Estimation of the Entropy of $Li/LiCoO_2$ Half-Cell as a Function of State-of-Charge

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Thermal modeling has been a popular and useful method of investigating thermal management, scale-up, and safety aspects of Li-ion batteries. An important input required to predict temperatures using the thermal models is the rate of heat generation during the operation of the battery. This heat generation rate can be classified into two – *(i)* the irreversible heat generated due to flow of charge against ohmic and charge-transfer resistances, and *(ii)* the reversible heat generated due to entropy changes undergone by the electrode materials in the process of intercalation or de-intercalation of lithium. While the irreversible heat generation has been included in all the thermal models, many researchers have assumed zero reversible heat generation primarily for want of experimental data on the entropy changes occurring in the system. Nevertheless, it has been shown by Hong *et al.*[1] that the reversible heat effects contribute significantly to the total heat generated in a Li-ion battery, especially when operated at low rates. Accordingly, many researchers have included the reversible heat generation in calculating the temperatures attained by Li-ion batteries.

In order to calculate the reversible heat generated, Hong *et al.*,[1] Hallaj *et al.*,[2] and Selman *et al.*[3] measured the entropy changes occurring in various commercial Li-ion batteries (full-cells), and Thomas *et al.*[4] in an experimental $Li/LiMn_2O_4$ half-cell. These researchers report not only a significant reversible heat effect, but also a significant variation of the magnitude of the reversible heat produced with state-of-charge or the lithium content of the electrode materials in question. Thus it becomes important to include a state-of-charge (SOC) dependent reversible heat generation term in thermal models as opposed to just a constant value used in the thermal models existing in the literature.

In this paper, we present a method for estimating the total cell entropy (see Fig. 1), and subsequently, the entropy of the $Li/LiCoO_2$ half-cell as functions of SOC, using low-rate (C/3) voltage-time and temperature-time data measured during the discharge of an $LiC_6/LiCoO_2$ system. The difference between the total heat generation rate calculated from the measured temperature at a particular SOC and the irreversible heat generation rate calculated from the electrochemical-thermal model[5] is used to obtain the cell entropy at that SOC. The value of the heat-transfer coefficient, required in calculating the total heat generation rate from the measured temperature data, is estimated from temperature decay with time measured during the relaxation periods. Adding the SOC-dependent entropy of the Li/LiC_6 half-cell obtained from Verbrugge and Koch[6] to the SOC-dependent cell entropy estimated above, the SOC- dependent entropy of the $Li/LiCoO_2$ half-cell is calculated as illustrated by Lampinen and Fomino[7] (see Fig. 1).

References

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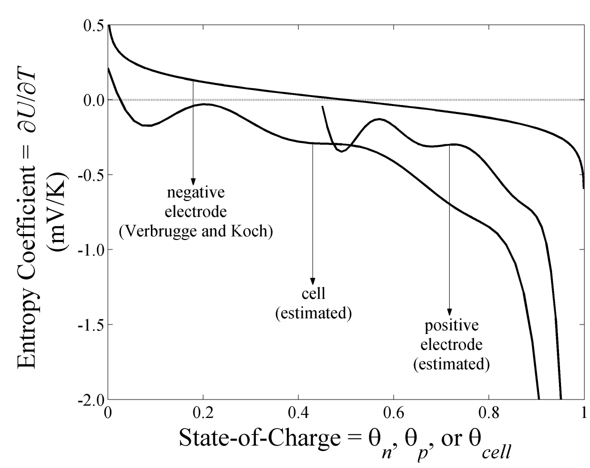

Fig. 1. Cell and electrode entropy coefficients estimated as functions of SOC from the measured temperature-time data and the electrochemical model.