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Challenges in Data-Based Degradation Models for Lithium-ion Batteries

Running head: Data-Based Degradation Models for Lithium-ion Batteries

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Abstract

This work summarizes the findings resulting from applying an aging modeling approach to four different capacity loss experimental datasets of lithium-ion batteries (LIBs). This approach assumes that the degradation trajectory of the capacity is a function of three variables: time, a kinetic constant, and a time-dependent factor. The analysis shows that the time-dependent factor α is cell-chemistry dependent, and cannot be averaged for calendar and cycling modes, and combined modes. This factor was also found to be a function of the stress factors. A quadratic model was used to obtain the kinetic constants per test, and statistical metrics were provided to evaluate the quality of the fitting, which was significantly affected when using averaged values of α and re-fitted kinetic constants. A set of test matrices is proposed for calendar, cycling, and mixed aging modes to overcome the challenges of data-based models developed from accelerated test approaches for modeling aging in LIBs. This work also proposes a methodology to develop these data-based aging models.

1. Introduction

Performance degradation of lithium-ion batteries (LIB) over their lifetime is inevitable, and it is related to chemical, electrochemical, and mechanical processes that occur inside the battery, which are influenced by the battery design, materials, and more importantly, by operational conditions or stress factors. This performance degradation, commonly referred to in the literature as *aging*, is usually quantified by battery health indicators that describe degradation effects such as capacity fade and resistance growth¹. There are two aging modes in LIBs: calendar aging, when the battery is disconnected from any load for a specific time, and cycling aging, when the battery is either charging or discharging. The predominant degradation mechanism during both calendar and cycling aging is the growth of a solid

electrolyte interphase (SEI) at the graphite anode¹. This SEI layer is a barrier that protects the anode from corrosion, which is created the first time that the cell is used and progresses as the cell is cycled. Over time, the SEI promotes the loss of lithium ions and the electrolyte decomposition, as well as graphite exfoliation¹. Another important degradation mechanism is lithium plating, which also appears at the negative electrode mostly during cycling aging, and it causes the shift of the pseudo-linear behavior of capacity fade with respect to time, characterized by the SEI growth, into a non-linear behavior^{2,3}. Pseudo-linear behavior is observed in primary applications such as electric vehicles (EVs), where steady degradation profiles are expected. Batteries are removed from EVs when their nominal capacity reaches approximately 80% of their beginning-of-life (BOL) nominal capacity, to be either disposed or used in less demanding applications, which are more permissive to non-linear behavior and drastic drops of performance compared to primary applications. Lithium plating is characterized as lithium deposited on the anode in the form of dendrites³. Both SEI growth and lithium plating are the predominant aging mechanisms on graphite anodes. Other additional degradation mechanisms in LIB graphite anodes include electrolyte decomposition, binder decomposition, graphite exfoliation, structural disorder, loss of electrical contact, electrode particle cracking, transition metal dissolution, and corrosion of current collectors. On the other hand, the main degradation mechanisms on the cathode include the interaction between the cathode element dissolved within the electrolyte and the anode, and electrolyte degradation. The stress factors promoting degradation during calendar aging are temperature and state-of-charge (SOC); while in cycling aging, the stress factors also include C-rate (rate of charge and/or discharge) and depth-of-discharge (DOD)⁴. More specifically, high temperatures ($> 40\text{ }^{\circ}\text{C}$) promote SEI growth, while low temperatures ($< 10\text{ }^{\circ}\text{C}$) promote lithium plating^{3,5,6}. Under high temperatures and high SOC ($> 80\%$), the SEI may dissolve and create lithium salts less permeable to the lithium ions, increasing the anode

impedance⁷. High C-rates and DODs also accelerate aging during cycling, due to SEI growth⁸. A comprehensive review of LIB degradation mechanisms is included in the work of Palacin⁹.

There are three different approaches for modeling the aging phenomena¹⁰: (1) ***physical-chemical models***, which include a performance module based on porous electrode theory -or its simplified version, the single-particle model- and a formulation for the parasitic reactions associated to the degradation mechanisms; (2) ***data-based models*** fitted to data from accelerated degradation tests of individual battery cells at different operating conditions; and (3) ***data-driven models***, based on online data measurements of battery performance parameters in primary and secondary applications. Physical-chemical models describe the electrode charge transfer process and the physical degradation of the components within the battery; their main challenge is the estimation of the electrochemical parameters required for modeling both the battery performance and aging models. Data-based models developed from accelerated aging tests can be empirical and semi-empirical, including parametric models fitted to experimental data from a design of experiments that attempts to reproduce conditions that capture the main degradation mechanisms. On the other hand, data-based models developed from online measurements do not consider the underlying physics and mostly rely on machine learning techniques for state-of-health prediction. The main disadvantages of data-based models from accelerated aging tests are related to test resource availability (time and equipment cost) to a data set that is large enough to obtain statistically significant results. In consequence, these data models are prone to misrepresenting (1) the interaction between stress factors, (2) degradation mechanisms that may not be observable in accelerated tests, and (3) module- or battery-level performance cause by cell spreading that may not be observable during tests with individual cells. Regarding the data-based models from online measurements, as per any other application using machine learning algorithms for prediction

purposes, they require extensive and quality datasets to train on, and an accurate interpretation of the results generated from their algorithms. The focus of this work is identifying the challenges of using data-based models from aging accelerated tests (DBM-AT) and presenting a methodology to develop these models.

Several DBM-AT models have been proposed for both calendar and cycling aging modes and different cell chemistries, mostly using the capacity fade as a health indicator^{11,12,13,14,15,16,17}; we will turn our attention first to calendar aging. Schmalstieg et al.¹⁸ performed calendar aging tests on 2.15 Ah lithium nickel manganese cobalt oxide (NMC) cells, and they fitted the data of capacity loss as a function of temperature, SOC and time using a set of quadratic equations. They demonstrated that the capacity loss rate follows an exponential behavior, in agreement with the Arrhenius law

$$r = Ae^{-\frac{E_A}{RT}}, \quad (1)$$

where A is the pre-exponential factor, E_A is the activation energy, and T is the temperature. Arrhenius-based correlations are power-law functional relationships. The evolution over time of the capacity loss in phenomena modeled with Arrhenius-based correlations is obtained by multiplying Equation 1 by the term t^α , where t is time, and α is a time-dependent factor.

Arrhenius-based correlations are also proven to represent capacity loss during calendar aging for other cell chemistries^{19,20,21,22,23}. For instance, Kaneko et al.²³ performed a set of accelerated calendar tests on 6.2 Ah lithium iron phosphate (LFP) cells, and they fitted the capacity loss using an Arrhenius-based correlation, where a capacity loss coefficient is correlated with the time term with an exponent equals to 0.5. Similarly, Redondo-Iglesias et al.²⁴ developed an empirical approach for estimating capacity loss during calendar aging based on a linear approximation of the Eyring equation, which has the same mathematical

form as the Arrhenius equation. The Arrhenius' and Eyring's equations only diverge significantly at high temperatures, where the rate of a chemical reaction continues to rise at high temperatures in the Eyring's equation, compared to the asymptotic behavior in the Arrhenius' equation. In the work of Redondo-Iglesias et al.²⁴, the exponential factor of the Eyring's equation is the ratio $\frac{E_A}{R}$, where E_A is a function of the DOD and C-rate. This correlation was tested with accelerated calendar tests for 350 Ah nickel manganese cobalt (NMC) cells.

Other semi-empirical approaches have also been used in DBM-AT degradation models of LIBs^{25,26,27}. For instance, Baghdadi et al.^{25,26} made an analogy of the degradation correlation presented by Dakin²⁸ to correlate the evolution of the capacity over time in LIBs

$$C(t) = C_0(1 - k_c t^\alpha), \quad (2)$$

where, C_0 is the initial capacity of the cell, k_c is a kinetic constant, α is a time-dependent factor, and t is time. This approach assumes that all degradation mechanisms, also referred to as side reactions, follow the same trajectory or degradation path for the capacity described by Equation 2. The kinetic constant is required to be estimated for each combination of stress factors values. This approach was validated by running a set of calendar aging tests on 15 Ah LFP cells.

Capacity loss has also been correlated using alternative or modified expressions of the Arrhenius' (Equation 1) and Eyring's equations. For instance, Kassem et al.²⁹ performed a calendar aging study on 27 commercial LFP cells stored at nine different temperatures and SOC. They found that the capacity loss is affected by the storage temperature, being this effect severe at maximum temperature and SOC (60 °C and 100%). They fitted the capacity loss using an empirical expression that includes the kinetic dependence of the capacity fade

with temperature and SOC during storage, as well as a temperature-dependent diffusion limitation term. Another example, also involving LFP cells, is the analysis of cell performance degradation conducted by Sarasketa-Zabala et. al.³⁰ at different SOC and temperature storage conditions, for modeling the dominant aging phenomenon (SEI growth). Their mathematical model¹¹ to obtain the capacity loss is an exponential function, including the reciprocal of the temperature and SOC, and time with an exponent of 0.5. As demonstrated in previous works^{21,22,29,30}, capacity loss during calendar aging follows the Arrhenius rate law. However, the Arrhenius-like behavior is not valid at sub-zero temperatures since lithium plating, instead of SEI growth, is the predominant aging mechanism³¹.

For cycling aging, on the other hand, Wang et al.¹⁹ also obtained an Arrhenius-based correlation to predict capacity loss during cycling-induced aging of 2.2 Ah LFP cells. They collected data following a test matrix that covers different temperatures (-30 to 60 °C), DODs (90 – 10%), and discharge C-rates (C/2 - 10 C). Based on their results, the authors concluded that capacity loss was strongly affected by the number of cycles and temperature, while DOD effects were less significant. They used a power-law model to correlate the capacity loss and the stress factors in which the Arrhenius equation accounted for the temperature effect; the activation energy was defined as a function of the C-rate, and the Ah-throughput—which is the energy delivered or stored in the battery—was used instead of the number of cycles to allow quantifying the capacity loss for different C-rates. Similarly, Cui et al.³² reported an exponential influence on the aging rate of LIBs, by determining the relationship between discharge rate, temperature and capacity loss on LCO/Meso carbon micro beads (MCMB) cells; the activation energy in their equation was also defined as a function of the C-rate.

In practical applications, batteries are exposed to both calendar and cycling aging; hence it is no surprise that several researchers have tried to model the combined effect of both aging

modes. Gering³³ segregated the degradation mechanisms (e.g., SEI and lithium plating) by fitting kinetics correlations per degradation mechanism, described with different degradation trajectories, and using validation data only from calendar tests. As in any LIB, the kinetics is dictated by the materials in the electrodes that promote the reactions involved in performance degradation; these reactions eventually become self-moderating, since the effect of these reactions is to diminish the active sites that promote the reactions, contributing to the SEI fracture and reformation, as well as particle fracture³³. For this reason, segregating the electrochemical reactions from the electrochemical processes promoted by similar operating conditions would require a considerable amount of tests to verify the shift from a degrading to a self-moderating behavior. Similarly, Santhanagopalan et al.²⁷ developed a segregated aging model as

$$q = \min(q_{Li}, q_{sites}) \quad (3)$$

$$q_{Li} = b_0 + b_1 t^\alpha + b_2 N \quad (4)$$

$$q_{sites} = c_0 + c_2 N \quad (5)$$

where, the capacity q , limited by cycleable lithium in the cell q_{Li} or electrode active sites q_{sites} , is estimated from a DBM-AT model that includes an independent term b_0 , a calendar term as a function of time t and a time-dependent factor α , and a cycling term as a function of the number of cycles N . The term $b_2 N$ represents low-to-moderate cycling conditions and $c_2 N$ represents a linear fade regime during cycling. A set of performance fade trajectories for different degradation mechanisms such as kinetic-controlled reaction, diffusion-controlled reaction, and cycling fade have been described in detail by Santhanagopalan et al.²⁷.

Capturing the dynamic degradation phenomena in LIBs using DBM-AT models poses several challenges: (1) the DBM-AT for a specific cell chemistry requires running tests for a

wide range of stress factors to accurately predict degradation, (2) different degradation mechanisms lead to different kinetic relationships that can coexist, and (3) performance degradation can later shift in time to an electro-chemo-mechanical process, such as SEI layer fracture. The balance between available testing resources, time, and model accuracy in reproducing aging should result in optimal strategies for collecting the minimum required data. For instance, Santhanagopalan et al.²⁷ proposed a test matrix with the minimum number of tests that intend reproducing the dominant degradation mechanisms for both calendar aging and combined calendar and cycling aging modes. Similarly, Mathieu et al.³⁴ ran several calendar, cycling, and mixed calendar-cycling tests with a set of cells made of a blend of lithium manganese oxide (LMO) and NMC chemistries, at a Δ SOC of 10% and different temperatures, SOC_s, and C-rates. They used the D-optimal design of experiment (DOE) to optimize the combinations of cycling tests while fixing the number of calendar and mixed tests. Their calendar/cycling data was preliminarily fitted using a multi-factor quadratic model. After statistical analysis of the resulting model coefficients, the authors proposed a simpler model with fewer terms, the structure of which suggests the minimum number of experiments.

In this work, we summarize the findings resulted from applying the aging calibration approach presented by Mathieu et al.³⁴ to four different datasets: (1) aging data from combined calendar and cycling tests of LMO/NMC cells³⁵, referred to as Dataset I; (2) aging data from calendar tests of lithium nickel cobalt aluminum oxide (NCA) cells³⁶, referred to as Dataset II; (3) aging data from calendar tests of NMC cells³⁶, referred to as Dataset III; and (4) aging data from calendar tests of LFP cells³⁶, referred to as Dataset IV. Mathieu's approach³⁴ was developed for calibration purposes of cycling aging models and was used in this work as a reference semi-empirical approach to developing a more accurate DBM-AT for calendar and cycling aging of LIBs. The estimation of the kinetic constants and time-dependent factor

of the capacity loss model resulted in discrepancies and inconsistencies that can be explained by challenging the assumptions of Mathieu's approach³⁴, such as the use of an average time-dependent factor and the combination of calendar and cycling aging in one correlation. Furthermore, the effect of the sample size on the statistical significance of the estimated model coefficients was also analyzed for the calendar aging datasets. In addition to p-values, we have included overall metrics for the fitting, such as F-statistics and R^2 , to estimate the goodness-of-fit of the model. Based on our statistical analysis, and supported by the kinetic and mechanistic understanding of the degradation phenomena in LIBs, we propose representative test matrices for calendar and aging tests, and further guidelines for developing accurate and physically meaningful DBM-AT degradation models for LIBs.

The main contributions of this work are (1) a robust methodology for the semi-empirical analysis of aging data of LIBs, (2) comprehensive test matrices that balance the need for covering the full operational envelope of LIBs in electric vehicles (EVs) and stationary applications with the need to keep the number of tests to a minimum, and (3) general guidelines for the development of DBM-AT aging models applied to multiple cell chemistries. In the next section, we describe the baseline approach reported by Mathieu et al.³⁴, followed by the data analysis methodology used to explore and compare the datasets. Next, in the results section, we discuss the exploratory data analysis of the datasets and the fitting of kinetics constants and model coefficients (β). Finally, we propose guidelines for developing accurate DBM-ATs of LIBs.

2. Baseline Approach

This section summarizes the aging model implemented by Mathieu et al.³⁴, hereafter referred to as the baseline approach. This approach assumes that the evolution of the capacity over time follows Equation 2, and that all side reactions follow the same trajectory described by this equation. A linear regression on the baseline dataset is then performed using the

following linearized form of Equation 2.

$$\ln \left[-\ln \left(\frac{C(t)}{C_0} \right) \right] = \ln(k_c) + \alpha \ln(t). \quad (6)$$

This baseline dataset^{12,37} used by Mathieu et al.³⁴ is different from the datasets explored in this work, but based on cells of the same chemistry blend as those of Dataset I (LMO/NMC-Graphite), and other chemistries like Dataset II (NCA-Graphite), Dataset III (NMC-Graphite) and Dataset IV (LFP-Graphite). Fitting all calendar and cycling data in the baseline dataset with Equation 6, preliminarily considering k_c and α as fitting parameters, resulted in values of α that varied between 0.532 and 1.098. Then, the authors considered a fixed, average value of α of 0.745 for the final implementation of the linear regression, claiming that calendar and cycling aging modes can be fitted with a unified expression that only has k_c as the fitting parameter. Their average coefficient of determination R^2 was 0.954, being the lowest value 0.619.

The next step in this approach is correlating the kinetic constants with the stress factors: reciprocal temperature ($1/T$), SOC as a fraction, charge current (I_C), and discharge current (I_D). Their initial model consisted of the following quadratic equation

$$\ln(k_c) = \beta_0 + \beta_T \frac{1}{T} + \beta_S SOC + \beta_C I_C + \beta_D I_D + \beta_{TS} \frac{SOC}{T} + \beta_{TC} \frac{I_C}{T} + \beta_{TD} \frac{I_D}{T} + \beta_{SC} SOC I_C + \beta_{SD} SOC I_D + \beta_{CD} I_C I_D + \beta_{TT} \frac{1}{T^2} + \beta_{SS} SOC^2, \quad (7)$$

where, the sub-indices of β coefficients in (Equation 7) are named after their corresponding stress factors: temperature (T), SOC (S), charge (C), and discharge (D). A quadratic model was chosen by Mathieu et al.³⁴ for modeling purposes since polynomial functions with a restricted domain are typically used for approximation of complex phenomena with DOE approaches³⁸. This means that DOE can be used on the principle that any function with one or more parameters can be fitted on a restricted domain of its parameters by a polynomial

function. Also, a quadratic function was used due to the limited available data: interactions between three and four factors were not considered since they could lead to overfitting when estimating unknown values, and quadratic effects of charge and discharge currents were confounded with the intercept value, and they were assumed negligible. Linear and quadratic effects of $1/T$, SOC, and charge/discharge on degradation rates are significant when linearizing Arrhenius-based models or used as quadratic polynomial models to successfully model capacity loss of LIBs^{16,39}. The authors fitted Equation 7 with data compiled from 27 experiments and evaluated the statistical influence of each coefficient. They estimated the individual p-values of each coefficient and set a threshold of 5%. Thus, those coefficients with p-values greater than 0.05 were discarded, leading to the following reduced model

$$\ln(k_c) = \beta_0 + \beta_T \frac{1}{T} + \beta_S SOC + \beta_C I_C + \beta_D I_D + \beta_{TC} \frac{I_C}{T} + \beta_{TD} \frac{I_D}{T} + \beta_{TT} \frac{1}{T^2} + \beta_{SS} SOC^2 \quad (8)$$

Equation 8 excludes the linear terms accounting for the interaction between temperature and SOC, and between SOC and current.

3. Methodology

This section describes the exploratory data analysis (EDA), implementation of baseline approach, kinetics and statistical analysis of results, and formulation of test matrices and degradation models.

First, we carried out an EDA to summarize and compare the main characteristics of the datasets, inspecting the evolution of the capacity loss over time as a function of the stress factors. Second, we applied the baseline approach to all datasets. The parameters k_c and α were estimated for each test using linear regression (LR) with the iteratively reweighted least-squares (IRLS) method in combination with M-estimators⁴⁰, a robust fitting approach that significantly reduces the sensitivity to the outliers. Then, we re-fitted k_c considering a fixed average value of α for all tests in a dataset. We also investigated the correlation of α

with the stress factors for calendar and cycling aging. Third, we estimated the β coefficients of the full quadratic model (Equation 7). The coefficients were re-fitted using the reduced model (Equation 8). In addition to the individual p-value of each β coefficient and the coefficient of determination R^2 , this work incorporates additional statistical diagnostic metrics such as the residual standard error (RSE), F-statistics, and global p-value to compare the performance of both models. All data analysis routines were coded in R, a robust programming language for statistical computing. Finally, we proposed guidelines for the formulation of test matrices and degradation models based on the systematic statistical analysis of aging data implemented in this work and supported by kinetics principles.

4. Exploratory Data Analysis

This section presents the findings of the EDA of all datasets in terms of the observed evolution of the capacity loss with the stress factors, the significance of the tests in the context of expected battery operational ranges in real applications, and predominant aging mechanisms promoted by the ranges of stress factors considered in each dataset.

Baseline Dataset.³⁴ This dataset consists of 27 calendar and cycling aging tests conducted on a prismatic cell with a rated nominal capacity of 43 Ah, whose anode is made of graphite, and cathode of a blend of LMO and NMC. As shown in Table 1, the test matrix consists of 17 cycling aging tests at four charge/discharge C-rate combinations ($1/1$, $3^{-1}/3^{-1}$, $1/3^{-1}$, and $3^{-1}/1$), three ambient temperatures (0, 25, and 45 °C), and four SOC_s (30, 65, 80, and 90%) cycled around $\pm 5\%$ of these average SOC_s (i.e., Δ DOD of 10%), for an equivalent time of approximately 500 days. This test matrix also considers ten calendar aging tests (denoted as 0/0) conducted over 500 days approximately at four ambient temperatures (0, 25, 45 and 60 °C) and six SOC_s (0, 30, 65, 80, 90 and 100%).

The calendar aging tests in the baseline dataset³⁴ focus mostly on the effect of different SOC_s at high (45 °C) and low (0°C) temperatures. High temperatures and high SOC_s

promote the evolution of SEI and the transition-metal dissolution, and low temperatures ($< 0\text{ }^{\circ}\text{C}$) promote lithium-plating during calendar aging. For cycling aging, the test matrix of the baseline data emphasizes the effect of moderate C-rates at maximum temperature, which promotes SEI formation and growth, and SEI fracture and reformation. Since some cycling tests were run at low temperature ($0\text{ }^{\circ}\text{C}$) and moderate C-rate (1C), lithium plating effects might be expected from these tests; however, these cycling conditions unlikely occur in an electric vehicle because the thermal management system is usually designed to keep the cell temperature within $15 - 40\text{ }^{\circ}\text{C}$ during operation and charging. Exposure to low temperatures is more likely to occur during calendar aging. This test matrix lacks the consideration of dominant SEI growth and lithium plating aging modes at higher C-rates ($> 2\text{C}$, mostly while charging). Also, it considers a ΔDOD of only 10% in all cycling tests, which impedes capturing other aging modes promoted at higher ΔDODs , like electrode and particle fracture.

Dataset I.³⁵ This dataset consists of 21 calendar and cycling aging tests conducted on a pouch cell with a nominal capacity of 26 Ah, whose anode is made of graphite, and cathode of a blend of LMO (30%) and NMC (70%). As shown in Table 2, the test matrix consists of 12 cycling aging tests at three charge/discharge C-rate combinations (1/1, 2/2, and 4/4), three ambient temperatures (25, 35 and $45\text{ }^{\circ}\text{C}$), and three SOC_s (15, 45, and 65%) up to 8000 equivalent full cycles around $\pm 5\%$ of these average SOC_s (i.e., ΔDOD of 10%). This test matrix also considers nine calendar aging tests (denoted as 0/0) conducted up to 600 days at three ambient temperatures (25, 35 and $45\text{ }^{\circ}\text{C}$) and three SOC_s (15, 75, and 90%).

The calendar aging tests in Dataset I³⁵ focus on the effect of low and high SOC_s in the medium-to-high temperature range ($25 - 45\text{ }^{\circ}\text{C}$). None of the experiments in this test matrix were conducted at low temperatures; therefore, no aggressive conditions promoting lithium plating are expected from this dataset. The cycling aging tests in Dataset I focus on the effect of low-to-medium SOC_s in the medium-to-high temperature range ($25 - 45\text{ }^{\circ}\text{C}$), considering

higher C-rates (2C and 4C) than those in the baseline dataset (up to 1C). Thus, these higher C-rates in Dataset I are expected to capture more SEI formation and growth than the baseline dataset, and potentially more SEI fracture and deformation mechanisms. For instance, as shown in Figure 1, the evolution of the capacity (as a percentage) at 35 °C and 15 % average SOC for Dataset I at different C-rates exhibit higher losses as the C-rate increases. Another example is included in Figure 2, where we can observe the evolution of the capacity for calendar mode at 35 °C and different SOC levels; further discussions including the implementation of Equation 2 on this sub-dataset are addressed in the next section of this work.

Datasets II, III, and IV.³⁶ These datasets consist of calendar aging tests conducted over 300 days on NCA cylindrical cells of 2.8 Ah (Dataset II), NMC cylindrical cells of 2.05 Ah (Dataset III), and LFP cylindrical cells of 1.1 Ah (Dataset IV). Each test matrix considers 48 calendar aging tests at three ambient temperatures (25, 40 and 50 °C) and 16 SOC levels (0 – 100 %). These datasets were chosen to evaluate the applicability of the baseline approach to other cell chemistries and to evaluate the effect of the sample size.

The calendar aging tests in Datasets II, III, and IV³⁶ focus on the effect of the full range of SOC levels (0-100%) in the medium-to-high temperature range (25 - 50 °C). As shown in Figure 3, this data reveals that the capacity loss does not increase steadily with the SOC. Instead, there is a transition zone in the 55-70% SOC range where the cells exhibit more aggressive capacity loss compared to the range 0-55%, for all cell chemistries tested. Interestingly, the capacity loss evolution under the same stress conditions is also different among cell chemistries. For instance, at 100% average SOC, 50 °C and 300 days, the NMC cells lost 23.2% of their capacity, compared to NCA and LFP cells, which lost 12.7 and 14.5%, respectively.

5. Fitting of Kinetic Constants and Time-Dependent Factor

This section presents the fitted kinetic constants k_c and time-dependent factors α for Datasets I, II, III, and IV. Table 3 shows these parameters for each test in Dataset I, along with the adjusted kinetic constants when considering (i) an average α per segregated aging mode (k_{c-s}) and (ii) an average α for both aging modes combined (k_{c-c}). For the baseline dataset, Mathieu et al.³⁴ obtained the same average value of $\alpha=0.745$ for both calendar and cycling modes, although different datasets obtained by other researchers proved that different values of α are obtained for both aging modes^{27,41,42}. For this reason, we first focus our attention on the suitability of assuming an average α in this fitting approach. Nevertheless, our analysis shows that the value of α ranges from 0.54 to 1.59 among calendar tests (those at zero C-rate), and from 0.20 to 1.34 for cycling tests, yielding average values of 0.94, 0.63, and 0.72 for calendar, cycling, and combined modes, respectively. Similarly, Tables 4, 5 and 6 show these fitted parameters for Datasets II, III, and IV, which only contemplate calendar tests. In these cases, α ranges from 0.50 to 1.22 among calendar tests in Dataset II, from 0.47 to 1.01 in Dataset III, and from 0.46 to 1.56 in Dataset IV, yielding average values of 0.67, 0.74, and 0.68, respectively. Regarding k_c , Although these values shall be analyzed along with their corresponding α value, quick visualization of the adjusted values for an average α allows observing that higher values were obtained as the stress conditions were more aggressive for both aging modes, for instance, at high temperatures and SOC.

Figure 1 shows the evolution of the capacity (as a percentage) at 35 °C, 15% average SOC for cycling aging data at C-rates 1C, 2C, and 4C; while Figure 2 shows the evolution of the capacity (as a percentage) at 35 °C for calendar aging data at SOC levels of 15%, 75%, and 90%. These figures illustrate how the quality of the fitting for both aging models is negatively affected when estimating capacity with Equation 2 using average α and re-fitted k_c .

(dotted lines), compared to the capacity estimated with individual values for k_c and α (solid lines). The quality of fitting also decreases as stress factors become more aggressive towards promoting the main degradation mechanisms, such as higher C-rates during cycling and higher SOC during calendar. Nevertheless, when comparing the quality of fitting for datasets II to IV, which includes only data for calendar aging, the capacity estimation is not affected, even at high C-rates, and the difference between cell chemistries is also negligible. This could be attributed to intrinsic differences due to cell chemistry, being LMO/NMC more affected at higher SOC compared to NCA, NMC and LFP. Also, we hypothesize that the wide variation of α among calendar and cycling aging tests is due to one or more of the following causes: (1) influence of additional stress factors during cycling aging that are not occurring during calendar; (2) influence of an extended range of stress factors for Datasets I to IV compared to the baseline dataset during cycling aging, for instance, high C-rates compared to moderate C-rates; (3) inability to segregate degradation mechanisms with different degradation trajectories for different combinations of stress factors, (4) dependence of α on the stress factors and (5) influence of stress factors and their interactions with cell chemistries on the variability of degradation trajectories.

The fitting of kinetic constants k_c and time-dependent factor α for Datasets I to IV is shown in Tables 3 to 6.

The influence of additional stress factors for cycling aging compared to calendar aging and extended range of stress factors can be inferred from the EDA of Dataset I and baseline dataset, where higher C-rates at the same temperature and average SOC, for instance, cause higher capacity loss over time than moderate C-rates. Similarly, the influence of cell chemistry on the degradation trajectory can be observed in Figure 3, where NMC cells exhibit more capacity loss than NCA and LFP cells from 60% average SOC. This could suggest, for the analyzed data for instance, that different average values of α grouped by SOC

ranges could be used, even for the same degradation trajectory within an aging mode. To quantitatively assist us in evaluating the strength of the correlation between α and the stress factors, we performed a set of linear analyses to fit the correlations of the following expression:

$$\alpha = \gamma_0 + \gamma_T \frac{1}{T} + \gamma_S SOC + \gamma_I I \quad (9)$$

The strength of the correlation is measured by the value of the coefficient γ , if it is significant. The values of each coefficient and its corresponding p-value are summarized in Table 7. The sub-indices of γ are related to their corresponding stress factor (T, SOC, and I for C-rate).

The individual p-values of the γ coefficients suggest that α strongly depends on the SOC for all chemistries ($p < 0.05$) in both aging modes, except for LFP (Dataset IV), in which the temperature also plays a significant role; while in cycling aging, α strongly depends on the C-rate. In addition, these findings also allow us to infer that, for a unique degradation trajectory, α cannot be averaged, either per each degradation mode or when combining calendar and cycling aging. We have quantified the impact of these assumptions, for instance, by calculating the relative error of the estimated capacity loss at 500 days for Datasets II, III, and IV using segregated and combined α with re-fitted k_c 's with respect to individual values of α and k_c per test, as shown in Table 8.

The maximum relative errors for Dataset III, corresponding to NMC cells, have a maximum value of 11.03%, and they are higher between 60 and 90% SOC, followed by low SOC. Based on our findings, we designed the following strategy for NMC cells to reduce these errors: (1) we assumed that the degradation trajectory is the same for the entire range of calendar aging, (2) we re-grouped the values of α as follows: an average value for 0 and 100% SOC, from 10 to 60% SOC, and from 70 to 90% SOC per each temperature, (3) we re-fitted

the kinetics constants k_c accordingly. With the implementation of our strategy, we reduced the maximum relative error to 2.82%. This exercise suggests that parametric sub-trajectories could be employed to improve the quality of the data fitting.

In our results above, it is clear that lithium-ion batteries are affected by several degradation mechanisms that are promoted by different operational and ambient conditions. These mechanisms result from the strong coupling of electrochemical, chemical, thermal, and mechanical phenomena. Therefore, it is expected that superposed aging effects define the battery state-of-health (SOH). Moreover, since C-rate and DOD are additional stress factors during cycling, both aging modes cannot share the same fade trajectory; the values of k_c and α are strongly related to the specific combination of stress factors, and they also depend on the cell chemistry. Therefore, different degradation trajectories shall be considered when developing DBM-ATs.

6. Correlation of Kinetic Constants to the Stress Factors

In this section, we present the detailed results regarding the fitting of β coefficients for all datasets. Although we have demonstrated that α cannot be averaged per segregated or combined aging modes, in this section we show and discuss the corresponding results of fitting the β coefficients as per the baseline approach. We introduced additional metrics for evaluating the quality of the fitting.

6.1 Calendar, cycling, and combined aging for the same cell chemistry

Table 9 includes a comparison between the baseline dataset and Dataset I, which have the same cell chemistry (LMO/NMC), using the quadratic model proposed by Mathieu et al.³⁴ This comparison is done for segregated calendar and cycling modes, and combined aging modes, following the baseline approach with average α values. Shaded values are statistically significant based on their p-value.

For calendar aging, the β coefficients differ significantly in magnitude. For Dataset I, all

individual p-values, except for the quadratic term of SOC, are discarding stress factors such as the linear or quadratic terms of the temperature reciprocal, that are supported by the physics of LIBs; in this case, we can hypothesize that the individual p-values of the coefficients do not provide enough information for discarding the β coefficients, unless the sample size is indeed significant. Unfortunately, there are no additional tests performed on this data to evaluate this effect. For this reason, additional metrics shall be considered for evaluating the quality of the fitting, such as R^2 , RSE, F-statistics and overall p-value. A good fit of the data for a specific model is therefore obtained when R^2 is close to 1, F-statistics is considerably greater than the critical value, and the overall p-value is less than the threshold value of 0.05. Based on these criteria, we can conclude that the quadratic model represents a good fit for Dataset I.

Similar trends in terms of magnitude are observed for cycling aging and combined modes. A considerable reduction of the p-values is observed for Dataset I when combining calendar and cycling modes, compared to segregated modes, supporting our hypothesis that the sample size could have an impact on the p-values, making significant the effect of the stress factors.

The quadratic model includes many fitting coefficients, and it could be affected due to limited data; hence reduced models should be used instead to obtain an excellent trade-off of precision when estimating these coefficients, and representativeness and interpretability of the resulting model, in terms of how it agrees with the underlying physical phenomena that we are modeling. Table 10 includes a comparison between the baseline dataset and Dataset I, which have the same cell chemistry (LMO/NMC), using the reduced model.

As shown in Table 10, the β coefficients differ significantly in magnitude for calendar, cycling and combined aging modes. We can observe more coefficients with p-values < 0.05 , since there are more degrees of freedom to estimate the coefficients. The quality of the fitting decreases compared to the quadratic model; however, the reduced model is a good fit.

6.2 Calendar aging for different cell chemistries

The results of the calendar aging comparison among different cell chemistries are shown in Tables 11 and 12. These tables show that β coefficients significantly differ among different cell chemistries, mostly in magnitude. As expected, the magnitudes of these coefficients also show that there is a strong dependence of capacity fade on temperature, in both terms, linear and quadratic, for all datasets.

As already discussed for Dataset I and the baseline dataset, individual p-values of the coefficients do not provide enough information for discarding the β coefficients. The reduced model has more degrees of freedom, therefore more reliable estimates of the coefficients can be obtained, since there is more evidence to discard those values that are not significant, without affecting the quality of the fit.

We previously discussed that the sample size could have an impact on the individual p-values of β coefficients. To evaluate this effect, we performed a cross-validation exercise on the calendar datasets to generate what is commonly referred to as the *learning curve*⁴³. Namely, we fitted the same model structure to different datasets of increasing sample size, which were randomly sampled (with replacement) from the available data. Figures 4, 5, 6, and 7 show how the p-value of the temperature (β_T , β_{TT}) and SOC (β_S , β_{SS}) coefficients of the reduced model change as the sample size increases.

As shown in Figure 4, the p-values of β_T fall below the threshold of 0.05 at 23 samples; less variability is also observed, as narrower error bars approach this threshold. This means that the linear effect of the reciprocal temperature becomes significant when running at least 23 tests. Regarding β_S , Figure 5 illustrates that p-values do not fall below the threshold; therefore, a considerable amount of tests (> 24) are required to verify if the linear effect of SOC exists. The quadratic effects of the inverse of the squared reciprocal temperature (β_{TT})

and SOC (β_{SOC}), illustrated in Figures 6 and 7, show similar trends, falling under the p-value threshold after 22 samples, also exhibiting narrower error bars as they approach this threshold. We can conclude that the linear and quadratic effects of the reciprocal temperature, and quadratic effect of the SOC can be observed in Datasets II, III, and IV after a specific number of samples, while Dataset III (NMC) exhibits an early linear effect of SOC, reaching the threshold at 13 samples. This demonstrates that, for an aging model including only five coefficients, several tests are required to represent the effect of two stress factors: temperature and SOC; this requirement is expected to considerably increase when adding stress factors, such as in the multi-factor quadratic model (Equation 7 and 8).

7. Guidelines for DBM-ATs in Lithium-ion Batteries

A set of considerations for DBM-ATs in LIBs are summarized in this section, based on the kinetics-statistical analysis of capacity loss data for different cell chemistries, including (1) test matrices, and (2) DBM-AT modeling considerations. We suggest that the performance fade parameter or health indicator for the DBM-AT should be the capacity fade since all degradation modes (loss of lithium inventory, loss of active anode material, and loss of active cathode material) contribute to this degradation effect.

7.1 Test Matrices

The test matrices to generate data for the aging correlation should consider (1) calendar aging mode, (2) cycling aging mode, and (3) mixed aging modes. When designing a test matrix for calendar mode, we should include high, medium, low and sub-zero ambient temperatures, to generate data that could eventually represent SEI growth and formation (high temperature), and lithium plating (sub-zero temperature), a transition zone at low temperature, and normal temperature, closed to the expected working temperature during real-life storage. In our analysis, we observed that α is mostly dependent on SOC in calendar aging. For this reason, we recommend large SOC intervals, but with a fair representation (shorter SOC steps) of the

SOC transition zone between 55% and 70% average SOC. This increment of SOC and temperature ranges in the test matrix should overcome the challenges of representing the interaction of the stress factors. The number of tests and the number of cells to be tested should be prioritized for the stress conditions that promote the dominant degradation mechanisms, this means, high temperature (45 °C) and SOC (80 and 100%), and sub-zero temperatures at 80% SOC. Based on these considerations, we suggest performing a set of aging tests according to the test matrix included in Table 13.

A total of 14 tests are recommended for calendar aging. The duration of tests is variable, depending on the threshold fixed for finalizing the tests, and the degradation pace, which is affected by the operating conditions. Thus, longer test durations are expected at 25 °C; for this reason, we only included a fair degradation pace represented at 80% SOC mean. Cell-to-cell variation, although statistically challenging to account for, should be considered by including more cells in those tests whose conditions promote dominant degradation mechanisms, such as tests at 45°C and -15°C. When running tests, we also recommend periodic cell characterizations every 100 days, including electrochemical impedance spectroscopy (EIS), which is proven as an efficient aging diagnostic tool that could help to identify degradation modes^{44,45,46,47}. Finally, tests at sub-zero temperatures become optional in those geographies where these ambient temperatures are not expected.

In designing a test matrix for cycling mode, we should include high, medium, and low temperatures. Battery thermal management systems (BTMSs) are expected to keep the temperature between 15 – 40 °C to maximize the battery lifetime²⁶. Therefore, sub-zero temperatures or very high temperatures should be discarded. The dominant degradation mechanism, the SEI growth and formation, is promoted by high temperature, high SOC and high C-rate; while lithium plating is promoted at low temperature and high C-rate. Other relevant mechanisms to be considered during cycling include are (1) SEI fracture and

reformation, promoted at high temperature and high C-rates, and (2) electrode and particle fracture, promoted at high C-rate and large Δ DODs. As can be seen in Table 14, we have selected an ambient temperature range of 10 – 45 °C instead of 15 – 40 °C to reduce the duration of the tests. We recommend including more cells simultaneously tested at high C-rates, extreme temperatures, and high DODs, for the visualization of cell-to-cell variation. We have arbitrarily defined 1C as a low C-rate and 4C as a high C-rate. However, charge and discharge conditions depend on several factors such as the application, cell specification, and charging method. In any case, it is recommended to include tests at low and high C-rates. We also recommend, if required, extending the tests beyond the 20% capacity fade threshold that has been commonly used by researchers and manufactures as the end of life in EVs, to observe the expected shift from pseudo-linear to non-linear trend in second-life.

Finally, a mixed set of tests (cycling with rest periods) at high temperatures and high C-rates are also recommended, as indicated by Santhanagopalan et al.²⁷. We propose running a set of mixed cycling/resting experiments at 45 °C as per Table 13. Although the degradation in LIBs is a multi-dimensional and complicated process, the test matrix shown in Table 14 will reasonably cover the operational envelope of electrical applications running LIBs and would reproduce their dominant degradation mechanisms.

7.2 Model development

Once the data is collected, we recommend the following methodology for developing the DBM-AT.

Step 1: Trajectory equations of performance fade parameters.

Select the trajectory equations of the performance fade parameter for each test and aging mode, and find the best local regression model for each test. For calendar aging, we

recommend a trajectory equation of the capacity fade as per Equation 2, with α as a function of average SOC, avoiding potential shifting to a different order of reaction. For cycling aging, we could select linear trajectory equations for first-life, at least for SEI formation and growth, but other options should be considered for accelerating mechanisms such as lithium plating and break-in process. A set of trajectory equations for these accelerating mechanisms have been suggested by Santhanagopalan et al.²⁷. In any case, we recommend representing any cycling trajectory in terms of Ah-throughput or number of cycles, to account for Δ DOD and C-rate. Local regression models from trajectory equations should be rated using a suite of statistical metrics, instead of relying solely on individual p-values for the estimated coefficients, and should also be qualitatively assessed for consistency vis-à-vis the underlying physical phenomena.

Step 2: Kinetic model shape and fitting coefficients.

Develop a coupled model calendar-cycling. We propose estimating the kinetic constant as a function of the stress factors as per the baseline approach, using a multi-factor quadratic model fitted with ISRL. We demonstrated that this quadratic model is statistically significant for all chemistries. The quality of the fitting should be measured by (1) individual p-values of β coefficients, (2) global metrics such as F-statistics, p-value, and R^2 , and (3) the effect of sample size.

Step 3: Performance fade model regression.

A global performance fade model shall be developed by integrating terms for calendar aging as a function of time and cycling aging as a function of Ah-throughput or number of cycles.

The quality of the fitting should be studied using statistics metrics such as the overall F-statistics, p-value, and R^2 , as described in Step 2.

8. Conclusions

In this work we summarized the findings resulted from applying the aging calibration approach presented by Mathieu et al.³⁴ to four different capacity loss datasets: (i) data from combined calendar and cycling tests of LMO/NMC cells³⁵, referred to as Dataset I; (ii) data from calendar tests of NCA cells³⁶, referred to as Dataset II; (iii) data from calendar tests of NMC cells³⁶, referred to as Dataset III; and (iv) aging data from calendar tests of LFP cells³⁶, referred to as Dataset IV.

We carried out an EDA to summarize and compare the main characteristics of the datasets, inspecting the evolution of the relative capacity over time as a function of the stress factors. Compared to the baseline dataset, Dataset I included the effects of higher C-rates for cycling conditions and medium-to-high temperature range; therefore, the test matrix is designed to mostly promote SEI growth. Calendar Datasets II, III, and IV include a full range of SOC (0-100%) and medium-to-high temperature range. They reveal that the capacity loss does not increase steadily with SOC and that there is a transition zone where the cells exhibit the fastest capacity loss for all cell chemistries tested. NMC cells experienced more aggressive aging than NCA and LFP.

We explored the suitability of assuming an average α when fitting kinetic constants and time-dependent factor. Our analysis showed wide ranges of α for all datasets. We hypothesize that this variation can be attributed to several causes. The EDA allowed us to conclude that additional stress factors for cycling aging compared to calendar aging and extended ranges of stress factors influenced this variation, as well as chemistry-dependent differences. In addition, we performed a linear regression analysis to evaluate the strength of the correlation between α and the stress factors, demonstrating that this factor is strongly correlated with

SOC for all chemistries in calendar aging and also with C-rate in cycling aging. We also performed an exercise suggesting parametric degradation sub-trajectories, using different α average values per range of SOC and temperatures, to improve the representation of aging.

Although we demonstrated that α cannot be averaged per segregated or combined aging modes, we fitted the β coefficients of the full quadratic model (Equation 7) and reduced model (Equation 8) as per the baseline approach. The individual p-values of some of the β coefficients showed not to be significant, mistakenly suggesting the rejection of stress factors such as the linear or quadratic terms of the temperature reciprocal that are supported by the physics of LIBs. To improve our analysis, we added statistical metrics for the global aging model to evaluate its goodness-of-fit, such as R^2 , RSE, global p-value, and F-statistics. Furthermore, we evaluated how the sample size affects the value of the individual p-values, seen as a reduction of the p-values (1) for Dataset I when combining calendar and cycling modes, and (2) for calendar datasets II, III, and IV as a result of a cross-validation exercise.

We proposed a set of test matrices for aging correlation considering calendar aging mode, cycling aging mode, and mixed aging modes. In calendar mode, we extended the range of temperature to also include sub-zero temperature, and shorter SOC steps in the transition zone between 50 and 70% average SOC. Cell-to-cell variation should be considered by including more cells in those tests whose conditions promote dominant degradation mechanisms, such as tests at 45°C and -15°C. We also recommend periodic cell characterizations every 100 days, including EIS for further aging diagnostics. For cycling mode, we include an extended range to evaluate aging at higher C-rates and large Δ DODs. Finally, our mixed set of tests (cycling with rest periods) are recommended at high temperature and high C-rate.

We also proposed a methodology for developing DBM-ATs. This methodology includes three steps: (1) Select trajectory equations of the performance parameter; (2) develop a

coupled kinetic model using a multi-factor quadratic model, as per Equation 7, fitted with IRSL, evaluating the quality of the fitting; (3) develop a performance fade model integrating the terms of calendar and cycling modes.

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Tables

Table 1. Test matrix for the Baseline Dataset.³⁴ Each test is represented by a charge|discharge C-rate.

Temperature, °C	60				0 0		
	45	0 0	0 0	0 0	0 0		0 0
			3 ⁻¹ 3 ⁻¹			3 ⁻¹ 3 ⁻¹	
					3 ⁻¹ 1		
	25						
				3 ⁻¹ 3 ⁻¹			
			3 ⁻¹ 1			3 ⁻¹ 1	
			1 3 ⁻¹		1 3 ⁻¹		
	0			1 1			
			0 0		0 0		0 0
					3 ⁻¹ 3 ⁻¹		
			3 ⁻¹ 1	3 ⁻¹ 1			
	1 3 ⁻¹						
				1 1			
	0	30	65	80	90	100	
	Average SOC, %

Calendar tests

Cycling at 10% ΔDOD

* 3^{-1} is equivalent to 1/3C

Table 2. Test matrix for the Dataset I.³⁵ Each test is represented by a charge|discharge C-rate.

Temperature, °C	45		0 0				0 0		0 0
		2 2	2 2	2 2	2 2	2 2	2 2	2 2	
						4 4			
	35		0 0				0 0		0 0
		2 2	2 2		2 2	2 2			
			1 1			1 1			
		4 4			4 4				
	25		0 0				0 0		0 0
		2 2	2 2	2 2	2 2	2 2	2 2	2 2	
						1 1			
	5	15	25	45	65	75	85	90	
		Average SOC, %							

Calendar tests

Cycling at 10% Δ DOD

Table 3. k_c and α for Dataset I.

Stress factors			Independent α				Constant α	
T, °C	SOC, %	C-rate	$k_c \times 10^{-5}$	α	R ²	RSE	$k_{c-s} \times 10^{-5}$	$k_{c-c} \times 10^{-5}$
25	15	0	0.02	1.66	0.858	0.046	1.66	6.28
25	75	0	191.29	0.51	0.799	0.004	16.17	56.52
25	90	0	166.86	0.54	0.930	0.003	16.53	57.84
35	15	0	0.46	1.27	0.845	0.045	3.56	13.18
35	75	0	130.43	0.66	0.993	0.001	21.56	77.66
35	90	0	65.26	0.75	0.985	0.002	28.12	96.90
45	15	0	0.43	1.34	0.758	0.006	4.90	17.92
45	75	0	96.30	0.84	0.994	0.001	53.03	186.55
45	90	0	89.80	0.79	0.995	0.001	38.84	136.85
25	5	2	322.07	0.41	0.626	0.136	61.10	33.00
25	15	2	60.27	0.63	0.695	0.188	57.66	31.22
25	25	2	85.37	0.63	0.900	0.046	88.26	49.12
25	45	2	86.27	0.70	0.945	0.031	142.04	78.42
25	65	2	66.81	0.73	0.934	0.042	140.00	77.14
25	75	2	143.67	0.66	0.924	0.040	176.23	98.98
25	85	2	323.44	0.53	0.760	0.075	177.07	104.16
35	5	2	238.06	0.37	0.665	0.084	41.39	22.46
35	15	2	155.97	0.47	0.460	0.149	55.32	29.79
35	45	2	91.57	0.69	0.942	0.027	138.65	77.38
35	65	2	51.24	0.81	0.945	0.041	169.01	93.63
35	15	1	0.05	1.32	0.572	0.222	9.67	5.01
35	15	4	1990.98	0.23	0.536	0.033	149.67	83.01
35	65	4	479.64	0.59	0.889	0.027	388.62	231.16
35	65	1	10.27	0.89	0.982	0.015	71.33	37.11
45	5	2	206.83	0.42	0.709	0.035	47.80	25.62
45	15	2	62.33	0.60	0.673	0.083	48.47	25.98
45	25	2	129.37	0.54	0.699	0.061	74.77	39.88
45	45	2	120.12	0.67	0.961	0.018	158.27	87.74
45	65	2	61.39	0.84	0.963	0.029	221.68	129.21
45	75	2	124.65	0.73	0.956	0.015	236.42	136.24
45	85	2	252.38	0.65	0.954	0.007	282.44	167.70

Table 4. k_c and α for Dataset II.

Stress factors			Independent α			Constant α
T, °C	SOC; %	$k_c \times 10^{-5}$	α	R ²	RSE	$k_{c-s} \times 10^{-5}$
25	0	1.56	1.22	0.920	0.274	30.8
25	10	17.38	0.86	0.971	0.113	54.6
25	20	47.65	0.72	0.984	0.070	71.7
25	30	61.19	0.68	0.995	0.037	75.5
25	40	38.03	0.76	0.977	0.089	72.3
25	50	33.92	0.80	0.995	0.043	77.1
25	60	166.18	0.59	0.994	0.035	131.6
25	70	233.95	0.55	0.999	0.012	147.9
25	80	283.93	0.51	0.998	0.018	151.3
25	90	183.56	0.60	0.996	0.028	153.7
25	100	173.61	0.62	0.998	0.020	160.3
50	0	9.61	1.05	0.942	0.211	78.4
50	10	105.96	0.69	0.996	0.037	135.6
50	20	160.06	0.64	0.989	0.054	165.5
50	30	235.56	0.60	0.998	0.022	192.0
50	40	268.73	0.58	0.994	0.036	203.8
50	50	238.38	0.61	0.995	0.034	207.5
50	60	532.22	0.50	0.996	0.026	262.3
50	70	549.69	0.54	0.988	0.052	335.2
50	80	621.40	0.52	0.991	0.039	338.1
50	90	656.55	0.52	0.996	0.026	352.9
50	100	518.55	0.58	0.997	0.026	379.6

Table 5. k_c and α for Dataset III.

Stress factors			Independent α			Constant α
T, °C	SOC; %	$k_c \times 10^{-5}$	α	R ²	RSE	$k_{c-s} \times 10^{-5}$
25	0	6.91	0.87	0.970	0.092	15.5
25	10	25.74	0.75	0.966	0.108	30.4
25	20	35.38	0.72	0.982	0.074	35.9
25	30	52.91	0.68	0.983	0.068	44.2
25	40	69.44	0.64	0.972	0.082	46.8
25	50	44.94	0.72	0.975	0.089	46.8
25	60	50.50	0.72	0.992	0.050	52.3
25	70	375.47	0.47	0.969	0.065	110.7
25	80	370.01	0.48	0.978	0.055	110.9
25	90	249.50	0.55	0.982	0.057	109.2
25	100	101.62	0.74	0.992	0.052	113.1
50	0	8.96	1.01	0.996	0.051	39.3
50	10	25.32	0.96	0.995	0.052	88.8
50	20	54.53	0.87	0.998	0.035	116.6
50	30	98.85	0.81	0.996	0.040	161.7
50	40	150.31	0.77	0.997	0.031	194.5
50	50	114.09	0.82	0.992	0.055	192.2
50	60	147.53	0.78	0.998	0.029	204.1
50	70	530.37	0.59	0.996	0.030	282.3
50	80	379.83	0.68	0.997	0.026	318.5
50	90	333.26	0.71	0.997	0.030	306.8
50	100	185.39	0.87	0.992	0.059	407.0

Table 6. k_c and α for Dataset IV.

Stress factors			Independent α			Constant α
T, °C	SOC; %	$k_c \times 10^{-5}$	α	R ²	RSE	$k_{c-s} \times 10^{-5}$
25	0	1.28	1.06	0.929	0.242	10.6
25	10	0.30	1.56	0.985	0.162	29.2
25	20	18.62	0.87	0.996	0.047	59.6
25	30	62.74	0.70	0.997	0.030	86.5
25	40	77.86	0.67	1.000	0.005	93.6
25	50	63.38	0.71	0.997	0.035	91.6
25	60	77.27	0.68	0.999	0.018	97.6
25	70	137.17	0.59	0.985	0.060	109.7
25	80	324.71	0.53	0.990	0.044	199.3
25	90	327.17	0.53	0.994	0.033	195.1
25	100	90.61	0.75	0.997	0.033	166.2
50	0	30.66	1.00	0.988	0.090	186.6
50	10	266.15	0.62	0.998	0.021	251.4
50	20	430.83	0.55	1.000	0.005	290.1
50	30	423.70	0.58	0.999	0.014	328.8
50	40	652.33	0.52	0.996	0.027	386.8
50	50	566.80	0.56	0.999	0.012	393.4
50	60	593.92	0.54	0.999	0.011	386.5
50	70	657.86	0.52	0.998	0.018	384.6
50	80	1133.64	0.46	0.997	0.019	484.0
50	90	864.43	0.52	0.999	0.010	491.8
50	100	802.32	0.54	0.999	0.012	506.0

Table 7. Linear regression analysis for α correlation.

Dataset I					Dataset II		Dataset III		Dataset IV	
Cycling		Calendar			Calendar		Calendar		Calendar	
	Estimate	p-value	Estimate	p-value	Estimate	p-value	Estimate	p-value	Estimate	p-value
γ_T	0.00036	0.946	-0.00117	0.915	-0.00450	0.089	0.00335	0.166	-0.00355	0.033
γ_S	0.00327	0.043	-0.01033	0.008	-0.00360	<0.001	-0.00287	0.003	-0.00235	0.013
γ_I	-0.19721	0.005	-	-	-	-	-	-	-	-
Statistics										
R ²	0.453		0.717			0.448		0.272		0.361
RSE	0.195		0.258			0.149		0.168		0.231
F-stats	4.9 / 3.2		7.6 / 5.1			8.9 / 3.4		6.0 / 3.4		6.2 / 3.4
p-value	0.011		0.023			0.001		0.001		0.007

Table 8. Errors when comparing capacity loss after 500 days estimated with average α and re-fitted k_c , versus individual α and k_c per test

Stress factors		% Error		
T, °C	SOC, %	Dataset II	Dataset III	Dataset IV
25	0	1.47	1.12	0.40
25	10	0.79	2.04	3.45
25	20	0.43	3.22	1.18
25	30	0.23	3.02	0.52
25	40	0.50	2.63	0.30
25	50	0.88	2.83	0.63
25	60	0.44	7.67	0.38
25	70	0.68	6.48	0.18
25	80	1.29	6.44	1.45
25	90	0.47	6.34	1.14
25	100	0.26	4.16	1.31
50	0	2.54	2.07	6.53
50	10	0.64	1.92	0.15
50	20	0.16	2.30	1.74
50	30	0.31	1.46	1.21
50	40	0.92	0.72	3.71
50	50	0.38	1.12	1.80
50	60	2.17	4.64	3.06
50	70	2.24	11.03	3.40
50	80	2.46	4.04	6.14
50	90	2.34	3.79	3.88
50	100	1.09	2.45	3.38

Table 9. Fitting of β Coefficients (standardized) with the quadratic model, comparison between baseline dataset and Dataset I.

	Calendar				Cycling				Combined Calendar and Cycling			
	Baseline Dataset		Dataset I		Baseline Dataset		Dataset I		Baseline Dataset		Dataset I	
	Est.	p-value	Est.	p-value	Est.	p-value	Est.	p-value	Est.	p-value	Est.	p-value
β_0	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000
β_T	-10.3	0.007	-0.9	0.877	-22.4	0.017	-3.4	0.608	-14.5	< 0.001	-16.2	0.044
β_S	2.8	0.010	2.0	0.352	0.06	0.978	6.8	0.003	1.9	0.039	4.9	0.077
β_C	-	-	-	-	2.3	0.458	2.1	< 0.001	-0.4	0.794	-7.1	0.036
β_D	-	-	-	-	-2.7	0.245	-	-	-2.2	0.093	-	-
β_{TS}	-1.3	0.128	0.8	0.683	-1.2	0.722	-5.1	0.015	-0.2	0.818	-3.2	0.240
β_{TC}	-	-	-	-	-2.5	0.471	-	-	0.9	0.499	7.7	0.025
β_{TD}	-	-	-	-	2.4	0.272	-	-	2.7	0.037	-	-
β_{SC}	-	-	-	-	0.6	0.286	-0.4	0.052	-0.08	0.633	-0.4	0.014
β_{SD}	-	-	-	-	0.7	0.257	-	-	-0.07	0.719	-	-
β_{CD}	-	-	-	-	0.2	0.754	-1.4	< 0.001	-0.2	0.128	0.3	0.149
β_{TT}	9.7	0.009	0.4	0.937	21.9	0.017	3.6	0.591	1.4	< 0.001	15.7	0.047
β_{SS}	-1.1	0.004	-2.0	0.015	0.8	0.564	-0.6	0.021	-1.2	< 0.001	-0.7	0.082
Statistics												
R^2	0.994		0.993		0.977		0.969		0.970		0.901	
RSE	0.121		0.136		0.343		0.222		0.240		0.368	
F-stats	122.7 / 6.3		86.6 / 9.0		10.4 / 8.7		51.5 / 2.8		35.2 / 2.6		22.4 / 2.4	
p-value	0.0002		0.002		0.04		< 1 x 10 ⁻⁷		< 1 x 10 ⁻⁷		< 1 x 10 ⁻⁷	

Table 10 Fitting of β Coefficients (standardized) with the reduced model, comparison between baseline dataset and Dataset I

	Calendar				Cycling				Combined Calendar and Cycling			
	Baseline Dataset		Dataset I		Baseline Dataset		Dataset I		Baseline Dataset		Dataset I	
	Est.	p-value	Est.	p-value	Est.	p-value	Est.	p-value	Est.	p-value	Est.	p-value
β_0	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000
β_T	-11.1	0.007	-0.8	0.866	-22.4	0.001	-21.9	0.025	-13.5	< 0.001	-10.3	0.225
β_S	1.7	< 0.001	2.8	0.001	0.6	0.420	1.3	0.005	1.7	< 0.001	1.1	0.016
β_C	-	-	-	-	0.2	0.890	0.6	< 0.001	-1.0	0.413	-8.0	0.038
β_D	-	-	-	-	-3.0	0.082	-	-	-2.1	0.088	-	-
β_{TC}	-	-	-	-	0.2	0.911	-	-	1.3	0.272	8.4	0.029
β_{TD}	-	-	-	-	3.4	0.057	-	-	2.4	0.048	-	-
β_{TT}	10.3	0.009	0.4	0.930	21.3	0.001	21.8	0.030	12.6	< 0.001	9.8	0.245
β_{SS}	-1.2	0.001	-2.0	0.005	-0.2	0.785	-0.6	0.170	-1.3	< 0.001	-0.2	0.602
Statistics												
R^2	0.989		0.993		0.953		0.891		0.959		0.852	
RSE	0.150		0.121		0.316		0.379		0.245		0.431	
F-stats	99.5 / 5.2		135.1 / 6.4		17.9 / 3.7		26.1 / 2.9		49.3 / 2.6		23.0 / 2.5	
p-value	0.00006		0.0002		0.0005		< 1 x 10 ⁻⁷		< 1 x 10 ⁻⁷		< 1 x 10 ⁻⁷	

Table 11. Fitting of β Coefficients (standardized) for calendar aging with the quadratic model for all chemistries.

	Dataset I (LMO/NMC)		Dataset II (NCA)		Dataset III (NMC)		Dataset IV (LFP)	
	Estimate	p-value	Estimate	p-value	Estimate	p-value	Estimate	p-value
β_0	0.0	1.000	0.0	1.000	0.0	1.000	0.0	1.000
β_T	-2.9	0.877	16.7	0.024	18.8	0.020	16.7	0.057
β_S	2.0	0.352	0.3	0.790	1.3	0.343	-5.1	0.002
β_{TS}	0.8	0.683	0.9	0.478	-0.1	0.937	6.3	< 0.001
β_{TT}	0.4	0.937	-17.7	0.020	-19.5	0.017	-17.8	0.043
β_{SS}	-2.0	0.015	-0.5	0.008	-0.5	0.015	-0.7	0.005
R^2	0.993		0.961		0.956		0.945	
RSE	0.159		0.222		0.237		0.263	
F-stats	86.6 / 9.0		93.6 / 2.7		81.5 / 2.7		65.6 / 2.7	
p-value	0.002		< 1 x 10 ⁻⁷		< 1 x 10 ⁻⁷		< 1 x 10 ⁻⁷	

Table 12. Fitting of β Coefficients (standardized) for calendar aging with the reduced model for all chemistries.

	Dataset I (LMO/NMC)		Dataset II (NCA)		Dataset III (NMC)		Dataset IV (LFP)	
	Estimate	p-value	Estimate	p-value	Estimate	p-value	Estimate	p-value
β_0	0	1.000	0	1.000	0.000	1.000	0	1.000
β_T	-0.8	0.866	17.0	0.022	18.8	0.017	17.1	0.151
β_S	2.8	0.001	1.2	< 0.001	1.2	< 0.001	1.1	0.001
β_{TT}	0.4	0.930	-17.7	0.018	-19.5	0.014	-17.8	0.134
β_{SS}	-2.0	0.005	-0.5	0.007	-0.5	0.013	-0.7	0.032
R^2	0.993		0.960		0.955		0.888	
RSE	0.121		0.219		0.231		0.365	
F-stats	135.1 / 6.4		119.7 / 2.9		107.2 / 2.9		40.0 / 2.9	
p-value	0.0002		< 1 x 10 ⁻⁷		< 1 x 10 ⁻⁷		< 1 x 10 ⁻⁷	

Table 13. Recommended test matrix for calendar and cycling tests. Each test is represented by a charge|discharge C-rate.

Temperature, C	45	0 0	0 0	0 0	0 0	0 0	0 0		0 0
							1 1 4 4*	1 1 4 4*	1 1 4 4*
	25						0 0 1 1 4 4		1 1 4 4
	10						4 4	4 4	1 1 4 4
	0		0 0		0 0		0 0		
	-15		0 0		0 0		0 0		
		0	30	55	60	65	80	85	100
		Maximum SOC, %

Calendar tests

Cycling at 20% ΔDOD

Cycling at 50% ΔDOD

Cycling at 100% ΔDOD

* Tests repeated at 50% and 80% duty cycle (charge/discharge)

Figures

Fig. 1. Evolution of the capacity at 35 °C and 15% average SOC for cycling aging data (Dataset I³⁵) at different C-rates: (a) 1C, (b) 2C, (c) 4C. Solid lines are fitted with k_c and α as free fitting parameters, and dashed lines with k_c as the only fitted parameter and α as averaged value.

Fig. 2. Evolution of the capacity at 35 °C for calendar aging data (Dataset I³⁵) at SOC levels: (a) 15%, (b) 75% and (c) 90%. Solid lines are fitted with k_c and α as free fitting parameters, and dashed lines with k_c as the only fitted parameter and α as averaged value.

Fig. 3 Capacity loss of three different chemistries (NCA, NMC, and LFP) at 50 °C and 300 days for different SOC_s³⁶

Fig. 4. P-values of β_T versus the number of samples for dataset III (NMC)

Fig. 5. P-values of β_S versus the number of samples for dataset III (NMC)

Fig. 6. P-values of β_{TT} versus the number of samples for dataset III (NMC)

Fig. 7 P-values of β_{SS} versus the number of samples for dataset III (NMC)