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Combined experimental and modeling approaches of the thermal runaway of fresh and aged lithium-ion batteries

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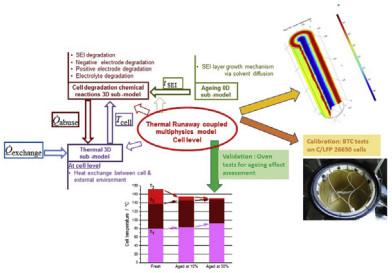
HIGHLIGHTS

- Development of an original 3D thermal runaway model including calendar ageing.
- Model includes 3D thermal, 3D chemical reaction, and 0D calendar ageing sub-models.
- Calibration of the model for cylindrical 26650 LFP/C cells using a BTC.
- Validation of the model for fresh as well as 10% and 30% aged cells in oven tests.
- Fresh and aged cells are compared in terms of critical temperatures under overheating.

GRAPHICAL ABSTRACT



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ABSTRACT

Li-ion secondary rechargeable batteries are becoming the preferred solution to store energy on board of new generation electric and hybrid vehicles or manage renewable energy in stationary applications. However, Li-ion batteries (LIBs) are still suffering limited lifetime, high cost and significant safety issues increasing their time to mass market. Thermal runaway is still nowadays considered as a major hazard of LIBs. This multiscale and multistep phenomenon originating at the microscale level potentially leads to uncontrolled fire and explosion of the battery. This work is focused on the development and validation of a 3D physical model of the LIB electro-thermal behavior nearby thermal runaway conditions. A combined modeling and experimental investigation provides a better understanding of the mechanisms leading to thermal runaway of LIBs, and of the ageing influence on this process. One major outcome of this work is also the proven fact that calendar ageing leads to a delayed onset of the cell self-heating temperature with a thermal runaway starting at a lower temperature. This is supported by computer simulations showing that the thickening of the solid electrolyte interface (SEI) hinders the diffusion of Li ions, which delays the degradation of the negative electrode and the occurrence of thermal runaway.

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1. Introduction

Lithium-ion batteries (LIB) are currently considered as the best available solution to store energy on board of new generation of electrical, plug-in, or hybrid electrical vehicles, or to develop stationary applications with alternative green energy sources (solar, wind, photovoltaic). However, their ageing, high cost, and safety aspects still represent critical issues for these storage systems.

To assess and mitigate these drawbacks, major research efforts have been carried out in the recent past. Thermal runaway has been identified as a major concern with LIBs on the full value chain, potentially leading to uncontrolled fires and explosions causing the failure of the entire battery pack [1]. Catastrophic hazardous events reported to originate from LIBs, albeit not so frequent, such as violent venting, smoke, fire, explosion [2] still act as a clear restraint to LIB market development for high power/high energy applications, and still even in rare cases for consumer market appliances [3,4].

The thermal runaway of LIBs has been described as a multistep process implying a series of exothermic reactions related to the decomposition of different components of the cell (electrodes, electrolyte, and binder), together with their interactions occurring above a critical temperature, which led to an increased temperature inside the cell [5].

The most consensual analysis of the thermal runaway of a LIB considers that the phenomenon proceeds in four main stages occurring successively according to the onset of exothermic decomposition reactions as follows:

1. The first degradation reaction leading to the initial subsequent increase in cell temperature is usually reported to concern the solid electrolyte interface (SEI) that forms a passivation film on the surface of the carbon negative electrode. The onset of this reaction is ranging between 90 °C and 120 °C depending on the chemistry of the cell [6].
2. When the SEI starts to decompose, the electrolyte reacts violently with the active material of the negative electrode, which accelerates the cell temperature rise [7].
3. At temperatures above 120 °C [8], the positive electrode materials start to decompose, leading to evolution of oxygen that can react with the electrolyte and generate additional heat. According to thermal stability studies of commercial LIBs, the onset temperatures of the exothermic reactions at positive electrode materials rank in the following order:

$LiNiO_2$ (~180 °C) < $LiCoO_2$ (~200 °C) < $LiMn_2O_4$ (~220 °C) < $LiFePO_4$ (> 240 °C).

$LiFePO_4$ is then considered as the most thermally stable material of positive electrodes [7].

4. The electrolyte, most commonly a lithium salt dissolved in a mixture of organic carbonates, can decompose exothermically at elevated temperatures (> 200 °C) depending on its composition (salt, solvents, additives) [9].

At the cell level, the thermal runaway features globally depend on the chemistry of the cell components, as well as the shape and design of the cell [10]. They also depend on the state of charge (SOC) of the cell. Cells of higher SOC have revealed a lower thermal stability in dedicated studies, meaning a lower onset temperature of the thermal runaway reactions [5] and a higher self-sustained rate of increase of the cell temperature [11]. Some recent studies have investigated the effect of ageing on the thermal stability of cells by performing thermal stability tests under abuse conditions (overcharge, overheating …) to determine correlations between battery ageing and safety [12–15]. For example, the influence of cyclic ageing on the thermal behavior of Li-ion cells with $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2/Li_yMn_2O_4$-blend electrode positive materials was studied by Fleischhammer et al. [12]. They showed that cells aged by high-rate cycling had about the same safety behavior as fresh cells. In contrast, a significant increase of self-heating was observed for cells showing plating of metallic lithium on the negative electrode due to low temperature charging. On the other hand, Röder et al. [13] studied the influence of calendar ageing (at full SOC and 60 °C) on the thermal stability of a commercial Li-ion cell containing a mixture of $LiMn_2O_4$ and $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ as positive electrode material and graphite as negative electrode. They showed that the self-heating onset temperature of the aged cells was much lower than that of the fresh cells. These experimental studies show that the ageing history of aged cells plays a strong role on their safety so that an open issue is the way battery ageing affects its sensitivity to thermal runaway, in particular for the graphite-$LiFePO_4$ (LFP/C) technology claimed to be safer than the others.

So far, battery safety studies have mainly consisted in experimental approaches based on safety and abuse tolerance tests as well as post-mortem battery analyses [16]. However, these approaches show significant shortcomings due to the complexity of the phenomena involved in battery operation. Moreover, the safety and abuse tolerance tests are destructive so that the cost in battery test samples becomes an issue. Modeling and simulation are then used to predict battery performance and safety and help the design of new batteries, especially as experimental databases are now available for model calibration and validation, at least at cell level.

The number of investigations on LIB safety has increased in the last decade, including safety studies implementing modeling approaches [17–19]. However, battery modeling in abuse conditions was exclusively aimed for some time at modeling single events leading to battery failures as short circuit, mechanical abuse, overcharge or fire propagation. Combined modeling of electrical, chemical, and thermal behaviors of LIBs in abuse operating conditions emerged only after 2012. NREL (National Refreshable Energy Laboratory), Battery design LLC, and Sandia National Laboratories works constitute a large step forward in battery modeling and simulation in abuse conditions at different scales (cell/module/pack). However, all models of thermal runaway in abuse conditions available at the cell level are presently based on the chemical degradation reactions considered in Kim et al.'s model [6], none of them taking into account the influence of cell ageing. In this context, the objective of the present work is the development and validation of accurate physical models of the thermal behavior of fresh and aged LIBs in conditions leading to thermal runaway, for further practical applications to sizing and design support of safer batteries. A 3D thermal runaway model including ageing phenomena was developed and calibrated for cylindrical 26650 LFP/C cells (A123 Systems) using a battery test calorimeter (BTC) before validation with oven tests. The thermal safety of such LFP/C cells (fresh and aged at two different residual capacity) was then experimentally determined for comparison with expectations from the model to find out the influence of calendar ageing on battery safety.

2. Materials and methods

In order to build a multi-scale predictive model of thermal runaway adapted to fresh and aged LIBs, two complementary studies were carried out in parallel, a modeling work to develop several sub-models and achieve a coupled multi-physics and multidimensional model, and an experimental work to initially calibrate the sub-models and validate the model. As indicated above, A123 (2.3 Ah) cylindrical LFP/C cells were used. Their characteristics are presented in Table 1. All the tests were carried out with fully charged cells (100% SOC), which is known to be the worst-case scenario [5].

2.1. Modeling approach

As mentioned above, thermal runaway models available at the cell scale are all based on the chemical degradation reactions introduced in