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A study on specific heat capacities of Li-ion cell components and their influence on thermal management

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HIGHLIGHTS

- Temperature and SOC dependent specific heat capacities.
- Simple correlations for application in thermal models.
- 2D-thermal model of an automotive PHEV Li-ion cell.
- Influence of specific heat capacity on thermal management.

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ABSTRACT

Thermal models of Li-ion cells on various geometrical scales and with various complexity have been developed in the past to account for the temperature dependent behaviour of Li-ion cells. These models require accurate data on thermal material properties to offer reliable validation and interpretation of the results.

In this context a thorough study on the specific heat capacities of Li-ion cells starting from raw materials and electrode coatings to representative unit cells of jelly rolls/electrode stacks with lumped values was conducted.

The specific heat capacity is reported as a function of temperature and state of charge (SOC). Seven Li-ion cells from different manufactures with different cell chemistry, application and design were considered and generally applicable correlations were developed.

A 2D thermal model of an automotive Li-ion cell for plug-in hybrid electric vehicle (PHEV) application illustrates the influence of specific heat capacity on the effectivity of cooling concepts and the temperature development of Li-ion cells.

1. Introduction

In the field of thermal modelling of Li-ion cells many improvements have been achieved in recent years. Particularly coupled electrochemical-thermal models and thermal management analyses have been intensely discussed. The complexity of numerical approaches with emphasis on thermal issues ranges from modelling of detailed reconstructed electrode microstructures [1] and sophisticated multiscale and multidimensional approaches (MSMD) [2–5] to lumped cell models for battery pack analysis [6–11].

Against the background of extensive activities in thermal modelling, surprisingly few publications address the determination of thermal material properties, namely thermal conductivity and specific heat capacity, of Li-ion cell components. It is well known that deeper insights of thermal material properties enhance the accuracy and validation of numerical models. Despite this obvious conclusion, many numerical models are parametrized with the same thermal material properties such as the frequently cited ones of Chen et al. [12]. Recently new investigations on the temperature dependence of thermal conductivities of electrodes [13] and the effect of ageing on thermal conductivity [14] contributed to a better understanding of thermal behaviour of electrodes.

Most of the scarce studies on specific heat capacities of materials of Li-ion cells focused on complex experimental set-ups only suitable for separators [15], special materials [16,17] or pure active

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materials at very low temperatures [18]. Probably the most relevant investigation was done by Maleki et al. [14], who applied differential scanning calorimetry to determine the averaged specific heat capacities of new and aged cells. However, a comparison of the experimental results with the calculated values based on the specific heat and mass fraction of each component showed a difference of 25% and puts the results into question. Additionally the specific heat capacities of the individual components were not evaluated as a function of temperature nor state of charge.

Apart from the mentioned work on individual components such as electrodes, some experimental set-ups to obtain the average specific heat capacity of full Li-ion cells have been introduced. These publications either consider pouch cells [19–22] or cylindrical cells [23–25] but the proposed methods are not applicable to prismatic hard case cells.

One of the key aspects, which has not been addressed in the previous studies, is provision of a consistent set of data suitable for thermal models regardless of the considered dimensions and chosen scale of resolution. As it is very cumbersome to analyse every single cell in depth, generally applicable functions to describe the specific heat capacity are required for reliable thermal modelling.

In this work the connection of specific heat capacity of pure raw materials, porous electrode coatings and average properties of full Li-ion cells are investigated and three mayor aspects are addressed:

(i) Is there a generally applicable correlation to describe the temperature and SOC dependent specific heat capacity of the most common anode and cathode materials? In a similar way, is there a general function to describe separators, electrolytes and pouch cell foils?
(ii) To what extend is porosity and thickness of the coatings influencing the specific heat capacity of common anode and cathode configurations?
(iii) What general conclusions can be derived for specific heat capacities of full Li-ion cells?

Beyond the experimental investigation addressing the aforementioned questions, this work illustrates influence of thermal material properties, particularly the heat capacity, on model predictions of thermal behaviour of Li-ion cells. For this purpose, a numerical study of the influence of specific heat capacity on the temperature development of an automotive Li-ion cell under different cooling conditions is provided.

Hence, this paper is divided into two parts. The first part focuses on the investigation of specific heat capacities of Li-ion cell materials by differential scanning calorimetry (DSC) in the temperature range of −40 to 60 °C, as it is mainly relevant for automotive application.

In Section 2 the experimental procedure of the DSC measurements is described, followed by comprehensive discussion of the investigation results in Section 3. Starting from raw materials for electrodes and individual Li-ion cell components, common electrode configurations and unit cells of jelly rolls/electrode stacks are investigated as well. In this context a unit cell is referred to as a stack of one separator layer, a double-side cathode, another separator layer and a double-sided anode. This composition is the smallest unit of volume that contains all of the structural information to build up a Li-ion cell.

Following this procedure, experimental data for all thermal simulation approaches such as microstructure reconstructions of electrodes, MSMD models, 3D or reduced order cell models are provided. To gain generally valid correlations, seven representative Li-ion cells of different manufacturers were selected to cover (i) the most common cell chemistries of cathodes such as LCO, NCA and NMC, (ii) prismatic hard case and pouch cell formats, and (iii) the relevant fields of application such as consumer vs. automotive cells and high power cells vs. high energy cells. All considered Li-ion cells are listed in Table 1.

In the second part of the paper (Section 4), a 2D thermal model of a Li-ion cell for PHEV application is introduced in order to highlight the influence of thermal material properties and their temperature dependency.

2. Experiments

Charging of the cells and determination of the capacity was conducted at room temperature according to the charge protocol of each cell. Subsequently the cells were discharged to the designated SOC. Afterwards the cells were inserted into a glovebox with argon atmosphere and dismantled. The materials were extracted and washed using Dimethyl-carbonate (DMC) solvent. The electrodes were prepared for DSC measurements by (i) careful removal of the coatings from the conductor foil to measure the coating material itself and (ii) punching out of small samples with a diameter of 4.5 mm to capture the properties of the full electrode. Subsequently the powders and electrode samples were dried for 12 h at 80 °C to remove remaining components of the solvent. All other investigated cell components were prepared in a similar manner.

The specific heat capacities of the electrodes were obtained by differential scanning calorimetry (DSC) with a Q2000 (TA Instruments) in the temperature range from −40 to 60 °C. Hermetic Aluminium pans were applied for liquid samples and materials soaked with electrolyte to prevent evaporation and mass loss. All measurements were conducted in N_2-atmosphere, with a flow rate of 50 ml/min.

Specific heat capacity of solid samples was evaluated by direct measurement with continuous heating rates of 20 °C/min after calibrating the DSC with a synthetic sapphire disk, which served as standard reference material. Three samples were taken from each material and five consecutive runs were executed for each sample to reduce measurement uncertainty. Samples containing liquids are more temperature sensitive and were analysed by zero-mean sinusoidal excitation with an amplitude of 0.5 K and a cycle duration of 100 s at discrete temperatures.

To calculate average specific heat capacities of electrodes and unit cells additional information on the morphology of the layers is necessary. Therefore, the thickness of each component was determined by a thin film thickness gauge with an accuracy of 1 μm. The porosity of the electrodes was obtained by gravimetric measurements and He-pycnometry (Pycnomatic ATC, Porotec) was applied to measure the density of the electrode coatings. The corresponding data of the considered Li-ion cells is summarized in Table 2. The density of the electrolyte was evaluated by oscillating u-tube measurements (DMA5000, Anton Paar) and the coefficients of the corresponding polynomic correlation are given in Table 3.

Table 1
Overview of Li-ion cells considered for specific heat capacity investigation in this study.

	Application	Type	Chemistry	Capacity/Ah
Prismatic hardcase cells				
Cell A	Consumer	Energy	LCO/C	1.9
Cell B	Consumer	Energy	LCO/C	6.8
Cell C	Automotive	Energy	NMC/C	60.0
Cell D	Automotive	Power	NMC/C	28.0
Pouch cells				
Cell E	Consumer	Power	LCO-NCA/C	3.2
Cell F	Automotive	Energy	NMC/C	50.0
Cell G	Consumer	Power	LCO-NCA/C	2.0