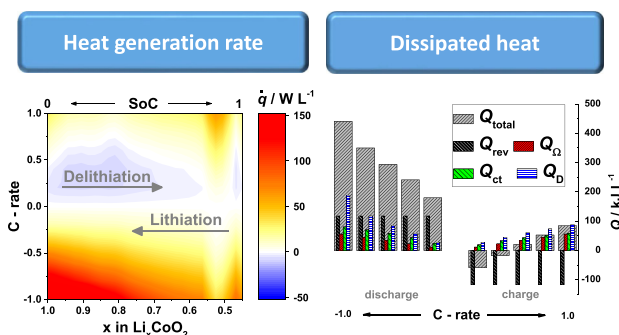


Detailed study of heat generation in porous LiCoO<sub>2</sub> electrodesC. Heubner<sup>b,\*</sup>, M. Schneider<sup>a</sup>, A. Michaelis<sup>a,b</sup><sup>a</sup> Fraunhofer IKTS Dresden, 01277 Dresden, Germany<sup>b</sup> Institute for Materials Science, TU Dresden, 01062 Dresden, Germany

## HIGHLIGHTS

- The contributions to the total heat generation are analyzed as  $f(I, T, x)$ .
- The reversible heat is most significant at high temperature and low C-rates.
- Mass transport limitations are most influential among the irreversible heats.
- Charge transfer limitations show the largest temperature dependence.
- Total heat generation is lower for lithiation compared to delithiation of Li<sub>x</sub>CoO<sub>2</sub>.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work the heat generation in porous LiCoO<sub>2</sub> based electrodes for lithium ion batteries is studied in detail. Irreversible heat generation rates due to ohmic resistance, charge transfer and mass transport limitations as well as the reversible heat of the electrode reaction are determined from electrochemical measurements as a function of the C-rate, the temperature and the lithium concentration in the active material. The results show that all the individual heat sources contribute significantly to the total heat generation in the electrode. The heat sources are functions of the C-rate and the temperature as well as the lithium concentration in the active material. The reversible heat contribution was found to be most significant at higher temperatures and lower C-rates, which tend to reduce kinetic limitations and irreversible heats, respectively. The heat generation rate due to mass transport limitations is most influential among the irreversible heats, whereas the ohmic contribution shows a minor impact. The total heat generation was found to increase with increasing C-rate and decreasing temperature. Furthermore, the heat generation is significantly reduced for charging compared to discharging due to the intrinsic asymmetry of the reversible heat and larger kinetic limitations for lithiation compared to delithiation of LiCoO<sub>2</sub>.

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## 1. Introduction

Temperature strongly affects performance, safety and lifetime of

lithium ion batteries [1]. Particularly, elevated temperatures can trigger exothermic reactions and decomposition of the solid electrolyte interphase or the separator resulting in a thermal runaway [2,3]. Degradation is enhanced at elevated temperatures [4] and the performance is drastically reduced at low temperatures [5]. As a consequence, the heat generation in lithium ion batteries is studied

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intensively. Temperature evolution and heat dissipation are investigated theoretically using 1D models assuming uniform heat generation as well as detailed thermal–electrochemical 3D models [1]. It turns out that such simulations require a detailed knowledge of material properties, thermodynamic and kinetic parameters as well as an accurate validation. Experimental investigations of the heat generation commonly deal with commercial and custom calorimeters or the measurement of the temperature of the battery using some kind of temperature sensor. Accelerated rate calorimetry [6,7] and isothermal heat conduction calorimetry [8–12] are primarily 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) [13–15]. Spatially resolved temperature measurements have been published that report the temperature distribution within commercial batteries designs, as cylindrical cells [16,17] and prismatic cells [18–20]. Our group studied the local heat generation rates in single stack lithium ion battery cells and the contributions of the components anode, separator, and cathode to the total heat generation using custom build electrochemical cells for local in-operando temperature measurements [21,22].

Assuming negligible heat of mixing [23] and no phase change except crystalline phase transitions, the local volumetric heat generation rate,  $\dot{q}$ , is given by Refs. [24,25]:

$$\dot{q} = \frac{I}{V} \left( \eta - \frac{T\Delta S}{zF} \right) \quad (1)$$

with  $I$ ,  $\eta$  and  $\Delta S$  being the absolute current related to the volume  $V$ , the overpotential and the entropy of the electrode reaction.  $T$ ,  $z$  and  $F$  are the absolute temperature, the valence and the Faraday constant. Several researchers analyzed the significance of the irreversible heat which is connected to the overpotential and the reversible heat related to the entropy change using full cells [26–29]. However, the particular contributions of the cell components anode, separator, and cathode to the total heat generation received only scant attention [30]. Furthermore, the individual contributions to the total overpotential,  $\eta$ , and the corresponding portions of the irreversible heat generation rate are usually not analyzed. The overpotential is caused by ohmic losses, the charge transfer resistance, and mass transport limitations. Thus, Eq. (1) can be written as:

$$\dot{q} = \frac{I}{V} \left( \eta_{\Omega} + \eta_{ct} + \eta_D - \frac{T\Delta S}{zF} \right) \quad (2)$$

with  $\eta_{\Omega}$ ,  $\eta_{ct}$  and  $\eta_D$  being the ohmic potential drop, the activation overpotential and diffusion overpotential. Based on this approach, four different heat sources can be defined according to the different contributions to the overpotential and the entropy change:

$$\dot{q} = \dot{q}_{\Omega} + \dot{q}_{ct} + \dot{q}_D + \dot{q}_{rev} \quad (3)$$

In the present study, these individual contributions to the total heat generation rate of a LiCoO<sub>2</sub> (LCO) based porous electrode are investigated. The kinetics and thermodynamics of the electrode reaction were studied as a function of the C-rate and the temperature. The results were used to estimate the heat generation rates related to the ohmic resistance of the LCO electrode, the charge transfer at the electrode–electrolyte interface, mass transport limitations and the entropy of the electrode reaction. Details of the investigated materials and the experimental techniques are provided in the next section. Thereafter, the kinetic and thermodynamic characterization of the electrodes is presented. Subsequently, the C-rate dependence as well as temperature dependence of the different heat sources is shown. Finally, the total

heat generation rate of the LCO electrode is computed and the significance of the different contributions is discussed.

## 2. Experimental and methods

Commercially available composite electrodes (*MTI Corp.*) containing active material LiCoO<sub>2</sub> (LCO) admixed with binder and conductive additives upon a 14 μm aluminum current collector foil were investigated. The active material proportion in the powder was 95%, the active material density was 20 mg cm<sup>-2</sup>. The geometrical properties of the electrodes were accurately examined using scanning electron microscopy. The average electrode thickness amounted to 95 μm and the mean particle size was 6 μm. The porosity was roughly estimated to 0.37. The separator was a borosilicate glass–microfiber filter (*Whatman*). Commercially available high purity 1 M LiPF<sub>6</sub> in ethylene carbonate (EC): diethyl carbonate (DEC) in a 1:1 weight ratio (*BASF, Selectilyte™*) was used as electrolyte. The electrochemical experiments were carried out in 3-electrode Swagelok® cells. The LCO foil was the working electrode, the counter electrode as well as the reference electrode consisted of metallic lithium. The assembly of the cells was carried out in an argon filled glove box (*MBraun*). Afterwards the cells were placed in a climate chamber. 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. Subsequently galvanostatic intermittent titration technique (GITT [31]) measurements were performed. The C-rate was varied from 0.2 C to 1.0 C and the measurements were carried out for three different temperatures (10 °C, 20 °C, and 30 °C). The  $t_{on}$  time of a single current impulse was varied with the C-rate in order to maintain the same change in lithium concentration during each pulse and to improve the comparability between the different C-rates.

The temperature dependence of the open circuit potential (OCP) was measured as a function of the lithium concentration  $x$  in Li<sub>x</sub>CoO<sub>2</sub>, in order to determine the entropy and the reversible heat of the electrode reaction, respectively. First, the cell was cycled three times at 20 °C and was then brought to the fully lithiated state (CCCV to 3 V). The OCP was then measured for 3 h, followed by a change of the temperature of the climate chamber (e.g. 30 °C). After the OCP was stable at the respective temperature, the temperature was changed to the next level (e.g. 10 °C), etc. Finally, the temperature was brought to the initial value of 20 °C to determine possible drifting from the initial voltage. Afterwards, the LCO electrode was delithiated using a C-rate of 0.1 C for 1200 s. After the stabilization of the OCP, the temperature – time protocol was repeated. The complete procedure was repeated until the cut-off potential of 4.3 V was reached.

## 3. Results and discussion

### 3.1. Kinetic characterization

In order to determine the heat generation rates connected to the ohmic resistance of the electrode, the charge transfer and mass transport limitations GITT measurements were performed at different C-rates and temperatures. GITT is well established for the investigation of intercalation kinetics [31,32]. Starting from an intercalation electrode of known composition and in electrochemical equilibrium, a constant current is applied to the cell and the potential response is measured. After a certain time, 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

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