

Calorimetric studies of lithium-ion batteries and their materials

C. Ziebert, W. Zhao, N. Uhlmann, C. Gebert, M. Rohde, H. J. Seifert
Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP),
Eggenstein-Leopoldshafen, Germany

Lithium-ion batteries are used as power sources in energy storage applications due to their adapted functionality and chemistry for both high energy and high power density as well as long cycle lifetime. The main challenges, not only for electric vehicles but also for smaller portable devices and high capacity stationary storage facilities, are related to thermal and safety behavior of the batteries under normal and abusive operating conditions. Understanding the heat generation and propagation in lithium-ion batteries and avoiding thermal runaway at high temperature is therefore a critical issue. To understand both the materials and the related cell behavior for regular and irregular operations as well as accident scenarios, it is important to investigate batteries and their constructive materials by *calorimetric studies*. Also, the thermodynamics of the constructive materials of lithium batteries governs the electrochemical performance of the lithium-ion batteries. Knowing the thermodynamic data resulting from calorimetry supports quantitative statements regarding energy density, capacity, open circuit voltage as well as thermal behavior and safety. Quantitative heat generation and dissipation data for batteries in operation enables the rational design of thermal management systems for mobile and stationary applications of lithium batteries.

Motivated by such coherencies, various types of calorimetry (Tian-Calvet, Differential Scanning Calorimetry) were used to measure battery materials heat capacities, enthalpies of formation and transformation, and enthalpy increments, respectively [1-3]. All these data are the input for CALPHAD-type modeling and electrochemical-thermodynamic calculations for studying battery performances. Additionally, heat effects of electrochemical cells during cycling were quantified by Tian-Calvet Calorimetry and Accelerating Rate Calorimetry (ARC), respectively. Such calorimeters are used for investigations of both electrochemical half/full cells and (commercial) batteries in operation (coin, cylindrical, pouch cell formats). Also, heat capacities for batteries are derived. Accelerating Rate Calorimeters are operated in isoperibolic and adiabatic modes, respectively. Temperature changes during electrochemical cycling at various C-rates and modes are analyzed [4]. Based on extensive calibrations, quantitative data for both heat generation and dissipation can be derived. For analyses of thermal runaway, cells and batteries are tested in the ARC using the heat-wait-see mode. The temperature changes and temperature rates before, during and after cell failure are recorded. Additionally, results from nail penetration and various short circuit tests are presented. This presentation will give an overview on all calorimetric investigations of lithium-ion batteries and their constructive materials at KIT.

[1] D.M. Cupid, P. Gotcu, A. Beutl, T. Bergfeldt, H. Giel, D. Henriques, A. Kozlov, M. Masoumi, J. Seidel, H. Flandorfer, T. Markus, F. Mertens, R. Schmid-Fetzer, H.J. Seifert, Interlaboratory study of the heat capacity of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111) with layered structure, *Int. J. Mater. Sci.* **108** (11) (2017) 1008-1021.

[2] M. Masoumi, D.M. Cupid, T. Reichmann, KK Chang, D. Music, J.M. Schneider, H.J. Seifert, Enthalpies of formation of layered $\text{LiNi}_x\text{Mn}_x\text{Co}_{1-2x}\text{O}_2$ ($0 \leq x \leq 0.5$) compounds as lithium ion battery cathode materials, *Int. J. Mater. Res.* **108** (11) (2017) 869-878.

[3] P. Gotcu, W. Pfleging, P. Smyrek, H.J. Seifert, Thermal behaviour of Li_xMeO_2 (Me = Co or Ni plus Mn plus Co) cathode materials, *Phys. Chem. Chem Phys.* **19** (2017) 11920-11930.

[4] E. Schuster, C.Ziebert, A. Melcher, M. Rohde, H.J. Seifert, Thermal Behavior and Electrochemical Heat Generation in a Commercial 40 Ah Lithium Ion Pouch Cell, *J. Power Sources* **286** (2015) 580-589.