Karlsruhe Institute of Technology

Summer School of the DFG Priority Programme
SPP 1473, WeNDeLIB:
Design of cathode materials for improved capacity, stability and safety for lithium ion batteries based on the system $LiMO_2$ (M = Co, Mn, Ni)

Institute for Applied Materials

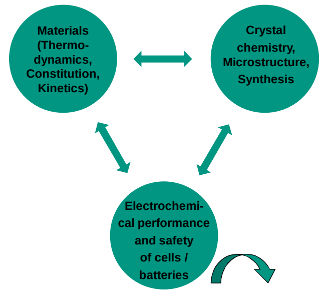
The Thermodynamics of Lithium-Ion-Batteries

Electrochemical-Calorimetric studies on safety fundamentals

E. Schuster, H.J. Seifert

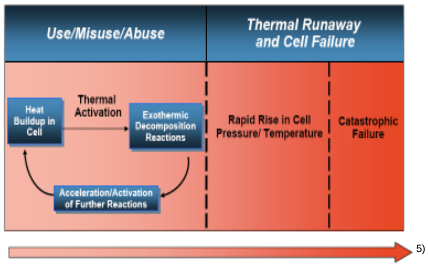
Introduction:
Li secondary batteries have been used for several years to power consumer electronics and are widely being investigated to power electric vehicles (EV's). A primary challenge for these batteries is safety, under abusive as well as normal operating conditions. During battery charge/discharge, various chemical and electrochemical reaction as well as transport processes take place. Some of these reactions and processes continue also under open circuit conditions. They are largely exothermic and may cause heat to accumulate inside the battery if heat transfer from the battery to the surroundings is not sufficient. This may be the case if the battery is operated under insulating conditions or in a hot environment. It will cause battery temperature to rise significantly, so ‚hot spots' may form within the battery, thereby risking thermal runaway.[1)]

To understand Batteries you have to understand the correlation of:



Field of work of the ARC

Accelerating rate calorimetry (ARC) :
The ARC is well suited to studying both the thermokinetics and thermodynamics of chemically reactive exothermic systems. The ARC has a number of options available, designed to study batteries during cycling and abuse. The Gibbs free energy (ΔG) of a system may be determined and used as an indicator of hazard potential. Further more, changes in ΔG based on calorimetric and electrometric data may be used to study the effects of cycling on battery efficiency. [2)]
The ARC provides an adiabatic environment in which a sample may be studied under conditions of negligible heat loss. The calorimeter configuration is such that the sample is suspended within an enclosed environment (a heavy duty cylinder with base and lid) whose temperature is controlled extremely precisely. Thus adiabaticity is achieved by tracking the temperature of the test sample closely when operating within the ARC's dynamic range.



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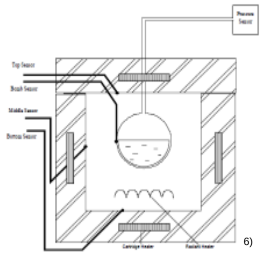


6)

Heat generation rates:
Heat generating rates inside the cell is derived from the thermodynamic relations:

$$Q = \Delta G + T\Delta S + W_{el}$$

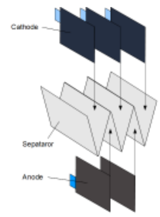
$$\Delta G = -nFE_{eq} \qquad \Delta S = nF\frac{dE_{eq}}{dT} \qquad W_{el} = -nF$$

$$q = I\left[\left(E_{eq} - E\right) + T\frac{dE_{eq}}{dT}\right] + q_p$$

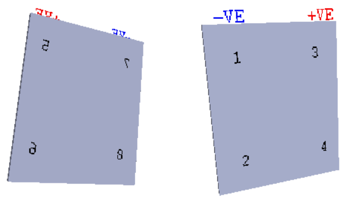
The thermodynamics of lithium-ion cells are complicated by the presence of liquid electrolyte mixtures as well as single-phase and multiphase solids. Heat generation may result from mixing and phase changes, as well as the main electrochemical reactions. Reliable prediction of temperature profiles of individual cells, and of a battery system as a whole requires first of all quantitative evaluation of the total heat generation rate.
Sources of heat generation:

1. The "reversible" heat released (or absorbed) by the chemical reaction of the cell $\quad q_{rev} = IT\frac{dE_{eq}}{dT}$
2. The "irreversible" heat generation by ohmic resistance and polarisation $\quad q_{irrev} = I(E_{eq} - E)$
3. The heat generation by "side reactions", i.e. parasitic/corrosion reactions and "chemical shorts" $\quad q_p$

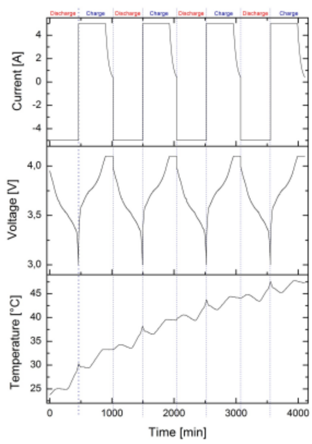
Measurements:



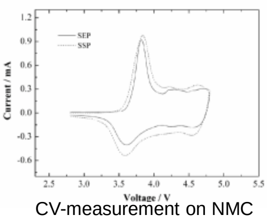
assembly of the pouch cell



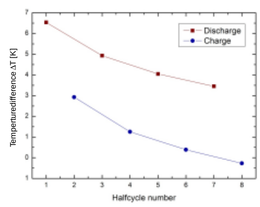
positions of the thermocouples on the pouch cell



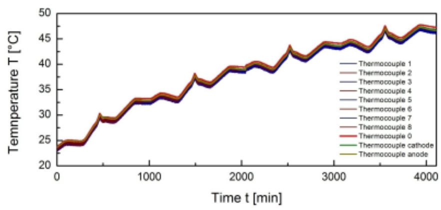
Temperature/voltage/current profile during cycling at C/8



CV-measurement on NMC



ΔT of the half cycles



Measurement with eight Thermocouples

Conclusion/Outlook:
- We point out that the battery showed a good cyclability with a net cooling effect during charge and a highly exothermic effect during discharge..
- The temperature difference becomes lower with higher temperature of the battery, because of the better battery performance at higher temperatures.
- Next step will be the measurements with a DC current interruption technique to determine the entropic coefficient.

[1)] S. A. Hallaj, M. Maleki, J.S. Hong, J.R. Selman, J. Power Sources 83 (1999) 1-8
[2)] S. Mores, M.R. Ottaway, Power Source Symposium (2001)
[3)] J.R. Selman, Said Al Hallaj, Isamu Uchida, Y. Hirano, J: Power Sources 97-98 (2001) 726-732
[4)] H.-B. Ren, X.-Y. Liu, H.-P. Zhao , Z.-H. Peng,Y.-H. Zhou, Int. J. Electrochem. Sci., 6 (2011) 727 - 738
[5)] Infomaterial THT,[6)] Technical Information Note 066, THT

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