms)	0.0036	0.0037	0.0033
Initial AC Spectral Impedance ESR (Ohms)	0.0041	NA	NA
Cell Power and Energy Density at 10C1 Rate (W/l, Wh/l, W/Kg, Wh/Kg)	NA	NA	1,068, 116, 653, 71
Cell Capacity and Recharge As A Function Of Temperature (Ah @ 35, 25, 0, -20, -30, and -40C)	NA	NA	10.41, 9.81, 7.26, 6.34, 4.67, 0.27
Cell Utility Cycle-Life PSOC Test (Cycles, % Capacity Loss)	8,394 / ~15%	NA	NA
Final DC Ohmic Resistance and Spectral Impedance (Ohms, ESR)	0.0042	NA	NA
Final AC Spectral Impedance ESR (Ohms)	0.0037		
Final Capacity Test C/2 (Ah)	8.91	NA	NA
Hybrid Pulse Power Test (Charge/Discharge Power (W) at 50% SOC)	NA	NA	198, 331
Over Voltage/Charge Abuse Test (Vent Temp, Max Temp, Fire Y/N)	NA	110°C, 160°C, N	NA

4. SUMMARY

Table 2 provides a brief summary of the test results on three cells. After capacity and impedance measurements cell #1 was PSOC pulsed cycled for 8,394 cycles (see Table 2). The other two cells were characterized for over voltage/charge, cell power, and capacity vs. temperature, as indicated in Table 2. These results indicate that the LiFeBatt cells meet the manufacturers specifications in capacity, internal ohmic resistance, max power, and specific energy. The temperature performance at 35, 25, 0, -20, -30, -40 °C show that both discharge capacity and recharge voltage are significantly affected by low temperature especially at temperatures below -20 °C. From -20 °C to 35 °C the capacity will increase by about 0.8% per °C. At temperatures below -20 °C the capacity drops dramatically to just 3% at -40 °C. The 10 second pulse power capability values can be used to scale up for larger pulse power applications and show power levels of 325 W/cell on discharge and 300 W/cell on charge at 50% SOC. The utility PSOC pulse cycle test results after 8,394 cycles suggests that the LiFeBatt cells will PSOC pulse cycle up to the 4C₁ rate for utility applications. Performance degradation was identified by capacity fade (10 to 15% loss - based on 9.61 or 10.14 Ah initial capacity) and by the increase in end of charge voltage during high power and medium power pulses. Based on the slow trend of capacity fade, the test cell should PSOC pulse cycle well beyond the 8,394 cycles tested before reaching 80% of initial capacity. This assumes that there will be no premature failure mechanisms that terminate life early. The ohmic resistance measurements and spectral impedance measurements before and after the PSOC pulse cycling have indicated only a slight increase in ohmic resistance and a very slight drop in ESR for spectral impedance. The ohmic value increased from 3.6 to 4.2 mohms, while the AC spectral impedance ESR value decreased from 4.01 to 3.74 mohms. This is a very minimal change, if any, and indicates no similar degradation as seen in the LiCoO₂ materials where increases in all of the impedances measured occur, and in some cases another passive film can form. Finally, the over charge/voltage abuse test indicated that the LiFeBatt cell can fail without fire, or damage to other external systems if those systems can handle the 160 °C max temperature and electrolyte venting.

5. REFERENCES

- [1] **Handbook Of Batteries**, 3th edition, G. W. Linden, McGraw-Hill Handbooks 1995, ISBN 0-07-135978-8,
- [2] D. Zhang, et al, “Studies on capacity fade of lithium-ion batteries,” Journal of Power Sources, 91, (2000), pp.122-129.

DISTRIBUTION

1	MS0161	Patent and Licensing Office	11500
1	MS0614	Cara Johnson	02540
1	MS0614	Thomas F. Wunsch	02546
1	MS0614	David Ingersoll	02546
1	MS0614	David Johnson	02546
1	MS0614	Manuel M. Contreras	02547
1	MS0614	Wes Baca	02547
1	MS0614	Nancy Clark	02547
5	MS0614	Thomas D. Hund	02547
1	MS0899	Technical Library	09536 (electronic copy)

