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Thermal conductivity and internal temperature profiles of Li-ion secondary batteries

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HIGHLIGHTS

- Thermal conductivity for Li-ion battery components are reported.
- Values are for different anodes, cathodes and separators.
- Values are with and without electrolyte and at different compaction pressures.
- We report corresponding internal temperature gradients for batteries in operation.

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ABSTRACT

In this paper we report the thermal conductivity for commercial battery components. Materials were obtained from several electrode- and separator manufacturers, and some were extracted from commercial batteries. We measured with and without electrolyte solvent and at different compaction pressures. The experimentally obtained values are used in a thermal model and corresponding internal temperature profiles are shown. The thermal conductivity of dry separator materials was found to range from 0.07±0.01 to 0.18±0.02 $WK^{-1}m^{-1}$. Dry electrode (active) materials ranged from 0.13±0.02 to 0.61±0.02 $WK^{-1}m^{-1}$. Adding the electrolyte solvent increased the thermal conductivity of electrode (active) materials by at least a factor of 2.

1. Introduction

Li-ion batteries have seen a major introduction to small scale hybrid and fully electric vehicles. As larger battery cells have become cheaper, Li-ion based batteries are currently seeing an introduction to large scale electric and hybrid electric vehicles [1], *e.g.*electric buses, hybrid electric buses and hybrid electric ships [2]. As larger vehicles take batteries into use, larger battery packs are needed, and more intense cycles are applied. Therefore, thermal management becomes more important, both internally and externally. The growing use of Li-ion batteries is not only due to their zero emission characteristic during operation and their rather low carbon footprint [3]. It has also been shown, that a more cost efficient application can be realized [2] but the specific energy of the battery is still a limiting factor, when we compare to gasoline-driven vehicles [4].

Fast charging of LIBs would require a good understanding of heat production and heat transfer within the battery. Effects like capacity fade, power fade, and self discharge within Li-ion batteries are well reported in the literature, *e.g.* by Bandhauer et al. [5]. Especially the temperature influence on different ageing mechanisms is well reported [6–9].

Performance and cycle life are also dependent on battery design [10,11], which will influence current distribution, state of charge (SOC), temperature and voltage distribution. This will influence local temperatures [12] and therefore, local degradation (ageing).

As a result, a correct determination and allocation of heat sources together with the thermal conductivities of the different components will allow modelling of internal temperature profiles. This can help a cooling system outside the battery or outside the

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battery pack. Moreover, improved thermal management will improve the understanding of local ageing mechanism and may lead to better battery designs and enhanced lifetimes. We find reports of several researchers using an *in-situ* measurement setup [13–16] to determine internal temperatures.

Finally, knowing internal temperature profiles at high current densities gives the possibility to predict and avoid conditions for thermal runaway, which is a key safety need for LIBs during operation at high current densities. One can see temperature behaviour of LIBs during thermal runaway in the publication of Wu *et al.* [17] who used an accelerated rate calorimeter technique. They showed the increase in temperature of a $LiCoO_2|C$ and a $LiFePO_4|C$ battery when exposed to high temperatures ($>100°C$).

Thermal conductivities of all components are key parameters for the modelling of temperature profiles. The materials' thermal conductivity is not necessarily isotropic. Usually, the terms ”in-plane” and ”cross-plane” are used. If we imagine a thin electrode, we differentiate between the direction perpendicular (cross-plane) and parallel to the plane (in-plane). There are reports on thermal conductivities of Li-ion secondary battery materials [18], but they are not thoroughly investigated [5]. In particular, there is not that many reports on thermal conductivity of separators. In the literature, we find values for separators, but these values vary from 0.33 to 1.29 $WK^{-1}m^{-1}$ [19–22]. Some of these values are assumed and there are almost no reports on the experimental determination of the cross-plane thermal conductivity of a separator. We found one paper from Vishwakarma and Jain [23], in which a transient DC heating method was used to obtain an in-plane thermal conductivity of a separator of 0.5 ± 0.03 $WK^{-1}m^{-1}$. Since the heat production is predominant in the separator-electrolyte region and to some extend within the solid electrolyte interface region at high currents [18], knowledge of the thermal conductivity of the electrolyte soaked separator is critical. In addition, temperature profiles of batteries will vary during operation, in terms of ageing, SOC and C-rate. Internal resistances are reported to increase during ageing [24–26], and this will influence the heat production inside the battery. In addition, the thermal conductivity of the graphite electrodes is reported to change for different graphite particle sizes, the relative amounts of polyvinylidene difluoride binder and carbon-black, and for different compaction pressures [27]. Last, the thermal conductivity is a function of temperature [27,28]. Using photothermal deflection spectroscopy, Logos et al. reported the thermal conductivity for different commercial electrodes and find a decrease of 0.025–0.045 $WK^{-1}m^{-1}$ per Kelvin for different negative electrodes and 0.005–0.050 $WK^{-1}m^{-1}$ per Kelvin for different positive electrodes.

In this paper we report the thermal conductivity for a wide range of pristine materials at different compaction pressures, dry, and soaked in electrolyte solvent. Thereafter, we use an already developed simple 1-dimensional thermal model [18] to compare these values and put them into a thermal context.

2. Experimental

2.1. Apparatus - thermal conductivity measurements

The thermal conductivity meter is presented in Fig. 1. It is explained in detail by Burheim *et al.* [29]. It measures the temperature at different equidistant places in the stainless steel cylinders, the temperature drop over the sample and the thickness of the sample. The thermal conductivity of the stainless steel was known, which made it possible to compute the heat flux through the system.

The average sample temperature was close to room temperature, because of a lower temperature of 10 °C and a higher temperature of 35 °C on the bottom and the top of the thermal conductivity meter, respectively. Measurements were carried out at compaction pressures of 2.3 bar, 4.6 bar 6.9 bar, 9.2 bar and 11.5 bar. When measuring electrolyte solvent soaked samples, materials were soaked in a 50:50 vol% mixture of diethyl carbonate and ethylen carbonate without the presence of $LiPF_6$. As one can see later, this does not significantly effect the thermal conductivity of the examined separator or the NMC-cathode, but an effect on the thermal conductivity of the graphite-anode of up to about 35% increase was measured.

2.2. Materials

We investigated separators from Viledon®, Celgard®, and Whatman. Table 1 gives an overview of all separators, their materials, and their impregnation (in case of the separators from Viledon®).

In addition, we investigated a $LiFePO_4$ electrode from MTI Corporation (bc-af-241lpf-ss), and $LiCoO_2$ (HS-LIB-P-Co-001) and graphite (HS-LIB-N-Gr-001) electrodes from Hohsen Corporation. Finally, we investigated materials from a commercial battery (XALT31HE, MODEL F910-0006), which had a nominal capacity of 31 Ah. The battery materials from XALT were measured after the disassembling of the battery and after cleaning them from remaining $LiPF_6$ salt.

3. Theory

3.1. Thermal conductivity measurements

The total thermal resistance R_{sample}, which is the sum of the thermal resistance of the sample and its contact resistance $R_{apparatus-sample}$ with the apparatus, were plotted as a function of sample thickness and the thermal conductivity was obtained as the inverse of the slope. Different thicknesses were achieved by stacking of samples. In case of electrodes, the thermal resistance of the sample had two contributions, the thermal resistance of the active material $\frac{\delta_{act.M.}}{k_{act.M.}}$ and the thermal resistance of the current collector $\frac{\delta_{foil}}{k_{foil}}$. Both contributions can be expressed by their respective thickness δ divided by their thermal conductivity k. It was shown before [24], that the total thermal resistance can be calculated by using the temperature drop over the sample and the heat flux q_{sample} through the sample.

$$R_{sample} = \frac{T_4 - T_5}{q_{sample}} = 2R_{apparatus-sample} + \frac{\delta_{act.M.}}{k_{act.M.}} + \frac{\delta_{foil}}{k_{foil}} \tag{1}$$

It was also shown, that additional contact resistances from stacking can be neglected [29]. The term δ_{foil}/k_{foil} in equation (1), which refers to the current collectors, equals zero in case separators, and can be neglected in case of electrodes [24].

3.2. Internal heat production

There are three heat sources within a Li-ion secondary battery: ohmic heat production, heat production or consumption due to the entropy change of the electrode reactions (reversible heat production) and heat production from the resistance of the electrochemical reaction. All heat sources were discussed in Ref. [24] and the total heat generation at charge and discharge of a LIB as a whole can be described as follows: