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Eyring acceleration model for predicting calendar ageing of lithium-ion batteries

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ABSTRACT

Modelling of lithium-ion batteries calendar ageing is often based on a semi-empirical approach by using, for example the Arrhenius acceleration model. Our approach is based on Eyring acceleration model, which is not widely used for electrochemical energy storage components. Parameter identification is typically performed without taking into account the state-of-charge (*SoC*) drifting. However, even in rest condition, battery cells' *SoC* drifts because of capacity losses (self-discharge and capacity fade). In this work we have taken into account the *SoC* drift during calendar ageing tests. For this, we considered available capacity (Ah) instead of *SoC* (%) as ageing factor. Then, the analytical solution of the problem leads to the use of the Lambert *W* function in the model formulation. Simulation results show that Lambert-Eyring model is more accurate and allows a reduction in the number of parameters to be identified.

1. Introduction

During the last decade, electric vehicles (EV) and hybrid electric vehicles sales have grown from 0.1 to 3% in France [1]. However, the low range and high purchasing price of EV's are the main obstacles to their market penetration. Range and price are directly related to the battery size which is the most expensive component of an electric vehicle. Currently, car manufacturers have found a compromise between price and range that fixes typically the range between 100 and 200 km for a purchasing price (including batteries) from 20 to 40 k€. Battery size of those vehicles vary from 16 to 24 kWh.

Electric vehicles can contribute to a cleaner mobility, but for this, the whole life cycle must be optimized in order to be less resource consumer and less waste producer than thermal vehicles.

Energy management of the vehicle is often optimized with an energy economy aim, but it can also be done for extending the battery longevity. The elaboration of this kind of strategies requires reliable and accurate ageing models.

In this paper, calendar ageing of lithium-ion LFP/C cells has been modelled. Calendar ageing seems to be predominant in batteries used in applications such as electric vehicle. LFP cells offer high durability, power and safety, which represent three crucial performances for transportation applications.

A classical approach of model parameter identification consists on a step by step identification: first step consists of identifying the temperature (*T*) influence and then the second step is for the state-of-charge (*SoC*) influence. For this, every factor (T and *SoC*) must be considered as being constant.

During calendar ageing tests, constant temperature is easily driven because battery cells are in rest condition and no heat is emitted by them. However, battery cells' *SoC* is not constant: *SoC* drifts over time because of capacity losses.

Consequently, *SoC* drift may be considered from the parameter identification phase in order to improve the ageing model accuracy. The chosen formulation in this work relies on the Eyring acceleration law [2]. This law allows a global approach where all parameters can be identified in a single step.

2. Calendar ageing

Calendar ageing of a battery cell is the degradation of its performances while being in rest condition, that is when no current is supplied or absorbed by this cell. This type of ageing must considered in transport applications because vehicles are parked 95% of the time [3].

Calendar ageing yields on ageing mechanisms caused by side reactions between the different chemical substances inside each

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Nomenclature

SoC	state of charge
T	temperature
Q_0	initial capacity
Q	current capacity
Q_a	available capacity
Q_d	used capacity
Q_{sd}	self-discharge (reversible capacity loss)
Q_L	capacity fade (irreversible capacity loss)

component of the battery (electrodes, electrolyte, etc.). Ageing mechanisms of lithium-ion batteries are numerous, complex and can interact with each other [4].

As on battery cells the main ageing mechanisms lie on chemical reactions, the battery performances degrade over time as these reactions advance. Thus, Arrhenius-like laws are commonly used to explain the thermal stress influence on performances. Eq. (1) is a general form for a performance ($y(t)$) degrading over time under a thermal stress (T) using the modified Arrhenius law. The performance $y(t)$ can be the internal resistance (power fade) [5–8] or the capacity fade [9–11] with T the absolute temperature (in K), A the pre-exponential factor, E_a the activation energy for the reaction (in eV), k the Boltzmann constant and $f(t)$ the time degradation function of $y(t)$ considered.

$$y(t) = AT^n e^{(Ea/kT)} f(t) \quad (1)$$

The Eyring law is also used on reliability studies [2] for example for mechanical components [12]. This law extends the Arrhenius law to other stress factors S_i such as pressure, current, voltage, etc. Eq. (2) is a general form for a performance ($y(t)$) degrading over time under two type of stresses (T and S_i) using the Eyring law. In the Eyring law each additional stress is added to the exponential function beside the thermal stress term (E_a/kT). The direct influence of a stress is B_iS_i and C_iS_i/kT represent an interaction term between temperature and S_i where B_i, C_i are stress-dependent constants.

$$y(t) = AT^n e^{(Ea/kT+B_iS_i+C_iS_i/kT)} f(t) \quad (2)$$

In this paper, we have modelled calendar ageing of A123 LFP/C cells (2.3Ah) from SIMCAL project [13]. The main calendar ageing mechanism in this type of cells is SEI (Solid Electrolyte Interface) formation [14]. The consequence of this ageing mechanism is the capacity fade due to a loss of lithium inventory.

In order to facilitate the results comparison, all capacity measurements and simulation are expressed relative to initial capacity (p.u.).

2.1. Accelerated ageing tests in SIMCAL project

Accelerated ageing tests were carried out in order to show up the ageing mechanisms responsible of battery degradation. These tests consist in putting battery cells to different levels of use constraints. The collected results can be used afterwards to establish remaining useful life or performance evolution laws.

In the case of calendar ageing, two factors have been identified as being responsible of battery degradation: temperature (T) and state-of-charge (SoC). In SIMCAL project [13], six technologies of batteries (one NMC/C, one NCA/C, one LMO/NMC blended/C and three LFP/C) were tested to study the influence of SoC and temperature as ageing factors. Target values of factors are 30, 45 and 60 °C for temperature and 30, 65 and 100% for SoC. Each couple of values (T, SoC) was assigned to three different cells to improve the representativeness of the results. Cells' performances were periodically measured by the means of RPTs (Reference Performance Tests) at 25 °C. The RPT protocol consisted in:

- Full charge/discharge cycle at 1C rate for capacity measurement
- Electrochemical Impedance Spectroscopy (EIS) and time response to pulse profiles at different values of SoC

In this work, we focused the analysis to one LFP/C technology and exploited only the capacity measurements.

Fig. 1 shows the capacity loss evolution (Q_L) of A123 cells under ageing tests from SIMCAL project. In this figure the temperature influence is clearly perceptible: if cells are grouped by SoC level, cell degradation is greater at higher temperatures (that is, degradation rate is higher for 60 °C than for 45 °C and than for 30 °C for each SoC level).

Nonetheless, the reciprocity of this sentence is not always true: the degradation rate is not always higher at higher SoC levels. At 30 °C cell degradation is greater when SoC is higher, that is degradation at SoC 100% is higher than when SoC is 65% and 30%. However, at 45 °C, degradation at SoC 100% is similar than when SoC is 65%. Even at 60 °C, degradation at SoC 100% is lower than when SoC is 65%. This behaviour seems to be atypical and highlights a strong interaction between the ageing factors (T, SoC).

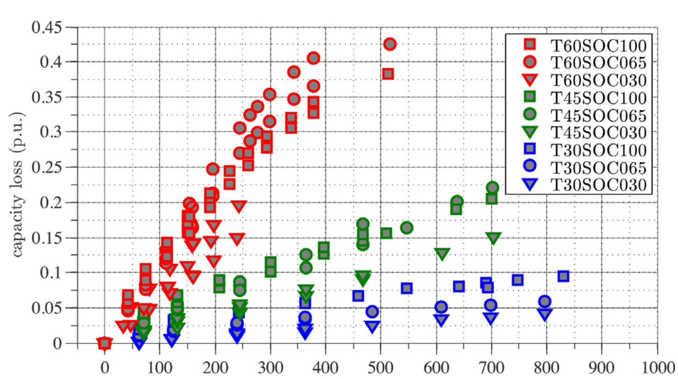

Fig. 1. Capacity loss of A123 cells from SIMCAL project.