Capacity and power fade cycle-life model for plug-in hybrid electric vehicle lithium-ion battery cells containing blended spinel and layered-oxide positive electrodes

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Abstract

This paper proposes and validates a semi-empirical cycle-life model for lithium-ion pouch cells containing blended spinel and layered-oxide positive electrodes. For the model development and validation experimental data obtained during an aging campaign is used. During the campaign the influence of charge sustaining/depleting operation, minimum state of charge (SOC), charging rate and temperature on the aging process is studied. The aging profiles, which are prescribed in power mode, are selected to be representative of realistic plug-in hybrid electric vehicle (PHEV) operation. The proposed model describes capacity fade and resistance increase as function of the influencing stress factors and battery charge throughput. Due to its simplicity but still good accuracy, the applications of the proposed aging model include the design of algorithms for battery state-of-health (SOH) moni-

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**Part of this research was conducted at the time she was Research Scientist at OSUCAR

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monitoring and prognosis, PHEV optimal energy management including battery aging, and the study of aging propagation among battery cells in advanced energy storage systems.

**Keywords:** Lithium-ion battery, Capacity and power fade, NMC-LMO cathode, Semi-empirical model, cycle-life prognosis, PHEV cycling

### 1. Introduction

A crucial step towards the large-scale introduction of plug-in hybrid electric vehicles (PHEVs) in the market is to reduce the cost of their energy storage devices. Lithium-ion (Li-ion) batteries are the preferred energy storage technology in PHEVs due to their high energy and power density [1]. One of the goals of U.S Department of Energy (DOE) Vehicle Technologies Program for hybrid electric systems is to, by 2022, reduce the production cost of Li-ion batteries by nearly 75 percent from 2012 costs. Currently, battery cycle and calendar life represents one of the greatest uncertainties in the total life-cycle cost of advanced energy storage systems [2].

Generally, battery aging manifest itself in a reduction in the ability to store energy and deliver power, performance metrics correlated with loss in capacity and increase in internal resistance [3], [4]. Among the micro-mechanisms of Li-ion battery aging we cite active particle loss and metal sediment or SEI film accumulation. A review of today’s knowledge on the mechanics of aging in Li-ion batteries can be found in [3], [5]. These physical-chemical mechanisms are enhanced by stress factors such as current severity (C-rate), operating temperature, state of charge (SOC), cycling rates, over-charge and over-discharge [3], [4]. The generation of long-term predictions of the evolution of capacity and/or resistance to predict when it will reach a predetermined threshold is referred as battery prognosis. Prognosis helps in
making informed and timely life cycle management decisions, reducing warranty and maintenance costs while improving serviceability, availability and safety. Prognosis is possible when an aging model describing the evolution of aging over time/cycle is available.

Battery aging models can be classified as physics-based [6, 7, 8, 9, 10, 11, 12, 13] and semi-empirical models [2, 14]. Due to its simplicity but still good accuracy, semi-empirical models have been used for on-line battery prognosis and state-of-health (SOH) estimation, and as part of other Battery Management System (BMS) tasks such as state-of-charge (SOC) estimation [4], [15]. Recently, semi-empirical models have been also used for PHEV optimal energy management including battery aging [16],[17] and for the study of aging propagation among cells in advanced battery systems [18]. Due to its potential applications, in this work, we choose to use the semi-empirical approach for the aging model development.

During the past years, the concept of blended electrodes composed of several active materials is attracting attention. Blended cathodes promise the combination of benefits of different metal-oxides into a hybrid electrode to allow performance optimization [19], [20]. In particular, blended cathodes composed of layered-oxide positive electrodes such as \( \text{LiNi}_{1/3}\text{Nm}_{1/3}\text{Co}_{1/3}\text{O}_2 \) (NMC) and spinel oxide positive electrodes such as \( \text{LiMn}_2\text{O}_4 \) (LMO) have been considered as one of the most promising candidates for PHEV applications [21], [22]. NMC positive electrodes have high specific capacity, good thermal stability and good cycle life. However, they have poor performance at high rates [21]. On the other hand, LMO positive electrodes, have a high rate capability and a low-cost. However, they have a low cycle life [19]. NMC-LMO blended positive electrodes have been reported to have the benefits of the two metal-oxides [23], [21].
There have been substantial efforts to conduct experimental campaigns to understand the influence of different stress factors on battery aging for various cathode materials: LiCoO$_2$ (LCO) [24, 25], LiNiO (LNO) [24], Li(Ni,Co)O$_2$ (NCO) [26, 27, 28, 29], Li(Ni,Co,Al)O$_2$ (NCA) [30, 25, 31, 32], LiFePO$_4$ (LFP) [2, 14, 32], NMC[33, 34, 35]. The majority of these studies have also included efforts to develop semi-empirical aging models. The main stress factors investigated have been SOC, $\Delta$SOC, C-rate, and Temperature. Recently, other PHEV related stress factors such as vehicle-to-grid services (V2G) [36], charging protocol [37] and SOC equalization [38] have been included.

Though NMC-LMO cathodes are considered an excellent candidate for PHEV applications, only few aging campaigns using this composite material have been published [39, 40, 41, 13]. In [39] the effect of temperature and SOC on calendar-life and charge sustaining/depleting cycle-life are studied within a large aging campaign. In [40], cycle-life is studied under two scenarios. In the first, the effect of thermal cycling superimposed to charge sustaining/depleting operation is studied. In the second, the magnitude and randomness of constant power pulses is investigated. None of these studies have included the development of suitable aging models for BMS and prognostics schemes.

Despite the efforts reported in the literature, there is still the need to understand battery aging under more realistic PHEV operation. In particular, the development of accurate aging models able to assess and prognose the life of the most advanced li-ion cathode candidates under realistic automotive scenarios is critical. This paper proposes semi-empirical capacity and power fade aging models for Li-ion pouch cells with NMC-LMO positive electrodes based on PHEV aging cycles. During the aging campaign
that provided data for the proposed model, the influence of charge sustain-
ing/depleting operation, minimum SOC, charging rate and temperature on
the aging process was studied [13].

This paper is organized as follows. Section 2 describes the design of
experiments and the methodology used during the periodic state of health
assessments. Section 3 presents the capacity fade experimental data and
describes the development and validation of an aging model based on em-
pirical relations of the stress factors with capacity fade. Section summarizes
and discusses the results in Section 3. Section 5 presents the resistance in-
crease experimental data and describes the development and validation of a
power fade model. Similarly, Section 6 sumarizes and discusses the results
in Section 5. In Section 7, the conclusions are presented.

2. Experimental Campaign

The United States Advanced Battery Consortium (USABC) defines two
operational modes for PHEVs, Charge-Depleting (CD) and Charge-Sustaining
(CS) [1]. In CD mode the vehicle is allowed to operate in electric mode (i.e.
the vehicle powered by the electric drive and onboard electric energy storage)
and hybrid mode (i.e. the vehicle is powered by the electric drive and/or
engine), with a net decrease in battery state-of-charge (SOC). Where the
battery SOC is defined as the available capacity expressed as a percentage of
rated capacity. In CS mode the vehicle is only allowed to operate in hybrid
mode with a relatively constant battery SOC. Figure 1 shows an schematic
of a typical SOC profile under PHEV cycle operation. During CD the bat-
tery is depleted starting from a battery SOC of $\text{SOC}_{\text{max}}$ and until reaching
a predefined $\text{SOC}_{\text{min}}$. During CS the battery SOC is kept within a window
UE\text{CS} with an average value of SOC\text{min} [1], see Figure 1. We define \( t_{CD} \) as the time spent in CD, \( t_{CS} \) as the time spent in CS, and \((t_{CD} + t_{CS})\) as the total operating time. The ratio of CD to the total operating time is then defined as the ratio of \( t_{CD} \) to \((t_{CD} + t_{CS})\),

\[
Ratio = \left( t_{CD} : (t_{CD} + t_{CS}) \right) = \frac{t_{CD}}{t_{CD} + t_{CS}}
\]

which indicates the fraction of time spent in CD mode over the total operation time. Therefore, \( Ratio=1 \) corresponds to CD operation i.e. all the operating time is spent in CD. \( Ratio=0 \) corresponds to CS operation, i.e all the operating time is spent in CS. Ratios such that \( 0 < Ratio < 1 \) correspond to mixed operation i.e. the total operating time is divided between CD and CS. For example, the SOC profile shown in Figure 1 corresponds to mixed operation with a \( Ratio \) of \( 1/2 \), i.e, half of the CD-CS operation time is spent in CD while the other half is spent in CS.

Battery charging is typically done through CC-CV protocol [37]. That is, a constant current (CC) is used until the battery voltage reaches a predetermined limit, followed by a constant voltage (CV) until the current declines to a predetermined value. In this work we express the current in terms of C-rate\(^1\). We refer to the CC expressed in C-rate as charging rate (\( CR \)).

2.1. Design of Experiments

In order to understand battery aging under a more realistic vehicle cycle-life scenario; in this work, the following stress factors are defined for PHEV operation:

\(^1\)A C-rate is a measure of the rate at which a battery is charge/discharged relative to its maximum capacity. Operationally, C-rate\(=\frac{I(t)}{S_0}\), where \( I(t) \) is battery input current and \( S_0 \) is the battery nominal capacity
• Charging rate, \( CR \)

• Battery skin temperature, \( T \)

• \( t_{CD} \) to \((t_{CD} + t_{CS})\) \( Ratio \)

• Minimum state-of-charge, \( SOC_{min} \)

To understand the dependence of aging on the stress factors, the experimental data obtained during an aging campaign conducted on pouch cells with composite NMC-LMO positive electrode and carbon graphite negative electrode is used. The design of experiments, previously reported in [13], is summarized in this section. Each cell has a nominal capacity of 15Ah at 1C-rate and a nominal voltage of 3.75V. The battery cell cycling equipment consisted on 400 channels with a maximum capability of 8V charge, 5V discharge and 400A, controlled using Labview.

The duty cycles used during the aging campaign are composed of the PHEV CD and CS micro-cycles defined by the USABC [1]. The duty cycles are prescribed in power mode, not current mode, preserving vehicle performance regardless of SOC and Temperature. In Figure 2 the power micro-cycles, which are scaled up to approximate a ten-mile CD range PHEV using a BSF of 94, are shown.

Three sets of experiments were conducted:

• One set for CD operation, i.e. \( Ratio =1 \)

\(^2\)Aging campaign design by [13] and aged cells produced by the CAR Industrial Consortium/CARTech LLC.

\(^3\)The Battery Size Factor (BSF) is defined as the minimum number of units (cells, modules or sub-batteries) of a given design required for a device to meet all U.S. Department of Energy Vehicle Technologies Program targets, including cycle life and calendar life [1].
• One set for CS operation, i.e. \( \text{Ratio} = 0 \)

• One set for mixed operation, i.e. \( 0 < \text{Ratio} < 1 \)

For the CD operation experiment, the power duty cycle consists of either five, six, or seven times a CD micro-cycle to cause an \( \text{SOC}_{\text{min}} \) of approximately 45, 35, or 25\%, respectively. Then the cell is charged using a \( \text{CR} \) of \( C/3 \), \( 3C/2 \), or \( 5C \) to a voltage of 4.15 V, where a CV portion finishes the charge to 95\% SOC and the entire cycle is repeated. A total of 9 CD experiments, one for each case, were conducted at 30\(^\circ\)C.

For the CS experiment, the SOC is set by using the cell OCV vs. SOC curve to select the voltage corresponding to an \( \text{SOC}_{\text{min}} \) of 45\%, 35\% or 25\%, respectively, then a CS micro cycle is repeated while keeping the voltage within a window of 10mV around the nominal setpoint. A total of 3 CS experiments, one for each case, were conducted at 30\(^\circ\)C.

For the mixed operation experiment, the power duty cycle consists of seven times a CD micro-cycle to cause an \( \text{SOC}_{\text{min}} \) of approximately 35\%, followed by CS micro-cycles repeated in \( \text{Ratios} \) of 1/2 and 1/4. Then the cell is charged using a \( \text{CR} \) of \( 3C/2 \) following the protocol previously described and the entire cycle is repeated. Three experiments corresponding to a \( \text{Ratio} \) of 1/2, each one conducted at 10\(^\circ\)C, 30\(^\circ\)C or 45\(^\circ\)C. One experiment corresponding to a ratio of 1/4 was conducted at 30\(^\circ\)C. A total of 4 experiments were conducted.

Table 1 contains the summary of the experiments during the aging campaign. The campaign duration was up to 3 months of effective cycling test time. The resulting charge throughput expressed in ampere-hour throughput (Ah) attained at the end of each experiment is shown in the last column of the table.
2.2. Cell Characterization

Prior to and after the aging campaign, each cell was characterized using the following tests:

- Capacity test;

- Hybrid Power Pulse Characterization (HPPC). Test used to assess discharge and regen power capability.

For the capacity test, the cell was fully charged and then discharged using a constant current of 1C (15A) to the lower voltage limit. The voltage limits used during the test were $V_{\text{max}} = 4.14\, \text{V}$ and $V_{\text{min}} = 2.8\, \text{V}$. The capacity was measured 3 times to establish repeatability.

The HPPC current profile consists of ten-second duration, high constant current inputs with a 40-second open circuit in between. After the pulse sequence, the cell is immediately discharged with 10% DOD increments to traverse the SOC range and rested for 1hr before the pulse sequence is repeated [1]. This test sequence is repeated 9 times. Using a BSF of 94, the discharge and regen pulses correspond to a current of 5C (75A) and 3.75C (56.25A) respectively, and a 2C (30A) discharge current to traverse the SOC range.

During the life cycle aging campaign, cells were stopped periodically for assessment using the procedures previously described (approximately every two weeks). All the characterization tests were conducted at $30^\circ\text{C}$. Figure 3 shows the voltage response during the capacity characterization tests for experiment #16 in Table 1. The cell charge throughput expressed in kAh before each test is indicated in parenthesis.

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4 The HPPC test is conducted using a BSF of 94
3. Capacity Fade Model Development

In a battery, the number of cycles is commonly expressed using the total ampere-hour throughput \([Ah]\) in both charge and discharge, i.e. \(Ah = \int_0^t |I(\tau)|d\tau\), where \(I(t)\) is the input current to the battery [42]. The capacity fade [%] of as a function of the battery charge throughput is then expressed as:

\[
S_{\text{loss}}(Ah) = 100 \cdot \frac{S_0 - S(Ah)}{S_0},
\]

where, \(S_0\) is the cell nominal capacity and \(S(Ah)\) is the cell capacity after \(Ah > 0\) charge throughput. It has been experimentally shown that the capacity fade in Li-ion batteries can be described using a power law relation with \(Ah\) [2], [14], [42]. Therefore, we adopt the following functional form for the capacity fade model,

\[
S_{\text{loss}}(Ah) = f_C(SOC_{min}, Ratio, CR, T) \cdot Ah^z
\]

where \(f_C(\cdot)\) is a nonlinear function of the aging factors investigated during the aging campaign, and \(z > 0\). Capacity characterization data are used to quantify the capacity fade for the model development. The capacity characterization points obtained from experiment \(i\) are fitted using the following expression:

\[
S_{\text{loss},i}(Ah) = f_{C,i} \cdot Ah^{z_i}
\]

where, the coefficients \(f_{C,i}\) and \(z_i\) are the fitting parameters for experiment \(i\). The optimal fitting coefficients are found using the Nonlinear Optimization Toolbox in Matlab. In particular, the nonlinear Levenberg-Marquardt algorithm is used to solve the data fitting problem in the least-squares sense. For the model development, a constant \(z = 0.48\), which corresponds to the
average of the $z_i$ is used[14], [42]. The values of $f_{C,i}$ depend on the aging factors: $Ratio$, $SOC_{min}$, $CR$ and $T$.

In the following subsections, the effect of each aging factor on capacity fade is studied and described. A semi-empirical model based on empirical relations of the relevant aging factors with capacity loss is developed and validated. The model is developed by fitting the experimental capacity severity factor data points $f_{C,i}$ into empirical relationships. All the data fitting problems are solved in the least-square sense and using Levenberg-Marquardt algorithm. The data obtained from experiment #1 in Table 1 is discarded because it does not show consistency. This experiment is currently being repeated.

3.1. Dependence of capacity fade on Charging Rate

Lithium loss has been reported as one of the main mechanisms of capacity fade in Li-ion batteries during charging [37], [43]. It is estimated that more than 90% of the cyclable lithium loss during a CC-CV charging occurs during the CV portion, while the rest occurs during the CC portion [43]. During CV, higher values end-of-charge voltage (EOCV) lead to higher rates of capacity fade [43]. It has been also reported that metallic plating and subsequent lithium loss can also occur during the CC portion even during a normal CC-CV charging if the charging current rate exceeds a certain value [37]. The experimental data obtained suggested that there is no significant dependence of capacity fade on $CR$ under the charging conditions used during the experiments. This may be explained because the $CR$s used are relatively low (C/3, 2C/3 and 5C). Similarly, besides the use of the same CV (4.15V) the EOCV reached while using $CR$s of C/3 and 2C/3 were pretty close, 4.117V and 4.116V respectively. Moreover, while using
the CR of 5C ("fast charging"), the EOCV reached was 4.087V, a lower voltage than with the other two CRs, which may have compensated, if any, the effect of using a higher CR. Therefore, the CR is not consider an stress factor for the development of the capacity fade model.

3.2. Dependence of capacity fade on Temperature

After eliminating the CR from the stress factors, capacity fade may be affected by SOC$_{min}$, Ratio and T. It has been reported by different authors that the dependence of capacity fade on temperature is a combination of different aging effects [2], [3],[32]. On one hand, at high temperatures, capacity fade follows an Arrhenius relation with operating temperature, a relation which describes the effect of temperature on the chemical side reactions responsible for battery aging such as SEI film accumulation [1],[3], [26], [28], [35]. For different cathode materials the Arrhenius relation describes the dependence of capacity fade on aging for temperatures greater that 15°C. On the other hand, at low temperatures, capacity fade may follow an exponential decay with operating temperature, probably related to metallic lithium plating and subsequent electrolyte decomposition by metallic Li [3],[32]. Up to now, and to the best of our knowledge, this latter empirical relationship has not been fully understood and validated with experimental data. For this reason and since the experimental campaign conducted in this work was not intended to fully understand this later phenomenon, the experimental point corresponding to 10°C is not used for the aging model development. Therefore, the following expression for capacity loss is adopted:

$$ S_{loss}(Ah) = f_C(SOC_{min}, Ratio, T) \cdot Ah^z $$

(5)
where, $f_C(\cdot)$ is the capacity severity factor function defined as [2], [26]:

$$f_C(\cdot) = a_C(SOC_{min}, Ratio) \cdot \exp\left(\frac{-E_{ac}}{R_g T}\right)$$  \(6\)

where, $E_{ac}$ is the cell activation energy for the capacity fade process, $R_g$ is the universal gas constant, and $T$ is the cell absolute temperature.

The data from the temperature experiments along with the best curve fittings are shown in Figure 4(a). The experiments correspond to a $Ratio$ of 1/2, $SOC_{min} = 35\%$ and a charging rate of $3C/2$, at two different temperatures, $T_1 = 30^\circ C$ and $T_2 = 45^\circ C$ (Experiments #14 and #16 respectively, see Table 1). The data from these experiments along with Equation (6) is used to find the value of $E_{ac}$. The following relationship is used:

$$\ln\left[\frac{f_C(35\%, 0.5, T_1)}{f_C(35\%, 0.5, T_2)}\right] = \frac{-E_{ac}}{R_g} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$  \(7\)

where, the values of $f_C(35\%, 0.5, T_1)$ and $f_C(35\%, 0.5, T_2)$ correspond to the optimal coefficients obtained from the data curve fitting and $\ln$ is the natural logarithm function. The activation energy obtained for the capacity fade process is $E_{ac} = 22406 \ [Jmol^{-1}]$. The rate of capacity fade increases while increasing the operating temperature for the temperature range under study.

### 3.3. Dependence of capacity fade on Ratio

The experiments conducted to study the influence of the $Ratio$ on capacity loss correspond to experiments #5, 11, 14 and 15 in Table 1. The experiments were conducted at $SOC_{min} = 35\%$, $T = 30^\circ C$, and ratios of 0, 1/4, 1/2 and 1, respectively. The experimental severity factor values are fitted to the following equation:

$$a_C(35\%, Ratio) = \alpha_1 + \beta \cdot (Ratio)^b$$  \(8\)
where, $\alpha_1 = 145$, $\beta = 420$ and $b = 0.34$ are the identified constants. Figure 5 shows the severity factor obtained from the experimental data best curve fittings, and the proposed empirical relationship for the dependence of capacity fade on the Ratio. The results of these experiments indicate that the rate of capacity fade increases while increasing the Ratio. The rate of capacity fade is the lowest at CS operating mode i.e. Ratio of 0 and increases rapidly while increasing the ratio, reaching the highest value during CD operation i.e. Ratio of 1. Figure 4(b) shows the capacity characterization points obtained from experiments #5, 11, 14 and 15 as markers, and the proposed empirical relationship, as solid curve. The results experiments #2, 5 and 8, are used to validate the proposed model. Figure 6 shows the experimental data obtained from these experiments and the proposed empirical relationship. The experimental data points show good fitting with the proposed empirical relationship.

3.4. Dependence of capacity fade on $SOC_{\text{min}}$

The experiments conducted to study the influence of $SOC_{\text{min}}$ on capacity fade correspond to experiments #10, 11, and 12 in Table 1. The experiments were conducted at $T = 30^\circ C$, with a Ratio of 0, and $SOC_{\text{min}}$ of 45, 35 and 25%, respectively. The experimental capacity severity factor values are fitted to the following equation,

$$a_C(SOC_{\text{min}}, 0) = \alpha_2 + \gamma \cdot (SOC_{\text{min}} - SOC_0)^c$$  \hspace{1cm} (9)

where $\alpha_2 = 137$ and $\gamma = 9610$ are the identified constants for $SOC_0 = 0.25$ and $c = 3$. Figure 7 shows the capacity severity factor points obtained from the experimental data best curve fittings, and the proposed empirical relationship for the dependence of capacity fade on $SOC_{\text{min}}$. The results of these
experiments indicate that the rate of capacity fade increases while increasing $SOC_{\text{min}}$, this effect is more pronounced for $SOC_{\text{min}} > 35\%$. Figure 4(c) shows the capacity characterization points obtained from these experiments and the proposed empirical relationship.

4. Capacity fade model

Summarizing, capacity fade can be described by:

$$S_{\text{loss}}(Ah) = a_C(SOC_{\text{min}}, \text{Ratio}) \cdot \exp\left(\frac{-E_{ac}}{R_g T}\right) \cdot Ah^z \quad (10)$$

where, $a_C(\cdot)$ is the capacity severity factor function given by:

$$a_C(\cdot) = \alpha_C + \beta_C \cdot (\text{Ratio})^b + \gamma_C \cdot (SOC_{\text{min}} - SOC_0)^c \quad (11)$$

where, the dimensionless constant coefficients $\alpha_C, \beta_C, \gamma_C, b, c, z, SOC_0$, and the dimensional constant coefficients $R_u$ and $E_{ac}$ and are given by:

$$\begin{cases}
\alpha_C = 137 \\
\beta_C = 420 \\
\gamma_C = 9610 \\
b = 0.34 \\
c = 3 \\
z = 0.48 \\
SOC_0 = 0.25 \\
E_{ac} = 22406 \quad [Jmol^{-1}] \\
R_g = 8.314 \quad [JK^{-1}mol^{-1}] 
\end{cases} \quad (12)$$

Figure 8 shows the fitted surface $a_C(\cdot)$ that describes the dependence of capacity fade on $SOC_{\text{min}}$ and $\text{Ratio}$. The capacity characterization data points from experiments #1,4,3,6 and 9 in Table 1 are used to validate the
model. All conducted at $T = 30^\circ C$ with a Ratio of 1. Experiments #3,6 and 9 with SOC$_{min}$=25%, while experiments #1 and 4 with SOC$_{min}$=45%. Figure 9 shows the experimental points obtained from these experiments and the proposed model. The proposed empirical capacity fade model shows consistency with the experimental data points used for validation.

The goodness of fit for the capacity fade model is evaluated through the root mean square (RMS) error defined as:

$$RMS_S = \sqrt{\frac{\sum_{1<i<N} \left( \hat{S}_{loss,i}(Ah_j) - S_{loss,i}(Ah_j) \right)^2}{\sum_{1<j<m_i} 1}}$$

(13)

where, $\hat{S}_{loss,i}(Ah_j)$ is the estimated capacity loss for experiment #$i$ at $Ah_j$ charge throughput, $S_{loss,i}(Ah_j)$ is the corresponding experimental point, $N$ is the total number of experiments, and $m_i$ is the total number of capacity assessment tests conducted during experiment #$i$ (including initial, final and periodical state of health characterization tests). The root mean square obtained is $RMS_S = 0.0047\%$.

The capacity fade process follows a power law with the ampere-hour throughput. The power law factor, $z$, is very close to 0.5, which indicates that one of the main mechanisms of capacity fade may be the growth of a solid electrolyte (SEI) layer, causing a square root of $Ah$ shaped behavior [26], [35]. Usually SEI growth takes place mainly at the beginning of cycling and continues steadily with cycling [3]. Capacity fade follows Arrhenius-like kinetics, which indicates that it may be caused by thermally activated process.
5. Power Fade Model Development

The internal resistance increase of a battery cell [%] as a function of ampere-hour throughput can be expressed as:

\[ R_{\text{inc}}(Ah) = 100 \cdot \frac{R(Ah) - R_0}{R_0} \]  \hspace{1cm} (14)

where, \( R_0 \) is the cell nominal internal resistance and \( R(Ah) \) is the cell internal resistance after \( Ah > 0 \) charge throughput. From observations of the obtained experimental data and aging studies reported in the literature the resistance increase in Li-ion batteries can be described using a linear relation with \( Ah \) [39]. Therefore, we adopt the following functional form for the resistance increase model:

\[ R_{\text{inc}}(Ah) = f_R(SOC_{\text{min}}, Ratio, CR, T) \cdot Ah \]  \hspace{1cm} (15)

where \( f_R(\cdot) \) is a nonlinear function of the aging factors.

In a battery cell, the internal resistance is a function of the operational conditions: SOC, temperature and input current, charge/discharge [44]. There are different methods to calculate the internal resistance of a battery cell. For example, HPPC test, identification techniques using an equivalent circuit models of the battery cell, or using the input-output cell response and Ohm’s law [1], [44]. The first two methods are not suitable for online applications, for this reason the third approach is selected to analyze the data. Using the experimental data, the battery cell internal resistance is calculated by observing the voltage response to every input current step increase/decrease and using Ohm’s law as follows [45]:

\[ \hat{R} = \frac{\Delta V}{\Delta I} = \left| \frac{V_{\text{final}} - V_{\text{initial}}}{I_{\text{final}} - I_{\text{initial}}} \right| \]  \hspace{1cm} (16)
As illustration, a schematic of the input current and cell voltage response during the first 100 seconds of a CD micro-duty cycle are shown in Figure 10. In the figure, the initial currents and voltages used for the resistance calculations are shown as square markers; the final currents and voltages as triangle markers; and the input current and voltage response as solid curves.

In order to reduce noise and capture the actual trend in resistance increase, outlier removal and filtering methods were applied. Resistance values greater than 3 standard deviations from the average were removed to reduce resemblance. The cutoff criteria was chosen to remove false resistance values and not to remove data that did not fit the normal distribution. The removed values, which were not representative of the overall trend, typically constituted less than 1% of the total set. After the outlier removal, a moving average technique was chosen to capture the actual trend in resistance growth. The moving average window used has a length of 250 points.

Figure 11 shows the resistance data from experiment #16 before and after the outlier removal and filtering. Similar resistance data processing results are obtained for the rest of the experiments. These simple calculations do not perfectly identify the actual value of the internal resistance; however, they provide a simple but still accurate approach to trace the overall trend of the resistance growth throughout the battery lifespan.

Resistance data processed as explained above are used to quantify the growth in internal resistance for the model development. The resistance points obtained from experiment $i$ are fitted using the following expression:

$$R_{inc,i}(Ah) = f_{R,i} \cdot Ah$$  \hspace{1cm} (17)

where, the coefficients $f_{R,i}$ is the fitting parameter. The fitting coefficients are found using a linear least squares approach. In the following subsections,
the influence of the stress factors on the resistance growth is studied. Since the approach for the model development is similar to the one used for the capacity fade model, just the main highlights are presented in the next subsections.

5.1. Dependence of resistance increase on Charging Rate

In contrast to the capacity fade process, the experimental data suggest that there is dependence of resistance increase on the CR. For this reason, CR is considered a stress factor for the model development in this case.

5.2. Dependence of resistance increase on Temperature

Following a similar approach as in Subsection 3.2 the following expression is used to describe the dependence of resistance increase on temperature:

\[
R_{inc}(Ah) = a_R(SOC_{min}, Ratio, CR) \cdot \exp \left( \frac{-E_{a_R}}{R_u T} \right) \cdot Ah
\]  

(18)

where, \(a_R(\cdot)\) is the resistance severity factor function which depend on \(SOC_{min}, Ratio, CR\); \(E_{a_R}\) is the cell activation energy for the resistance increase process; \(R_u\) is the universal gas constant; and \(T\) is the cell absolute temperature. The activation energy obtained for the resistance growth process is \(E_{a_R} = 51800 \ [Jmol^{-1}]\). Figure 12(a) shows the resistance characterization points obtained from experiments as markers, and the model, as solid curve. The rate of resistance growth increases while increasing the operating temperature for the temperature range under study.

5.3. Dependence of resistance increase on Ratio

The experiments conducted to study the influence of Ratio on resistance increase correspond to experiments #5, 11, 14 and 15 in Table 1. These experiments were conducted at Ratios of 0, 1/4, 1/2 and 1, respectively.
The experimental severity factor values obtained for Ratios of 1/4, 1/2 and 1 may be consider the same while the one obtained for Ratio=0 is significantly different from the others. This result suggest that the underlying influence of Ratio on resistance increase is the fact that during CS the battery is not fully charged (during CS the battery is operated during a narrow SOC window). Therefore, for the model development a "equivalent" CR of zero is assigned for the CS operation. Therefore, the following equivalent CR function is defined:

\[
CR_{eq}(Ratio) = \begin{cases} 
0 & \text{Ratio} = 0 \\
CR & \text{Ratio} > 0
\end{cases}
\] (19)

6. Resistance increase model

Sumarazing the results from the model development, the resistance growth can be described by:

\[
R_{inc}(Ah) = a_R(SOC_{min}, Ratio, CR) \cdot \exp \left( -\frac{E_{aR}}{R_uT} \right) \cdot Ah
\] (20)

where, \(a_R(\cdot)\) is the resistance severity factor function given by:

\[
a_R(\cdot) = \alpha_R + \beta_R \cdot (SOCC_{min} - SOCC_0)^{\sigma_R} + \gamma_R \cdot \exp \left[ d \cdot (CR_0 - CR_{eq}) + e \cdot (SOCC_{min} - SOCC_0) \right]
\] (21)

where, \(CR_{eq}\) is a function of Ratio given by:

\[
CR_{eq}(Ratio) = \begin{cases} 
0 & \text{Ratio} = 0 \\
CR & \text{Ratio} > 0
\end{cases}
\] (22)
and, the dimensionless constant coefficients $\alpha_R, \beta_R, \gamma_R, c_R, d, e, \text{SOC}_0$ and
the dimensional constant coefficients $R_u$ and $E_{aR}$ and are given by:

\[
\begin{align*}
\alpha_R &= 3.2053e + 05 \\
\beta_R &= 1.3674e + 09 \\
\gamma_R &= 3.6342e + 03 \\
c_R &= 5.45 \\
d &= 0.9179 \\
e &= 1.8277 \\
\text{SOC}_0 &= 0.25 \\
CR_0 &= 5 \\
E_{aR} &= 51800 \ [Jmol^{-1}] \\
R_g &= 8.314 \ [JK^{-1}mol^{-1}]
\end{align*}
\]

Figure 13 shows the resistance severity factor surface $a_R(\cdot)$ that describes
the dependence of resistance growth on $\text{SOC}_{min}$ and $CR_{eq}$. The results indi-
cate that the rate in resistance growth increases while increasing $\text{SOC}_{min}$, and
the rate in resistance growth increases while decreasing $CR_{eq}$. Figures
12(b,c,d) show the resistance characterization points obtained from experi-
ments #2 to 12 and #14,16 along with the proposed model.

Since the model objective in this case is to capture the trend on the
resistance growth and not to predict the instantaneous value of the battery
internal resistance; the goodness of fit for the model is evaluated through
($RMS$) error defined over the resistance severity factor as:

\[
RMS_R = \sqrt{\frac{\sum_{1<i<N} \left( \hat{f}_{R,i} - f_{R,i} \right)^2}{N}}
\]

where, $\hat{f}_{R,i}$ is the estimated severity factor for experiment #i, $f_{R,i}$ is their
corresponding experimental severity factor point, and $N$ is the total number
of experiments. The root mean square obtained is \( RMS_R = 2.0495 \times 10^{-5} \).

The resistance increase process follows a linear relationship with \( Ah \). Additionally, the power loss process follows an Arrhenius-like kinetics, which indicates that the resistance growth may be caused by a thermally activated process.

7. Conclusions

This paper presented the results of an experimental campaign conducted on Li-ion pouch cells with NMC-LMO positive electrodes. During the campaign the influence of charge sustaining/depleting operation, minimum SOC, charging rate and temperature on the aging process is studied. The results show that capacity fade and resistance increase are influenced by \( \text{Ratio} \), \( \text{SOC}_{\text{min}} \), \( CR \) and temperature. Using a non-linear curve fitting technique, a semi-empirical aging model which describes the capacity fade and resistance increase as a function of the influencing stress factors and the ampere-hour throughput was proposed based on the experimental data. The proposed aging model is intended to be used for predicting battery cycle-life under realistic PHEV operation. For its simplicity but still good accuracy, the model can be used for the design and sizing of PHEV energy storage systems; for the design and implementation of algorithms for battery state-of-health assessment and end-of-life prediction (prognosis); as part of PHEV optimal energy management schemes including battery aging, among others. The aging model may be also used for more research-oriented purposes such as the study the propagation of aging among cells in battery systems.
ACKNOWLEDGEMENTS

The authors wish to thank the CAR Industrial Consortium\textsuperscript{5}/CARTech LLC for producing the aged cells. This material is based upon work supported by the National Science Foundation under Grant Number NSF-1301238 and the Department of Energy under Award Number DE-PI0000012.

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\textsuperscript{5}The CAR Industrial Research Consortium receives funding through annual membership fees paid by: GM, Ford, Cummins, Chrysler, Honda, Oshkosh Truck, Bosch, Eaton, Caterpillar, Lubrizol, Case-New Holland, Renault, Samsung, Tenneco, TRC Inc.
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Figure Captions

Figure 1: Schematic of SOC profile under PHEV operation: charge depleting (CD), charge sustaining (CS) and charging.

Figure 2: Charge depliting (CD) and charge sustaining (CD) power micro-cycles [1].

Figure 3: Voltage Response during the capacity characterization tests for experiment 16.
Figure 4: Capacity loss for: (a) temperature experiments; (b) Ratio experiments; (c) SOC$_{min}$ experiments (all conducted with a Ratio of 0). Experimental data are shown as markers, and the model, as solid curve.

Figure 5: Capacity severity factor function from Ratio experiments. Capacity severity factor points obtained form the experimental data best curve fittings are shown as markers, and the model, as solid curve (Equation 8).

Figure 6: Capacity loss for all the experiments conducted with a Ratio of 1 at SOC$_{min}$=35%. Experimental data are shown as markers, and the model, as solid curve.

Figure 7: Capacity severity factor function from SOC$_{min}$ experiments, all conducted with a Ratio of 0. Capacity severity factor points obtained from the experimental data best curve fittings are shown as markers, and the model, as solid curve (Equation 9).

Figure 8: Capacity severity factor map. The experimental points are shown as markers, and the severity function, as solid surface (Equation 11).

Figure 9: Capacity loss for SOC$_{min}$ experiments, all conducted with a Ratio of 1. Experimental data are shown as markers, and the model, as solid curve (Equation 20), (a) Experiments conducted with SOC$_{min}$=25%, (b) Experiments conducted with SOC$_{min}$=45%

Figure 10: Schematic of the input current and cell voltage response during the first 100 seconds of a CD micro-duty cycle. The initial currents and voltages used for the resistance calculations are shown as square markers; the final currents and voltages as triangle markers; and the input current and voltage response as solid curves.

Figure 11: Resistance data from experiment #16 before and after the outlier removal and filtering.

Figure 12: Resistance increase for: (a) temperature experiments; (b)
SOC \text{min} = 25\% \text{ experiments}, T = 30C^o; (c) SOC \text{min} = 35\% \text{ experiments}, T = 30C^o; (d) SOC \text{min} = 45\% \text{ experiments}, T = 30C^o. Experimental data are shown as markers, and the model, as solid curve.

Figure 13: Resistance severity factor surface. Resistance severity factor points obtained from the experimental data best curve fittings are shown as markers, and the model, as solid surface (Equation 21).

Table Captions

Table 1: Summary of aging experiments
<table>
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<th>Experiment #</th>
<th>Operating mode</th>
<th>Ratio ($t_{CD}+t_{CD+CS}$)</th>
<th>SOC$_{min}$ [%]</th>
<th>Charging C-rate</th>
<th>Temperature [C°]</th>
<th>Charge throughput* [Ah]</th>
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*attained by cell at the end of the experiment
Figure 1

[Graph showing the battery's state of charge (SOC) over time, with key points labeled as $t_{CD}$, $t_1$, $t_{CS}$, $t_2$, $t_{Charging}$, $t_3$, and the final state $UE_{CS}$.]
Figure 2

CD power micro cycle

CS power micro cycle
Figure 4

(a) Charge throughput [kAh] vs. Capacity loss [%] for different temperatures:
- T = 30°C (Experiment #14)
- T = 45°C (Experiment #16)

(b) Charge throughput [kAh] vs. Capacity loss [%] for different charge ratios:
- Ratio=1, (Experiment #5)
- Ratio=1/2, (Experiment #14)
- Ratio=1/4, (Experiment #15)
- Ratio=0, (Experiment #11)

(c) Charge throughput [kAh] vs. Capacity loss [%] for different SOCmin:
- SOCmin=45% (Experiment #10)
- SOCmin=35% (Experiment #11)
- SOCmin=25% (Experiment #12)
Figure 5

The graph shows the relationship between $a_C(35\%, \text{Ratio})$ and the ratio. The equation is

$$\alpha + \beta^*(\text{Ratio})^b$$

The data points are shown as red circles.
SOC_{min} = 35\% \ (Experiments \ #2,5 \ and \ 8)
\[ \alpha_2 + \gamma^*(\text{SOC}_{\text{min}} - \text{SOC}_0)^c \]

Experimental data
Figure 9

(a) 

Capacity loss [%] vs Charge throughput [kAh]

- SOC$_{\text{min}}$ = 25% (Experiments #3, 6, and 9)

(b)

Charge throughput [kAh] vs Capacity loss [%]

- SOC$_{\text{min}}$ = 45% (Experiments #4 and 7)
Figure 10
Figure 11: Graph showing the relationship between charge throughput [KAh] and internal resistance [mΩ]. The graph includes experimental points and a moving average. The x-axis represents charge throughput [KAh], and the y-axis represents internal resistance [mΩ].
Figure 12

(a) Resistance increase [%] vs. Charge throughput [kAh] for T=30°C (Experiment #14) and T=45°C (Experiment #16).

(b) Resistance increase [%] vs. Charge throughput [kAh] for CR=0, SOCmin=25% (Experiment #12), CR=C/3, SOCmin=25% (Experiment #3), CR=3C/2, SOCmin=25% (Experiment #6), and CR=5C, SOCmin=25% (Experiment #9).

(c) Resistance increase [%] vs. Charge throughput [kAh] for CR=0, SOCmin=35% (Experiment #11), CR=3C/2, SOCmin=35% (Experiment #5,13,14,15), and CR=5C, SOCmin=35% (Experiment #8).

(d) Resistance increase [%] vs. Charge throughput [kAh] for CR=0, SOCmin=45% (Experiment #10), CR=3C/2, SOCmin=45% (Experiment #4), and CR=5C, SOCmin=45% (Experiment #7).