Li-ion thermal issues and modeling in nominal and extreme operating conditions for HEV / PHEV's

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***Abstract*—The technical and commercial success of hybrid-electric vehicles (HEV) and plug-in hybrid-electric vehicles (PHEV) is strongly related to the security, cost and lifetime of the traction battery. Temperature is one of the most significant factors impacting the security, performance and life of an electrochemical battery. Regardless the cooling system adopted, the essential issue is to control the temperature gradient within each element in addition to the temperature profile across the entire energy storage system. An underestimation of internal temperatures would lead to non-uniform material ageing, but would also increase the risk of thermal runaway for some Lithium-based battery technologies. In this work, an original 0D impedance-based hybrid thermal/electrical model is developed, validated against experimental data and coupled with radial and axi-symmetric 2D model taking into account geometrical properties of a commercial cylindrical $LiFePO_4$/Carbone 2,3 Ah cell.**

I. INTRODUCTION

High-power secondary batteries for plug-in hybrid and electric vehicle applications generate much more heat during rapid charge and discharge cycles at high current levels. The use of batteries at high power will pose serious thermal-stability problems, even more when the battery size increases and many cells are interconnected to form large packs. Especially, Lithium ion battery systems require careful thermal engineering because temperature is intricately coupled to performance, life and safety of the chemistry. Bad thermal balance, at both the cell [1] and the pack level [2], shortens the pack lifetime. As battery size increases, cooling area to heat generating volume ratio decreases and internal temperature gradients can develop inside the cell. If temperature excesses 70-90°C during extreme conditions, exothermic chemical reactions can be triggered leading to thermal runaway [3]. To prevent safety issues and understand thermal behaviour in nominal and extreme conditions, intensive investigations were dedicated to model thermal behavior of battery technologies integrating kinetics and thermodynamics of these electrochemical systems. Two main thermal models approaches can be distinguished in literature. The main differences rely on whether or not an electrical/electrochemical model is coupled with a thermal one, be it global or local [4]. In this work, an original 0D impedance-based hybrid thermal/electrical/electrochemical model is developed, validated against experimental data and used as a building block in radial and axi-symmetric 2D coupled electrical/thermal model taking into account geometrical properties of a commercial cylindrical $LiFePO_4$/Carbone 2,3 Ah cell. A simplified thermal abuse model based on Hatchard and Kim work is also presented. 2D models are powerful tools to get insight into thermal behavior of the cell and detect potential extreme operational conditions (as very fast discharge) leading to safety issues that cannot be detected with 0D lumped models and simple skin temperature measurements.

II. EXPERIMENTAL

The experimental work was performed on 2,3Ah commercial cylindrical $LiFePO_4$/Carbone Li-ion cells. On the one hand, charge/discharge cycles following a Hybrid Pulse Power Characterisation-Like test [5], so called HPPC-Like test, were applied on Li-ion cells at different temperatures in a climatic chamber. A Digatron 200A/50V test bench was used at 25°C to perform other power tests like fast discharge. On the other hand, electrochemical tests were performed on a VMP2 multi-potentiostat. The application of Electrochemical Impedance Spectroscopy (EIS) with a 2-electrode set-up can help determine electrochemical phenomena occurring in the system [6].

III. MATHEMATICAL MODEL

A 0D impedance-based model was calibrated on a commercial 2,3Ah $LiFePO_4$/Carbone cell. It takes into account the main Li-ion electrochemical phenomena like electro-migration inside the electrolyte at high frequencies, Butler-Volmer electrochemical charge transfer kinetics in the medium frequency range associated with electrochemical double layer capacitance, and diffusion of ionic species in the electrodes in the low frequency range. All the previous phenomena follow an Arrhenius law. From simplified Butler-Volmer formalism for a redox reaction, charge transfer current density can be explained as

$$i = i_0 \left\{ \exp\left(\frac{\alpha_{ox} nF}{RT} \eta \right) - \exp\left(\frac{-\alpha_{red} nF}{RT} \eta \right) \right\} \qquad (1)$$

with i_0 the exchange current density, n the number of electrons transferred. An hypothesis of symmetry is made concerning the non-linearity between the charge and the discharge ($\alpha_{ox}=\alpha_{red}=0.5$) giving charge transfer resistance R_{ct} as a function of current i. The diffusive impedance is often represented by a Warburg impedance which expression differs as the mass transport boundary conditions vary [7]. Diffusion impedance is then expressed as

$$Z_w(s) = R_d \frac{\tanh \sqrt{s \tau_D}}{\sqrt{s \tau_D}} \qquad (2)$$

with R_d (Ω) the diffusion resistance, and τ_D the characteristic diffusion time (s) of the phenomenon, and s is Laplace variable. This impedance function is often

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implemented in the temporal domain as a transmission line be it a finite-length Cauer or a Foster-type electric network [8].

The equation for energy balance inside the cell can be expressed as

$$mC_p \frac{\partial T}{\partial t} = Q_{elec,gen} - q_n \tag{3}$$

where m is the cell mass (kg), C_p the calorific thermal capacity (J/kg/K), T the temperature (K) inside the cell, $Q_{elec,gen}$ the total heat generated (W) by the cell as the current flows in it, q_n the heat exchanged with the ambient (W). The reversible heat generation rate Q_{rev} in watts released by an electrode is given by

$$Q_{rev} = -\frac{\partial U_{th}}{\partial T} IT \tag{4}$$

Based on experimental data performed at IFP Energies nouvelles, the evolution of entropic term as a function of SOC was implemented in our model. The irreversible heat generation rate generally known as Joule losses is always exothermic and is given by

$$Q_{irrev} = R_i I^2 \tag{5}$$

where R_i, the internal resistance of the cell, is the sum of Ohm resistance, charge transfer resistance and the diffusion one. In the previous equation, other terms can be added as chemical abuse heat generation, or heat released when short occur in the cell. The total heat generated in the cell is the sum of electrical, chemical abuse reaction, shorts and is given by

$$Q_{total} = Q_{elec,gen} + Q_{abuse} + Q_{short} \tag{6}$$

Based on Kim and al. work [3], a simple lumped thermal abuse model was developed. It integrates exothermic reactions that can be triggered when internal temperature of the cell excesses 70 to 90°C. In this model, four main decomposition reactions are considered. The first reaction is SEI layer decomposition near 70°C to 90°C, then occurs the Negative-Solvent reaction around 120°C followed by the Positive–Solvent reaction and finally if temperature excesses 200°C electrolyte decomposition is considered. The consumption rate of active material due to decomposition reaction are given by

$$\frac{dC_{species}}{dt} = -A_{species} C_{species}^{\;m_{species}} \exp\left(\frac{-E_{a,species}}{RT}\right) \tag{7}$$

where $C_{species}$ (%) is the normalized concentration of Li^+ inside active material, $m_{species}$ is the order of the reaction, $A_{species}$ (s^{-1}) is the frequency factor of the reaction and $E_{a,species}$ (J/mol) is the activation energy of the decomposition reaction. The specific heat release is then computed as

$$Q_{species} = H_{species} W_{species} R_{species} \tag{8}$$

where $R_{species}$ (s^{-1}) is the reaction rate of the active species,$H_{species}$ is the specific heat release (J/g), and $W_{species}$ is the specific active material content ($g.m^{-3}$). The global volumetric chemical heat release is then expressed as

$$Q_{abuse} = \sum_{i=1}^{4} Q_{species,i} \tag{9}$$

IV. 0D THERMAL-ELECTRICAL MODEL VALIDATION

Continuous discharge tests were performed at various current discharge rates of C/2, 1C and 2C. Skin temperature was measured by means of a thermocouple put in the lateral surface. Electrical and thermal comparison between simulations and experimental data are respectively shown on the Figure 1.

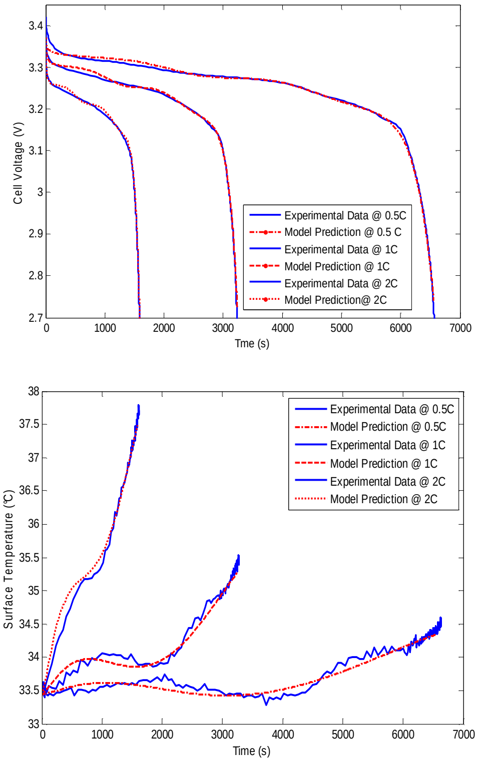

Figure 1 Voltage a) and skin temperature b) comparison between simulated and experimental data at C/2, 1C, 2C discharge rates

V. SIMULATION STUDY

0D thermal electrical model was coupled with 2D models in which thermal properties of each battery components were considered. Impact of air inside the cell, impact of cooling on temperature gradients in nominal operational conditions but also extreme conditions like oven test or very fast discharge were investigated. A representation of thermal gradients inside the cell at the end of a 2C discharge at 33°C are shown on Figure 2. During nominal or extreme operational conditions, measured temperature doesn't reflect internal thermal state. Commercial specifications for very fast continuous discharge is -70A.

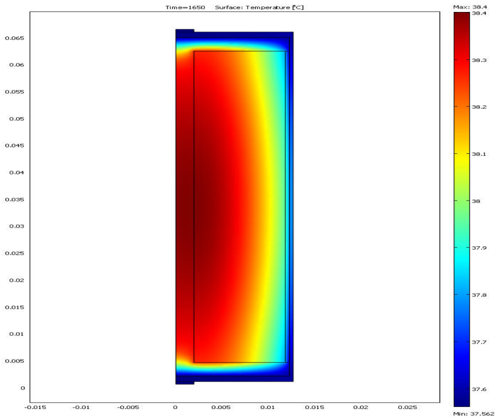

Figure 2 Temperature gradients computed by axi-symmetric model on a 2C-discharge at 33.4°C after 1700s.

To check this up, a -70A discharge at 0°C with free convection was simulated as represented on Figure 3. Interestingly, it was observed that skin temperature reached 62°C at the end of discharge which corresponds to the manufacturer maximum authorized value of 60°C. Concerning internal temperature, the simulation gives 80°C which is the onset temperature zone of SEI decomposition reaction.

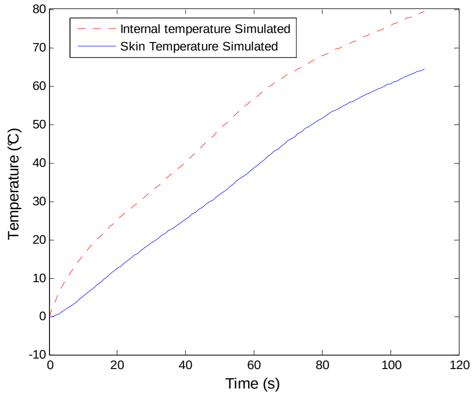

Figure 3 Evolution of internal and skin temperature during a 70 continuous discharge at 0°C

An oven test simulation was run for the commercial cylindrical cell based on Guo and al. [1;9] who tested a 55Ah LFP prismatic cell. A 155°C oven test was simulated to see how a LFP/C charged battery could react. As observed on Figure 4, a slight thermal runaway phenomenon is obtained. SEI and negative-solvent reaction occur. LFP-solvent reaction is triggered but not fully completed. Thermal evolution caused by LFP decomposition is not enough to trigger electrolyte decomposition and stronger thermal runaway.

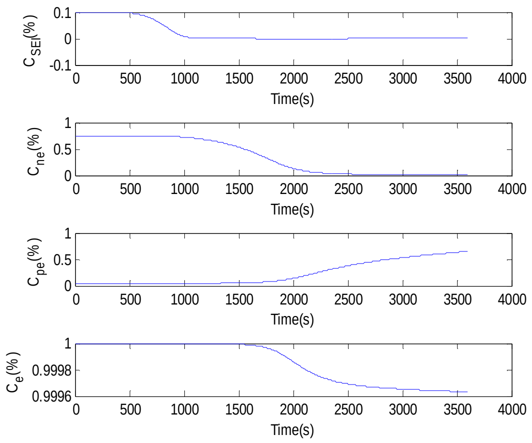

Figure 4 Evolution of normalized active material concentration as the chemical exothermic reactions develop.

VI. CONCLUSIONS

A multi-scale hybrid thermal/electrical and electrochemical modeling methodology has been developed to simulate nominal and extreme behavior of a commercial cylindrical Lithium Iron Phosphate ($LiFePO_4$) cell. These multi-dimensional models were validated against experimental and literature data. These developments can be used to understand thermal behavior of Li-ion cells, size modules and packs, and optimize thermal management strategies for HEV, PHEV and EV's.

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