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Methodology to determine the heat capacity of lithium-ion cells

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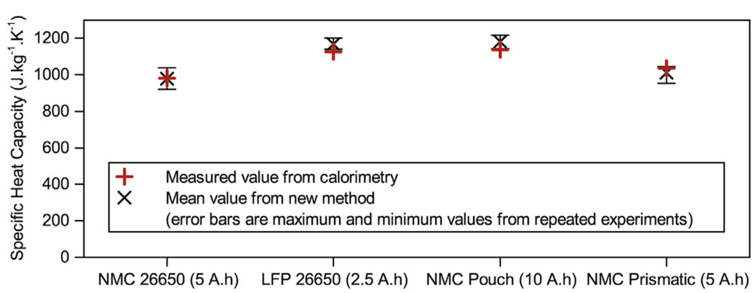
HIGHLIGHTS

- New method to determine the specific heat capacity of lithium-ion cells.
- Same method is applicable to cylindrical, pouch and prismatic cells.
- Results verified using calorimetry.
- Method uses common, inexpensive equipment found in many laboratories.
- Thermal model results validated experimentally for a range of operating conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper a novel method to determine the specific heat capacity of lithium-ion cells is proposed. The specific heat capacity is an important parameter for the thermal modelling of lithium-ion batteries and is not generally stated on cell datasheets or available from cell manufacturers. To determine the specific heat capacity can require the use of an expensive (> £100 k) calorimeter or the deconstruction of the cell whereas the method proposed by the authors in this paper uses common equipment found in most battery laboratories. The method is shown to work for cylindrical, prismatic and pouch cells, with capacities between 2.5 Ah and 10 Ah. The results are validated by determining the specific heat capacity of the cells with use of a calorimeter and a maximum error of 3.9% found. Thermal modelling of batteries is important to ensure cell temperatures are kept within specified limits. This is especially true at rates over 1C, such as the fast charging of electric vehicles, where more heat is generated than lower rate applications. The paper ends by demonstrating how the thermal model that underpins the authors' methodology can be used to model the surface temperature of the cells at C-rates greater than 1C.

1. Introduction

Energy storage is a topic that has gained much research attention in recent years, primarily with the end goal applications in either the transportation or electricity grid support sectors. Lithium-ion batteries have emerged as the dominant energy storage technology for transportation applications and are also used for many grid support applications. Operating lithium-ion batteries within a limited temperature range, usually between 15 °C and 35 °C, is important for extending the lifetime of battery [1]. Operating outside the specified temperature range will reduce the lifetime of the battery and, in addition, if the battery becomes too hot and the temperature exceeds the

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thermal runaway onset temperature, thermal runaway can occur leading to catastrophic failure [2]. Thermal modelling of lithium-ion batteries is therefore required during the battery design process to ensure the battery is designed to operate safely within the specified limits.

The thermal modelling of lithium-ion batteries becomes essential when batteries are operated at high rates where more heat is generated. Electric vehicle batteries may be required to operate at rates above 1C continuously while charging. The aim to increase charging rates in the future means thermal modelling and thermal management of the batteries will become even more important [3]. Hybrid and plug in hybrid electric vehicles have smaller capacity batteries than electric vehicles, however the cells have to operate at much higher rates and so thermal modelling is also important. An example are the Blue Energy cells, which are installed in many hybrid vehicles, these cells have a capacity of 5 Ah but may have to operate at up to 300 A for short periods during regenerative braking [4].

Thermal models of lithium-ion cells often start with a simple heat balance at a single point [5]. The rate heat is released or absorbed at the point is equal to the rate heat is generated or consumed at the point plus the rate heat is transferred to or from the point, this is described in more detail in Section 2. One and two dimensional models of lithium-ion cells that use few points can be created by programming the finite difference calculations [6]. More detailed three dimensional models using many points may require finite element modelling to predict the temperature in more complicated scenarios [7–10].

Differences between thermal models of lithium-ion cells arise due to the complexity of the cell geometry and the details of the different materials used in the cell, including their exact locations within the cell and the types of heat generation and consumption considered, this is described in more detail below. As with all modelling a trade off between accuracy and complexity must be considered.

The specific heat capacity of the cells is a critical thermal parameter that is required for all cell thermal models, irrespective of the thermal model employed. The heat capacity of an object is a measure of how easy it is to change the temperature of the object by transfer of heat. Depending on the required model complexity there may be one value for the heat capacity of the entire cell or multiple values at different locations within the cell [11–13], representing the different materials that the cell is constructed from. It should be noted that the specific heat capacity is not stated on cell datasheets and manufacturers often do not have data on the specific heat capacity of their cells. This paper focuses on modelling cases where a single value for the heat capacity is used.

One common method to find the heat capacity involves a weighted sum of the heat capacities of the materials inside the cell [14] however this either requires deconstructing the cell and determining the materials chemically or having detailed information regarding the make up of the cell, which normally is not available. A second common method is to use calorimetry [15], however the equipment to perform this calorimetry is expensive, often costing more than £100,000 and not commonly available in many laboratories. In this paper we demonstrate a novel method to determine the specific heat capacity of cells using common equipment found in most battery laboratories, the method requires only a battery analyser, temperature sensors and a fan.

As well as the specific heat capacity of a cell, a second parameter required for many thermal models is the thermal conductivity of the cells [16]. The thermal conductivity of the cell is a measure of how easily heat is transferred through the cell by conduction. The thermal conductivity varies within a cell depending on the direction of heat transfer [17]. Take for example a spirally wound cylindrical cell, the thermal conductivity will be different longitudinally and radially. Longitudinally, the heat is travelling through the same material, for example along a copper current collector. Radially, the heat is travelling through many layers of different materials, for example through the current collector, electrode, separator, etc. As an approximation, the model used in this paper does not differentiate between directions and uses a single value for the internal thermal resistance.

In the single point heat balance mentioned above, the rate at which heat is released or absorbed at a point and the heat transfer to and from a point are standard equations for thermal models, while the rate heat is generated or consumed in the cell is particular to lithium-ion battery thermal models. The estimation of the heat generation and consumption in a cell again depends on the model complexity and often four different terms of heat generation and consumption are discussed [18]: ohmic heating; reversible entropic heat; heat produced or consumed by any chemical reaction; heat of mixing.

In many thermal models of lithium-ion cells only the ohmic heating and reversible entropic heat terms are considered as they have the largest impact on temperature [19,20]. The ohmic heating term is the heat generated as current passes through the cell and is always generating heat when the current exists, it is equal to the current squared multiplied by the resistance. The entropic heat term is the entropy change of the cell reaction and it can either generate or consume heat, it is equal to the current multiplied by the temperature multiplied by the rate of change in open circuit voltage of the cell with temperature, which varies depending on the cell state of charge. The entropic heat term therefore requires significant cell characterisation of the open circuit voltage versus temperature across the range of state of charge which is a time consuming task [21]. Depending on the current rate of charge or discharge of the cell, either the ohmic heating term or the reversible entropic heat term may dominate, however note that the ohmic heating term is proportional to the current squared while the entropic heat term is only directly proportional to current.

This paper is structured as follows. The theory and description of the thermal model used by the authors is described in Section 2 and the experimental setup required for determining the specific heat capacity is described in Section 3. The novel method to determine the specific heat capacity of the cells is then described in Section 4. Section 5 presents the standard method to determine the specific heat capacity using a calorimeter and Section 6 compares the specific heat capacity values from Sections 4 and 5 for two cylindrical cells, one pouch cell and one prismatic cell. Section 7 discusses how the model can be used to predict the surface temperature of the cells during cycling with further discussion of surface temperature variations in Section 8. The paper conclusions are presented in Section 9.

2. Description of the cell thermal model

The lithium-ion cell thermal model used has previously been reported for a lithium-ion iron phosphate cell [22]. In this model heat is generated at a point inside the cell where this point has a specific heat capacity and a mass. The heat is then transferred from the inside of the cell to the cell surface where there is no mass or specific heat capacity. Finally, the heat is transferred from cell surface to the ambient environment as shown in Fig. 1. The internal and external heat transfer

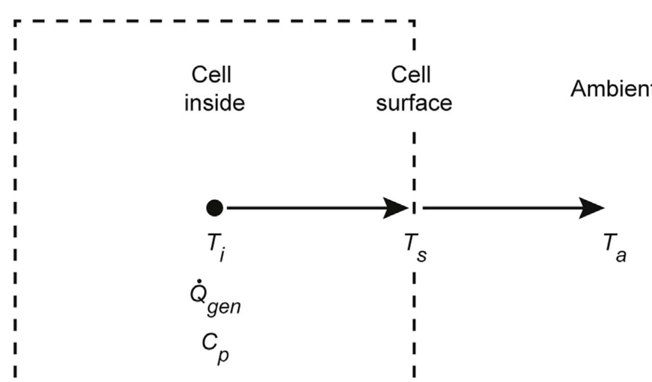

Fig. 1. Overview of cell thermal model.