# Isothermal calorimeter heat measurements of a 20Ah lithium iron phosphate battery cell

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Abstract—The heat generation of a 20Ah lithium iron phosphate pouch battery is characterized in this paper through the conduction of isothermal calorimeter measurements. The influence of temperature and current on battery heat generation is examined by including different operating conditions to the testing matrix, and the influence of the SOC on the battery heat rates is also studied throughout stepped current pulse procedures. Besides, the influence of reversible and irreversible heat contributions is also examined by analyzing the obtained output data. The presented examination was carried out as part of the design process of the battery system for EVs within the context of the JOSPEL project.

Keywords—lithium iron phosphate (LFP), isothermal calorimeter, calorimetry, entropic coefficient, lithium-ion.

## I. INTRODUCTION

Temperature is known to be one of the most influencing factors on the electrochemical processes within lithium-ion cells, affecting the life, cost, performance, and safety of the batteries [1]. While low temperatures slow down the electrochemical activity, diminishing extensively the power capabilities of any lithium-ion battery [2], high temperatures can eventually lead to the so-called thermal runaway, occasionally causing fire or even an explosion of the battery [3]. Moreover, capacity and power fade faster at extreme temperatures [1,4,5].

For these reasons, large battery packs such as the ones demanded in EVs or HEVs, require on the one hand of the development of battery thermal management systems (BTMS) to keep the batteries in the desired operating temperature range (usually 20-40°C) and to minimize temperature gradients across the battery pack [6].

On the other hand, accurate temperature estimation is also critical for the precision of battery management systems (BMS), which include algorithms for cell balancing and for estimating the state of charge (SOC) and state of health (SOH) of the batteries.

In order to predict the temperature in battery systems, numerical modeling appears as one of the most powerful tools, from micro to macroscopic scales and from nondimensional to fully spatially resolute simulation schemes. However, experimental investigation of the battery heat generation might still be necessary to validate the simulation models.

Characterizing or measuring the battery heat generation presents still a daunting number of challenges, especially due to the high reactivity of lithium with air or moisture. Isothermal heat conduction calorimetry arises as one of the best state-of-the-art existing tools, giving direct information of the heat dissipation rate of the battery sample from a systems perspective.

In this paper, the results of a set of isothermal calorimeter measurements conducted at Fraunhofer ISE on a 20Ah pouch lithium iron phosphate (LFP) commercial battery are presented. The proposed procedures have the objective to spotlight the potential of this characterization methodology.

#### II. BACKGROUND

The general partial differential equation (PDE) which describes the distribution of heat and the variation of temperature within a battery or pack can be written as

$$mC_P(dT/dt) + \nabla \cdot \boldsymbol{q} = q_{gen} - q_{dis} \tag{1}$$

where, by Fourier's law, the heat flow within and through the body of the battery itself is determined by

$$\boldsymbol{q} = -\lambda \,.\,\boldsymbol{\nabla}T \tag{2}$$

Note that, apart from the external heat dissipation  $q_{dis}$  (which includes external heat conduction, convection and radiation), equations 1 and 2 are dependent on the thermo-

physical properties of the battery (density, heat capacity and thermal conductivity) and on the heat generation rate of the battery sample,  $q_{gen}$ .

The thermo-physical properties of the battery are difficult to be experimentally determined, because of the complexity of the sandwich/layered structure of the active cell materials (thus, highly anisotropic properties) and the composition of each of the viscous or porous components. Besides, the internal inspection of the components is expensive and difficult, and requires working in an inert atmosphere due to the high reactivity to air and moisture of most of the components.

Similarly, the battery heat generation is difficult to estimate, due to the complexity of the electrochemical processes and its sensitivity to different operating conditions. Heat generation in electrochemical cells includes reaction terms, joule effects, and phase change and mixing effects [1,7], and is usually estimated in the literature from the energy balance derived by Bernardi et al. in the mid-1980s [8]. This enthalpy balance is normally presented in a simplified form, where average heat capacity and isothermal conditions are assumed and the effects of mixing and phase change terms are neglected [9]. This is written

$$q_{gen} = I \left( V - U \right) + IT \left( \frac{dU}{dT} \right)$$
[W] (3)

where the term I(V-U) corresponds to the irreversible heat contribution, whereas IT(dU/dT) reflects the reversible sources, corresponding to entropy changes. *V* is the operating voltage, *U* is the equilibrium voltage (or opencircuit), T is the temperature, and dU/dT is the so-called entropic factor.

However, this energy balance does not consider the ohmic heat in the current collectors, and this can be considerable in large pouch batteries due to constriction/spreading effects near the current tabs [10,11]. These effects may eventually lead to temperature inhomogeneities among the battery surface, as observed by IR imaging in [12,13] and, as a result, in electrochemical or electrical imbalance within the battery.

Furthermore, knowing that LFP cells show open-circuit voltage hysteresis [14], that the entropic factor is very difficult to measure, and that the operating voltage V is already difficult to estimate on its own (normally requiring of the adoption of Kalman filter strategies to amend SOC imprecisions [15]), it can be deducted that this model equation (eq. 3) is, in practice, very difficult to apply.

Thus, for all the previous reasons, and since the computation of the temperature is that important, it is recommended to experimentally measure or verify the battery heat generation rate by calorimetric tests.

## III. EXPERIMENTAL SETUP

## A. Instrument

The employed isothermal calorimeter is the *Netzsch IBC284*, and consists of an analysis chamber submerged in an isothermal bath of a 50/50 mixture of glycol and deionized water that permits the reach of below zero degrees temperatures without freezing.

The thermal bath temperature is controlled to a precision of  $\pm 0.01$  °C, and the heat that flows in/out the experimental chamber is measured by an array of high sensitivity type K thermocouples with an accuracy of  $\pm 15$  mW.

As compared to accelerated-rate calorimeters (ARC), where adiabatic conditions are foreseen, the isothermal calorimeter appears as a better characterization tool for batteries. The main reasons are:

- Constant thermal bath temperature minimizes the battery operational temperature increase. Instead, the battery temperature increases drastically more in ARC.
- Direct measurement of the heat flux, no need for estimating the battery heat capacity.



FIGURE 1: CUT-AWAY OF THE CALORIMETER, ADAPTED FROM [16].

# B. Calibration

A calibration factor is necessary to convert the voltage that is generated in the heat flux gauges (due to thermoelectric effects) to heat flux energy.

In order to obtain the calibration factor, several current pulses are applied to a high precision shunt resistor which is placed in the analysis chamber. After running several calibrations, the obtained calibration factors are observed to be slightly dependent on the bath temperature set point, as it was expected and as it can be seen in Fig. 2. The calibration factor variations are maintained under 2% as it was specified by the manufacturer, proving its repeatability and the overall precision of the instrument.

During the experimental testing phase presented here, the calibration has been repeated before and after every

battery test, and an average calibration factor is used to process of the obtained data.



FIGURE 2: OBTAINED CALIBRATION FACTORS

## C. Test procedure

Once the calorimeter has been calibrated, the investigated battery sample is placed inside the analysis chamber as shown in Fig. 3. Inside the testing chamber, the battery is connected to a copper busbar, which is externally controlled by a *Digatron MCT 300-05-3 ME* battery cycler.

Four different temperature sensors are placed on the surface of the pouch battery, two near each of the current collector tabs, one at the middle, and one next to the battery edge.



FIGURE 4: TEST PROCEDURE

Two voltage sensors are used: one at the busbar, and one at battery terminals, allowing for the direct calculation of the parasitic ohmic losses generated from the contact resistances and the connection between the battery and the busbar, which can be written

$$q_{batt} = q_{measured} - I(V_{busbar} - V_{batt})[W]$$
 (5)

The main influences in the magnitude of the battery heat generation are expected to be the current, the temperature, and the SOC. With this in mind, a test is designed for the Digatron battery cycler including the procedures (all at a fixed current rate) shown in Fig. 4.

The designed test procedure gives, on the one side, information on the full cycle processes, which is interesting because of the fast charge procedures that are often demanded in EVs and HEVs applications to charge the batteries in the shortest time possible. On the other side, the stepped charge and discharge procedures give insight on the SOC dependency of the battery heat, by means of a set of discrete/averaged interval data values.

In order to investigate the temperature and the current influences, this same procedure is tested at different temperatures and current rates. Since the tested battery efficiency is very good, and due to a lower interest, only currents higher than 1C are included in the experimental matrix.



FIGURE 3: BATTERY SETUP IN THE ANALYSIS CHAMBER

#### D. Data evaluation

A plot of the typical bare output that is obtained from current pulses is shown in Fig. 5.

The interpretation of the recorded heat flux (blue) or temperature (red) values at a concrete time instant is difficult because of the system complexity. For example, the instantaneous heat dissipation rate inside the chamber is unknown, as well as the thermal power that controls the bath to a stable temperature. Besides, the experimental chamber itself might also absorb some thermal energy, slightly increasing the temperature, when a thermal event is undergoing in the testing sample. Therefore, the value of the heat flux at any precise time is non representative. Conversely, if we take a time interval  $(t_1, t_2)$  that starts and ends up in equilibrium conditions, defined as

$$T(t_1) = T(t_2)$$
$$(dT/dt)|_{t^1} = (dT/dt)|_{t^2} = 0$$

it can be derived that the temporal integration of the measured heat flux corresponds to the overall thermal energy that the battery has dissipated within this time interval.

This means that, after any test procedure (applied current pulse), and before the next thermal event, a relaxation time must be necessarily ensured to recover equilibrium conditions in the calorimeter. Then, from the integrated heat flux area, which corresponds to the dissipated heat energy, an average battery heat power rate can be estimated for every event as

$$q_{batt,avg} = (\int_{tl}^{t^2} q_{batt} dt) / (t^2 - t^1) [W]$$
 (6)

and, by further integration of the electrical input, the average battery efficiency can also be obtained as

$$\eta_{batt} = (1 - q_{batt} / P_{elec,in}).100 \ [\%] \tag{6}$$

where  $P_{elec,in}$  is the electrical power that has been introduced or subtracted to the battery.

As multiple area integrations are needed during the evaluation of the obtained data, an automated data evaluation script has been developed to increase the efficiency of the data evaluation process. The automated heat flux integration avoids, besides, the possible human errors that are subject to the manual definition of the time integration limits of every thermal event.



FIGURE 5: EXAMPLE PLOT OF THE CALORIMETER OUTPUT

Moreover, the script's algorithm automatically subtracts the contact Joule dissipation effects from the heat

energy (equation 5), and estimates the portion of reversible and irreversible heat contributions by:

- 1. First, the open-circuit voltage curve U is estimated from stationary voltage data, obtained after 6h relaxation, and with a resolution of X%SOC (see Fig. 4).
- 2. Then, according to equation 3, the irreversible heat is obtained by the temporal integration of the curves belonging to the experimental current, and the difference of the obtained voltage V and the open-circuit voltage U.
- 3. Finally, the reversible contribution is estimated subtracting the irreversible heat to the total heat energy measured.

Last but not least, and using a similar procedure as the one suggested in [17], once the contributions of the reversible and irreversible heat sources have been separated, the internal resistance of the battery and the entropic factor can be estimated by

$$R_{batt} = q_{irrev} / (I^2)$$
 (7)

$$\frac{dU}{dT} = q_{rev} / (IT)$$
(8)

where average battery temperature and current are used from the time interval of the analyzed current pulse.

#### IV. RESULTS AND DISCUSSION

## A. Full cycle

The integrated heat flux results for full cycles at a current of 1C are gathered in the Table 1. In all the table cells, the upper value corresponds to charge and the lower value, conversely, to discharge processes. In this table, the values are compared to the sum of the energy released during the stepped processes at the same current of 1C (presented in the following section).

As presented in Table 1, the released thermal energy is observed to be higher at colder temperatures, as it was expected due to the sluggish electrochemical reactions and ionic transport rates. This can also be observed from the post-processed battery efficiency values,  $\eta_{batt}$ , computed as in equation 6 and included in Table 2.

TABLE 1: FULL CYCLE THERMAL ENERGY DISSIPATION

		T=0°C	T=20°C	T=40°C
Full cycle @1C	char	15646 J	10515 J	6696 J
	disch	20867 J	14801 J	6643 J
SUM 10x(10% SOC	char	14845 J	10111 J	5930 J
steps @1C)	disch	20634 J	10689 J	5899 J

TABLE 2: FULL CYCLE BATTERY EFFICIENCIES

		T=0°C	T=20°C	T=40°C
Full cycle @1C	char	93,7 %	95,9 %	97,4 %
	disch	85,7 %	91,3 %	97,3 %
MEAN (10% SOC steps @1C)	char	94,1 %	96,1 %	97,8 %
	disch	89,3 %	95,1 %	97,4 %

Note that the charge thermal efficiency is always greater than that of discharge. Furthermore, it can be seen that the difference between charge and discharge thermal efficiencies increases at lower operating temperatures.

Going back to the values presented in Table 1, it might be observed that the sum of the thermal energy release undergoing the stepped process differs from the values obtained during the CCCV full cycle procedures, especially in the case of the 20°C discharge test. In the results of the conducted experiments, the full cycle's heat dissipation is always slightly higher than the sum of the stepped processes. Nonetheless, the sources leading to these differences between stepped and continuous processes include different factors whose influence is difficult to be quantified. For example, the battery temperature increases slightly more in the case of full cycles, even if the calorimeter bath temperature keeps stable at all times. Another difference might be related to the transient establishment of the battery overpotential, which takes a higher importance in the case of the stepped processes. Another non-negligible influence is the different time duration of the constant-voltage (CV) phase, which is in most cases slightly longer in full cycle process than during the stepped pulses.

## B. Stepped process

The current pulse step time duration has been fixed in this paper to 10% SOC. The integration of the recorded heat flux during such stepped procedure yields to the average battery heat generation power presented in Figs. 6 and 7.

In these figures it can be seen that, in the case of the LFP battery under investigation, the peaks of the heat generation undergoing discharge processes are almost twice the maximum heat rates during charge. Besides, it is observable that the shape of the obtained heat generation rates is drastically different from charge to discharge processes, and thus the thermal behavior of the battery, which must be attributed to the reversible effects.

At this point, it is worthwhile mentioning that the nonfilled plotted points, found at high SOC in charging and low SOC in discharging procedures, do not correspond to galvanostatic or constant current regimes, since the cut-off voltages -2V and 3.6V- are reached. Then, the battery cycler stops applying a constant current (CC), and a constant voltage (CV) phase starts.

With this in mind, it is clear that the heat generation power (Figs. 6 and 7) tends to increase, towards high SOC when charging, and towards low SOC when discharging. This has necessarily to be attributed to diffusion limitations, which slow down the insertion of lithium ions when the active electrodes get full. This is reflected in Figs. 8 and 9, where the associated internal resistance of the battery, obtained from equation 7, is shown for the charge and discharge processes at a current rate of 1C.

As explained in the previous section, the irreversible heat is estimated from the recorded operating voltage, V, and by an approximation of the open-circuit voltage U. In this case, the open-circuit voltage is approximated by a linear interpolation of the scattered voltage data that is obtained after the 6 hours relaxation that is required after every thermal event (see Fig. 10).



FIGURE 6: AVERAGED BATTERY HEAT GENERATION DURING CHARGE



FIGURE 7: AVERAGED BATTERY HEAT GENERATION DURING DISCHARGE



FIGURE 8: ESTIMATED BATTERY INTERNAL RESISTANCE DURING CHARGE @1C



FIGURE 9: ESTIMATED BATTERY INTERNAL RESISTANCE DURING DISCHARGE @1C

The results in Fig. 10 show the open-circuit voltage's hysteresis that is expected in lithium-ion batteries, especially in those with LFP cathode, and the obtained values are comparable to the detailed voltage path dependency presented in [14].

Regarding the reversible heat contribution, Fig. 11 gathers the results for the entropic coefficient estimation, which is derived from the obtained experimental data by equation 8. The derived entropic coefficient values for the 1C tests at 0°C, 20°C, and 40°C show an average standard deviation of 4,5e-2 mV/K, confirming the negligible dependency of the entropic coefficient on the temperature.

Moreover, the obtained values are quantitatively in good agreement with the results that were conducted previously for the same battery and presented in [18], in this case, employing a high precision potentiostatic method. Comparatively, regarding experimental time-consumption, the values for the entropic coefficient have been obtained within 5-7 days using the presented calorimetric procedure, being this less than the one third of the time that the high-precision potentiostatic method required.



FIGURE 10: OBTAINED OPEN-CIRCUIT VOLTAGE (STATIONARY)



FIGURE 11: DERIVED ENTROPIC FACTOR FROM THE STEPPED PROCESSES @1C

#### V. CONCLUSIONS

In this paper, isothermal calorimeter measurements of a 20Ah LFP pouch battery are presented for full cycle and stepped current pulses procedures.

The heat dissipation rate results show complete different shape between charge and discharge procedures, which is attributed to diffusion limitations and reversible entropic changes. The strong influence of the operating current and temperature, as well as the SOC, on the battery heat production rate are confirmed by the experimental results.

The current is proved to be the major influence, contributing to both the irreversible and reversible contributions. The decrease of heat generation with increasing temperature has to be explained by the internal resistance decrease, as it has been seen that the entropic effects are approximately invariant in temperature.

It has been identified that CV phases at the low and high end cut-off voltages complicate the analysis of the data. Therefore, procedures including CV phases might only be used to obtain direct information about the heat rates undergoing these concrete kind of phases (especially important for testing fast charge procedures), but might not be useful for model parametrization purposes.

The described test and data analysis is suggested as a general testing procedure for thermal testing of batteries since, as shown, different meaningful output data can be obtained and analyzed from a unique test, including stationary open-circuit voltage, efficiency, internal resistance and entropic factor of the sample of study.

## ACKNOWLEDGMENT

The authors would like to thank for the funding the JOSPEL project has received from the European Union's Horizon 2020 research and innovation program under Grant Agreement n° 653851.

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