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Battery Technology Life Verification Testing and Analysis

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Abstract

A critical component to the successful commercialization of batteries for automotive applications is accurate life prediction. The Technology Life Verification Test (TLVT) Manual was developed to project battery life with a high level of statistical confidence within only one or two years of accelerated aging. The validation effort that is presently underway has led to several improvements to the original methodology. For example, a newly developed reference performance test revealed a voltage path dependence effect on resistance for lithium-ion cells. The resistance growth seems to depend on how a target condition is reached (i.e., by a charge or a discharge). Second, the methodology for assessing the level of measurement uncertainty was improved using a propagation of errors in the fundamental measurements to the derived response (e.g., resistance). This new approach provides a more realistic assessment of measurement uncertainty. Third, the methodology for allocating batteries to the test matrix has been improved. The new methodology was developed to assign batteries to the matrix such that the average of each test group would be representative of the overall population. These changes to the TLVT methodology will help to more accurately predict a battery technology's life capability with a high degree of confidence.

Keywords: batteries, life prediction, stress factors, Monte Carlo, uncertainty.

1. Introduction

Accurate life prediction is a critical component to the successful commercialization of high-power battery technologies for various applications, including the automotive industry. As part of the U.S. Department of Energy's Advanced Technology Development Program, the Technology Life Verification Test (TLVT) Manual [1] was developed to estimate a battery's life expectancy based on its anticipated usage (e.g., 15 years and 150,000 miles) at a target confidence interval with only one or two years of accelerated aging. The manual incorporates the FreedomCAR (Freedom Cooperative Automotive Research) goals and requirements, and can be applied to numerous applications (minimum power assist, maximum power assist, plug-in hybrids, ultracapacitors, etc.). This paper presents an overview of the TLVT process, followed by some lessons learned and subsequent improvements to the methodology as a result of the validation effort.

2. Technology Life Verification Testing

A general flow diagram of the TLVT process is shown in Figure 1. Prior to use in any TLVT-related application, a battery technology must first be thoroughly characterized and understood. In the absence of such knowledge, a series of short-term preparatory tests are conducted to help identify aging mechanisms and battery stress levels. Both prior knowledge and data from such preparatory testing are then used to develop a life model for a particular chemistry. Both a life model and error model are necessary for a viable experiment. The life model (either empirical or physics-based) reflects the typical degradation over time as a function of the identified life-limiting wearout mechanisms. Common stress factors include temperature, state-of-charge, energy throughput, and pulse power levels for both discharge and charge. The error model accounts for both the variability due to measurement error and manufacturing differences.

A full factorial core-life test matrix (i.e., a matrix that accounts for all of the degradation parameters identified in the life model) provides adequate coverage of these stress factors at various acceleration rates (e.g., three temperatures and two states-of-charge) to estimate life with a desired degree of confidence. The limiting values of these degradation mechanisms must also be identified so that the stress level is not increased to a point where a battery's failure rate is different than under normal use conditions. Once the core matrix is designed, Monte Carlo simulations are used to generate a large number of independent simulation trials for each experimental condition using random perturbations to the model parameters, measurement error, and manufacturing variability. The set of simulations provides a distribution of estimated average battery life. If the Monte Carlo simulations do not yield the desired life at the desired confidence limit (i.e., 15-year life at 90% lower confidence level), then the number of cells, and/or allocation of cells within the core matrix has to be modified. This process is repeated until an acceptable confidence limit is reached using Monte Carlo simulations.

The Monte Carlo simulations are then verified with actual battery testing. The performance results are modeled and analyzed for lack-of-fit using statistical methods (i.e., bootstrap) that create multiple realizations of the test data to assess the uncertainty in the life-on-test estimates. If the confidence limit is acceptable and matches reasonably well with the Monte Carlo simulation results, then the model can be used for accurate life prediction. Otherwise, the model needs additional development, and the process then repeats. Ideally, the test matrix would include a substantial number of batteries to minimize error, but that may not be practical or economically feasible. Other options include testing a small number of batteries at each test condition within the matrix, or a larger number of batteries at only a few of the test conditions. These options will depend on the levels of manufacturing variability and measurement error as well as the number of available batteries and test channels. For example, if the manufacturing variability is high, then more batteries need to be placed at each test condition. After initial characterization, both the batteries and test facilities should be checked for desired levels of repeatability and accuracy.

A supplemental test matrix is typically executed in parallel to the core testing. This matrix is intended to verify various assumptions about performance degradation in the model. These assumptions may include factors such as path independence, low temperature operation, and the effects of cold cranking. These factors would be tested to verify that they do not have an impact on battery life. If the assumptions are proven invalid, then the model has to be re-developed, and the core matrix simulation and testing has to be repeated.

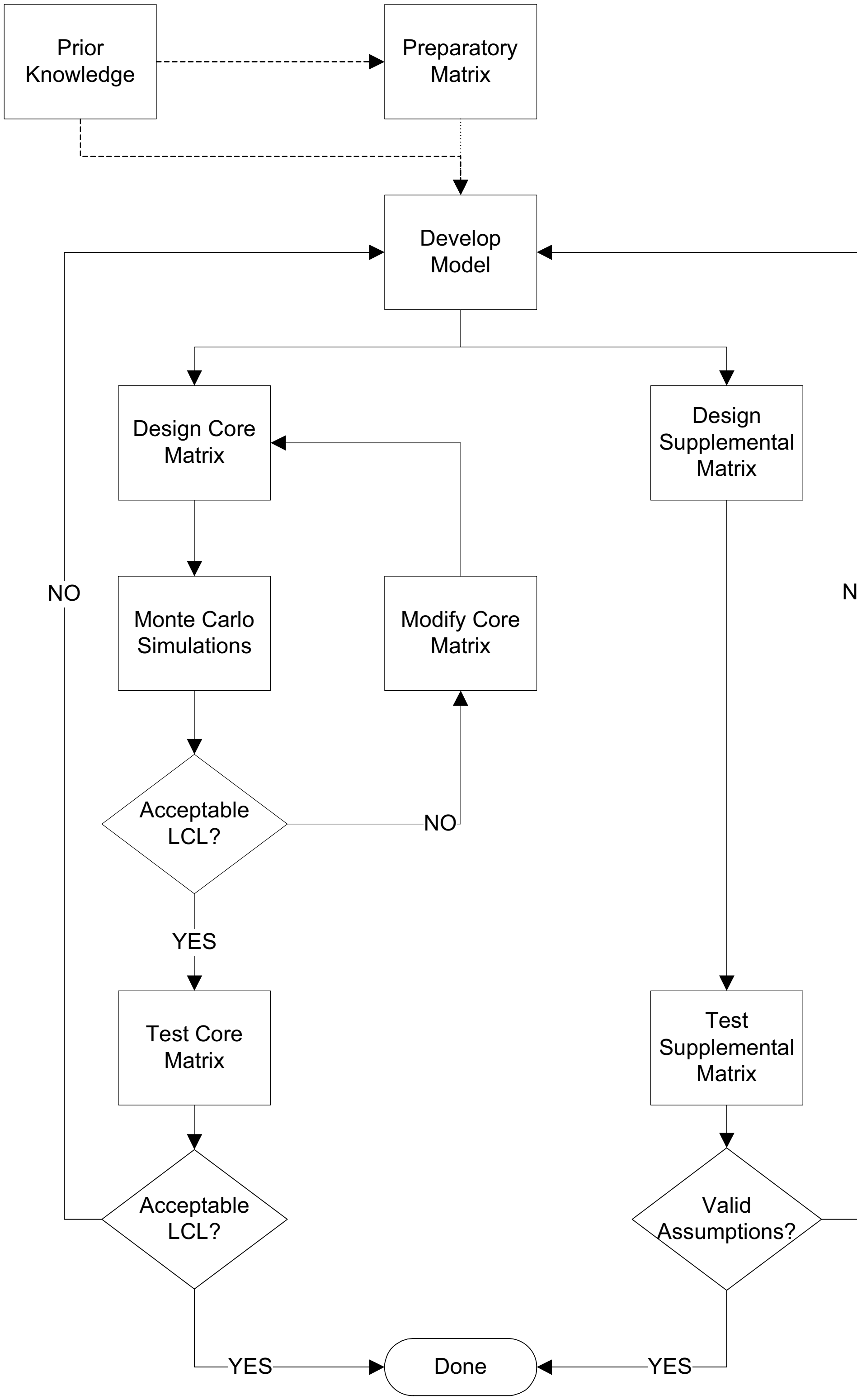

Figure 1: TLVT flow diagram

3. Lessons Learned

3.1 Minimum Pulse Power Characterization

The standard method of measuring performance degradation under the FreedomCAR Program is with a hybrid pulse power characterization (HPPC) test [2]. The profile is shown in Figure 2 and consists of a 10-s discharge pulse (typically at a $5C_1$ rate), and 40-s rest period, then a 10-s charge (more appropriately regenerative braking or "regen") pulse (typically at a $3.75C_1$ rate). There is a one-hour rest at open-circuit immediately prior to the discharge pulse to allow the battery to reach electrochemical and thermal equilibrium. This profile is repeated at each 10% depth-of-discharge increment (as determined from the beginning of life rated capacity), starting from a fully charged state, and ending at a fully discharged state. In other words, a fresh battery would be subjected to a total of nine HPPC pulses, ranging from 10 to 90% depth of discharge. From these data, the resistance, power, and energy can be calculated using the procedures defined in the FreedomCAR Manual [2]. For example, discharge resistance is determined using Equation (1), where V_{t0} is the open-circuit voltage immediately prior to the discharge pulse.

$$R_{dis} = \frac{V_{t_0} - V_{t_1}}{I_{t_1} - I_{t_0}} \tag{1}$$

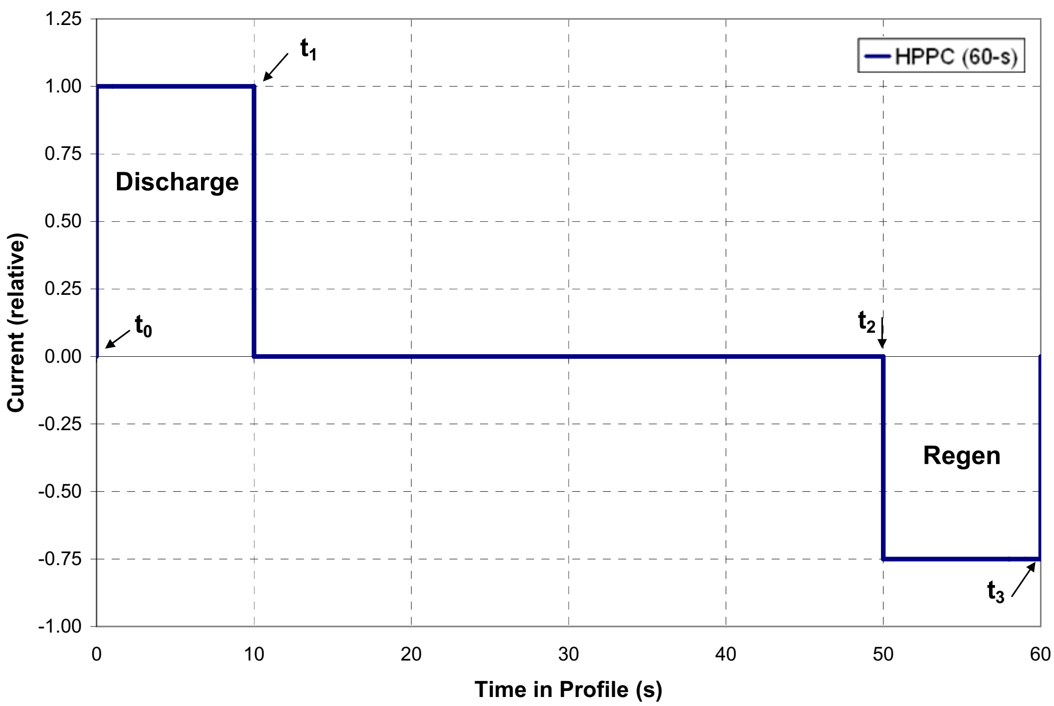

Figure 2: Hybrid pulse power characterization profile

The TLVT Manual replaced the standard HPPC test with a newly-developed minimum pulse power characterization test (MPPC) [1]. The MPPC profile is shown in Figure 3, and consists of an HPPC pulse profile at only two state of charge (SOC) conditions, known as SOC_{MAX} and SOC_{MIN}, which are meant to cover the expected operating range of the battery while in use. (All life testing is, therefore, also usually performed at or between these SOC conditions as well.) An

HPPC pulse profile is performed first at SOC_{MAX}, followed immediately by a taper discharge to the SOC_{MIN} target condition and a one hour rest at open circuit, then another HPPC pulse profile at SOC_{MIN}.

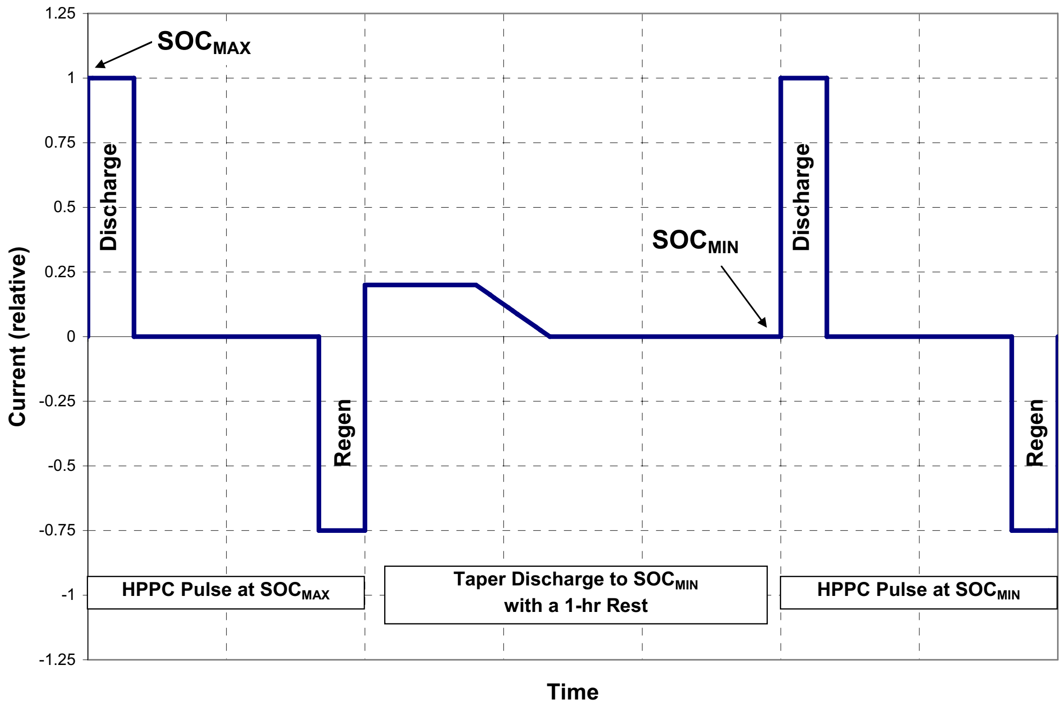

Figure 3: Minimum pulse power characterization profile

Since time spent at full charge has a negative impact on lithium-ion battery performance [3], the MPPC was designed to operate only within the specified SOC window and never let the battery reach a fully charged state. Consequently, the batteries are charged to the specified SOC_{MAX} target from a lower SOC condition. However, a study with the MPPC test revealed that fast rate charges to a specified target condition do not yield the same resistance values as when discharged to the same SOC for lithium-ion cells [4]. Figure 4 shows the difference in resistance values between an MPPC and HPPC test for a fresh and aged lithium-ion cell developed for the Advanced Technology Development Program. The cell chemistry for these cells was a $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ positive electrode, a MAG-10 graphite negative electrode, with an electrolyte consisting of 1.2 M $LiPF_6$ in EC:EMC [5]. As shown in Figure 4, the resistance values at SOC_{MIN} (approximately 3.65 V) are similar regardless of the test profile since the battery was always discharged to this SOC. However, at SOC_{MAX} (approximately 4.0 V), there is a noticeable difference in resistance values. The HPPC pulse was preceded by a discharge to SOC_{MAX} whereas the MPPC pulse was preceded by a charge. Table 1 shows the discharge resistances from the MPPC and HPPC profiles at SOC_{MAX}; the percent difference between them are 11.5 and 5.5% for the fresh and aged cell, respectively. These data not only indicate that there is a path-dependence effect, but also that the measured rate of resistance growth is apparently affected by the path as well. The aged cells seem to show less path dependence than the fresh cells. Additionally, the resistance behavior observed from the MPPC profile appears to be more erratic than the corresponding HPPC profile. These observations were also seen in other lithium-ion chemistries as well [4]. Obviously, changes in impedance growth have a strong impact on life prediction, and, thus, must be measured consistently to ensure accuracy and high confidence. These data suggest that the MPPC profile is inadequate for that purpose and should be replaced.

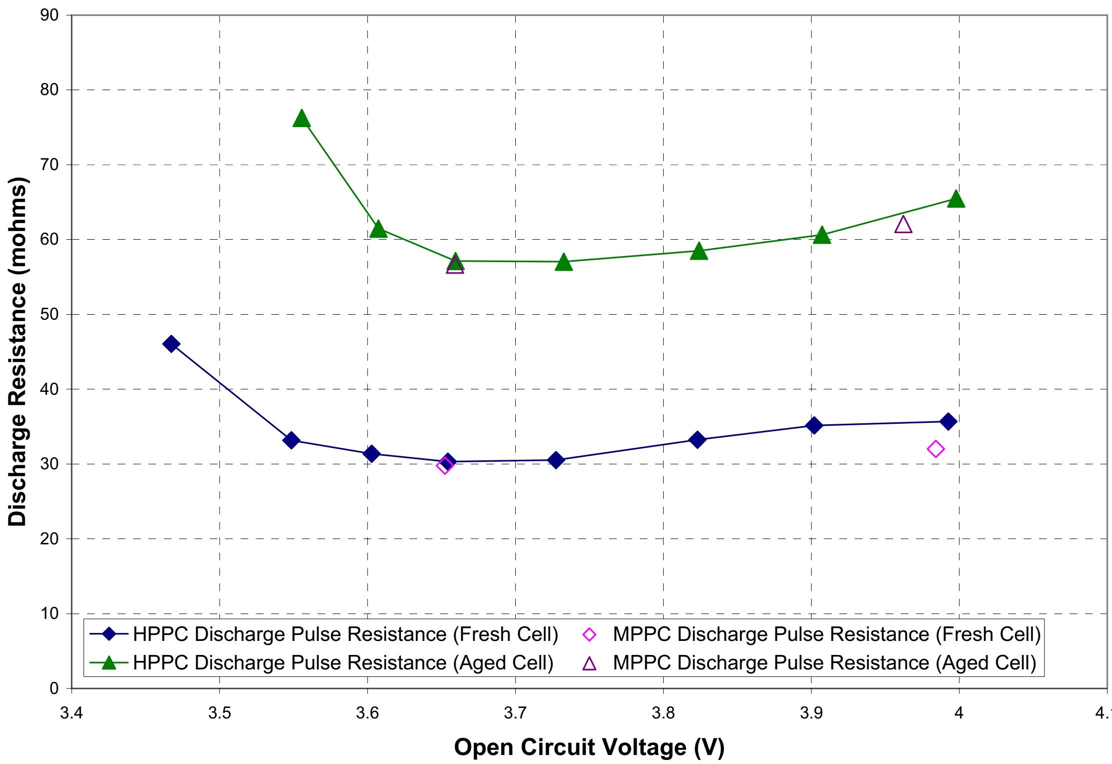

Figure 4: Discharge resistances for a fresh and aged cell (HPPC and MPPC)

Table 1. Discharge resistance values at SOC_{MAX} from the MPPC and HPPC tests

	MPPC (mohms)	HPPC (mohms)	%-Difference
Fresh Cell	32.01	35.68	11.5%
Aged Cell	62.08	65.47	5.5%

3.2 Measurement Uncertainty

Accurate life prediction requires the incorporation of both cell-to-cell manufacturing variability and test measurement error. The original TLVT Manual estimated measurement error from the test data, but this was found to be inadequate. A more direct approach was implemented based on the uncertainty studies performed at the Idaho National Laboratory [6,7]. Prior to battery aging, the test equipment is calibrated based on the manufacturer recommendations. After calibration, accuracy measurements are taken from the test channel at various different voltage and current levels within the full scale range using an independent digital voltmeter and calibrated shunt (to measure current). These data are then used in conjunction with the calibration errors from the digital voltmeter and shunt to determine the total equipment and channel error. These error values are used to determine if the test channel is yielding data within the claimed repeatability range (e.g., 0.02% of full scale).

These calibration data are also useful for determining the uncertainty range of derived parameters such as resistance, power, and energy. Since the only actual measurements taken during a test are voltage and current (temperature is treated elsewhere), the uncertainty of any derived parameter is calculated using a propagation approach based on a sequence of Taylor Series partial derivatives that layer down to the independent measured parameters (i.e., voltage and current). The resulting uncertainty expression incorporates the standard deviations determined from the accuracy check, the calibration errors, and the full-scale test channel levels. For example, Equation (2) shows the uncertainty expression for pulse resistance, where V_{FS} and I_{FS} are the test channel's full scale voltage and current, respectively; $\%errV_{CAL}$ and $\%errI_{CAL}$ are the calibration errors due to the digital voltmeter and shunt from the independent measurements; and $\%errV_{STD}$ and $\%errI_{STD}$ are the standard deviations determined experimentally from the accuracy measurements.

$$\%R_S = \left[2\left(\frac{\%errV_{STD}}{V(t_a)-V(t_b)} V_{FS} \right)^2 + 2\left(\frac{\%errI_{STD}}{I(t_a)-I(t_b)} I_{FS} \right)^2 + (\%errV_{CAL})^2 + (\%errI_{CAL})^2 \right]^{1/2} \quad (2)$$

Figure 5 shows the discharge resistance vs. open-circuit voltage curve from an HPPC test on a fresh and aged cell (the same data as in Figure 4) with the associated upper and lower uncertainties (i.e., dashed lines) as determined from Equation (2). The error bars are hard to see because the measurement uncertainty is very low. Table 2 shows the uncertainty of the discharge pulse at each 10% depth-of-discharge increment. The fresh cell shows an average error of approximately 0.36%, and the aged cell has an average error of only 0.13%. The aged cell uncertainty is smaller because the voltage difference (i.e., "$V(t_a) – V(t_b)$" in the denominator of Equation (2)) is larger. Since the measurement uncertainty is so low, the data can be used for accurate life prediction.

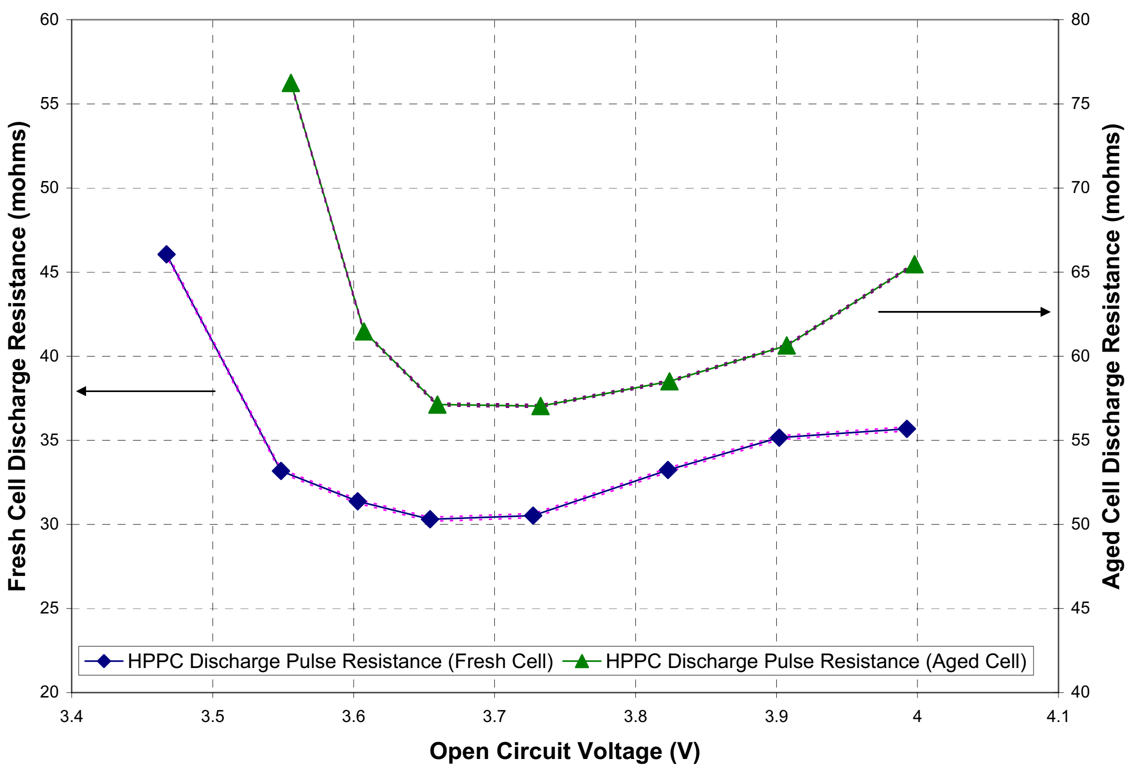

Figure 5: Discharge resistances for a fresh and aged cell (HPPC and MPPC)

Table 2. Measurement uncertainty for a fresh and aged cell

Fresh Cell Open-Circuit Voltage (V)	Fresh Cell Discharge Resistance (mΩ)	%-err	Aged Cell Open-Circuit Voltage (V)	Aged Cell Discharge Resistance (mΩ)	%-err
3.99	35.68	0.34%	4.00	65.47	0.12%
3.90	35.16	0.35%	3.91	60.64	0.13%
3.82	33.23	0.37%	3.82	58.51	0.13%
3.73	30.52	0.40%	3.73	57.04	0.14%
3.65	30.30	0.40%	3.66	57.13	0.14%
3.60	31.37	0.39%	3.61	61.47	0.13%
3.55	33.17	0.37%	3.56	76.25	0.11%
3.47	46.06	0.27%			
	Average:	**0.36%**		**Average:**	**0.13%**
	Standard Deviation:	**0.04%**		**Standard Deviation:**	**0.01%**

3.3 Rank Ordering of Cells

Another important aspect to accurate life modeling is the appropriate allocation of cells into a test matrix based on manufacturing variability. Ideally, manufacturing variability will be sufficiently low such that the cells can be distributed into a matrix at random, but this is not yet practical or economically feasible. Consequently, a methodology was developed to "randomly" assign cells to the matrix such that the average of each test group is representative of the overall population with respect to resistance and capacity. The deviation in resistance and capacity from the average for each cell is determined using Equations (3) and (4), respectively, where "Q" is cell capacity, and "R" is cell resistance. The cells are then randomly assigned to each group within the matrix such that the overall group average deviation within a test condition is less than or equal to some predetermined limit using the process shown in Figure 6. Once a deviation limit is chosen (i.e., 0.5), a random sample of cells is chosen to match a particular matrix condition such that there are no duplicates (i.e., the same cell number is chosen twice) or repeats (i.e., a cell that has already been placed in another matrix condition). The average deviation in resistance and capacity are then determined (i.e., the average of "R_{dev}" and "Q_{dev}" for each cell in the matrix condition). If the averages are below the deviation limit, then the cells are kept in the matrix condition. Otherwise, they are placed back into the pool of available cells again, and the process repeats until all the matrix conditions have been filled. Figure 7 shows an example rank ordering of cells based on a simple random assignment (squares) and a random assignment within a deviation limit of 0.5 (diamonds). As shown, the group averages for the rank ordering of cells are much tighter with a deviation limit.

$$R_{dev} = \frac{R_{cell} - R_{avg}}{R_{std}} \tag{3}$$

$$Q_{dev} = \frac{Q_{cell} - Q_{avg}}{Q_{std}} \tag{4}$$

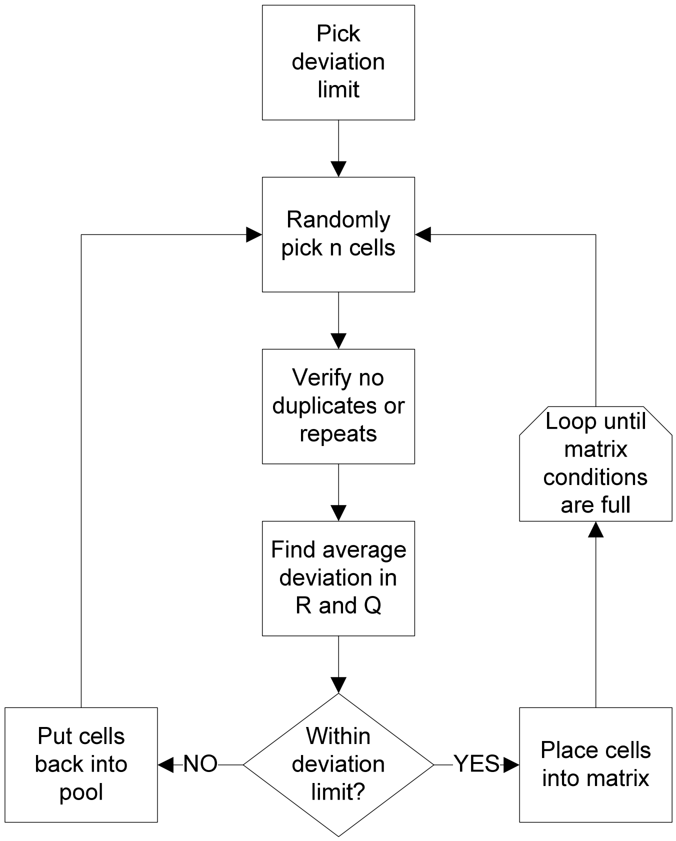

Figure 6: Rank ordering of cells flow diagram

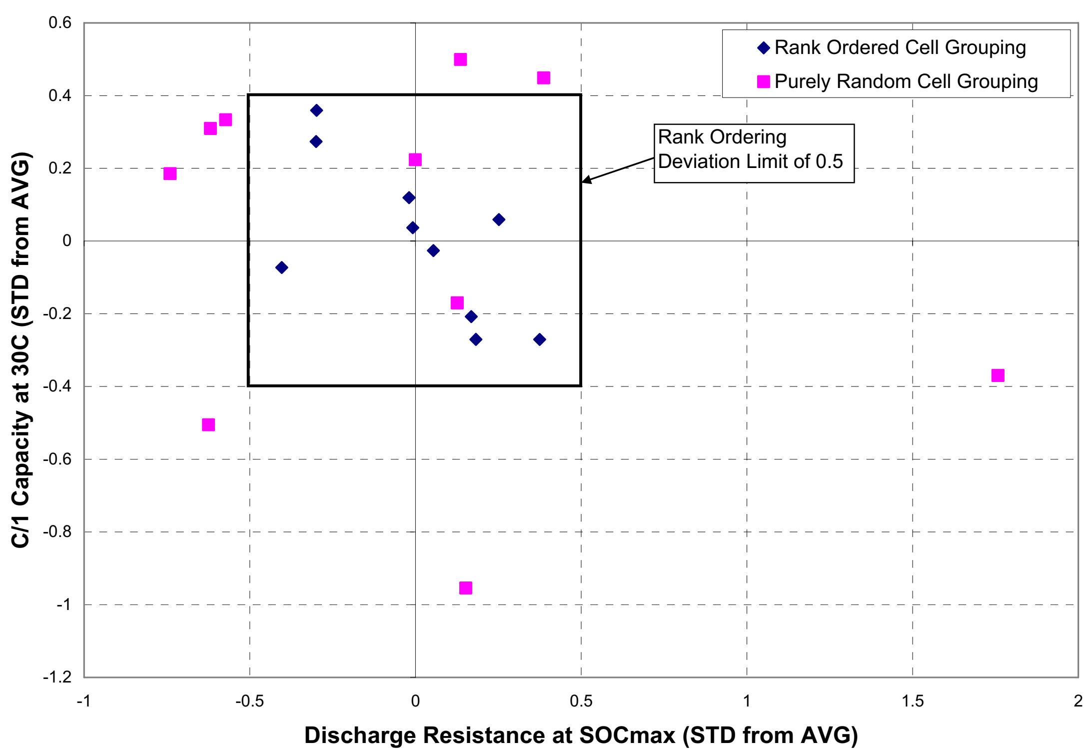

Figure 7: Sample rank ordering of cells with a deviation limit of 0.5

4. Future Work

The TLVT Manual validation effort is continuing, and there are other aspects of the methodology that need to be investigated. Of particular importance is a generalized empirical degradation model that can be applied to a set of data in the absence of a manufacturer's mechanistic model. The generalized model has the form shown in Equation (5), where "μ" is the average response in the battery population (e.g., resistance), "X_i" is the level of the i^{th} stress factor (e.g., temperature, SOC, etc.), and the "β_i" and "ρ" terms are model parameters. The error model is shown in Equation (6), where $Var(Y(X_1,X_2,\ldots,X_q;t))$ is the variance of the response ("Y") at time "t" for batteries stressed by the experimental condition specified by $\{X_1, X_2,\ldots,X_q\}$. The variance of a random cell-to-cell proportional effect (induced by manufacturing variability) is given by σ_δ^2, and σ_ε^2 is the measurement error variance (which can now be determined independently, as discussed above). This model is still under development, and will be part of a software tool package that will accompany the next version of the TLVT manual.

$$\mu(X_1, X_2, \ldots, X_q; t) = 1 + \exp\{\beta_0 + \beta_1 \cdot X_1 + \beta_2 \cdot X_2 + \ldots + \beta_q \cdot X_q\} \cdot t^\rho \qquad (5)$$

$$Var(Y(X_1, X_2, \ldots, X_q; t)) = \sigma_\delta^2 \cdot (\mu(X_1, X_2, \ldots, X_q; t) - 1)^2 + 2 \cdot \sigma_\varepsilon^2 \qquad (6)$$

Also of interest is the path dependence effect due to aging. Path dependence is applicable to a mix of calendar (i.e., shelf-life) and cycle life aging, thermal cycling, or SOC swings. These effects must be determined experimentally, and the life model should account for them as well. Lastly, the validation effort to date has centered on only one lithium-ion chemistry. Other chemistries will also be addressed to further validate the methodology and the general form of the life model.

5. Summary and Conclusions

The TLVT methodology is a useful tool for predicting battery life with a high degree of statistical confidence. The test matrices (core and supplemental) are statistically designed with a suggested allocation of cells based on the stress factors and levels, number of batteries available for test, and number of test conditions. Using an empirical or physics-based model, battery life is estimated using Monte Carlo simulations of the various test conditions in the core matrix. Once the simulation is satisfactory, batteries are placed on test to verify accuracy of the life model and the assumed levels of random variability from manufacturing and testing. Also, the statistical methods such as the bootstrap are used to assess the uncertainty in the life-on-test estimates derived from the experimental data.

A validation effort for this manual has yielded a number of lessons learned and methodology improvements. Testing with the newly developed minimum pulse power characterization test showed a path dependence effect on voltage when a target condition was approached by a charge or a discharge. The resistance growth behavior is therefore also impacted by the path dependence as well. Consequently, the MPPC test is considered inadequate for TLVT applications and needs to be replaced. Another critical component of accurate life prediction is a low measurement error during aging. The Taylor Series derivation of parameters such as resistance based on calibrations and independent checks appears to give the most accurate uncertainty range, and thus provides the most accurate life estimation. Finally, the appropriate allocation of cells into a core or supplemental matrix is highly dependent on manufacturing variability. If the manufacturing variability is too high, a new approach to randomly assign cells to a test matrix is developed such that the group average is representative of the entire set of batteries in the matrix based on deviations from the average in both capacity and resistance.

Additional work is underway on the development of a general life model that accounts for the identified stress factors and is capable of separating the effects of measurement error (determined independently) and manufacturing variability from the test data. Path dependence studies that include aging (calendar or cycle life), temperature, or state of charge are also being considered. Lastly, a TLVT life prediction using various lithium-ion chemistries is also vital for validating the general model.

6. References

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7. Acknowledgements

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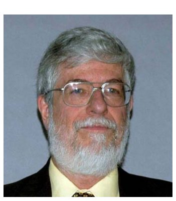

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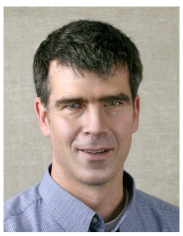

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