Abs. 428, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Heat Generation of Lithium-ion Batteries in High Rate Charge and Discharge

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In recent years, R&D of Lithium-ion batteries with high power are accelerated which are expected as an auxiliary power sources for fuel cell electric vehicles (FCEV). Lowering of internal resistance and polarization is one of important subjects because these are cause of energy loss and results in large heat generation during charge and discharge. In my previous study,[1] I performed calorimetry for a lithium-ion battery commercially available, and confirmed that the main causes of heat generation during charge and discharge are the battery reaction (entropy change of the reaction) and the polarization (resistance).

$$P = - I\, T\, (dV_{ocv}/dT) + I\, \eta \qquad (1)$$

where P, I, T, V_{ocv}, and η are generated heat, discharging current, temperature, open circuit voltage and overvoltage, respectively. In this work, heat generation behavior of lithium-ion batteries that are trial manufactured for high power usage is studied.

The test battery which was cylindrical shape with 400 mAh of nominal capacity, C, was cycled in a twin-type calorimeter, C80-22 (Setaram). The temperature in the calorimeter was hold at 298 K. The cycling rate was varied from $0.05C$ A to $5C$ A. Cut-off voltage in charge was 4.2 V while 2.5 V in discharge. The rest time between charge and discharge was 10 h. The State of charge (SOC) of the battery was normalized by $0.2C$ A discharging with 2.5 V of cut-off voltage by which SOC was set up at 0 %, fully discharged state. The normalization of SOC was carried out just before changing the cycling rate. The time constant of the calorimetric system was 370 s, and the thermal delay of the measured value was corrected.

Figure 1 shows the voltage and heat generation curves during discharge of various rates. Larger amount of heat was dissipated in higher rates with larger overvoltage. In Fig. 2, voltage at SOC 50% during discharge was plotted, and it showed linear relation with discharging current. From the slope of this I-V plot, the resistance of polarization, R, is evaluated as 84.4 mΩ, and overvoltage, η, can be described as 0.0844 I. The heat generation in the battery at SOC 50% is shown in Fig. 3. The relation between heat and discharging current agree well with following equation.

$$P = 0.0350\, I + 0.0844\, I^2 \qquad (2)$$

Since the temperature was 298 K, dV_{ocv}/dT was estimated as $- 1.17 \times 10^{-4}$ from (1) and (2), and the entropy change of the battery reaction would be - 11.3 J K^{-1} mol^{-1} at SOC 50%.

On the while, heat generation during charge couldn't be described as equation like (2). The negative electrode material in the battery was non-graphitizable carbon, and this would be a cause of complicated heat generation during charge. Note that the condition of preceding discharge affected the heat generation behavior during the following charge in the lithium-ion battery in which non-graphitizable carbon was used.[2]

The total amount of generated heat during cycling between normalizations of SOC by $0.2C$ A discharging is well balanced with the energy loss caused by the overvoltage in any cycling rates.

Acknowledgements

This work was conducted as the partial R&D of METI and NEDO. The sample batteries were supplied from Matsushita Battery Industrial Co. Ltd. The author also thanks K. Takano for his help to prepare experimental system.

References

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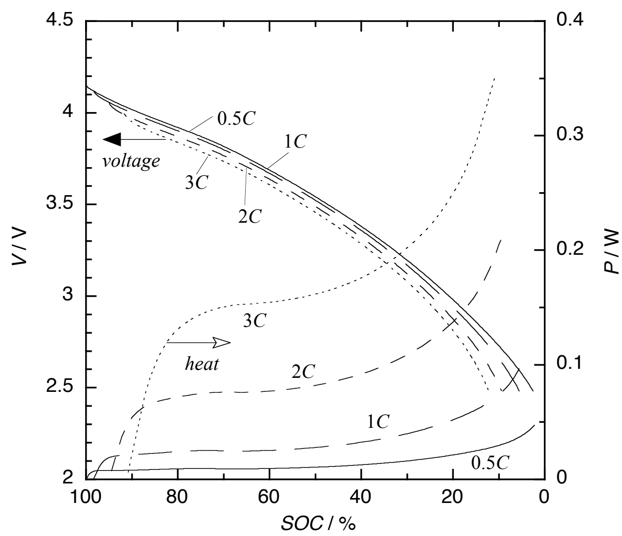

Fig. 1 Voltage and heat generation curves of the test battery during discharge of various rates.

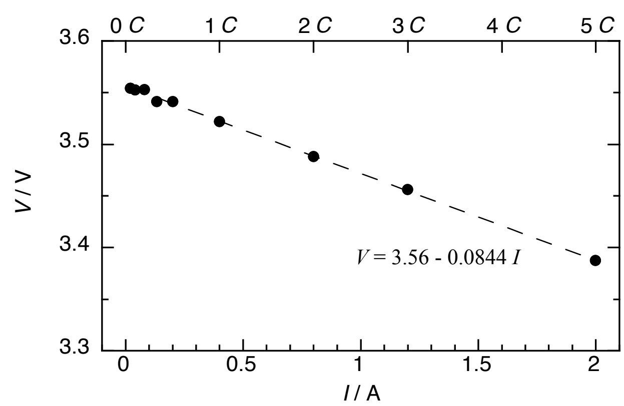

Fig. 2 Voltage of the battery at SOC 50% during discharge of various rates.

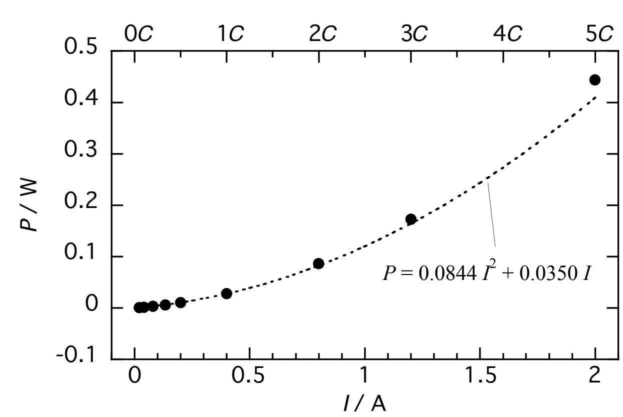

Fig. 3 Heat generation in the battery at SOC 50% during discharge of various rates.