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Local Heat Generation in a Single Stack Lithium Ion Battery Cell

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ABSTRACT

The local heat generation in a single stack lithium ion battery cell was investigated as a function of the C-rate and state of charge (SoC). For that purpose, a custom build electrochemical cell design developed for local in-operando temperature measurements is used. The local temperature evolution in both electrodes and the separator is compared with local heat generation rates calculated from galvanostatic intermittent titration technique (GITT) measurements. The impact of reversible and irreversible heats is evaluated as a function of the C-rate and the SoC. The results reveal substantial differences in the local heat generation rates of the individual components of the battery cell related to their kinetic and thermodynamic properties. Significant SoC dependencies of the local reversible and irreversible heat generation are reflected by both the local temperature measurements and the heat generation rates calculated from GITT. A distinct asymmetry between charging and discharging is revealed which results from the intrinsic asymmetry of the reversible heat as well as differences in the kinetic limitations of the lithiation and delithiation of active materials. This study indicates, that the heat generation rates of the individual cell components should be considered accurately in order to build up basics for targeted material-, design- and thermal management optimization to handle thermal issues in large battery packs.

1. Introduction

Performance, safety and lifetime of lithium ion batteries are strongly affected by temperature [1]. The degradation is enhanced at elevated temperatures [2] and the performance is drastically reduced at low temperatures [3]. The self-discharge is usually expected to be negligible at room temperature but becomes significant at temperatures above 50 °C [4]. Furthermore, elevated temperatures can trigger exothermic reactions and decomposition of the SEI or the separator resulting in a thermal runaway [5,6]. The optimization of lithium ion batteries, regarding these problems, requires a fundamental understanding of the heat generation. Many researchers studied heat generation, temperature evolution and heat dissipation theoretically using 1D models assuming uniform heat generation as well as detailed thermal-electrochemical 3D models [1]. However, associated simulations require a detailed knowledge of material properties, thermodynamic and kinetic parameters as well as an accurate validation. Some researchers investigated the heat generation experimentally by using commercial and custom calorimeters or simply measuring the temperature of the battery. Accelerated rate calorimetry [7,8] and isothermal heat conduction calorimetry [9–14] are primary applied to measure the heat that is dissipated from the battery. Temperature measurements are commonly done by placing a thermocouple on the surface of the battery(system) [15–20]. All these measurements suffer from the fact that the measured temperatures are integral values of the investigated setup consisting of the actual electrochemical cell and periphery (housing, current collector tabs, etc.). Actually, the heat generation within the individual components of the battery cell, which are the negative electrode, the separator and the positive electrode, distinctly differs due to different material properties as well as electrochemical kinetics and thermodynamics [21,22]. Consequently, a detailed understanding of the temperature evolution in the battery cell requires the knowledge of local heat generation rates. Recently, spatially resolved temperature measurements have been published [17,20,23–25]. However, the achieved resolution is much lower than required to resolve the spatial dimensions of the individual battery cell components which are in the sub-millimeter range. The presented techniques are well suited for the investigation of design effects but did not include any information about the local heat generation rates of the positive and the negative electrode or the separator.

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In this study a custom build electrochemical cell developed for local in-operando temperature measurements is used to investigate the local temperature evolution in a single stack lithium ion battery cell. In a previous paper the proper functioning of this setup has been demonstrated [21]. In the present paper, this setup is used to investigate the influence of the C-rate on the local heat generation as a function of state of charge (SoC) and the lithium concentration in the active materials, respectively. The local temperature measurements were compared to local heat generation rates calculated from galvanostatic intermittent titration technique (GITT) measurements.

2. Experimental and Methods

The investigation of local heat generation rates is carried out on the example of a well-established reference system for high energy density applications. Commercially available composite electrodes (*MTI Corp.*) were investigated. The active materials of the positive and the negative electrode were $LiCoO_2$ (LCO) and graphite (C), respectively. The separator was a borosilicate glass-microfiber filter (*Whatman*). Commercially available high purity 1 M $LiPF_6$ in ethylene carbonate (EC): diethyl carbonate (DEC) in a 1:1 weight ratio (*BASF*, Selectilyte^{TM}) was used as electrolyte. The geometrical properties of the electrodes and the separator were estimated by scanning electron microscopy. Geometrical and physical properties of the battery components are displayed in Table 1.

The assembly of electrochemical cells was carried out in an argon filled glove box (*MBraun*). For the electrochemical experiments a multi-channel potentiostat / galvanostat with integrated frequency response analyzer (VMP3, *Biologic*) was used. First, the cells were subjected to a CCCV procedure as formation and to determine the capacity of the cell (3.55 mAh), which was close to the theoretical capacity (3.85 mAh) based on the mass of LCO in the positive electrode. Hereinafter, local in-operando temperature measurements were carried out in parallel to a rate capability test including C–rates from 0.2 C to 1.0 C.

Fig. 1 displays an overview of the experimental details. For local in-operando temperature measurements a custom build electrochemical cell is used, which was introduced in a previous paper [21]. Within this cell the local temperature measurements are realized by a specific arrangement of three thermocouples schematically shown in Fig. 1. The type K thermocouples with a diameter of 0.25 mm are covered with a heat conducting but electrical insulating epoxy resin. The small volume results in small heat capacity and a very fast response characteristic. The electrical isolation reduces noise from the surroundings. The finally utilized thermocouples were carefully selected after preliminary investigations concerning the offset in thermal equilibrium and the thermoelectric voltage response in dynamic temperature tests ranging from 15 °C to 30 °C. Thermocouples that exhibit a thermoelectric voltage in a range of $39.1 \pm 0.4\,\mu V\,K^{-1}$ were selected for the experiments. Offsets between the three thermocouples were corrected as a part of the calibration. Two of the thermocouples are pressed against the backside of the electrodes. A third one penetrates the anode and is pressed against the separator. The thermocouples are spring mounted to realize a reproducible positioning and thermal contact. The electrode stack itself is spring mounted within the cell body to guarantee a reproducible contact pressure between the components. The electrodes were connected from the backside by electrical contacts implemented into the cell body. The cell body consists of polyetheretherketone (PEEK). All connections were sealed twice with gaskets. The cell and the device for data acquisition and analog to digital conversion (DT9874 MEASURpoint, *Data Translation*) were placed in a climate chamber (20 °C) with forced convection resulting in a stable surface temperature (±0.1 °C) of the cell body and the cold junction. Measurements were conducted after a relaxation period of 24 h to ensure thermal equilibrium. The raw data were smoothed using a simple moving average algorithm in order to reduce the noise and to improve the discriminability between the local temperatures.

In addition to the temperature measurements identical electrodes were investigated by GITT. GITT is well established for the investigation of insertion kinetics [27]. Starting from an insertion electrode of known stoichiometric composition and in electrochemical equilibrium, a constant current is applied to the cell and the potential response is measured. After a certain time interval, the current is interrupted and concentration gradients within the electrode and the electrolyte relax by diffusion of the mobile species accompanied by a drift of the electrode potential towards a new steady state value. This procedure is repeated until a defined cut-off potential is reached. In this study GITT was used to determine the overpotential of the electrode reactions as a function of the applied C – rate and the SoC. For that purpose 3-electrode Swagelok® cells were prepared with LCO and graphite being the working electrode, respectively. A sheet of lithium metal was used as counter electrode. As reference electrode the tip of a flattened lithium metal wire (<0.5 mm in diameter) was embedded in a double-layer separator peripherally at the electrodes. GITT studies were performed using the identical pretreatment and C-rates as for the temperature measurements. Local heat generation rates were calculated from the GITT results and compared to the local in-operando temperature measurements.

3. Results and discussion

3.1. Local in-operando temperature measurements

Fig. 2 presents an overview of the experiment including voltage profiles and local in-operando temperature measurements for

Table 1
Geometrical and physical properties of the investigated battery components.

	(Active) material	Thickness $d/\mu m$	Mean particle radius $r/\mu m$	Porosity $\Phi/\%$	Heat capacity $c_p/J\,g^{-1}\,K^{-1}$	Density $\rho/g\,cm^{-3}$	Volume V/cm^3
Positive electrode	$LiCoO_2$ (LCO)	120[a]	3[a]	33[a]	1.27[b]	2.33[b]	0.014
Negative electrode	Graphite (C)	110[a]	5[a]	35[a]	1.43[a]	1.35[b]	0.013
Separator	Borosilicate glass	150[a]	–	83[d]	1.93[a]	1.33[e]	0.019
Electrolyte	$LiPF_6$ in EC/DEC	–	–	–	2.06[b]	1.22[c]	–

[a] Estimated from SEM micrographs (see supplementary material).
[b] Taken from Ref. [26].
[c] Taken from Selectilyte^{TM} datasheet.
[d] Estimated from the ratio of the mass density compared to bulk borosilicate glass.
[e] Estimated from the values for bulk borosilicate glass and electrolyte, weighted with respect to the porosity.