



Investigation of path dependence in commercial lithium-ion cells chosen for plug-in hybrid vehicle duty cycle protocols

Kevin L. Gering^{a,*}, Sergiy V. Sazhin^a, David K. Jamison^a, Christopher J. Michelbacher^a, Bor Yann Liaw^b, Matthieu Dubarry^b, Mikael Cugnet^b

^a Energy Storage & Transportation Systems, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2209, USA

^b Hawaii Natural Energy Institute, University of Hawaii at Manoa, 1680 East-West Road, POST 109, Honolulu, HI 96822, USA

ARTICLE INFO

Article history:

Received 31 March 2010

Received in revised form 26 May 2010

Accepted 28 May 2010

Available online 8 June 2010

Keywords:

Lithium-ion battery

Path dependence

Aging mechanisms

PHEV

Thermal cycling

ABSTRACT

There is a growing need to explore path dependence of aging processes in batteries developed for long-term usage, such as lithium-ion cells used in hybrid electric vehicle (HEV) or plug-in hybrid vehicle (PHEV) applications that may then be “retired” to be utilized in grid applications. To better understand the foremost influences on path dependence in the PHEV context, this work aims to bridge the gap between ideal laboratory test conditions and PHEV field conditions by isolating the predominant aging factors in PHEV service, which would include, for example, the nature and frequency of duty cycles, as well as the frequency and severity of thermal cycles. These factors are studied in controlled and repeatable laboratory conditions to facilitate mechanistic evaluation of aging processes. This work is a collaboration between Idaho National Laboratory (INL) and the Hawaii Natural Energy Institute (HNEI). Commercial lithium-ion cells of the Sanyo Y type (18650 configuration) are used in this work covering two initial independent studies of path dependence issues. The first study considers how the magnitude of power pulses and charging rates affect the aging rate, while the second seeks to answer whether thermal cycling has an accelerating effect on cell aging. While this work is in early stages of testing, initial data trends show that cell aging is indeed accelerated under conditions of high discharge pulse power, higher charge rates, and thermal cycling. Such information is useful in developing accurate predictive models for estimating end-of-life conditions.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Path dependence is emerging as a premier issue of how electrochemical cells age in conditions that are diverse and variable in the time domain. For example, a laptop battery might be used sporadically, or lithium-ion cells in a vehicle configuration will experience a variable combination of usage and rest periods over a range of temperature and state of charge (SOC). This is complicated by the fact that some aging can actually become worse (or better) when a lithium-ion cell is idle for extended periods under calendar-life (calL) aging, as opposed to cycle-life (cycL) conditions where the cell is used within a predictable schedule. The purpose of this study is to bridge the gap between highly idealized and controlled laboratory test conditions and actual field conditions regarding PHEV applications, so that field-type aging mechanisms can be mimicked and quantified in a repeatable laboratory setting. The main parameters here involve the magnitude of power pulses, frequency of duty cycles, as well as the frequency and

severity of thermal cycles, looking at isothermal, mild, and severe scenarios.

Although there is little published literature that covers comprehensive aging and path dependence work, there are articles that address key issues, either singly or in some combination [1–10] (as a short list). This work advances this body of literature by having a comprehensive and consistent basis for testing and analysis, given the context of a PHEV application.

To date, little is known about lithium-ion aging effects caused by thermal cycling superimposed onto electrochemical cycling, and related path dependence. This scenario is representative of what lithium-ion batteries will experience in vehicle service, where upon the typical start of a HEV/PHEV, the batteries will be cool or cold, will gradually warm up to normal temperature and operate there for a time, then will cool down after the vehicle is turned off. Such thermal cycling will occur thousands of times during the projected life of a HEV/PHEV battery pack. We propose to quantify the effects of thermal cycling on lithium-ion batteries using a representative chemistry that is commercially available (Sanyo Y).

Electrochemical cycling is based on PHEV-relevant cycle-life protocols that are a combination of charge-depleting (CD) and charge-sustaining (CS) modes discussed in the Battery Test Manual

* Corresponding author. Tel.: +1 208 526 4173; fax: +1 208 526 0690.

E-mail address: kevin.gering@inl.gov (K.L. Gering).

Table 1
Sanyo Y cell ratings and specifications (as received).

V_{\max} = 4.2 V (100% SOC)
V_{\min} = 2.7 V (0% SOC)
90% SOC = 4.07 V
70% SOC = 3.94 V
35% SOC = 3.65 V
Electrode area: 800 cm ² (estimated)
$C_1/2$ discharge capacity: 1.9 Ah
$C_1/1$ discharge capacity: 1.86 Ah
Maximum recommended continuous discharge current: 5.7 A
Maximum operating temperature during discharge: 60 °C

for Plug-in Hybrid Electric Vehicles [11]. A realistic duty cycle will involve both CD and CS modes, the proportion of each defined by the severity of the power demands. There are innumerable ways to define and configure such PHEV-type cycling profiles. However, we can at least provide some boundaries to narrow our field of operating conditions. We assume that the cells will start each cycling day at 90% SOC, and that they will not be allowed to go below 35% SOC, with operation around 70% SOC being a nominal condition. The 35, 70, and 90% SOC conditions are also being used to define critical aspects of the related reference performance test (RPT) for this investigation. There are three primary components to the RPT, all assessed at room temperature: (A) static and residual capacity (SRC) over a matrix of current, (B) kinetics and pulse performance testing (PPT) over current for SOC of interest, and (C) EIS for SOC of interest. The RPT is performed on all cells every 28-day test interval, as well as a pulse-per-day to provide a quick diagnostic snapshot. Where feasible, we utilize various elements of Diagnostic Testing to characterize performance of the cells and to gain mechanistic-level knowledge regarding both performance features and limitations.

Herein we present the rationale behind the experimental design, early data, and discuss the fundamental modeling tools used to elucidate performance degradation mechanisms. While we recognize that the datasets are underdeveloped due to recent commencement of these tests, we are able to see early-life trends of key performance metrics, which have bearing on upfront issues such as ohmic resistance and the extent of completion of cell formation. The benefit of this work, upon completion, will be the testing approach used to explore aging path dependence, and to provide more realistic and accurate life predictions by accounting for the influence of thermal cycling effects and related path dependence on aging mechanisms.

2. Materials and methods

2.1. Test cells

The secondary lithium-ion cells used in this study are Sanyo Y cells of the 18650 configuration that have a nominal capacity rating of 1.9 Ah, and consist of a $\{\text{LiMn}_2\text{O}_4 + \text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2\}$ cathode of proprietary mixture and a graphite anode. A summary of salient properties is given in Table 1, and a photograph of a portion of these cells in their test fixtures is given in Fig. 1. The capacity and current specifications in Table 1 are provided by the manufacturer, and are presumably at room temperature, 25–30 °C. These cells are high quality, showing good stability and low cell-to-cell variability in early testing. Thorough characterization was achieved for these cells at beginning-of-life (BOL) through diagnostic testing that covered several issues of cell performance over regimes of temperature, current, cycling mode (charge vs. discharge), and SOC. There are 42 cells under test for the two path dependence studies discussed herein, which are part of a larger group of over 100 cells collectively being studied between INL and HNEI.



Fig. 1. Photograph of selected 18650 Sanyo Y cells on test at the INL, as placed within an environmental chamber.

2.2. Test equipment

Cell testing is facilitated through Maccor series 4000 testers with multi-range test channels. The multi-range capability enables good data resolution for a wide range of current. Cells are housed in temperature-controlled environmental chambers for the entire duration of their cycling and characterization. There is an added challenge to provide chambers that operate independently from each other and that undergo the prescribed thermal cycling (temperature ramping) in concert with their duty cycling, as described below. EIS measurements are performed over a frequency range of 100 kHz to 10 mHz with Solartron equipment, potentiostat 1287 A and frequency response analyzer 1260.

2.3. Test methods

This work covers two studies concerned with path dependence (PD) of cell aging. The first study (initiated September 2009) entails constant-power pulses of various magnitudes, using a time-average cumulative discharge energy that is equal for all scenarios. This study seeks to answer the fundamental question: *Is there an aging path dependence due to severity and randomness of power pulses?*

The second study (initiated December 2009) considers a combination of cell cycling (PHEV protocol, CD + CS) and thermal cycling. This study is aimed at answering the question: *Is there an aging path dependence due to cells operating under ambient temperature ramping?* Such thermal cycling will occur thousands of times during the projected life of a HEV/PHEV battery pack.

2.3.1. Path dependence Study 1

The purpose of this study is to investigate the influence of aging effects tied to relative magnitude and randomness of constant-power pulses, as well as look at aspects of charge depletion and substituting constant-current charge pulses in one scenario. The information gained from this work will allow an assessment of path dependence of cell performance degradation, as related to the main parameters. The breadth of this study is encompassed by Scenarios 1–5 given in Fig. 2, which are self-explanatory. The scenarios range from uniform, regularly spaced constant-power pulses to pseudo-random pulses of different magnitudes. A total of fifteen (15) cells are used for this task, allowing three cells per scenario. All testing is performed at 30 °C.

As is seen in Scenarios 1–5, cells are operating at or below the maximum power, P_{\max} , which in this case is constrained by the maximum amperage of the available test channels (5 A). For Sanyo

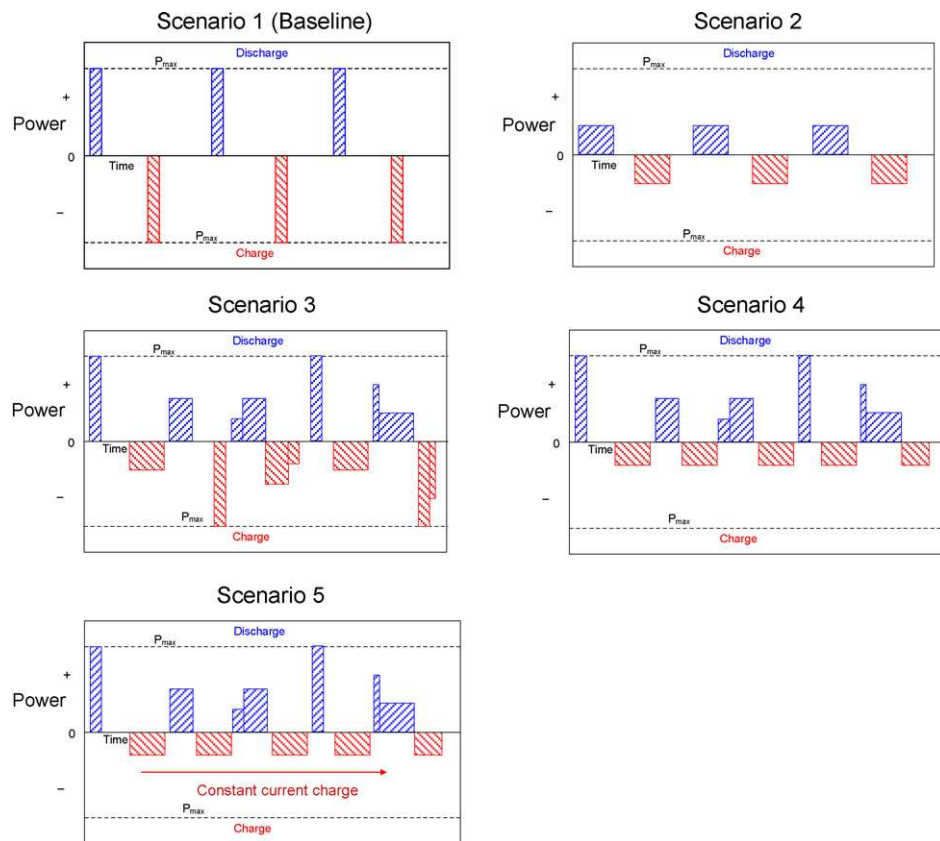


Fig. 2. Cycling profiles for the five scenarios comprising PD Study 1. The time-average cumulative discharge energy is equal for all scenarios.

Y cells operating between 70 and 90% SOC, 4 W cell^{-1} is a reasonable power at 5 A, which allows for a margin due to aging. Although this is a somewhat mild power level, it will allow for a finer determination of aging trends over time and so is more likely to give critical mechanistic information about performance degradation rates.

Using P_{\max} as the basis, the various profiles for Scenarios 1–5 were derived, where an important criterion is that the average cumulative discharge energy must be equal for all scenarios to ensure that basis is consistent throughout the study. Rest times were chosen to reflect the consistent basis of energy-per-time for discharge pulses. For example, if the pulses shown in Scenario 1 are 2-s each, then 8-s rest steps will give an overall profile duration of 60 s as shown. Using this discharge energy per minute basis, the other profiles were designed, knowing that their net repeatable profile would likely vary from the 1 min duration of the baseline Scenario 1.

An important aspect about PD Study 1 is that the charging method is also variable, ranging from constant-power, pseudo-random, to constant-current. Lithium-ion cells can be particularly sensitive to charging protocol, and aging mechanisms can become more pronounced under unfavorable charging conditions. The information gained herein can help guide the design of charging procedures implemented in HEV and PHEV applications.

2.3.2. Path dependence Study 2

To date, little is known about lithium-ion aging effects caused by thermal cycling superimposed onto electrochemical cycling, and related path dependence. This scenario is representative of what lithium-ion batteries will experience in vehicle service, where upon the typical start of a HEV/PHEV, the batteries will be cool or cold, will gradually warm up to normal temperature and operate there for a time, then will cool down after the vehicle is turned off. Such thermal cycling will occur thousands of times

during the projected life of a HEV/PHEV battery pack. In practice, some thermal management will be had in keeping batteries from becoming too hot. However, there appears to be little focus on keeping batteries from residing at colder temperatures at the beginning of their duty cycle. Our work will quantify the effects of thermal cycling on lithium-ion batteries using a representative chemistry that is commercially available. Electrochemical cycling is based on PHEV-relevant cycle-life protocols, and the resultant data will be extremely valuable toward developing models that correlate cell aging with thermal cycling conditions. The immediate benefit will be to provide more realistic and accurate life predictions by accounting for the influence of thermal cycling effects and related path dependence on aging mechanisms. Since an effective thermal cycle will be somewhat dependent on global location, testing parameters can be chosen to target a specific region of interest (e.g., New York City, Los Angeles, Vancouver, London, and Berlin). Table 2 gives the matrix of conditions investigated at the INL, where the shown times are adjustable to suit a particular duty cycle. In this table, temperature range refers to ambient temperature surrounding the cells while in their environmental chamber. T_{\max} is consistent throughout to avoid biasing the matrix with conditions of higher T that would cause undue accelerated aging. A total of twenty-seven (27) cells are employed in PD Study 2.

There are nine conditions representing PHEV cycle-life testing, and one calendar-life condition.

The main parameters are (1) the magnitude and frequency of the thermal cycling, looking at *isothermal*, *mild*, and *severe* scenarios, and (2) frequency of duty cycle. Fig. 3 summarizes the thermal profiles per each complete thermal cycle. This study is valuable in transitioning between idealized lab data and actual PHEV field data. Added value is gotten through INL/HNEI synergy. HNEI brings expertise in Diagnostic Analysis of data, and has

Table 2
Thermal cycling matrix for PD Study 2.

Test condition	Test type	Number of cells	T range	Time from T_{\min} to T_{\max}	Time at T_{\max}	Time from T_{\max} to T_{\min}	Thermal cyc. frequency
1	Isothermal	2	0 °C	NA	NA	NA	NA
2	Isothermal	2	20	NA	NA	NA	NA
3	Isothermal	2	40	NA	NA	NA	NA
4	Mild thermal cycling	3	10 to 40	30 min ^a	1 h	2 h ^b	Twice daily
5	Mild thermal cycling	3	10 to 40	30 min ^a	1 h	2 h ^b	Continuous
6	Mild thermal cycling	3	10 to 40	15 min ^a	1 h	1 h ^b	Continuous
7	Severe thermal cycling	3	–20 to 40	30 min ^a	1 h	2 h ^b	Twice daily
8	Severe thermal cycling	3	–20 to 40	30 min ^a	1 h	2 h ^b	Continuous
9	Severe thermal cycling	3	–20 to 40	15 min ^a	1 h	1 h ^b	Continuous
10	Severe thermal cycling; OCV ^c	3	–20 to 40	30 min ^a	1 h	2 h ^b	Continuous
Total cells	27						

“Continuous” thermal cycling frequency refers to the scenario whereby a PHEV undergoes repeated commutes throughout a day that each have a thermal cycling period (per above), covering up to 16 h day^{–1} and within a maximum permissible number of 1-h commutes.

^aLinear temperature ramping is assumed.

^bLinear temperature ramping is assumed; conditions are under no electrochemical cycling (vehicle off).

^cA baseline condition where cells at OCV undergo thermal cycles but no duty cycles (calendar-life).

demonstrated such on Sanyo Y cells (incremental capacity analysis and residual capacity).

2.3.2.1. Duty cycle for path dependence Study 2. The concept of a duty cycle for PHEV-relevant cycle-life testing is based on the charge-depleting (CD) and charge-sustaining (CS) modes discussed in the Battery Test Manual for Plug-in Hybrid Electric Vehicles [11]. A realistic duty cycle will involve both CD and CS modes, the proportion of each defined by the severity of the power demands. We utilize the Maximum PHEV profile as defined in this manual. We do not include a cold-crank (CC) profile at the beginning of each testing day, since it is unclear if CC pulses will add an aging artifact and hence complicate analysis of the cycle-life aging mechanisms.

An overall *standard cycle-life profile* is defined here as consisting of one CD profile (360 s each) for every 10 CS profiles (90 s each), giving an overall profile duration of 1260 s, or 21 min, while three consecutive standard profiles will require slightly more than 1 h to complete. It is assumed that the CD profile will begin each testing day, followed by 10 CS profiles. Herein we define a *duty cycle* as three standard cycle-life profiles in sequence, that is, the net profile that represents a 1-h one-way commute. Fig. 4 indicates the CD and CS profiles used for this work (scaled per the size of the cells), while Fig. 5 shows the basic definition of the cycle-life profiles and the duty cycle.

There are innumerable ways to define and configure PHEV-type cycling profiles. However, we can at least provide some boundaries

to narrow our field of operating conditions. We chose that the Sanyo Y cells will start each cycling day at 90% SOC (4.07 V), and that they will not be allowed to go below 35% SOC (3.65 V), with operation around 70% SOC (3.94 V) being a nominal condition. The 35, 70, and 90% SOC conditions are also being used to define critical aspects of the related RPT for this study.

Current is scaled at SOC according to the particular power goals stipulated under the Maximum PHEV protocol (per figures for CD and CS specifications), using an assumed battery size factor (BSF) of 2000. In order to use similar profiles for Sanyo Y cells operating at a *low temperature target*, it is sometimes necessary to slightly increase the BSF. These test conditions are achievable utilizing a 24-channel 25 A channel^{–1} tester for test conditions 1–9 and three channels at 5 A channel^{–1} for test condition 10 (Table 2). Note that of the 27 cells tested under this PD Study 2, 24 are cycle-life tested utilizing an identical electrochemical duty cycle, while three are kept at OCV or calendar-life conditions. Currently, the PHEV manual [11] does not assume manufacturer's protocol (MP) is used for cell charging (if the MP or low-magnitude charge currents are applied to CD/CS, the primary aging mechanisms will be related to discharge conditions).

The effect of temperature is another consideration since the cells will be tested under a variety of temperature conditions per Table 2. We suspect and probably should plan that the cells will not be able to meet power goals at the lowest temperature(s), especially as they become well aged. Since this is a realistic scenario for PHEV cells, it is acceptable that cells fail the power goals under such conditions. In fact, we want a mixture of failure/success conditions to promote the related aging mechanisms. An important issue then is what temperature range do we want the cells to meet the goals, and will they still meet the goals as they age. As a start, we have chosen a reasonable criterion to have the cells just barely meet power goals at 0–10 °C.

2.3.3. Reference performance test (RPT) and pulse-per-day (PPD)

The overarching goal of a given RPT is to query the cells to reveal pertinent performance data without adding undue aging or requiring excessive RPT completion time. The RPT designed for this work reflects the pursuit of more mechanistic-level information regarding cell performance and aging. There are three components to the RPT, all assessed at room temperature:

- static and residual capacity (SRC) over a matrix of current,
- kinetics and pulse performance testing (PPT) over current for SOC of interest,
- EIS for SOC of interest (90, 70, and 35%).

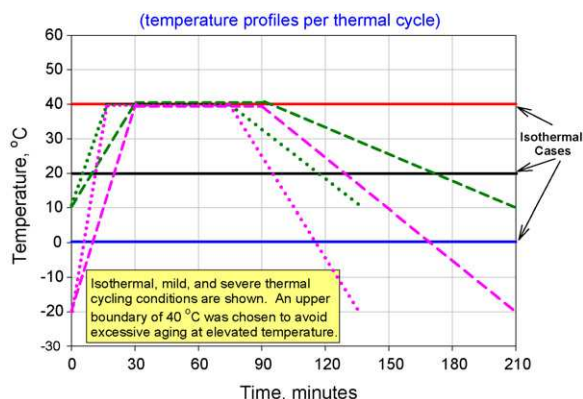


Fig. 3. Summary of temperature profiles for the various thermal cycling conditions under PD Study 2. The thermal cycles are synchronized with applicable duty cycles, requiring some thermal cycles to be repeated continuously, while others are performed twice daily as per a round trip scenario (see Table 2).

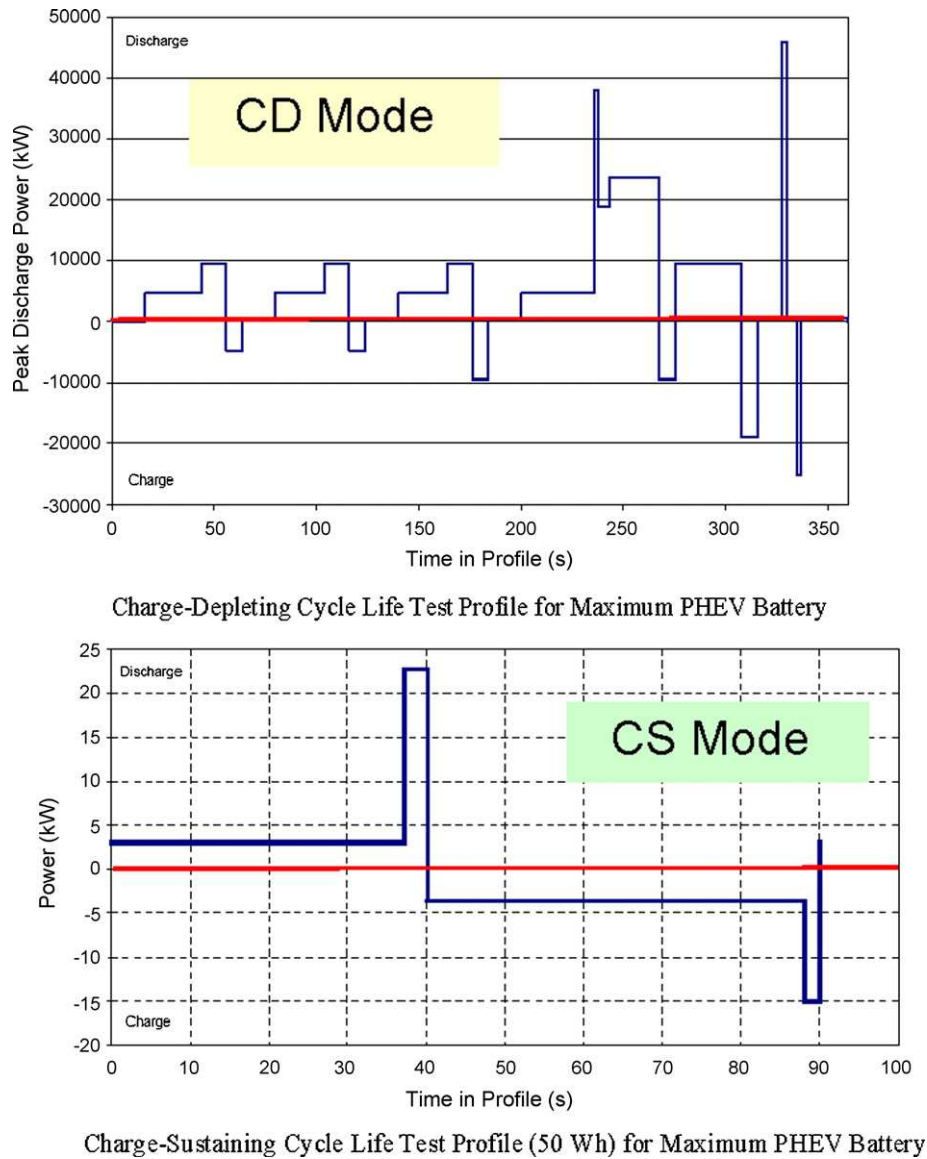


Fig. 4. Charge-depleting (CD) and charge-sustaining (CS) cycle-life profiles as defined for the Maximum PHEV Battery [11]. Power levels were scaled to reflect the size and power capabilities of the 18650 cells using a BSF of 2000.

The RPT is performed on cells every 28-day test interval. A “pulse-per-day” is also performed to provide a quick diagnostic snapshot (20-s discharge and charge pulses at 90% SOC, 30 °C).

This RPT concept is a combination of INL and HNEI interests, containing components that can serve more than one purpose. Also, this RPT does not assume that a manufacturer’s protocol is used for cell charging, and thus, includes a matrix of charge conditions.

The purpose of RPT component (A) is to quantify charge and discharge capacity dependence on current and the associated residual or unrealized capacity, and to determine how these quantities change over cell aging. The combined RPT components of (B + C)

enables impedance data to be obtained over a matrix of current and SOC, provides data toward kinetic analyses, and yields complex impedance spectra at the SOC of interest. The pulse testing is designed to cover a range of current that would capture conditions that could serve as surrogate low-power hybrid pulse power characterization (L-HPPC) conditions. Hence, HPPC is not explicitly performed, but equivalent results can be derived and interpolated from the resultant matrix of data. This simplifies the testing, placing power goal issues as an end application of the data, and not an upfront driver for stipulating test conditions.

In addition to monthly RPTs, all cells in PD Study 2 undergo a short standardized PPD at the end of each cycling day to gain daily information on cell integrity, and to provide a means to detect transitions between cell aging mechanisms (which would otherwise be crudely facilitated using a monthly RPT). Since we want the cells to be characterized at a meaningful SOC and to be ready for the next cycling day afterward, we perform the PPD at 90% SOC and 30 °C, using 20-s $C_1/1$ discharge and charge pulses with a rest in between. It is assumed that daily conditions just prior to the PPD have left the cells at a condition of $\leq 90\%$ SOC. The PPD mimics what might be performed through an “overnight diagnostics” algorithm, and is

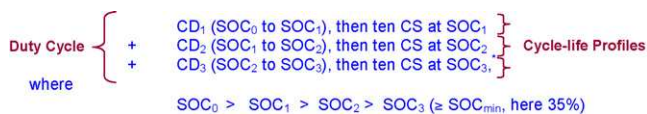


Fig. 5. General duty cycle concept for PD Study 2, showing the hierarchy between CD, CS, cycle-life profiles, and the complete duty cycle. As shown, the duty cycle approximates a 1-h one-way commute, starting at SOC₀ (90% SOC), and ending as low as SOC_{min} (35% SOC).

meant to be a spot check of cell health, not an intensive quantitative analysis.

3. Concept of aging path dependence

An understanding of “aging path dependence” is needed to design experiments related thereto and to interpret test data. Path dependence is an important factor for any batteries that will undergo prolonged usage in one or more applications, especially if usage patterns change appreciably during service life. In the context of lithium-ion cells in arbitrary service (vehicle applications, laptops, and consumer electronics), the extent of aging experienced by a cell at a given point in its life depends on the cumulative stress encountered under aging conditions by the cell at that point. Path dependence asserts that the *sequence* of aging conditions (as well as the nature of conditions) has a direct influence on the rate of aging and net aging along the timeline. Given such knowledge, an ideal scenario would be to ascertain an optimal path that would minimize aging, while meeting performance goals, thereby maximizing cell life. Such an optimal path is best understood in the context of reaction kinetics and thermodynamics, which collectively govern the extent and rate of degradation reactions that affect electrochemical cells.

One way to regard aging path dependence is to consider Fig. 6, wherein an arbitrary relative performance loss (capacity loss and power fade) is plotted against aging time, showing four distinct aging regions. This is an idealized plot for illustration purposes. The reference extent of performance loss (*) is shown for the four aging regions or periods being in the particular order they are in Fig. 6. Under a true path-dependent scenario, a random rearrangement of the order of aging periods will not necessarily yield the

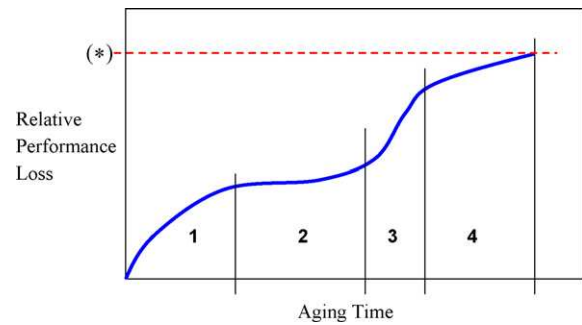


Fig. 6. Generalized diagram of relative performance loss over aging time (hypothetical case), illustrating four distinct periods of different aging conditions. Path dependence asserts that a randomized rearrangement of the four conditions will likely not reproduce the reference aging of (*) by the end of the fourth period.

identical loss of (*) at the end of the fourth period. In fact, based on the principles of reaction kinetics that proceed from an intermediate state and related thermodynamic constraints, we should expect the cumulative performance loss under a random rearrangement of aging conditions to produce net aging that is different from any other rearrangement.

4. Results and discussion

Work is progressing for PD Studies 1 and 2, which will illuminate fundamental performance limitations, aging mechanisms, and path dependence thereof for cells under these aging conditions. Data analysis is underway for the huge amount of information gathered so far during testing for PD Studies 1 and 2. In particular, pulse-per-day impedances (charge and discharge) and monthly RPT data

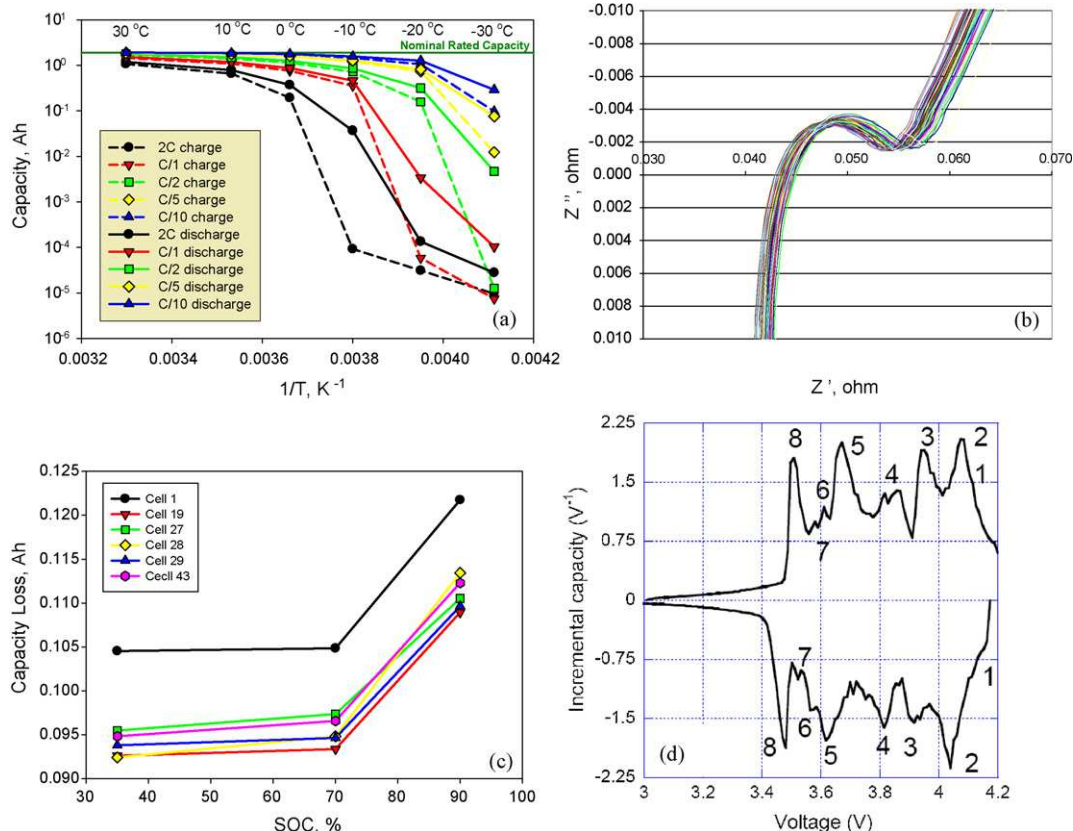


Fig. 7. Examples of Sanyo Y characterization data useful in capturing performance limitations and aging trends. Shown are (a) polarization study covering charge and discharge over a large matrix of temperature and current, (b) EIS results at 70% SOC, (c) 7-day self-discharge test results, and (d) incremental capacity analysis (ICA). All results at cell BOL.

is being evaluated. Given below is a concise discussion of early data subsets. A more complete discussion and analysis will be published in one or more follow-on papers at the conclusion of this work.

Overall, we have found the Sanyo Y 18650 cells to be an excellent platform from which to study aging path dependence issues. These cells are well made and BOL data showed very little cell-to-cell variability. So far, the rate of aging is manageable and commensurate with obtaining mechanistic-level information as the studies continue.

Various examples of BOL cell data are given in Fig. 7, where the type of each analysis targets specific issues of cell performance or characterization. This figure highlights issues of polarization behavior, interfacial impedance, self-discharge, and incremental capacity (akin to differential capacity). Such data can be obtained periodically (RPT) and tracked over aging time, where the data trends can be informative toward diagnostic analysis of aging mechanisms. We will perform such diagnostic analysis as the data sets become more fully developed over time.

Of particular value is incremental capacity analysis (ICA) that is made possible through plots like that of Fig. 7(d) that represent near-equilibrium conditions of cell cycling. This technique is finding growing utility for analysis of aging processes in electrochemical cells (e.g., [7,12–15]). Through ICA the predominant features of the dQ/dV profiles are indexed over voltage at beginning-of-life, and then tracked through successive aging periods. The modeling approach is built upon careful analysis of changes in attributes of the indexed items which are due to changes in the cell and electrode chemistry; not based on first principles models or empirical models. Therefore, the ICA approach produces information derived from mechanistic basis, which can be formulated for rate, temperature, and other effects derived from external factors. Also, since the incremental capacity analysis is based on voltage and capacity information, it provides us information with temporal resolution. Two issues with post-mortem analysis is that the end results do not provide such temporal resolution to allow accurate prediction, and results can be adversely affected by improper sample handling of the harvested cell materials. However, post-mortem analysis is useful and powerful as a validation tool. Lastly, using the incremental capacity analysis, one can investigate and analyze the behavior of the positive and negative electrodes separately (this aspect shall be discussed in a separate article). Since the incremental capacity peaks that are associated with each electrode can be indexed, tracing the changes in the electrode reaction on each electrode can be performed for analysis.

Regarding PD Study 1, Fig. 8 shows that pulsing at P_{\max} generally results in the most $C_1/1$ capacity loss, while having constant-current charge pulses attenuates the rate of loss. These are very early trends that need more maturity to provide detailed

information about the possible number and type of degradation mechanisms regarding capacity and impedance. However, early results are useful for assessing BOL trends and initial estimates of parameters for aging models, and it seems apparent in both the $C_1/1$ and $C_1/25$ cases that the capacity loss mechanisms are different or somewhat mitigated for Scenario 5 wherein we impose constant-current charging rather than constant-power charging. Future RPTs will reveal the number and magnitude of capacity loss mechanisms, and typically, at least 1 year of testing is needed to provide sufficient data for mechanistic analysis.

Regarding PD Study 2, Fig. 9 gives snapshots of PPD discharge impedances for selected aging scenarios given in Table 2: (a) 20°C isothermal (test condition 2), (b) 40°C isothermal (test condition 3), (c) mild (test condition 4), and (d) severe thermal cycling (test condition 7). These contours are made by plotting total pulse impedance against pulse time and cumulative test time (aging). Total impedance for a given PPD was calculated by an Ohm's law analysis ($R(t_{\text{pulse}}) = \Delta V(t_{\text{pulse}})/I$). This figure provides three key pieces of information: the ohmic resistance is closely approximated by the beginning-of-pulse condition (extrapolated to zero pulse time), the climb of impedance during the 20-s pulse, and the trending of these two quantities over the aging timeline. As such, from a single graph we can gauge how ohmic and capacitive contributions to impedance are tracking over cell aging for each test condition. Although the data in Fig. 9 covers approximately 1 month of collective testing, early trends indeed indicate that impedance growth is accelerated for cases of elevated temperature and more severe thermal cycling. This has obvious consequences for cells that will be in service in regions that impose wider thermal swings in daily and seasonal use of the batteries. This result also underscores the need for thermal management schemes that will not only cool the batteries as needed, but also keep the batteries above a critical minimum temperature to avoid cycling from cold temperatures. Again, it is imperative that these cells undergo extended testing for at least 1 year to determine mature trending behavior within the key metrics of capacity, impedance, and power.

Regarding fundamental analysis and modeling tools that will be used to elucidate aging artifacts of our mature datasets, degradation mechanisms will be analyzed using a combination of non-invasive electrochemical techniques, including incremental capacity analysis, inference from relaxed cell voltage during rest periods, EIS measurements, changes in kinetic performance, and other data over successive RPTs that reflect clear aging trends. ICA can trace the changes in the cell reactions, which in turn provide crucial information of such changes for mechanism inference. The relaxed cell voltage during rest period will provide assessment of the state of the cell without polarization, thus we can relate the phenomena of degradation to proper state of charge of the cell.

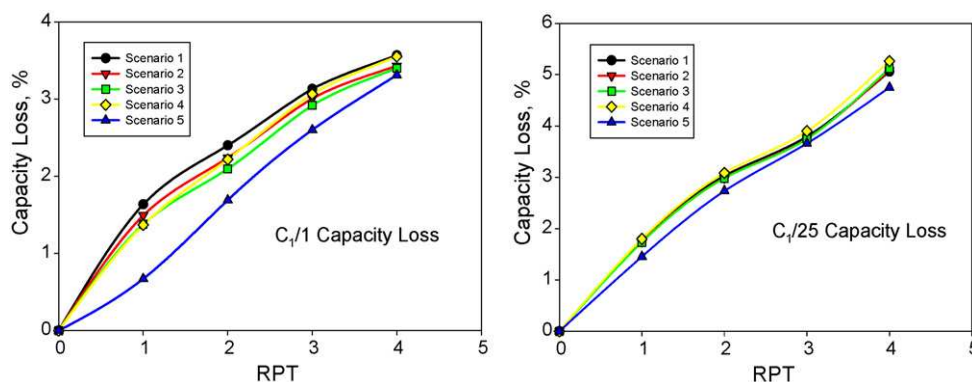


Fig. 8. $C_1/1$ and $C_1/25$ capacity loss data for PD Study 1, showing the effect of scenario conditions on the rate of aging relative to cell capacity. Although early indications are that the constant-current charge scenario promotes less capacity degradation, prolonged aging is required to determine the relative magnitude of all degradation mechanisms.

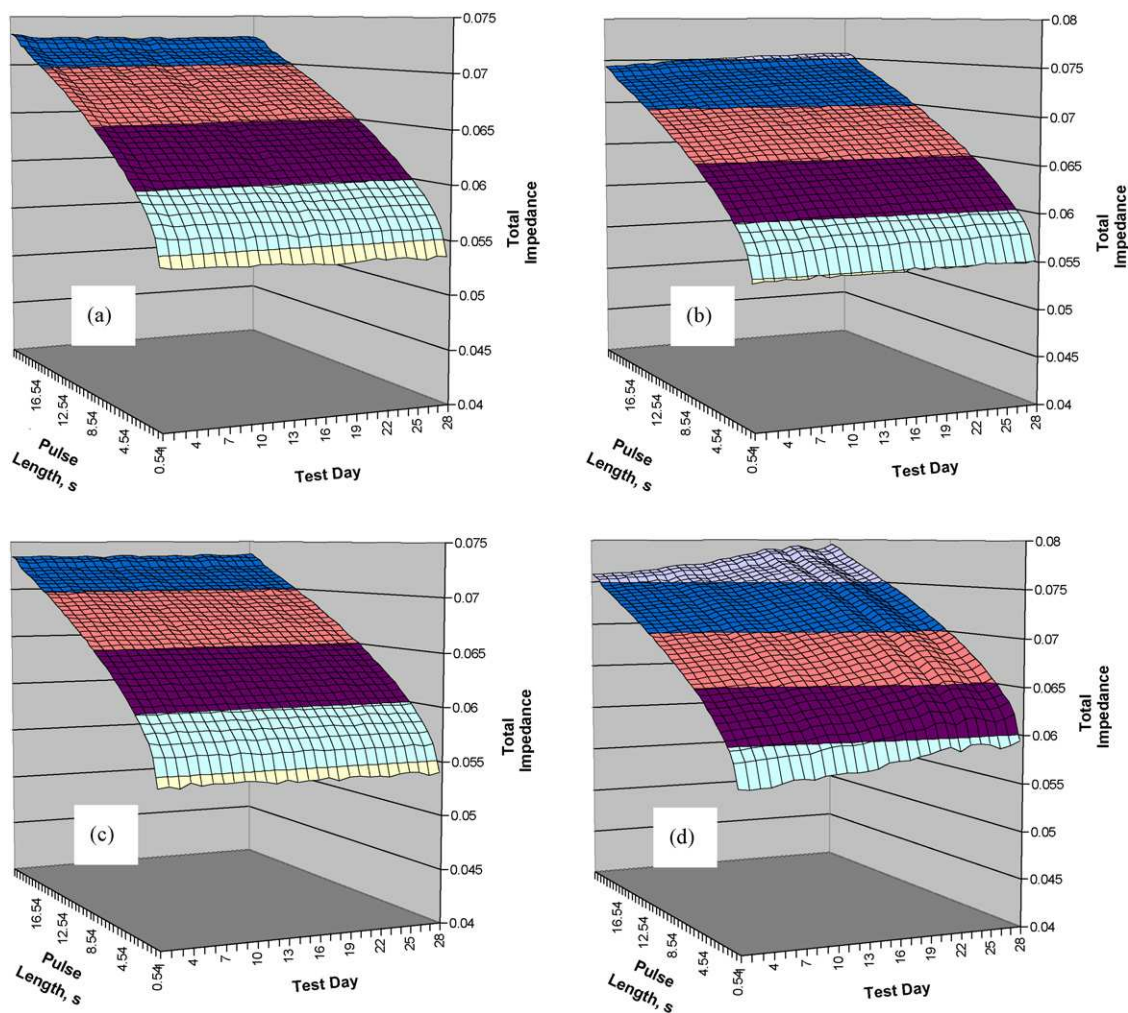


Fig. 9. Early PPD discharge impedances for selected cells in PD Study 2 that are undergoing (a) 20 °C isothermal, (b) 40 °C isothermal, (c) mild, and (d) severe thermal cycling. For this 1-month period, impedance growth is greater for cases of elevated temperature and more severe thermal cycling. Extended testing over at least 12 months will be performed to obtain mature trends in cell aging.

EIS measurements over cell aging will yield information regarding the magnitude of interfacial impedance and ohmic resistance, while kinetic performance data will track fundamental parameters related to equilibrium processes (e.g., exchange current density). When proper information of the cell degradation can be quantified for the state of the battery, the change of the degradation rate can then be incorporated into an advanced set of modeling tools being developed within our research group to predict path dependence on cell degradation. Some of these tools view degradation of cell performance in terms of the cell being a batch reactor encountering variable usage conditions over its life. Such sophisticated modeling tools are approaching final development and are beyond the scope of this paper.

As final analysis and modeling tasks are underway, a key issue will be the statistical quality of the data, since it is important to know what uncertainties might undermine the data in terms of experimental error and manufacturing variability. We will monitor data quality to determine if the deviation of key data (e.g., capacity fade) between various test groups is greater than the statistical variance within the groups. In other words, we will establish whether the differences seen are meaningful in terms of true path dependence or if they have more of a basis in experimental and measurement errors. This issue will be covered in a future publication that reports on the final outcome of this work.

5. Conclusions

Through the collaboration of INL and HNEI, a set of path-dependent studies have been initiated that focus on fundamental factors regarding the use of lithium-ion cells in PHEV-type applications. Early performance data over test time indicates that our test cells experience a slightly higher rate of aging at higher magnitude power pulses, higher temperature, and more severe thermal cycling. These results, although somewhat intuitive, allow us to quantify aging effects in the laboratory that have relevance to operating conditions in electric-drive vehicles, particularly PHEVs. However, much more data over aging is required to make substantive observations and conclusions on aging processes and path dependence. We will continue to monitor the aging trends over the next several months, and will perform mechanistic analyses and modeling on mature data sets at the completion of this work to determine the extent of path dependence of cell aging.

Thermal cycling should be considered as a standard aging condition for batteries intended for vehicle applications (HEV, PHEV, EV), and could be useful as an accelerated aging condition. There is much yet to be learned about how a particular cell chemistry and the physical design of a cell responds to repeated thermal cycling. If indeed a strong correlation exists between thermal cycling and aging rates, this will have a sobering consequence toward meeting

battery warranties for HEV, PHEV, and EV systems, since in many such cases battery life was elucidated from a series of isothermal studies.

The immediate benefits of this work will be to provide more realistic and accurate life predictions by accounting for the influence of thermal cycling effects and related path dependence on aging mechanisms, and provide a basis for improving battery development and management. Future work can assign the test parameters to reflect the choice of global location to target a specific region, country, or city of interest. In so doing, the aging path dependence and battery technology limitations tied to the global location can be quantified and used to design and optimize lithium-ion technologies for that region.

Acknowledgements

The authors gratefully acknowledge funding provided by the Office of Energy Efficiency and Renewable Energy within the United States Department of Energy, per Contract No. DE-AC07-05ID14517.

References

- [1] B.Y. Liaw, E.P. Roth, R.G. Jungst, G. Nagasubramanian, H.L. Case, D.H. Doughty, *J. Power Sources* 119–121 (2003) 874.
- [2] T. Osaka, S. Nakade, M. Rajamaki, T. Momma, *J. Power Sources* 119–121 (2003) 929.
- [3] K. Asakura, M. Shimomura, T. Shodai, *J. Power Sources* 119–121 (2003) 902.
- [4] B.Y. Liaw, R.G. Jungst, G. Nagasubramanian, H.L. Case, D.H. Doughty, *J. Power Sources* 140 (2005) 157.
- [5] B.Y. Liaw, M. Dubarry, *J. Power Sources* 174 (2007) 76.
- [6] M. Dubarry, V. Svoboda, R. Hwu, B.Y. Liaw, *J. Power Sources* 174 (2007) 366.
- [7] M. Dubarry, V. Svoboda, R. Hwu, B.Y. Liaw, *J. Power Sources* 165 (2007) 566.
- [8] M. Dubarry, N. Vuillaume, B.Y. Liaw, T. Quinn, *J. Asian Elec. Vehicles* 5 (2) (2007) 1033.
- [9] L.O. Valoen, M.I. Shoesmith, The effect of PHEV and HEV duty cycles on battery and battery pack performance, in: *Proceedings of the PHEV*, 2007.
- [10] M. Dubarry, N. Vuillaume, B.Y. Liaw, *J. Power Sources* 186 (2009) 500.
- [11] Idaho National Laboratory, Battery Test Manual for Plug-in Hybrid Electric Vehicles, INL/EXT-07-12536, revision 0, March 2008.
- [12] J. Barker, M.Y. Saidi, R. Koksang, *Electrochim. Acta* 41 (1996) 2639.
- [13] M. Dubarry, V. Svoboda, R. Hwu, B.Y. Liaw, *Electrochem. Solid State Lett.* 9 (10) (2006) A454.
- [14] M. Dubarry, V. Svoboda, R. Hwu, B.Y. Liaw, *J. Power Sources* 174 (2007) 1121.
- [15] M. Dubarry, B.Y. Liaw, *J. Power Sources* 194 (2009) 541.