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Life Cycle Testing of High Power 18650 Lithium-Ion Cells

Terry Unkelhaeuser, David Ingersoll
Sandia National Laboratory, Mail Stop 0613, Albuquerque, NM 87185-0613
Chet Motloch
Idaho National Engineering Laboratory
Vince Battaglia and Ira Bloom
Argonne National Laboratory
Harold Haskins
Ford Motor Company

Contact: T. Unkelhaeuser, phone: 505-845-8801 fax: 505-844-6972; e-mail: tmunkel@sandia.gov

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Near Term Objectives

- Develop a life cycle test protocol for characterization of high-power 18650 lithium-ion cells.
- Demonstrate the adequacy of the test protocol using commercially available cells and prototype Generation 1 Baseline cells.
- Design an experimental test matrix that encompasses test parameters known to affect cell performance, such as state of charge and temperature.
- Specify a series of pre- and post-test electrical studies that will allow for characterization of cell degradation mechanisms.
- Identify the testing resources necessary for implementation the test plan.
- Develop a post-test diagnostic schedule for each cell in the test matrix.

Approach

- Modify existing PNGV test protocols for use for high-power characterization of 18650 cells.
- Perform an evaluation of the modified test protocols using commercially available cells and prototype Generation 1 Baseline cells by placing these cells on a limited test schedule.
- Identify critical cell test parameters, such as state of charge and temperature, based on previous experience or by performing limited experimental testing.
- Develop a complete test matrix encompassing this critical parameter space.
- Populate the matrix within the constraints of limited cell resources beginning with the high value matrix elements.
- Identify test resources required for implementation of the test matrix.
- For each cell in the matrix, identify a post-test diagnostic schedule.

Accomplishments

- A fully automated high-power life cycle test was developed that allows for control of the state-of-charge of the cell on each cycle of the test and which also obviates the need for performing the Operating Set Point Stability Test described in the PNGV test protocol. This was accomplished by using the cell voltage as a measure of the state-of-charge of the cell and employing a controlled voltage step as the last element in the pulse profile. Enough flexibility of the test protocol has been attained such that this procedure has general applicability to a wide variety of cells.

- A prototype test fixture was developed to ensure maintenance of a uniform and stable cell temperature during testing. Due to the high currents passed in the test and the small but finite cell resistance, it was anticipated that the cell would exhibit significant i^2R heating, resulting in a significant deviation of cell temperature from the target value. This was experimentally verified, and a prototype cell fixture was designed and tested in order to eliminate this effect.
- A test plan was developed and published. This plan identifies the test matrix and test conditions for each and every cell. It also describes handling procedures, as well as pre- and post-test electrical characterization of the cells.
- The requisite test facilities necessary for plan implementation were identified. Due to the large number of cells and test conditions employed, it was clear that no single test facility could successfully implement the plan. Consequently, three sites were deemed necessary for full plan implementation. These sites are Argonne National Laboratory, Idaho National Engineering Laboratory, and Sandia National Laboratories.
- The testing of the 79 cycle life Gen 1 cells is completed. They were tested under two state-of-charge conditions (60% and 80%), three delta state of charge conditions (3%, 6%, 9%), and four temperatures (40°C, 50°C, 60°C, 70°C).
- All of the cell test data have been processed. The complete analysis of all of the data is continuing and will be completed before the Gen 2 testing program begins.

Future Directions

- Finish analyzing cell performance data.
- Development of the Generation 2 test plan.
- Implementation of the test protocol on Generation 2 Baseline cells.

It is well recognized that the conditions of use of a cell will affect its performance, as well as influence its eventual failure and mechanism of failure. Hence, in order to gain an understanding of the potential failure mechanisms of the cell, and perhaps to make predictive statements regarding cell performance under actual use conditions, it is necessary to subject the cell to a wide variety of test conditions within the expected performance envelope. A series of diagnostic tests aimed at exploring the fundamental characteristics of the cells, such as the structural changes of the cathode material for example, could then be performed. These tests would be performed either at the end of test in the case of destructive diagnostic methods of analysis, or interspersed during execution of the test in the case of non-destructive tests. Following this approach, a life cycle testing protocol was designed and developed which was applied to the Generation 1 Baseline cells. In order to gain a fundamental understanding of cell behavior as well as perhaps to aid in future cell design, this protocol will continue with the Generation 2 Baseline cells.

The Gen 1 cycle life cells were tested under two state-of-charge conditions (60% and 80%), three delta state of charge conditions (3%, 6%, 9%), and four temperatures (40°C, 50°C, 60°C, 70°C). Control of the state-of-charge during each cycle of the test was accomplished by making a fundamental change in the way that the state-of-charge is recognized. Normally, this is accomplished strictly on the basis of capacity and relative capacity added and/or removed from the cell. We initially adhered to this protocol and obtained voltage vs. capacity data at a low rate (C/25). However, we then tied these capacity levels to the open circuit voltage (OCV) of the cell, and in essence generated a calibration curve of OCV vs. state of charge. During the course of the test we controlled to this value, and a reset was done as the last step in a complete pulse profile.

The basic pulse profile used consists of a series of controlled current steps. One of the profiles is shown in Figure 1. Also contained in the figure is a table that summarizes the various current levels and time duration for each pulse. The final pulse, and the key to maintaining the state of charge on each cycle, is a controlled voltage step. In this way, by bringing the cell back to the desired voltage, the state of charge can be maintained at the desired level.

ATD Life Cycle 3% SOC Pulse Profile

Step Time (s)	Cumulative Time (s)	Current	Charge (A-s)	Cumulative Charge (A-s)
14	14	7.20	100.80	100.80
10	24	0.00	0.00	100.80
2	26	-6.48	-12.96	87.84
2	28	0.00	0.00	87.84
32	60	-2.745	-87.84	0.00
20	80	Adjust CV, as necessary, starting with OCV - SOC		

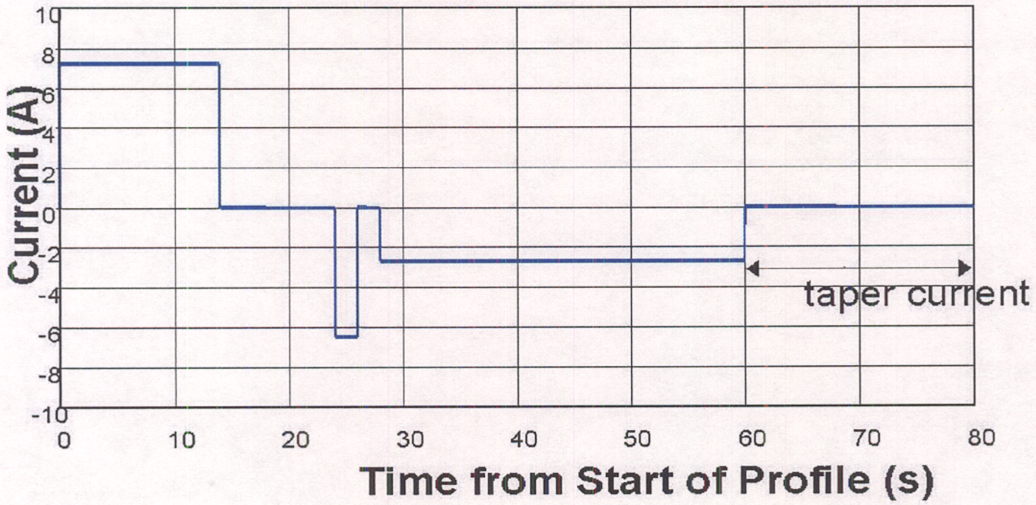

Figure 1. Life Cycle Test Profile for Generation 1 Baseline Cell

The amount of charge added to or removed from the cell during the pulse profile, that is the delta state of charge (ΔSOC), can significantly affect cell performance. We recognized this as one of the critical test parameters in our program, and three ΔSOCs corresponding to 3%, 6%, and 9% were included in our test design. Each of the different levels was obtained by using either one, two, or three repetitions, respectively, of the basic life cycle test profile shown in Figure 1. A comparison of the three different profiles is shown in Figure 2.

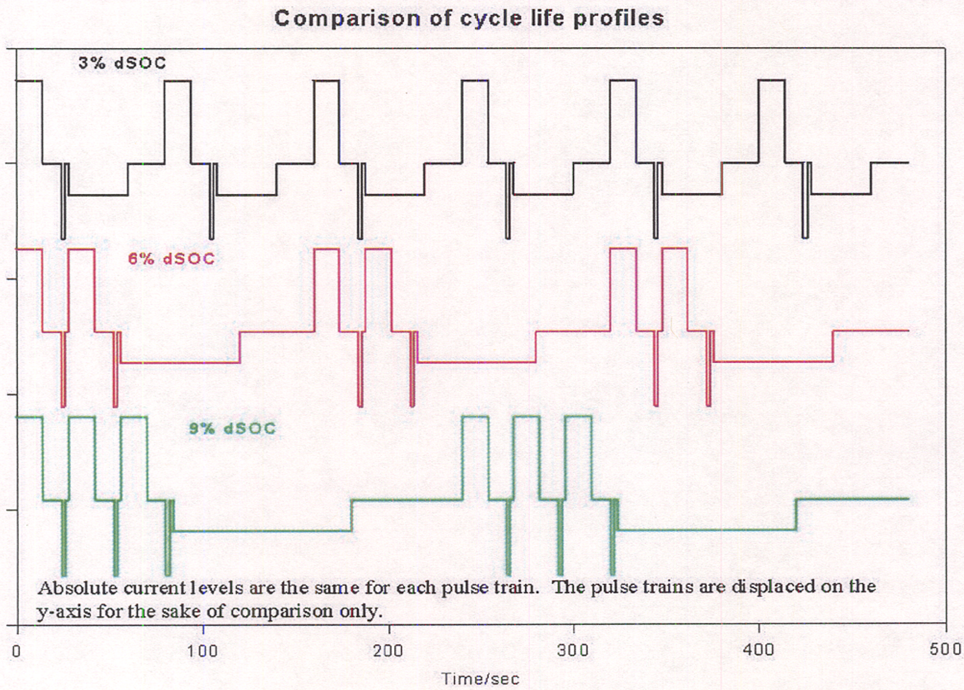

Figure 2. Life Cycle Test Profiles Corresponding to 3%, 6%, and 9% ΔSOC

From the above discussion it is evident that the critical parameters are state-of-charge, ΔSOC, and cell temperature. Based on these, three test matrices were developed that span the parameter space given the limited resources. Three matrices are used since three test sites, each with their own unique capabilities, are utilized to implement this program. Tables 1 – 3 show each of these matrices.

Matrix for ATD GEN 1 Baseline Cells at INEEL					
SOC	ΔSOC	Test Temperature			
		40 °C	50 °C	60 °C	70 °C
80%					
	zero (calendar life)	3	3	3	3
	3%			3	
	6%			3	
	9%			3	
60%					
	zero (calendar life)	3	3	3	3
	3%	3	3	3	3
	6%	3	3	3	3
	9%	3	3	3	3
40%					
	zero (calendar life)				
	3%				
	6%				
	9%				
TOTALS		15	15	24	15

Table 1. Life Cycle Matrix Implemented at INEEL

Matrix for ATD GEN 1 Baseline Cells at Argonne National Laboratories					
SOC	ΔSOC	Temperature			
		40 °C	50 °C	60 °C	70 °C
80%					
	zero (calendar life)				
	3%				
	6%				
	9%				
60%					
	zero (calendar life)	3	3	3	3
	3%				
	6%			3	
	9%				
40%					
	zero (calendar life)	3	3	3	3
	3%				
	6%				
	9%				
Totals		6	6	9	6

Table 2. Life Cycle Matrix Implemented at ANL

Matrix for ATD GEN 1 Baseline Cells at Sandia National Laboratories					
SOC	ΔSOC	Temperature			
		40 °C	50 °C	60 °C	70 °C
80%					
	zero (calendar life)	3	3	3	3
	3%	3	3		3
	6%	3	3		3
	9%	3	3		3
60%					
	zero (calendar life)				
	3%				
	6%				
	9%				
40%					
	zero (calendar life)				
	3%				
	6%				
	9%				
Totals		12	12	3	12

Table 3. Life Cycle Matrix Implemented at SNL

The testing of the 43 cycle life Gen 1 cells (39 + 4 replacements) assigned to SNL is complete. The test results were combined with the results from INEEL and ANL to present a unified testing result to the ATD and DOE program managers. Nineteen cells have been shipped to diagnostic labs and 20 cells are in cold storage (10°C). Three cells vented during testing and were replaced in the matrix.

The average capacity fade of the Gen 1 cells was higher at 80% SOC. Also, at 80% SOC, only the 40°C data have a steady increase in capacity fade with increasing dSOC. Capacity fade at other temperatures is somewhat insensitive to dSOC. At 60% SOC, a steady increase in fade is observed up to 70°C. These trends are shown in Figures 3 – 6.

	0%dsoc	3%dsoc	6%dsoc	9%dsoc
4 week 40 ° C	7.5	12.6	13.5	17.0
4 week 50 ° C	12.2	16.5	18.9	17.3
4 week 60 ° C	14.8	20.9*	21.0*	15.0*
2 week 70 ° C	16.0	19.9	19.9	20.1
Average	12.6	17.5	18.3	17.4

* = INEEL Data

Figure 3. Average % Capacity Fade at first RPT (80% SOC)

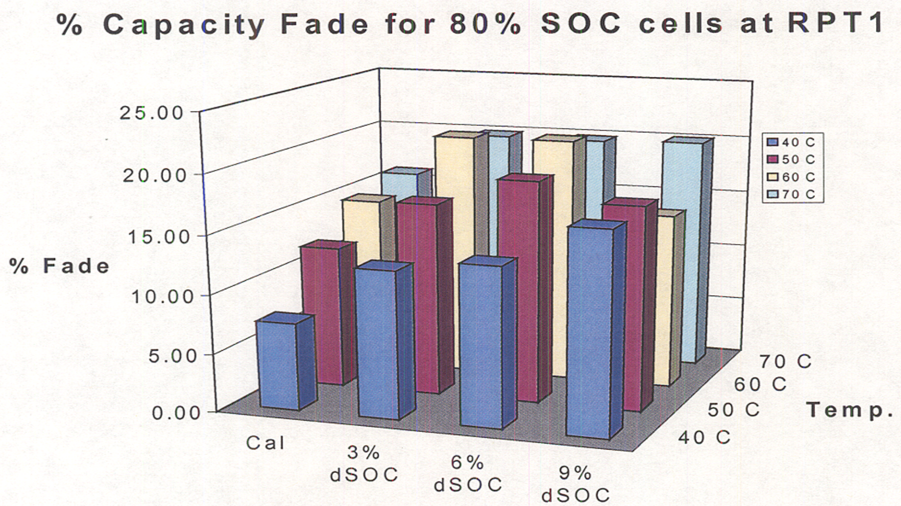

Figure 4. Higher Temperature and Higher dSOC Cause Higher Capacity Fade – 80% SOC Data

	3% dsoc	6% dsoc	9% dsoc
4 week 40 °C	7.9	9.0	11.0
4 week 50 °C	8.7	10.6	10.6
4 week 60 °C	9.9	10.5	12.5
2 week 70 °C	13.0	13.4	13.4
Average	9.9	10.9	11.9

All Data is from **INEEL**

Figure 5. Average % Capacity Fade at first RPT (60% SOC)

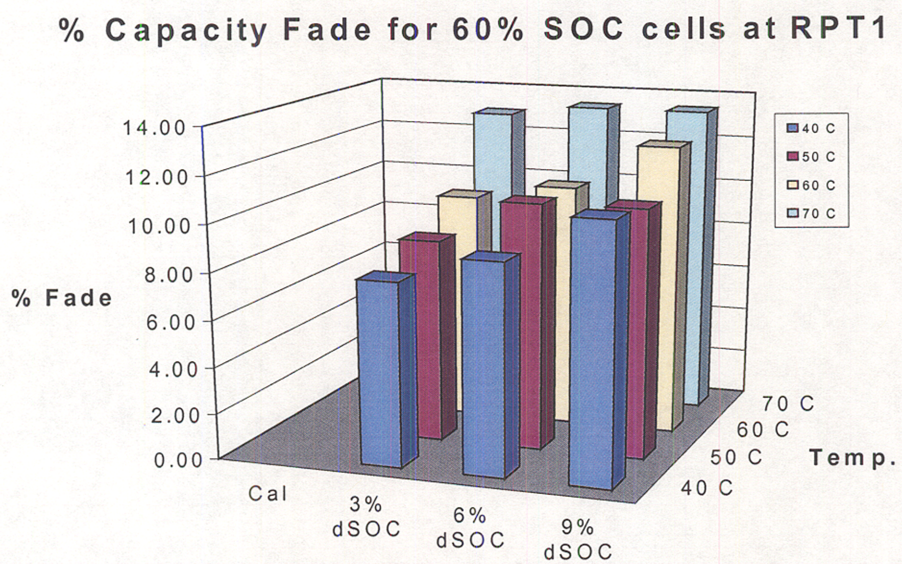

Figure 6. Higher Temperature and Higher dSOC Cause Higher Capacity Fade – 60% SOC Data

Pulse power fade was also observed for the Gen 1 test cells. For the INEEL test cells at 60% SOC, the average pulse power fade from characterization to the zero week RPTs was 10.6%. From zero week to the first RPT, the average pulse power fade ranged from 34% to 38% for the 70°C cells down to 21% to 26% for the 40°C cells.

The average pulse power fade from zero week to the first RPT for the 80% SOC cells tested at SNL ranged from 37% to 44% for the 70°C cells down to 24% to 34% for the 40°C cells. These results show that pulse power fade increases with higher SOC and higher dSOC. Figures 7 and 8 graphically illustrate the trend in increased pulse power fade.

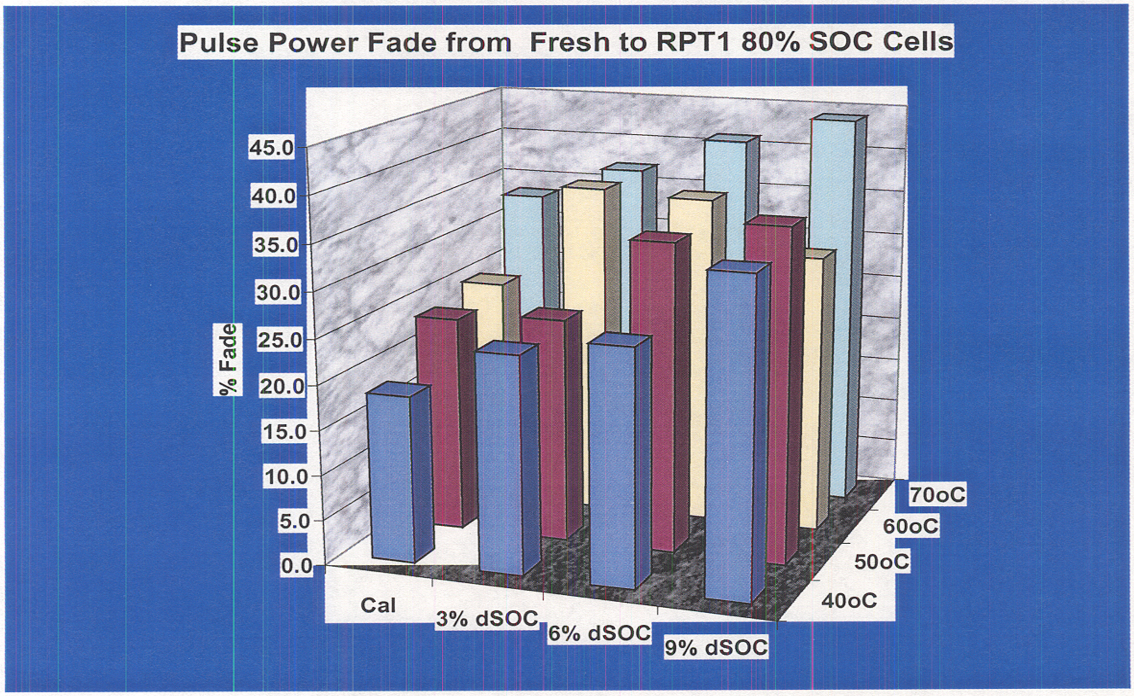

Figure 7. Pulse power fade, fresh to RPT 1 for 80% SOC cells

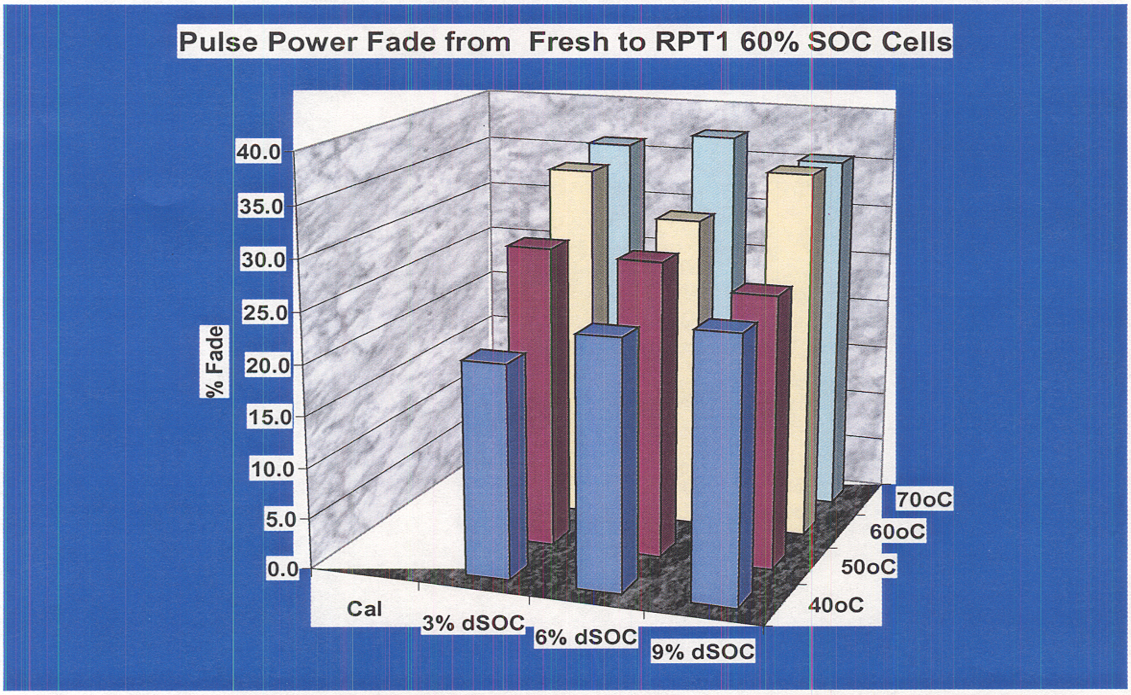

Figure 8. Pulse power fade, fresh to RPT 1 for 60% SOC cells

The mid-level Hybrid Pulse Power Characterization Tests (M HPPC) show that the increased resistance of the Gen 1 cells is primarily due to charge transfer resistance with a secondary ohmic resistance effect. This can be seen by examining the first 7.2A, 18 second pulse of the M HPPC test. The charge transfer resistance increases at a faster rate as the cell ages. Figure 9 illustrates the contribution of ohmic and charge transfer resistance to cell performance. Note, however, that Figure 9 is not corrected for the ohmic drop in the nickel tabs and test leads connected to the cell. We are in the process of making the appropriate measurements to correct the readings for the nickel tabs and test leads.

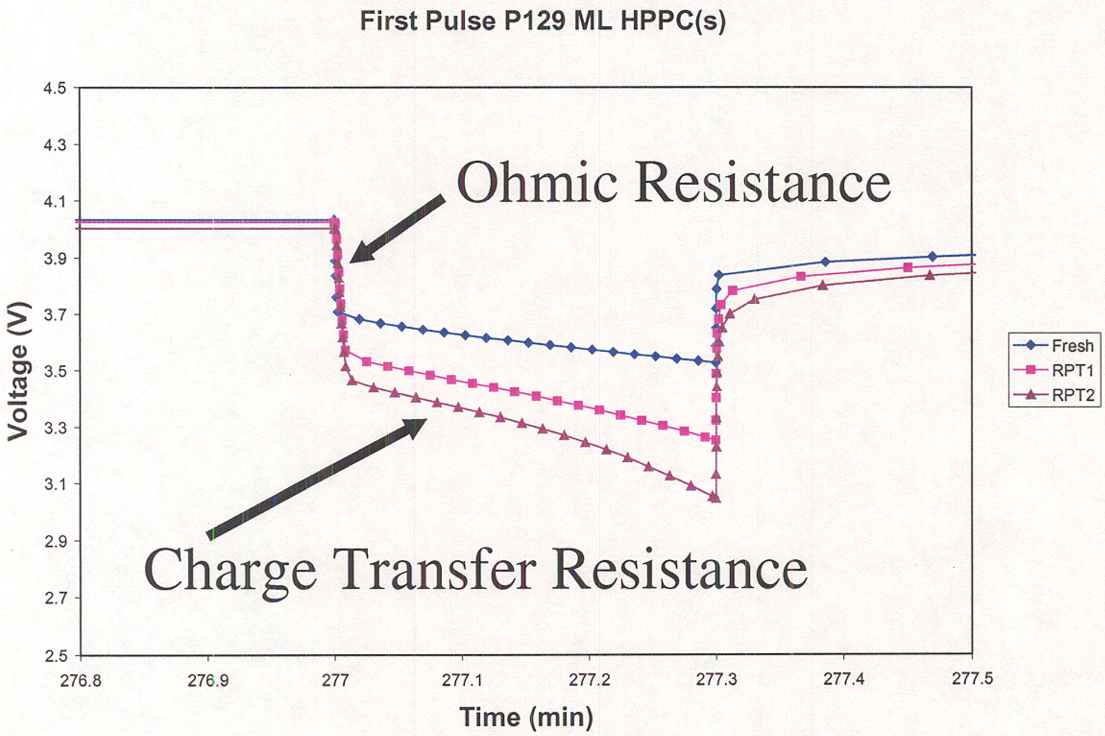

Figure 9. Typical first 7.2A, 18-second discharge pulse showing ohmic vs. charge transfer effects.

Acknowledgments

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