Calorimetric Investigations into commercial Li-ion electrochemical cells

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Calorimetry is a useful tool for the investigation of electrochemical cells. Nowadays, cells based on Li-ion chemistry are the preferred techniques due to their relatively high and power energy densities. This causes, however, safety concerns which are addressed by calorimetry. Furthermore, calorimetry can also serve as a tool to optimize the performance of an electrochemical cell. Therefore, a great demand for reliable and precise data for the heat generation or consumption of the battery under varying environmental and operational conditions exists.

Commercial calorimeters for the examination of cells and batteries are available. One disadvantage of these calorimeters is their application range. They are either constructed as so-called *isothermal heat conduction calorimeters (IHC)* to measure the minute heat generation during normal operation or as *accelerating rate calorimeters (ARC)* to measure the large heat generation during thermal runaway.

Experiments on the same cell under identical conditions show large discrepancies: Sony 18650, C/$LiCoO_2$: IHC, 0.92 C discharge 13.3 - 84.5 W L^{-1}; ARC, 1 C discharge 0.0 - 15.5 W L^{-1} [1]; underpinning the need for traceable measurements.

A new design of a versatile calorimeter for pouch or prismatic cell types was developed at PTB, s. Fig 1. The calorimeter comprises a heat sink, a thermometer, a heat flow sensor, and a calibration unit. The size of the calorimeter can be adjusted to the cell size by combining several of these repeating units, each having a size of 40 x 40 mm².

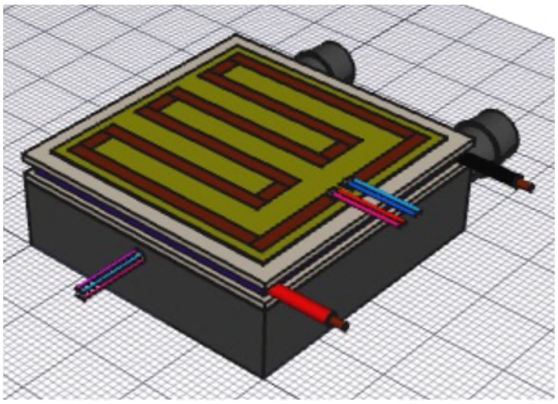

Figure 1: Basic calorimeter set-up

Figure 2 shows the typical heat flow pattern for a C//$LiCoO_2$ pouch cell measured with a calorimeter built of 9 repeating units.

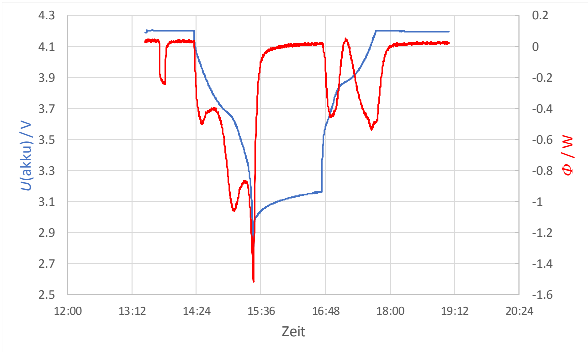

Figure 2: Voltage and heat flow during discharge and charge of a 5 Ah commercial pouch cell at ±1 A; (n(Li) ≈ 0.2 mol)

As an obvious but nevertheless technologically very important application, this information can be used to design, construct and optimize the thermal management system of electric vehicles.

Heat flow due to Joule heating and heat flow due to heat of reaction are distinguished by their signs during charge and discharge, s. Fig. 3. The pattern of the heat flow as a function of the charge of the cell correlates well with phase transitions within the carbon anode and the $LiCoO_2$ cathode.

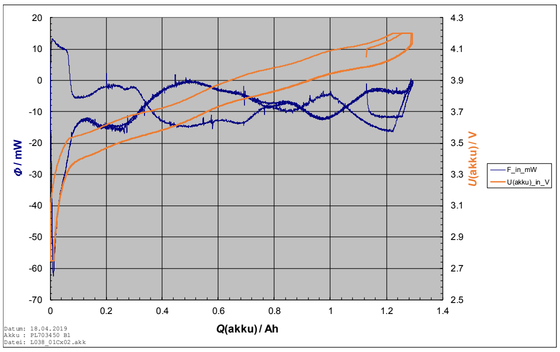

Figure 3: Heat of reaction for a 1.3 Ah C//$LiCoO_2$ pouch cell at I = 0.1 C_{nom}; (n(Li) ≈ 0.05 mol)

Effects due to temperature, charge and discharge current, electrode and electrolyte compositions, age etc. are readily inferred from the heat flow curves as shown exemplarily in Fig. 4 for a low quality Chinese make of a Li-ion battery und used to improve the performance of the cell.

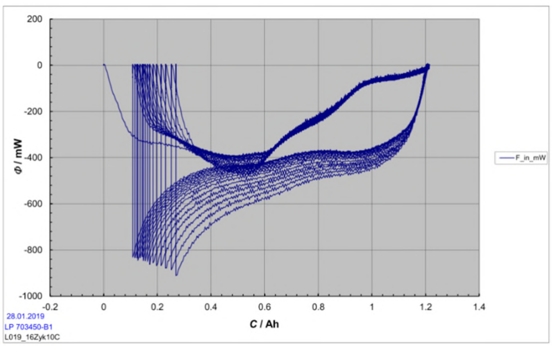

Figure 4: Aging of a Li ion battery during cycling at I = ±1 C_{nom}. Total number of cycles is approx. 60.

[1] T. M. Bandhauer, S. Garimella, T. F. Fuller, *A Critical Review of Thermal Issues in Lithium-Ion Batteries*, J. Electrochem. Soc. **158** (2011) R1-R25