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Development of an empirical aging model for Li-ion batteries and application to assess the impact of Vehicle-to-Grid strategies on battery lifetime

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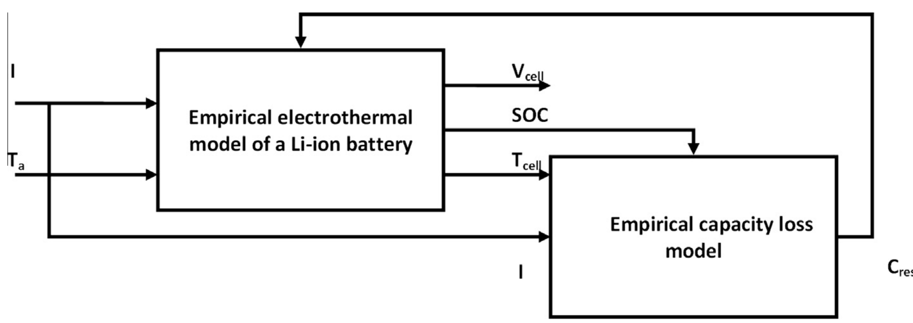
HIGHLIGHTS

- Empirical capacity loss model for Li-ion batteries.
- Both calendar and cycle aging were modeled.
- Calibrated and validated on LFP/C and NCA/C cells using experimental data.
- Real life application to assess the influence of V2G on aging for both technologies.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper an empirical capacity fade model for Li-ion batteries has been developed, calibrated and validated for a NCA/C and a LFP/C Li-ion cell. Based on extensive experimental work, this original, generic model is well suited for system simulation approaches, and is able to describe both cycle and calendar effects on aging. The stress factors taken into account for each aging mode are the state of charge and the temperature for calendar aging, and the temperature and the current for cycle aging. A simple approach has been adopted in order to instantaneously apply either cycle aging or calendar aging according to operating conditions and thus accurately model aging effects due to dynamic operating conditions. This model has then been coupled to an electrothermal model and integrated in a system simulation software application in order to assess the effect of charging rates, charging strategies and V2G on battery lifetime. When compared, the two battery chemistries exhibited different behaviors when submitted to V2G scenarios. Light V2G scenarios caused relatively low aging for the LFP/C based battery but tended to slightly increase the aging of the NCA/C based battery according to simulations.

1. Introduction

In order to reduce fossil energy dependence and the environmental impact of vehicles, new regulations are encouraging car manufacturers toward vehicle electrification. This trend raises the issue of electrical energy storage. Li-ion batteries are one of the most promising solutions to store the energy needed for highly electrified vehicles: hybrid electrical vehicles (HEV), plug-in hybrid vehicles (PHEV) or full electric vehicles (EV). However, energetic and power performance of Li-ion batteries is known to decrease during their service lifetime [1].

Although the cost of battery packs is decreasing [2], they comprise a significant proportion of market vehicle price, which means car manufacturers have to provide a guaranteed longevity ensuring

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a safe and sufficient battery performance throughout the vehicle service lifetime. Therefore, battery aging studies are of particular interest in order to optimize battery systems in terms of size and cooling requirements, and also to devise management strategies well suited along the vehicle lifetime. Providing a minimum level of performance is also mandatory to ensure financial viability for electrified vehicles. For such concerns, modeling is essential to provide car designers with information and reduce development costs.

While the main microscopic aging phenomena of Li-ion cells have been identified [1,3] and described, for instance Li plating at low temperature [4], loss of active material at elevated temperature [5] or solid electrolyte interphase (SEI) growth at the negative electrode/electrolyte interface [6,7], aging of Li-ion batteries remains difficult to predict [8,9]. In most aging models, considering that SEI growth is the main cause of aging for Li-ion batteries with graphite negative electrode leads to a quadratic evolution shape of the capacity loss in the beginning of the battery life as put forward by Spotnitz [10].

To find the main impact factors, research efforts have been dedicated to model macroscopic Li-ion cell capacity loss and impedance increase [11,12]. The main aging factors are the state of charge, *SOC*, the depth of discharge during cycle, *DoD*, the temperature, *T*, and current, *I*. Another key impact factor is the battery usage [13] which can be described in two contributions to aging:

- Calendar aging ($I = 0$): the battery is stored without being used so there is no current through the battery.
- Cycle aging ($I \neq 0$): the battery is either charged or discharged.

It has been shown that the two types of aging will lead to different battery behaviors with usually a higher capacity loss and higher power loss during cycle aging [13].

In order to model aging phenomena, two different approaches have been put forward in the literature, which are physical modeling [14–16] and empirical modeling [10,17]. Usually empirical models will address either calendar aging [10,13] or cycle aging [11]. Some other modeling works include both cycle and calendar aging behaviors [18–20] but, despite describing cycle aging, the proposed model did not take into account the charging rate on aging. The resulting model assesses the capacity loss as a function of time and constant stress factors which has little application in use [21–24]. It is not convenient to use this kind of modeling for system simulation where stress factors are dynamically varying, for instance due to environmental conditions (temperature variations due to seasons and day and night successions) or due to vehicle use (storage SOC depending on the duty cycle).

In this paper, we introduce an original empirical capacity fade model suitable for system simulation application. This generic approach for Li-ion batteries is applied on two Li-ion technologies and validated against experimental data. Once validated, it can be used in a system simulation to assess the usefulness of different charging strategies in order to preserve the batteries' performance throughout their lifetime in various realistic operating conditions.

2. Model development

The capacity fade model is based on 2 contributions leading to different capacity losses in Ah: Q_{loss}^{cal} due to calendar aging and Q_{loss}^{cyc} due to cycle aging.

2.1. Calendar aging

As often discussed the two main stress factors for calendar aging are temperature and State of Charge (SOC). Usually [11,22,25] an empirical aging law is given as below

$$Q_{loss}^{cal} = B_{cal}(SOC)\exp\left(-\frac{Ea_{cal}}{RT}\right)t^{z_{cal}} \tag{1}$$

In this expression B_{cal} is a pre-exponential factor depending on *SOC*, expressed in $\frac{Ah}{s^{z_{cal}}}$, Ea_{cal} is the activation energy, expressed in J mol^{-1}, which evaluates the dependency of calendar aging on temperature *T*, expressed in K, and z_{cal} is a dimensionless constant. Considering a capacity loss phenomenon linked to SEI growth and diffusion limitations, this exponent should be around 0.5.

This expression is well suited to rapidly evaluate the capacity lost during long term storage but it is not suitable when many different operating conditions are happening. As a consequence, this expression has been differentiated against time in order to evaluate infinitesimal variation of capacity due to calendar aging:

$$\frac{dQ_{loss}^{cal}}{dt} = z_{cal}B_{cal}(SOC)\exp\left(-\frac{Ea_{cal}}{RT}\right)\left(\frac{Q_{loss}^{cal}}{B_{cal}(SOC)\exp\left(-\frac{Ea_{cal}}{RT}\right)}\right)^{1-\frac{1}{z_{cal}}} \tag{2}$$

This expression can then be linked to other capacity loss phenomena like cycle aging.

2.2. Cycle aging

For cycle aging a similar approach based on Wang et al. [11] is used. In this study the capacity loss due to aging is influenced by two major stress factors: current and temperature. The formulation encountered is then:

$$Q_{loss}^{cyc} = B_{cyc}\exp\left(\frac{-Ea_{cyc} + \alpha|I|}{RT}\right)Ah^{z_{cyc}} \tag{3}$$

In this expression, B_{cyc} is a pre exponential factor in $Ah^{1-z_{cyc}}$ which depends on current, Ea_{cyc} is an activation energy for cycle aging expressed in J mol^{-1}, α is a coefficient for aging acceleration due to current expressed in J mol^{-1} A^{-1}, z_{cyc} is an exponent constant that should be around 0.5 for diffusion limited process. Finally, *Ah* stands for Ah throughput, that is the amount of charge sent into the cell. For the same reason as for calendar aging, this expression has been differentiated against time:

$$\frac{dQ_{loss}^{cyc}}{dt} = \frac{|I|}{3600}z_{cyc}B_{cyc}(I)\exp\left(\frac{-Ea_{cyc} + \alpha|I|}{RT}\right)\left(\frac{Q_{loss}^{cyc}}{B_{cyc}(I)\exp\left(\frac{-Ea_{cyc}+\alpha|I|}{RT}\right)}\right)^{1-\frac{1}{z_{cyc}}} \tag{4}$$

In this expression, the Ah throughput term, once differentiated, is proportional to the current in the cell.

2.3. Switch between calendar and cycle aging

Once the influence on aging has been expressed for both behaviors, it is necessary to find a way to decide what kind of aging is occurring based on the actual operating conditions. In some approaches it has been assumed that the cycle aging contribution does not take into account calendar effects [22,23]. Both contributions are then added to get the total aging. In our work, the assumption is that when the modeling of cycle aging has been performed, calendar aging occurring during cycle mode is already taken into account. As a consequence, we need to find a condition describing the switch between calendar and cycle mode.

First, taking as a major phenomenon of capacity loss the SEI formation at the negative electrode, it is known that the parasitic reaction of SEI formation is accelerated when the negative electrode potential is lower (i.e. during charge or when the SOC is high). As a consequence it has been assumed that cycle aging only occurs when the battery is in charge and the current is above a