A Simplified Model for improving Thermal Stability of Lithium-ion Batteries

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Lithium ion batteries represent a well established technology in a range of applications (laptops, mobile phones, etc.) but they are becoming key factors in many other areas were reliability and safety are of paramount importance (e.g. the space and automobile industries). However, a number of drawbacks still raise concerns about their wider use and hamper a more structured introduction in these additional applications.
In particular, the management of heat effects remains a challenge, as an excessive temperature rise can cause reduction of cycle life, battery failures and, above all, may lead to thermal runaway of individual cells or of an entire battery pack, with associated damages to the surrounding people or environment. In the present paper, a simplified model capable of predicting the thermal behaviour of a battery pack refrigerated with a cooling fluid, is presented. It allows to quickly estimating the efficiency of a given cooling system under specific working conditions, and thus identify the range of operation within which a given energy storage system can safely operate.

1. Introduction

For high-power battery packs, considerable amount of heat can be generated in the cells as a result of high discharge currents during duty cycles, causing rapid rise in cells' temperature. An uncontrolled temperature rise, besides causing a number of operational consequences (such as the reduction of cycle life) is also recognized as one of the main causes of a series of harmful events such fires and explosions (Wang et al., 2012; Hendricks et al., 2015; Bubbico et al., 2018a). For optimal performance of a battery pack, working temperatures of the cells in the pack should be limited to within a proper range (generally between 20 °C to 40 °C). Different cooling methods can be selected for battery packs, such as air cooling (see for example Lou, 2007; Sabbah et al., 2008; Sun et al., 2012; Yang et al., 2015, just to name e few), liquid cooling (Valøen et al., 2005; Malik et al., 2018; Zaho et al., 2018), heat pipe cooling (Guo et al., 2011) and phase change materials (PCM) (Sabbah et al., 2008; Ling et al., 2015; Lin et al., 2015; Bubbico et al., 2018b). In order to properly predict the efficiency of any such systems, mathematical modelling is of great importance. CFD modelling is a very powerful tool to get detailed results, however, in most cases it is still too time consuming in terms of setup and calculation time; conversely, simplified one-dimensional models can provide good enough results in a much shorter time, which is very useful when many different configurations need be preliminarily assessed.
One of the earliest thermal and electrochemical analyses focused on battery systems was reported by Bernardi et al. (1984): the battery temperature was assumed constant over the battery surface, being only a function of the time, which can be considered a reasonable assumption for thin batteries such as in the case of the pouch type.
Different phenomena occur within a single battery cell: electrochemical reactions, mass transfer, phase changes, mixing effects and so on, and each of them can be associated with a thermal effect. As a consequence, the energy balance for a cell can be written as:

$$\frac{\partial H_{tot}}{\partial t} = \dot{Q} - IV \tag{1}$$

where H_{tot} represents the overall enthalpy of the different phases, V is the cell voltage, I is the current, which is positive or negative depending on the operation phase (i.e. charging or discharging, respectively), and t is the time.

From Eq (1), the heat generated per unit time can be calculated as:

$$\dot{Q} = I(V - E_0) - IT\frac{\partial E_0}{\partial T} - \sum_i \Delta H_i^{avg} r_i - \int \sum_j (\bar{H}_j - \bar{H}_j^{avg})\frac{\partial c_j}{\partial t} du \tag{2}$$

where, E_0 is the Open Circuit Voltage (OCV), T the cell temperature, ΔH_i^{avg} is the enthalpy variation associated with the i-th chemical reaction, r_i its reaction rate, $\bar{H}_j$ the partial enthalpy of species j, $\bar{H}_j^{avg}$ the average enthalpy of species j, and c_j its concentration. In addition, u is the battery volume and "avg" indicates any property calculated at the average volumetric concentration.

According to Thomas et al. (2003), Eq (2) can be further simplified, and the generated heat can be split into two distinct terms which can be written as:

$$\dot{Q}_{irr} = I(V - E_0) = RI^2 \tag{3}$$

$$\dot{Q}_{rev} = IT\frac{\partial E_0}{\partial T} = T\Delta S\frac{I}{nF} \tag{4}$$

Eq (3)**Errore. L'origine riferimento non è stata trovata.** represents the exothermic irreversible effects associated with the Joule effect, which depend on the internal resistance of the cell. Eq (4) is the reversible heat associated with the entropy variations caused by the cell reactions (Bernardi et al., 1984); this heat effect can be positive or negative depending on the circulating current (whether during charge or discharge) and on the state of charge (SOC) of the cell (Nazari et al., 2017).

Based on the above considerations, a simplified one-dimensional model is presented here, capable of quickly predicting the temperature trend for a battery pack, provided with a cooling system, during charge and discharge phases. This will allow to estimating the expected temperature rise within a battery pack, in a very short time, which can be very useful for example for a preliminary comparison of different cooling fluids efficacy. A few dielectric oils have been selected, based on a compromise between cooling efficiency and safety considerations: the results obtained with four different commercial thermal fluids have been compared with air and reported. It can be seen that in all cases the use of a dielectric liquid is much more efficient than air in keeping the battery temperature within safe limits.

2. Battery Thermal Model

A one-dimensional model has been developed in Labview language (National Instruments) to predict the temperature trend during the charge/discharge phases of a pack of pouch type cells, refrigerated with a cooling fluid flowing in the space between the cells. A simplified approach was used assuming that the temperature of a battery varies with time but remains uniform throughout the system at any time. According to these hypotheses, the energy balance for a refrigerated cell (which can be easily extended to a whole battery pack) can be written as in the equation below:

$$MC_p\frac{dT}{dt} + hS(T - T_r) + \varepsilon S\sigma(T^4 - T_r^4) - \dot{Q} = 0 \tag{5}$$

In this equation, the first term represents the thermal energy variation of the cell, the second one is the heat removed by the cooling fluid by convection, and the third one is the possible radiant fraction of the heat exchanged with the cooling fluid. Tr is the average temperature of the cooling fluid.

Last term in Eq (5) is the already mentioned generated heat (see Eq (3) and Eq (4)):

$$\dot{Q} = \dot{Q}_{irr} + \dot{Q}_{rev} \tag{6}$$

If the radiant heat can be neglected, the trend of the temperature with time is then given by:

$$T(t) = \left[T_i - \frac{\beta}{\alpha}\right]e^{-\alpha t} + \frac{\beta}{\alpha} \tag{7}$$

with:

$$\alpha = \frac{2hS\Gamma_r c_{pr}}{(2\Gamma_r c_{pr} + hS)Mc_p} \tag{8}$$

$$\beta = \frac{\dot{Q}}{Mc_p} + \frac{2hS\Gamma_r c_{pr}}{(2\Gamma_a c_{pr} + hS)Mc_p}T_{ri} \tag{9}$$

Besides the already specified terms, in all the above equations, T_i = initial temperature of the battery pack [K], C_p = specific heat of the battery [J/kgK], C_{pr} = specific heat of the cooling fluid [J/kgK], Γ_r = cooling fluid mass flow rate [kg/s], h = heat transfer coefficient W/m^2K], R = battery internal resistance [Ohm], I = discharge current [A], M = mass of the battery [kg], S = heat transfer surface [m^2], σ = Stefan-Boltzmann constant, ε = surface emissivity, T_{ri} the refrigerating fluid inlet temperature.

The following correlations have been used to evaluate the Nusselt number (and subsequently the heat transfer coefficient) under the different flow regimes which might establish:

- Churchill and Chu correlation (Hewitt, 1992) for natural convection;
- Shah (Shah et al., 1978), Baehr-Stephan, Stephan-Preuber (Stephan, 2010), Hausen (Liu et al. 2011) correlations for laminar flow;
- Colburn correlation and Gnielinski correlation for transitional/turbulent flow (Thirumaleshwar, 2006, Kakac et al.,1987).

In summary, in order to obtain the temperature trend of a lithium ion cell under load, the setup model requires the following information to be specified:

- cell's parameters: geometrical configuration (height H and length L), capacity (C), mass (M), specific heat (c_p), internal resistance (R);
- refrigerating fluid properties: pressure (P), initial temperature (T_{ri}), velocity (v);
- room temperature (T_a);
- current value of the discharge/charge cycles (I);
- distance between the cells in a module;
- duration of the discharge/charge cycle.

3. Model validation and results

The model has been validated against experimental tests carried out on a facility available at the ENEA laboratories of the Casaccia Research Center (Bubbico et al., 2017). Cooling air flowed between four EiG pouch cells 20 Ah, with a 3 mm gap between each other, and the temperature was detected by means of 14 thermocouples placed as illustrated in Figure 1.
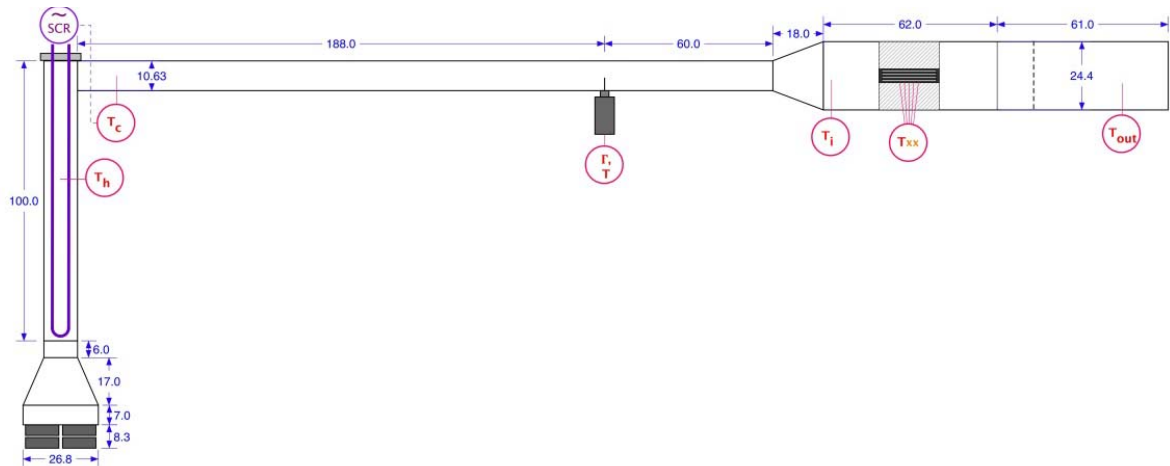

Figure 1: Experimental loop for the cooling tests (Bubbico et al., 2017)

The cooling tests with air have been carried out adopting high batteries discharge rates (4C), and assessing the cooling efficiency at different air flow rates. The reversible heat term has been derived by the experimental

data for $\frac{\partial E_0}{\partial T}$ as a function of the cells state of charge (SOC %) provided by Viswanathan et al. (2010) and by Schuster et al. (2015).

In Figure 2, a comparison between model predictions and experimental results is reported, for a 4C discharge phase and an air flow rate of 1.5 10^{-3} m^3/s. The small differences in the two curves can be explained by considering the following issues: at the beginning of the experimental test, a small delay is required by the cycler to generate the full regime current, which has not been taken into account in the simulation. On the other hand, at the end of the discharge, the experimental temperature rises more rapidly than predicted; this is probably due to the higher resistance characterizing an aged cell at low SOC (%) (Waag et al., 2013), while a constant resistance has been adopted in the theoretical model.
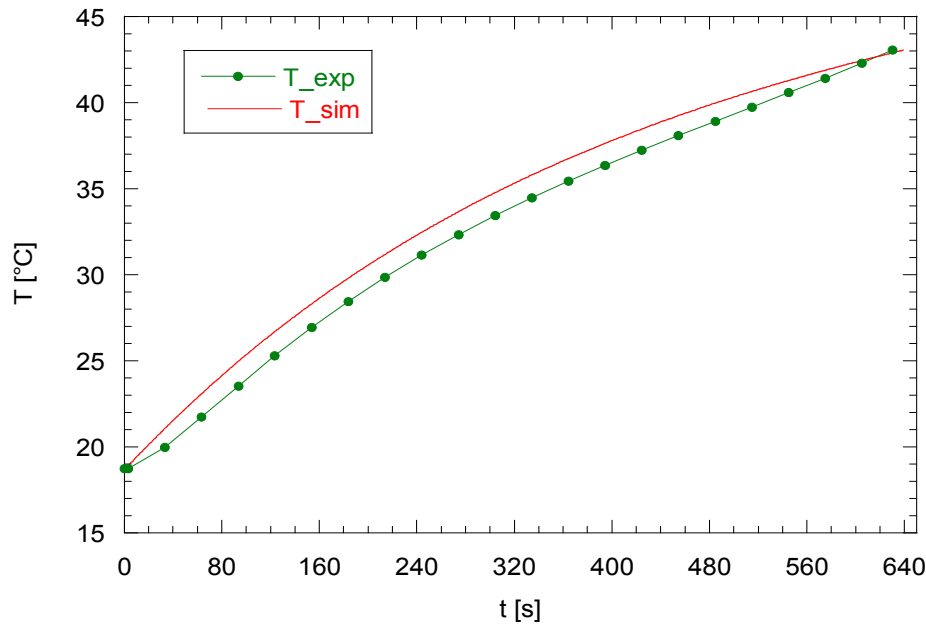

Figure 2: Comparison between model predictions and experimental data, for a 4C discharge and air velocity of 4 m/s (1.5 10^{-3} m^3/s flow rate).

After validation, the model has been applied to assess the cooling efficacy of a number of dielectric liquids. Based on a compromise between cooling efficiency and safety considerations, 4 liquids have been finally selected (see **Errore. L'origine riferimento non è stata trovata.**) out of 18 initially considered. The respective temperature trends as a function of time have then been compared with that obtained with air, and the results are reported in Figure 3. In order to have a more meaningful comparison, the temperature profiles reported in the figure have been derived assuming a constant pumping power of 0.02 W for all the runs and a discharge rate of 5C.

Table 1: Dielectric fluid properties

	Clearco STO50	Clearco 125	PM-Midel 7131	Midel ICE
ν (cSt)	50	125	29	7.7 (at 40°C)
μ (Pa.s)	0.048	0.134	0.0281	0.007
ρ (kg/m^3)	960	1070	970	915
T_{PP} (°C)		-51	-60	-75
k (W/mK)	0.15	0.14	0.15	0.13
c_p (kJ/kg)	1.5	1.498	1.8	1.947
T_b (°C)	-	-	>300	-
T_{FP} (°C)	>300	315	260	190

PP=Pour Point, FP=Flash Point, b=boiling

Overall, it is apparent from Figure 3, that the use of a dielectric liquid is always much more efficient than air in keeping the battery temperature within safe limits, with a difference of about 25 °C at the end of the simulation time; in particular, the final temperature of 50 °C reached in the tests with air, may result well beyond the safe

range for a number of commercial cells. As far as the various liquid refrigerants are taken into consideration, from a strictly thermal point of view, a difference of about 3 degrees was registered among each other, with the Clearco PM125 oil showing the worst performance due to its high viscosity. However, based on the data by the manufacturer, the Clearco PM125 has also the highest flash point (315°C), which makes it the best candidate from a safety point of view, since it could better withstand extreme thermal conditions associated with overheating or even a possible thermal runaway. This factor, as well as many others such as toxicity, availability, cost, etc., should also be taken into consideration for a final choice. As a first approximation, the Clearco STO50 seems to represent a good compromise.
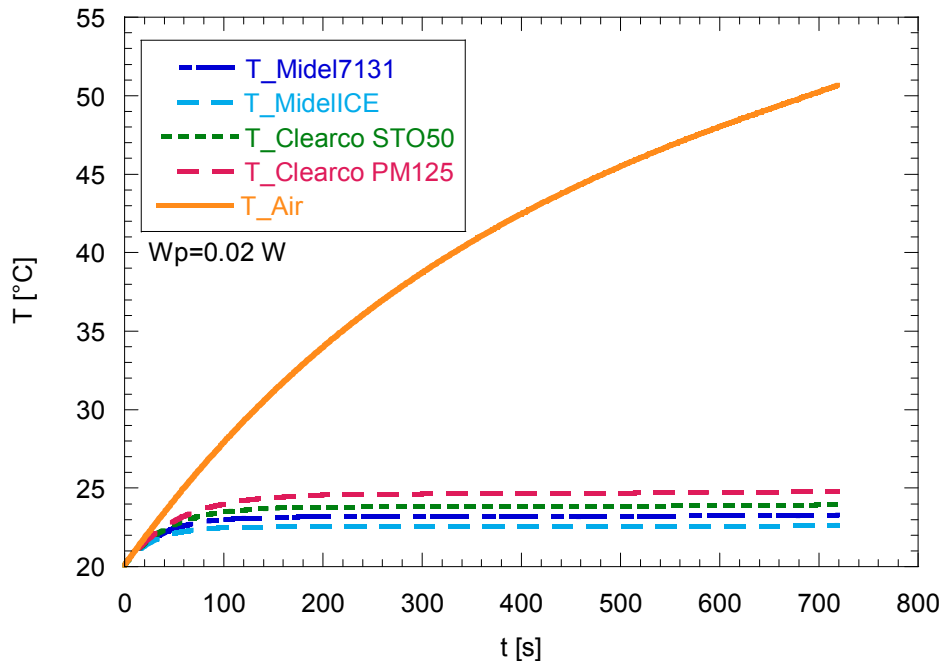

Figure 3: Battery pack temperature profiles obtained using air and the dielectric oils of Table 1 (@ 5C discharge rate and 0.02 W pumping power)

4. Conclusions

In the present paper, a one-dimensional model has been set up and applied to simulate the temperature trends within a battery pack of Li-ion pouch cells, in connection with the use of different cooling fluids.

After validation against experimental tests, the model has been applied to assess the cooling performance of four dielectric liquids. The fluids adopted have been selected considering both their thermal and hazardous properties. It has been shown that the cooling efficacy of the dielectric oils, at the same pumping power, is always higher than that of air; under certain conditions, it was possible to reduce the maximum temperature of the batteries by more than 25°C at the end of the simulation time. This difference can be significant since, given the usual operating temperature range of common cells, it can discriminate whether a given system might be used or not for a particular application.

The model is simple, flexible, and provides results in a very short time, so that the performance of new cooling fluids can be quickly assessed. This can be useful in a number of practical applications where the possibility of adopting a given battery system has to be preliminarily assessed in order to avoid the occurrence of damaging accidents for the surrounding people or the environment, which are often caused by an excessive cell temperature.

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