Development of High Sensitive Calorimeter for Coin-Type Lithium-ion Cell

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Calorimetry is a useful method to discuss energy conversion efficiency for lithium-ion battery (LIB)[1, 2]. It also gives information on the inner resistance and the reaction entropy of LIB as well as dissipated or absorbed heat directly during operation which are essential parameters for thermal simulation for ensuring safety and reliability. Since the entropy change of intercalation reaction has relation to the crystal structure of the active electrode materials, the calorimetry has possibility to utilize as a nondestructive analysis method for degradation of the active materials. Lots of calorimeter have been used for LIB up to this day. However, in most of previous reports, cylindrical cells commercially available were used from the limitation of size of sample holder and from the sensitivity of calorimeter. Recently, demand from developer of LIB is rapidly increasing for calorimetry to apply characterization of coin-type cell, by which they can characterize thermal behavior of candidate materials for next generation LIB from the initial stage of development. Kobayashi has been using high sensitive calorimeter produced by Tokyo Riko for coin-type cell[3]. Unfortunately, Tokyo Riko had already finished their business, and new alternative calorimeter with high sensitivity is required. Hence, we are aiming to develop a new calorimetric system which is available to coin-type cell.

As the heat flow sensor of our calorimeter, Peltier element (ThermaTEC™ Thermoelectric Modules from Liard) was selected. Two elements were used for one cell holder, and heat flows from both end faces of a sample cell were detected. The side face of the cell was covered by a thermal insulator. From summation of measured heat flows, total heat dissipated from the cell was evaluated. Between the sample surface and the sensor, an aluminum thin plate was held as a heat receiving unit which was also functioned as an electrode terminal for current impressing. For calibration of the system, a dummy cell that include a metal film resistor (400 Ω) was used. The thermal sensitivity of the system was approximately 5 W V^{-1}. In order to prevent increase in cost of the system, temperature control unit was omitted. However, if the calorimetric system is set into a thermostatic chamber, measurement can be carried out under constant temperature condition. For precise calorimetry, influence of baseline drift should be suppressed, and differential measurement method using a reference holder is applied as like DSC. Figure 1 is a typical result of calorimetry using the developed system for a coin-type cell of $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) cathode and lithium metal anode of which capacity is *ca*. 3.7 mAh, and small heat of several decade μW order during 0.1C rate can be detected.

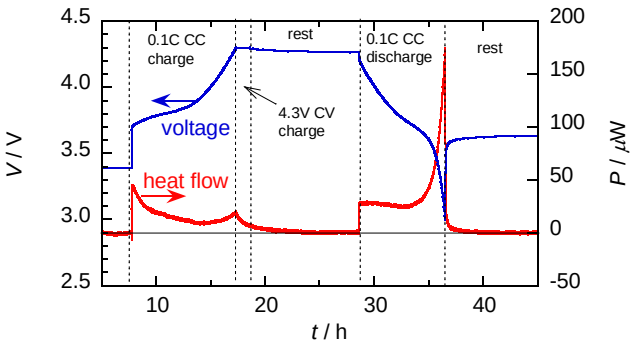

Fig. 1. Heat generation profile of a coin-type cell of NMC cathode with lithium metal anode during charge and discharge at 0.5°C.

References:
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