Thermodynamic profiles of Li-Ion Batteries – quantitative relation to anodes, cathodes, and their compositions

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Thermodynamic measurements on batteries gained an increase of attention in the recent past. They provide deeper insights look into the electrochemical processes [1,2] and are also useful for improved modeling of the thermal behavior of cells. [3]

The measurements themselves aim at the equilibrium open circuit cell voltage E_0 and its temperature dependence $(\partial E_0/\partial T)_{p,x}$, where p and x are the pressure and the state of charge (SOC), respectively. Due to the varying composition of anode and/or cathode as a function of the SOC, both values show a pronounced dependence on x.

The response of the open circuit voltage E_0 on temperature changes allow is proportional to the differential charge/discharge entropy $\Delta_r S(x)$ according to

$$\left(\frac{\partial E_0(x)}{\partial T}\right)_{p,x} = \frac{1}{nF}\left[\frac{\partial}{\partial x}S(x)\right]_{p,x}.$$

Based on the cell voltage E_0 in combination with this slope, one may also calculate the charge/discharge enthalpy $\Delta_r H(x)$ according to

$$\Delta_r H(x) = nF\left[E_0(x) + \frac{\partial E_0(x)}{\partial T} - E_0\right]_{p,x},$$

where F the Faraday constant. The variation of $\Delta_r S(x)$ as a function of the Li content x in the electrode yields to characteristic "entropy profiles" that serve as a kind of "fingerprint" spectrum reflecting structure and chemistry of anode and cathode. Similarly, also $\Delta_r H(x)$ varies with SOC.

In this work, we will report on first results of a broad analysis of the thermodynamic properties of commercially available 18650 Li ion cells. We will demonstrate in how far the respective $\Delta_r S(x)$ and $\Delta_r H(x)$ profiles can be broken down to additive contributions of anode and cathode, and in how far selected features of those anode and cathode profiles can be quantitatively related to their structure and composition. For this purpose, we disassembled the commercially available full cells and analyzed structure and chemical composition of their anodes and cathodes. Furthermore, we studied those anodes and cathodes separately in coin cells with metallic Li as counter electrodes. Figures 1 and 2 exemplarily show the $\Delta_r S(x)$ and $\Delta_r H(x)$ profiles of the cathodes of commercial NCM and NCA cells, respectively.

Apart from an analysis of the profiles themselves, we will also comment on the importance of a proper compensation for time-dependent relaxation effects of the measured open circuit value E_0, which for many cell chemistries does not reach steady state values even after waiting times of more than two hours. We will show that ignoring those relaxation effects can lead to substantial misinterpretation of thermodynamic measurement data.

We will further discuss the applicability of entropy profile measurements under operating conditions, as a supplement to existing methods for SOC and State-of-Health monitoring.
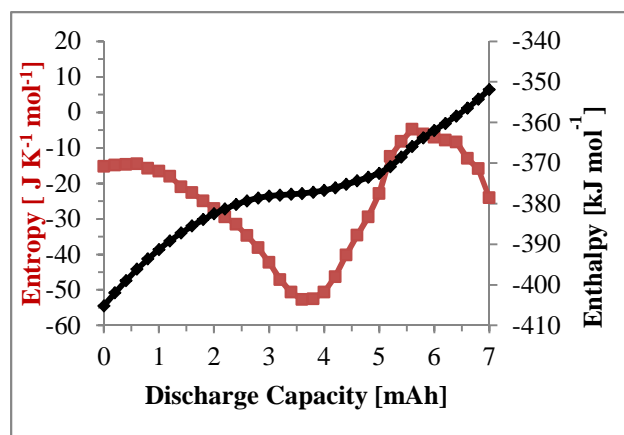

Fig. 1 Entropy and Enthalpy of a NCM cathode, taken out of commercial available 18650 cell
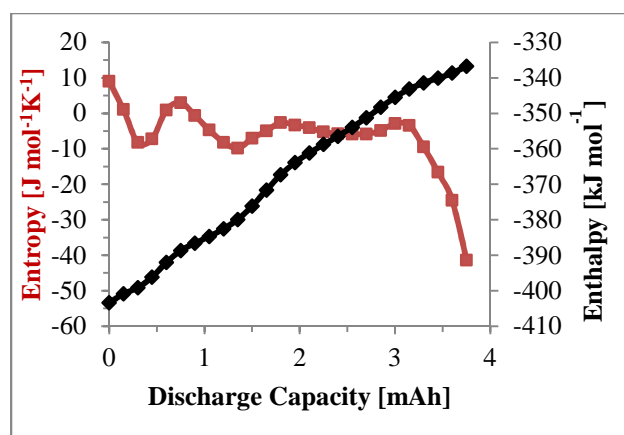

Fig. 2 Entropy and Enthalpy of a NCA cathode, taken out of commercial available 18650 cell

References:

[1] Y. Reynier, J. Graetz , T. Swan-Wood, P. Rez, R. Yazami, B. Fultz, Phys. Rev. B 70 (2004) 174304.

[2] Y. Reynier, R. Yazami, B. Fultz, J. Power Sources 119-121 (2003) 850.

[3] V.V. Viswanathan et al., J. Power Sources 195 (2010) 3720.