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Pedro V. H. Seger, Pierre-Xavier Thivel, Delphine Riu. A second life Li-ion battery ageing model with uncertainties: From cell to pack analysis. *Journal of Power Sources*, 2022, 541, 10.1016/j.jpowsour.2022.231663 . hal-04051083

**HAL Id: hal-04051083**

**<https://hal.science/hal-04051083>**

Submitted on 22 Jul 2024

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# A Second Life Li-Ion Battery Ageing Model with Uncertainties: from Cell to Pack Analysis

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## Abstract

The increasing availability of Second Life Li-ion Batteries (SLBs) makes so that accurate ageing modeling can be a powerful tool to estimate the impact of a certain utilisation profile. However, several stress factors can impact the ageing, and uncertainties are an important issue for the second life, due to the sometimes unknown first life utilisation and the natural variability of electrochemical devices. In this work, we propose an empirical, event-based model for the second life of li-ion cells. Its parameterization is supported by real data of **Li-NMC (Lithium Nickel Manganese Cobalt oxides)** cells and considers cycling ageing with three stress factors: current, cycle depth and mean State of Charge (SoC). The model takes uncertainties in consideration, and we provide all the parameters in Open Data fashion. This simple model can be easily implemented and coupled to cycle counting algorithms in order to predict a lifetime range for a given SoC profile. Finally, we analyse the effect of individual cell uncertainties and their impact on a battery pack. Simulation results show that the model is able to properly simulate the second life duration when compared to practical results available in the literature.

*Keywords:* Second Life Battery, Li-Ion, Ageing Model, Cyclic ageing, Event based, Uncertainty

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## 1. Introduction

The increased demand of Li-ion Batteries (LIBs) observed on the last decade is expected to continue expanding for many years, mainly due to the growth of the Electric Vehicle (EV) fleets all over the world. This implies an estimated availability of several **gigawatt-hours (GWh)** per year in Second Life li-ion Batteries (SLBs) in the future [1].

The significant environmental impact of the manufac-

turing and recycling of LIBs is a motivating factor for their reuse [2]. This opens up the way for a second life of these cells in less demanding stationary applications, such as ancillary services associated to renewable energy sources and charging stations [2, 3].

Proper modeling of the ageing of these batteries can be an important tool for engineers, either for online estimation of their State of Health (SoH) or for analysis and prognostic related to a certain application.

Accurate modeling of the capacity loss is, however, a daunting task. The ageing of a battery is a function of several external stress factors, such as the current and cycle depth. Moreover, LIBs are electrochemical devices, so

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uncertainties associated to their ageing can play an important role - specially during their second life.

### 1.1. Ageing modeling

Regarding the modeling of the capacity loss of LIBs, distinct approaches are identified in the literature - a detailed review is available in [4].

One possible technique is the *electrochemical* and/or *physical* modeling, where detailed equations are used to model phenomena related to the mechanical and/or chemical degradation. Works such as [5–8] are good examples of this approach. The main drawbacks of such models are the related to their complex nature: difficulties to parameterize, to consider the uncertainties and to implement them programmatically.

Another common approach is the *statistical* modeling, such as presented in [9–11]. This approach is based on data, with the utilisation of statistical methods and the development of models capable of predicting the capacity loss. These models can be adaptive and online, correcting their prediction as the ageing takes place. The main drawback of this technique is that they are limited by their own data, risking to under-perform if the real utilisation of the batteries is different than expected.

The *empirical* or *analytical* approach consists of models where the equations and parameters are found through empirical fitting of observed data. This is the case in works such as [12–15]. This method is limited by the complex ageing nature of LIBs: finding an equation or a set of equations able to consider several stress factors is a daunting task, requiring a significant amount of data.

The capacity loss of LIBs is usually characterised by a fast degradation starting at a SoH of around 80%, the so-called *ageing knee*, and a slower degradation when the cell is deeply aged - this is visible in the experimental data of

[12]. Empirical models usually rely on exponential and/or polynomial equations to represent this behaviour.

However, ageing models considering specifically the second life are, to the extent of our knowledge, underdeveloped in the literature. As the model presented in this work concentrates on the second life (i.e. a SoH between 80% and 50%), we believe a simple exponential can provide an adequate representation - this is explained in detail in Subsec. 3.2

### 1.2. Ageing stress factors

Several stress factors have been identified in the literature for the ageing of LIBs [5, 13–21]. Regarding cyclic ageing, the main ones are the cycle depth, the current, the mean SoC and the temperature. For calendar ageing, the stress factors usually considered are the time, the temperature and the storage SoC.

The *cycle depth*, hereby called  $\Delta SoC$ , can be defined as the range between the initial and final SoC of a charge or discharge segment. This variable is also known as  $\Delta DoD$  in the literature. A larger cycle depth is more detrimental to the lifetime of the battery, as the chemical volume changes during cycling are increased, causing a loss of active material [20, 22].

The *current* or *C-rate* is a well known source of stress for batteries, and a main role of any Battery Management System (BMS) is to monitor this variable. Usually, the higher the current, the more the capacity loss is accelerated due to increased Solid Electrolyte Interphase (SEI) growth and electrode cracking [23, 24]. This is a known problem of the so-called *fast charge* of LIBs [25, 26]. Furthermore, high currents induce higher losses due to the internal resistance of the cell, also impacting its temperature.

The *mean SoC* or  $SoC_m$  in which the cell is cycled is another important factor that plays on cycle ageing: for example, a cycle with a  $\Delta SoC = 20\%$  around a  $SoC_m = 90\%$  impacts the ageing more than around a  $SoC_m = 50\%$ ; this is well documented in the literature [17, 18].

The *temperature* is well described in the literature as a stress factor for both cyclic and calendar ageing. High temperatures induce SEI growth and decomposition reactions in the electrolyte, SEI and binder [22, 23] - all these induce a loss of lithium inventory, reducing the capacity of the cell. Low temperatures induce lithium plating and dendrite formation, causing a loss of active material [20, 23]. Continuous cycling at a given temperature plays a major role in the dominant ageing mechanism [27].

The *time* and the *storage SoC* also play an important role on calendar ageing. Time is usually correlated with the SEI growth and modeled with a square root relation [23, 24, 28]. Storage at high or low values of SoC is a source of degradation due to loss of active material and lithium on both electrodes, as shown in [17, 20, 23].

### 1.3. Uncertainties related to LIBs

The uncertainty related to the ageing rate of LIBs is often visible in works that present experimental results of several cells. Even though most works concentrate on first life ageing, some interesting literature showcase the importance of considering the ageing variability.

Baumhöfer et al (2014) [29] present ageing data from 48 identical cells cycled under the same conditions, showing how the capacity deviation from mean increases as the cell ages. It is visible in their data how this deviation is specially significant on the second life. The same data set is later used in [12] to propose a long-term ageing model.

In [30], 96 cells connected in series are aged and the individual capacity of each cell is presented. The fact that

the weakest cell limits the entire pack is visible in their results. In [31], the voltage dispersion of cells coming from eight different packs is studied.

The utilisation of empirical data to parameterize LIB uncertainties is a common approach when there is enough data, with the main advantages being the reliability of real-life experimentation and the flexibility of the approach. One example is found in [30], where the authors use data from over 20000 cells to parameterise a distribution of the cell capacity at the beginning of their lives. This is then used on the proposed ageing models.

Other works focus on the impact of the cell uncertainties in a battery pack. In [32], a statistical method is used to detect cells with shorter lifetime, whereas [33] shows the importance of considering cell imbalances when estimating the behaviour of a pack.

Moreover, as this work focuses on the second life, another uncertainty is also important: the SoH at the beginning of the second life utilisation. In real life applications, where batteries are retrieved for a second life, it is clear that they will not all be at the same SoH: not only can SLBs come from different sources (thus different first lives), but also cells coming from the same source can have an ageing variability as shown in [29].

### 1.4. Article objective and structure

The objective of this work is to propose a simple yet accurate model for cyclic ageing of second life batteries, including cell-level ageing uncertainties.

This model is intended as a prognostic tool, suited for offline analysis of second life applications. We also propose a straightforward way to model the ageing uncertainties. The goal of the model is to be a feasibility analysis tool, allowing for an estimation of the lifetime range for any SoC profile.

The main characteristics of our model are:

1. A classic exponential-based modeling of capacity loss.
2. Consideration of three stress factors: cycle depth, mean SoC and current value.
3. Parameterization based on experimental data and made available in open data fashion.
4. Modeling of two types of uncertainty (initial SoH value and rate of ageing).
5. Simple software implementation.
6. Easily coupling to cycle counting algorithms to estimate a lifetime for any given SoC profile.

We believe this work bridges two important gaps on the literature: the modeling of second life ageing and the consideration of uncertainties on the capacity loss.

We understand that these contributions can be valuable for anyone studying second life applications, the impact of the utilisation on the lifetime of the batteries and the effect of cell uncertainties on a pack.

This work is organized as follows: Sec. 2 presents the methodology used in this work. Sec. 3 explains in detail the modeling approach and identified parameters, Sec. 4 shows the results of our model both in cell and pack level, and finally Sec. 5 concludes this work.

## 2. Methodology

### 2.1. Formal Definitions

The following paragraphs define some key concepts and abbreviations used in this work.

The *State of Charge* - SoC is the instantaneous amount of charge  $Q$  of the cell divided by its actual capacity  $Q_a$ , as shown in Eq. 1. Using this convention, the SoC values are always between 0 and 100 %.

$$SoC[\%] = \frac{Q}{Q_a} \cdot 100 \quad (1)$$

The *State of Health* - SoH is the actual capacity  $Q_a$  of the cell divided by its nominal capacity  $Q_n$ , as shown in Eq. 2. We assume the common definition that the *Second Life* of a LIB begins around a *SoH* of 80 %.

$$SoH[\%] = \frac{Q_a}{Q_n} \cdot 100 \quad (2)$$

We consider that, in a given SoC profile, a *cycle* can be defined by three parameters: the depth  $\Delta SoC$ , the mean value  $SoC_m$  and its current C-rate (which is the slope of the SoC).

The *C-Rate* is defined by the electric current going through the battery divided by its nominal value. A C-rate of 1C represents a charge at the nominal current, whereas  $-C/2$  represent a discharge at half the nominal current.

### 2.2. Initial assumptions

The model developed in this work concentrates on the cyclic ageing, with three stress factors as an input: the cycle depth, the mean SoC and the C-rate. More specifically, we use data from Li-NMC cells (Lithium Nickel Manganese Cobalt oxides).

An important assumption is that our model is *event-based*, meaning that the total ageing is considered to be caused by several events, each one with a small capacity loss associated. In our case, the events are the cycles that the battery go through during its life. As described in [34], this incurs some assumptions, notably: that the capacity loss of each cycle is small, and that it is not directly dependant of the previous cycles.

Another choice in this work is that we do not consider the calendar ageing. Usually, if a cell is stored in adequate conditions, the calendar ageing is a long-term effect,

sometimes even reversible [35]. We consider that the utilisation of second life batteries implies a short to medium term application, where the calendar effect would not play a major role when compared to the cyclic ageing.

Finally, we choose not to consider the temperature as a stress factor, even though it is a well known source of ageing. Considering the temperature would require another layer of modeling and parameterization, as it is closely related to other stress factors such as the current and the cycle characteristics.

The temperature of a cell is also a function of its shape and physical properties, e.g. how the cells are arranged in a pack, air flow, etc. A thermal model would be needed to properly consider this.

Moreover, the objective of our model is to be a tool of analysis of SoC profiles when coupled to a cycle counting algorithm such as the Rainflow method. The temperature of each cell would be an extra input that is often not available on real data.

Furthermore, we consider that second life applications will normally operate in conditions that do not induce strong heat in the batteries - for example, avoiding high currents or high depths of discharge seems to be reasonable practical choices.

### 2.3. Modeling methodology

One of the most important challenges of any ageing model is to correctly evaluate the impact of several possible combinations of stress factors (the inputs) on the capacity loss (the output).

As previously discussed in Subsec. 1.2, several published studies concentrate on the impact of stress factors on cyclic ageing. However, it is uncommon to find results of an extensive testing considering all the factors and the relation between them.

This is due to the increased number of tests that would be needed to consider all possible cases - a monumental work would be needed to test all possible conditions of cyclic ageing. Moreover, ageing results available in the literature concentrate mainly on the first life, and there are few works with data on second life ageing.

In this work, our modeling and parameterization are based on an approach that considers our own experimental data, but also the results of selected works from other researchers. The steps to do so are the following:

1. We depart from experimental data of cyclic ageing of several cells during the second life, previously presented in [27, 36]. The characteristics of these cells are shown in Table 1. All these cells were cycled with the same profile: a C-rate of  $\pm C/2$ , a  $\Delta SoC$  of 100% and a temperature of 25 °C - we consider these to be the *standard conditions* of our model. We use these results to find the *standard model* and its parameters; this is done with well known curve-fitting techniques.
2. We observe that, in our experimental data, there are two types of uncertainty: the initial SoH value and the behaviour throughout the second life (faster or slower ageing). We compare our data with other publicly available results, then we model and parameterize the uncertainties for our *standard conditions*
3. We find works in the literature that have cycled Li-ion batteries (of similar technology as ours) in the same *standard conditions*, but also on other conditions. For example, we select a work that has cycled NMC cells at a C-rate of  $C/2$  and at other values of current [24]. This gives us an idea of the *relative* impact of these conditions on the standard model developed on step 1.

4. We carefully select and treat this data from other works to parameterize a *relative ageing term* that impacts our standard model. This term is responsible for making the ageing tendency slower or faster depending on the stress factors (inputs).

The details of these steps are explained in Sec. 3.

Table 1: Investigated cell characteristics

<b>Cell Format</b>	18650
<b>Positive Electrode</b>	NMC + LMO (Lithium Nickel Manganese Cobalt Oxide + Lithium Manganese Oxide)
<b>Specific Capacity</b>	158.5 mAh g <sup>-1</sup>
<b>Negative Electrode</b>	Graphite
<b>Specific Capacity</b>	309 mAh g <sup>-1</sup>
<b>Cell Capacity</b>	2.15 Ah (nominal), 1.72 Ah at SoH = 80%
<b>Nominal Voltage</b>	3.65 V

Once the model is fully parameterized, we perform several simulations of second life ageing, considering multiple cells and various conditions. We compare these results to practical ageing results available in the literature in order to validate our model.

We also study the impact of individual cell uncertainties on a pack: this is done by considering that the weakest cell limits the total capacity of the pack. We perform Monte Carlo simulations with different pack sizes in order to assess how the uncertainties spread from the cells to limit the total expected lifetime of the pack.

### 3. Ageing Modeling

The capacity loss model proposed in this article is shown in Eq. 3 below.

$$Q_{loss} = a e^{\sigma b \varepsilon Q_c} - c \quad (3)$$

Where:

- The capacity loss  $Q_{loss}$  used in this work is specific to the second life: a value of  $Q_{loss} = 0$  represents a cell at a SoH of 80%.
- $Q_c$  is the cumulative cycled capacity of the cell: it is the abscissa of our model.
- $a, b$  are parameters from our standard model, calculated from a fit of experimental data from previous works [27, 36].
- $\sigma$  is a *relative ageing term*, a function of our cycling stress factors: the  $\Delta SoC$ ,  $SoC_m$  and the C-rate.
- $c, \varepsilon$  are parameters used to model the uncertainties.

The meaning, hypothesis and parameterization methodology of each one of these parameters will be detailed in the subsections below.

#### 3.1. Cumulative cycled capacity $Q_c$

Several battery ageing models available in the literature are a function of the number of cycles that the cell went through. We believe this is not an ideal choice for the abscissa of an ageing model, specially on second life, as the definition of a cycle is limited: as the cell ages, a cycle of a given SoC depth  $\Delta SoC$  implies less and less energy cycled.

Various authors use the notion of Full Equivalent Cycles (FEC) to counter this limitation, where the total amount of ampere-hours cycled by the battery is divided by the initial capacity. This is an easy way to represent the lifetime of the cell, but it does not represent the fact that the actual energy throughput in a cycle gets smaller as the cell loses capacity.

In this work, we choose the abscissa of our model to be simply the cumulative cycled capacity  $Q_c$  of the battery, or the total amount of ampere-hours cycled. This choice

has the advantage of being simple to comprehend and implement in real life. Moreover, it can easily be transformed into Full Equivalent Cycles.

### 3.2. Standard model and parameters $a$ , $b$

The experimental data we use to model and parameterize the standard model comes from the cycling of several cells during their second life. These results have originally been published in [27], where a study of the chemical impact of the cell conditions was shown. A dynamic model for the second life has also been proposed based on this data [36].

As described in these previous works, the cells underwent cycling conditions at a C-rate of  $\pm C/2$ , a  $\Delta SoC$  of 100% and a temperature of 25 °C, with a check-up characterisation cycle performed at every 50 cycles to assess the capacity of the cell.

Some of the cells had their first life at a temperature of 0 °C and others of 25 °C. In this work, we ignore their first life condition in the ageing model, as we make the hypothesis that the first life conditions might be unknown in real life applications. Moreover, the uncertainty terms can be used to represent a cell that has a degraded second life due to a stressful first life operation.

Five of these cells have been selected for the ageing model proposed in this work. By performing curve-fitting to the capacity loss curve of each cell, we notice that a simple exponential model is sufficient to adequately represent their behaviour. We then average the fit of each cell in order to obtain the parameters  $a$ ,  $b$  of our model, available in Table 2.

Figure 1 show the ageing curves of each of the cells, as well as the average fit obtained and an uncertainty range representing two standards deviations (more details about the uncertainties in Subsec. 3.4).

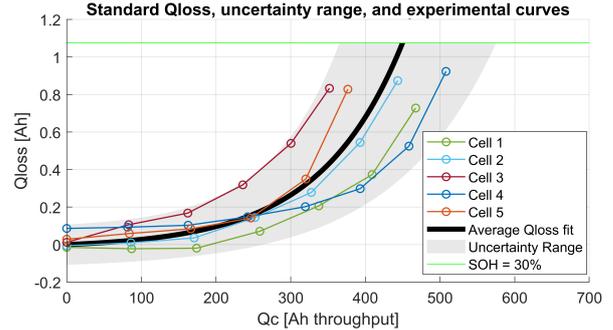


Figure 1: Experimental curves, average fit and uncertainty range

As previously discussed in Sec. 1.1, double exponential models are often used to model LIBs capacity loss. We believe that a single exponential is adequate for our model, as the second life is often characterised by the so-called *ageing knee* [12], i.e. a faster tendency to lose capacity.

Moreover, our choice for a simple exponential model is explained by the behaviour of our data and the focus of this work in the second life. However, we believe the same method - the idea of using variables  $\sigma, \varepsilon$  to expand and compress the exponential term - could be used for double exponential models.

The exponential described in Eq. 3 along with parameters  $a, b$  consist what we call the *standard model*. All the other parameters of the model are supposed to modify the standard model, making the lifetime loss faster or slower, or adding uncertainties.

### 3.3. Relative Ageing Term $\sigma$

The  $\sigma$  function in our model represents the impact of the stress factors on the ageing. Cycling the battery in stressful conditions (such as with a high current or a large cycle depth) should yield bigger values of  $\sigma$ , meaning that the exponential capacity loss of Eq. 3 will be faster.

As previously mentioned, the stress factors that we retain for the second life are the cycle depth  $\Delta SoC$ , the mean state of charge  $SoC_m$  and the current (C-rate). The

$\sigma$  term is then, naturally, a function of these three factors, as shown in Eq. 4 below.

$$\sigma = \gamma(\Delta SoC, SoC_m) \cdot \delta(C_{rate}) \quad (4)$$

The detail of these two functions and their associated parameters will be discussed below.

### 3.3.1. $\gamma$ , a function of $\Delta SoC$ and $SoC_m$

The impact of the cycle depth on ageing is usually represented by the so-called Wöhler curves [34, 37], where the expected number of equivalent cycles is plotted as a function of the cycle depth  $\Delta SoC$ . Some manufacturers test their cells and make this information publicly available on the datasheets, however that is not always the case.

The objective of the  $\gamma$  function is, then, to establish a weight to each possible pair of  $\Delta SoC$ ,  $SoC_m$ . This function is naturally limited by the following relation:

$$SoC_m \pm \frac{\Delta SoC}{2} \in [0 \ 100]\% \quad (5)$$

Meaning that the combination of these two inputs must be contained in a SoC between 0 and 100% - for example, a cycle with a  $\Delta SoC = 100\%$  is only possible around a mean SoC of  $SoC_m = 50\%$ .

In order to model and parameterize this function, we select the work from Ecker et al. (2014) [17], in which NMC cells similar to ours were tested in different conditions of  $\Delta SoC$  and  $SoC_m$  during the first life of the cells.

We make the observation that a  $\Delta SoC$  of 100% is the worst possible case for the ageing of a battery. The  $\gamma$  function is built so that a value of 1 is attributed to this condition, and all other possible  $\Delta SoC$ ,  $SoC_m$  combinations yield a value between 0 and 1.

In order to adapt the data from Ecker et al. (2014) to our desired function, we make the hypothesis that the

relative ageing between two conditions remain the same in the second life.

For example, let us consider that a cell (a) cycled at  $\Delta SoC = 100\%$ ,  $SoC_m = 50\%$  lasted 500 cycles on the first life, and a cell (b) cycled at  $\Delta SoC = 50\%$ ,  $SoC_m = 50\%$  lasted 1000 equivalent cycles at the same C-rate. We suppose that cell (b) would also last twice as long on the second life - this relation is true if an exponential is chosen to model the capacity loss. The  $\gamma$  function would, then, return a value of 1 for the conditions of cell (a), and a value of 0.5 for the conditions of cell (b). This would effectively make cell (b) capacity loss be two times slower in our model.

We use this approach to normalize the cycling results of this experimental data set, then we fit a function that approximates the observed behaviour. This results in Eq. 6 below:

$$\gamma = r_1 \cdot (SoC_m\%)^2 + r_2 \cdot SoC_m\% + r_3 + \frac{\Delta SoC\%}{100} \quad (6)$$

Where parameters  $r_1, r_2, r_3$  are available on Table 2.

The resulting fit of the  $\gamma$  function is visible on Fig. 2 below, as well as the experimental points calculated from the data of Ecker et al. (2014) [17].

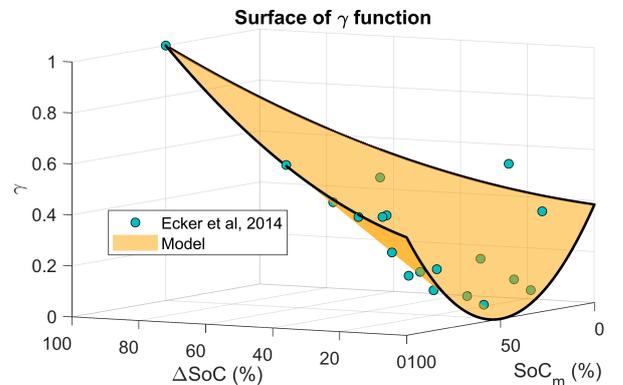


Figure 2: Experimental points identified from Ecker et al. (2014) [17] and surface of the proposed gamma function

The chosen  $\gamma$  function shows a  $1/\Delta SoC$  behaviour as observed in [17]. In the  $SoC_m$  axis, we observe that a parabola represents a good fit of the experimental data; its parameters are limited so that the axis of symmetry (lowest point) is around  $SoC_m = 50\%$ . This parabolic relation is also observed in [18].

The choices explained above for the fitting of this curve are made so that a physical relation is observed: that the capacity loss induced by a cycle is intensified the bigger its value of  $\Delta SoC$  is and the farther away from  $SoC_m = 50\%$ .

Nonetheless, error calculations between our  $\gamma$  function and the experimental points deduced from Ecker et al. (2014) show that our fit is representative of the reality. We obtain a Mean Absolute Error (MAE) of 0.056 and a Root Mean Square Error (RMSE) of 0.070.

As the values of  $\gamma$  are contained between 0 and 1, these metrics can be understood as a  $MAE\%$  of 5.6% and a  $RMSE\%$  of 7%. We consider these values to be acceptable as (a) the objective of the fit is to capture a physical relation, not the most precise passage between the points and (b) the experimental nature of the data from Ecker et al. (2014), which is uncertain by nature.

### 3.3.2. $\delta$ , a function of the current rate

For the modeling and parameterization of the current effect, we select the work of Wang et al. (2014) [24], where NMC cells similar to ours were cycled at different values of current, cycle depth and temperature.

In this work, the authors notice that the rate of capacity loss has a near-exponential behaviour with the increase of the C-rate. We consider that their model equation for a temperature of  $20^\circ\text{C}$  (near ambient temperature) is the one closer to our own results. This relation is shown in Eq. 7 below.

$$\delta = \alpha \cdot e^{\beta \cdot |C_{rate}|} \quad (7)$$

Where  $\alpha$  and  $\beta$  are parameters identified and available on Table 2. We also choose to consider the absolute value of the C-rate, meaning that we make the hypothesis that the impact of the C-rate on ageing is the same for both charge and discharge of the battery.

In order to find these parameters, we adapt their equation using the same approach previously described for the  $\gamma$  function. This means that the  $\delta$  function yields a value of 1 for a C-rate of C/2 (our standard conditions). Higher values of current should return values bigger than one, thus making our capacity loss function *faster*, and smaller values of current should return values smaller than one.

### 3.4. Uncertainties modeling - parameters $c, \varepsilon$

When analysing experimental data of several cells cycled in the same conditions [27, 29], two types of ageing uncertainties are visible: the initial capacity and the ageing trend.

The initial capacity uncertainty refers to the variability of the capacity when the cell is obtained. This is true even for cells fresh out of the industry: some have a capacity slightly higher or lower than the nominal expected value. As this work concentrates on the second life, this uncertainty is even more important: the batteries recuperated for these applications might have had very different first lives, and will certainly not always be at a SoH of precisely 80%.

In this work, we model the initial capacity uncertainty through the parameter  $c$ , as shown in Eq. 3. If the value of  $c$  is equal to the value of parameter  $a$ , the cell starts the second life precisely at a SoH of 80%, or a capacity of 1.72 Ah.

The parameter  $\varepsilon$  works similarly as the  $\sigma$  function, in that a value of 1 represents no uncertainty, and values bigger or smaller represent faster or slower ageing, respectively.

For practical purposes, the values of  $c, \varepsilon$  should be defined at the beginning of a simulation (c.f. Appendix A). This means that the cell will have its initial capacity *and* its ageing trend fixed. The interest in using these two variables is to simulate several cells, each one with a different ageing behaviour.

We propose, then, that probability distributions should be used to attribute values to  $c$  and  $\varepsilon$ . Regarding  $c$ , our data analysis indicates that an adequate representation is attained with a normal law with a **Mean ( $\mu$ )** at  $c = a = 0.0190Ah$  and a **Standard Deviation (SD)** of  $\frac{5}{3} \cdot \frac{2.15}{100} = 0.0358Ah$ . This translates to a law centered at a SoH of 80% and with three standard deviations spanning the interval  $SoH \in (75 \text{ } 85) \%$ . A cell with  $c > a$  represents, in our model, a  $Q_{loss} < 0$  at the beginning of a simulation - this means simply a cell starting their second life at a SoH higher than 80%.

Concerning parameter  $\varepsilon$ , a normal distribution can also be used to represent a faster or slower ageing trend. We propose a law with a **Mean  $\mu = 1$**  and a **Standard Deviation of  $SD = 0.1$** . Three standard deviations represent, then, up to 30% faster or slower ageing.

An user of the model proposed in this work can, of course, propose different behaviours for these parameters, such as other distribution laws or standard deviations.

### 3.5. Model Overview and Utilisation

The proposed model, described by Eqs. 3-7 in the previous subsections, has all its identified parameter values available in Table 2.

Table 2: Identified parameters of the proposed model

Name	Value	Unit
a	0.0190	Ah
b	0.0090	Ah <sup>-1</sup>
$r_1$	$1.5365e - 02$	–
$r_2$	$1.5365e - 04$	–
$r_3$	0.3841	–
$\alpha$	0.8277	–
$\beta$	0.3904	–
c	Normal law with $\mu = 0.0190$ , $SD = 0.0358$	Ah
$\varepsilon$	Normal law with $\mu = 1$ , $SD = 0.1$	–

We believe the same modeling approach could be used for other cell technologies and capacities, with a different data set needed to parameterize the model.

The algorithm to implement our model programmatically is proposed in a flowchart, available in Appendix A. This is ideally coupled to a cycle counting algorithm, such as Rainflow Counting, which can identify cycles with any combination of stress factors, different C-rates and even half cycles.

## 4. Model Applications and Results

### 4.1. Cell-level Analysis

A first demonstration of the applications and results achievable with our model is to consider the effect of regular cycling under different conditions.

This is shown in Fig. 3, where the capacity loss is simulated for three different cases. In each case, two stress factors are constant and one is variable. In these simulations, the solid lines correspond to a cell with no uncertainties, and the shaded areas represent two standard deviations of parameters  $c, \varepsilon$ .

The abscissa of these curves is the cumulative cycled capacity  $Q_c$ . If we consider the nominal cell capacity of 2.15 Ah, we can see that, in terms of Full Equivalent Cycles (FEC), the second life would last from a few dozen cycles

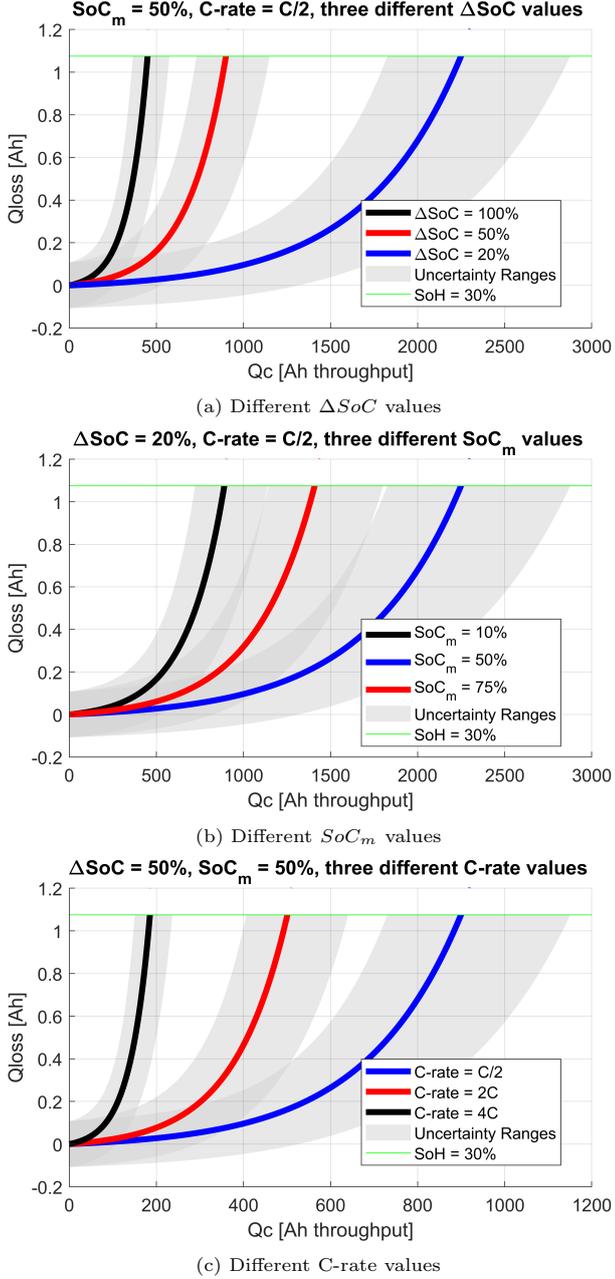


Figure 3: Simulation results showcasing the impact of the stress factors. In each subfigure, two stress factors remain constant and one is made variable.

in stressful conditions (such as a current of 4C on Fig. 3c) to around a thousand cycles in milder conditions (such as a  $\Delta SoC = 20\%$  on Fig. 3a).

These durations seem to be consistent with works that cycled LIBs during the second life, such as [12]. The relation between the stress conditions is consistent with the works used to develop our ageing model (c.f. Subsec 3.3).

As we force the stress factors to remain constant, the charge throughput (value of  $Q_c$ ) of each cycle on the simulation gets smaller as the cell ages - a  $\Delta SoC$  of 100% represents more cycled energy at a  $SoH$  of 80% than at a  $SoH$  of 70%, for example.

One hypothesis of our uncertainties modeling is also visible on these results: our model is built so that the uncertainty range is affected by the stress conditions. This means that cell cycled at stressful conditions will have a narrower uncertainty range.

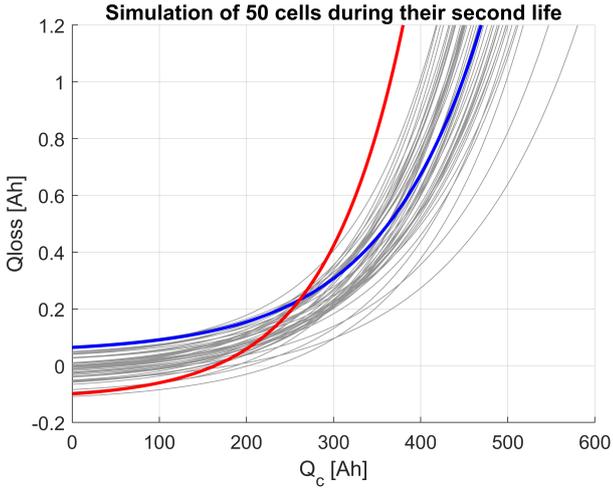
Once these initial results are established, our next proposition is to evaluate the effect of our uncertainty modeling. This is shown in Fig. 4a, where 50 independent cells were simulated with the following stress factors:  $\Delta SoC = 100\%$ ,  $SoC_m = 50\%$ ,  $C-rate = C/2$ . Each cell had different parameters  $c, \varepsilon$  originated from the probability distributions as proposed in Table 2.

Figure 4b is heavily inspired by Fig. 7 of Baumhöfer et al (2014) [29], a work that shows experimental data of 48 cells aged under the same conditions. By comparing the results of our model with the experimental data in [29], it is visible that our uncertainty modeling is able to successfully represent the ageing variability of LIBs on cell level.

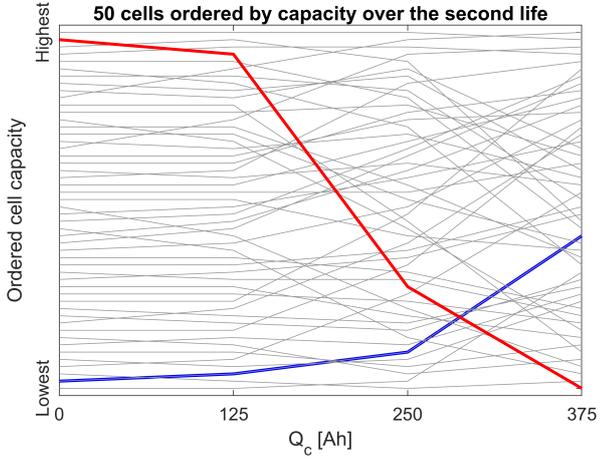
#### 4.2. Pack-level Analysis

The results presented thus far motivate us to analyse the impact of individual cell uncertainties in a battery pack, notably consisting of cells in series.

It is well known that the weakest cell in a series connection of batteries limits the capacity of the entire branch (given that a BMS is used to protect the cells from being overdischarged). Even if a BMS is used to balance the cells in a pack during a charge, the discharging capacity is always limited by the cells with the lowest capacities.



(a) Capacity loss behaviour of the 50 simulated cells



(b) Cells ordered by their capacity over the second life

Figure 4: Simulation of 50 independent cells, each one with different uncertainty parameters. Two cells are highlighted: in red, a cell starting with a high capacity and having a fast ageing trend; in blue, a cell starting with a smaller capacity and having a slower ageing trend.

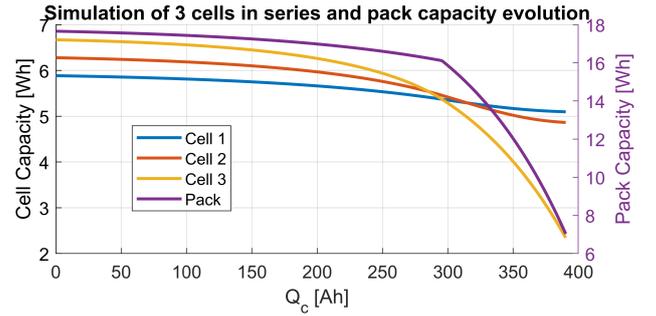
We imagine, then, a simple connection of 3 cells in series, with each cell having different uncertainty parameters:

- Cell 1:  $c = -0.0885$ ,  $\varepsilon = 0.8$
- Cell 2:  $c = 0.0190$ ,  $\varepsilon = 1$
- Cell 3:  $c = 0.1265$ ,  $\varepsilon = 1.2$

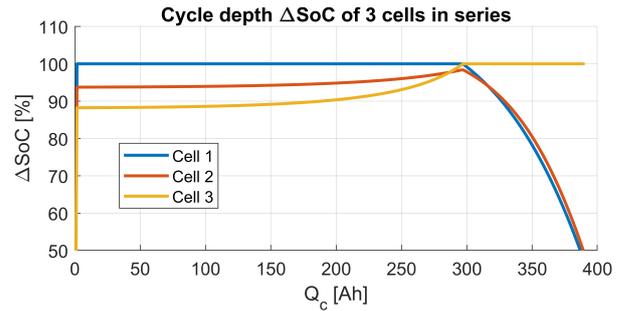
We then perform a cycle-by-cycle simulation, where the cells always have a  $SoC_m = 50\%$  and a  $C_{rate} = C/2$ . At each cycle, the capacity of the weakest cell is identified:

this cell will be cycled at a  $\Delta SoC = 100\%$ . The other cells will be limited by the capacity of the weakest cell, having a smaller cycle depth. We consider the pack capacity in ampere-hours then to be that of the weakest cell; the capacity in watt-hours (storable energy) is obtained by multiplying by the cell nominal voltage  $V_{nom} = 3.65 V$ .

The simulation results are shown in Fig. 5.



(a) Capacity of 3 cells in series (left y-axis) and the total pack capacity (right y-axis)



(b) Cycle depth  $\Delta SoC$  of 3 cells in series

Figure 5: Simulation of three cells in series with the weakest cell limiting the pack capacity

Figure 5b illustrates that the  $\Delta SoC$  of each cell in the pack evolves as the cells age. The impact of this is visible in Fig. 5a - the pack capacity has initially a slower capacity loss trend, as it is dominated by Cell #1, which has a smaller value of  $\varepsilon$ . Eventually, Cell #3, which has a faster ageing trend (larger  $\varepsilon$ ) takes its place as the weakest cell; the capacity of the pack starts deteriorating faster.

These results indicate that our model is capable of successfully simulate sudden increases in the rate of capacity loss of a pack, due to the limiting induced by a weaker cell. We presume it can be used as a prognostic tool of such

situations when coupled with real measurements from a battery pack.

Finally, we propose another test based on the number of cells in series in a pack. As observed in Fig. 5a, a single cell can reduce the lifetime of the entire pack.

We assume the association of four different number of cells in series ( $N_s$ ): 1, 3, 10 and 50. We choose to limit our analysis to series-connected cells, even though a real pack comprises  $N_p$  cells in parallel, as the objective is to examine the limiting effect of the weaker cells in a pack.

Then, for each value of  $N_s$ , we simulate the capacity loss until an arbitrary End of Second Life (EOSL). This is done with a similar procedure as used in Fig. 5: each individual cell has different uncertainty parameters  $c, \varepsilon$ , and the  $\Delta SoC$  of each cell is calculated at each cycle so that the pack is limited by the weakest cell.

We then perform these simulations 1000 times for each value of  $N_s$ , in a Monte Carlo method. At each simulation, we store the cumulative cycled capacity  $Q_c$ . The idea is to obtain a distribution representing a lifetime range for each pack size.

The simulation results are presented in boxplot fashion in Fig. 6. These should be read as representation of the data distribution; for example, the black dashed lines (called *whiskers*) represent 99.3% of the data. For the single cell, the boxplot showcases that 99.3% of the simulations yielded a  $Q_c$  between 345 and 575 Ah at the EOSL.

It is visible that, the more cells are associated in series, the narrower is the range of cycled capacity of the pack. This is due to the fact that, with more and more cells in series, the higher is the probability of having a weak cell with a fast capacity loss tendency that will limit the entire pack.

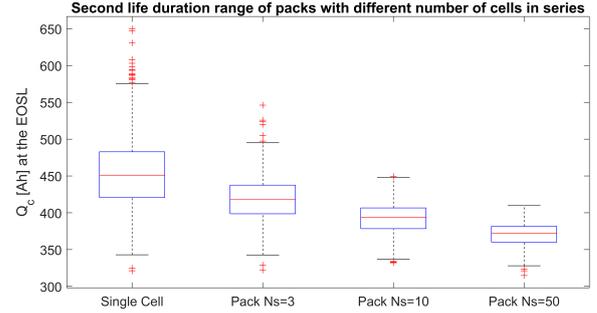


Figure 6: Results of Monte Carlo simulations of the lifetime range of different pack sizes

We believe this is an interesting result, as it showcases the impact of individual cell uncertainties in a pack. If a second life battery pack is to be assembled with random cells (in a *remanufacturing* process), we understand that an association of a large number of cells in series is to be avoided for the aforementioned reason.

Nonetheless, a battery pack needs to have a certain voltage level depending on the application; minimizing the number of cells in series at all costs would raise the requirements on interfacing elements, such as power electronic converters, which would create other issues. Ultimately, a compromise is to be found.

## 5. Conclusion

In this work, an ageing model applied for second life Li-ion cells was proposed. This empirical model is built and parameterized with experimental data of Li-NMC cells, and is intended to simulate cyclic ageing of cells considering three stress factors: current, cycle depth and mean SoC.

The novelty of the model is in its focus on the second life and the ability to easily simulate uncertainties related to the ageing, which are not negligible. Moreover, all the equations and parameters are provided in open data fashion

Results show that this ageing model is capable of predicting the lifetime range for different operating conditions of the Li-ion cells. The simulated capacity loss trends obtained are compatible with experimental results available in the literature, indicating the plausibility of the proposed model.

The modeling of uncertainties is shown to successfully emulate the real ageing variability of LIBs. Moreover, it allows for the simulation of the effects of cell-level uncertainties in a battery pack.

This work bridges a gap related to the specific modeling of the second life ageing, as well as the increasing associated uncertainties. We believe this model can be useful to anyone considering the deployment of second life batteries and desiring to simulate their ageing.

Future works will go in the direction of using this model as the intended prognostic tool it is, analysing SoC profiles and the feasibility of second life applications. **The addition of a thermal model is also considered in order to increase the completeness of the model and to expand the possible applications that can be studied.**

## 6. Acknowledgement

This research is supported by the French National Research Agency under the "Investissements d'avenir" program (ANR-15-IDEX-02) through the Cross Disciplinary Program CIRCULAR.

The authors would also like to thank the researchers from the ISEA institute of the RWTH Aachen University for kindly sharing the source data from their 2014 article [17] - these results were used to parameterize an important part of our model.

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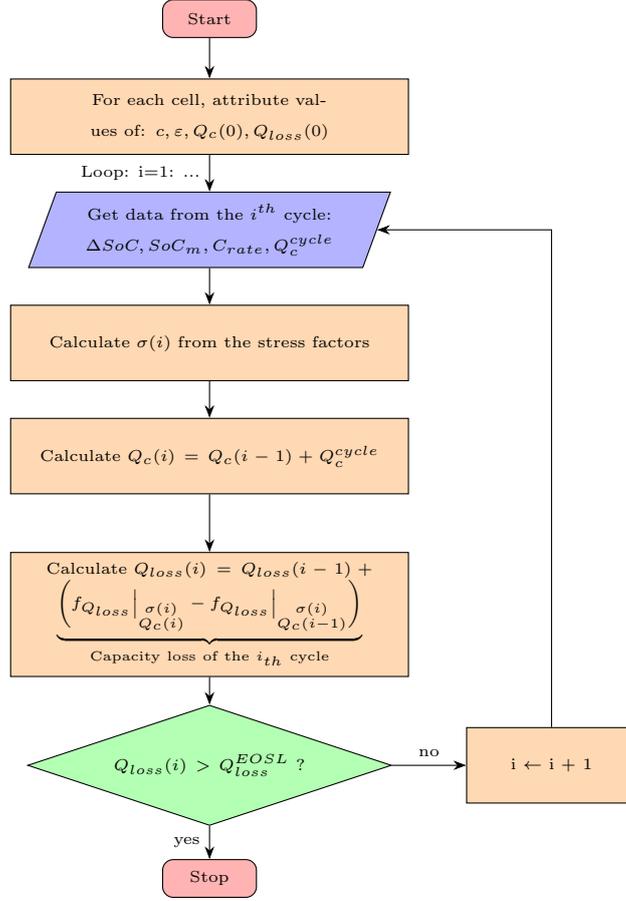
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## Appendix A. Model implementation algorithm for a given SoC profile



Where:

- $f_{Q_{loss}}$  is Eq. 3.
- $\sigma(i)$  is calculated with Eq. 4.
- $Q_{loss}^{EOSL}$  is an arbitrary constant determining the End Of Second life.
- Parameters  $c, \varepsilon$  come from a probability distribution as explained in Subsec. 3.4.
- $Q_c^{cycle}$  is the cycled charge (in Ampere-hours) of the cycle in question.

For the sake of simplicity, the algorithm above works for *regular* SoC profiles, i.e. profiles consisting of repeated cycles with the same stress factors (same charge and discharge C-rates). If this is not the case, the algorithm simply has to be adapted to calculate  $f_{Q_{loss}}$  for the charge and discharge segments separately when calculating  $Q_{loss}$ .