

Characterization of reaction in lithium-ion cells by calorimetry and staircase voltage step coulometry

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Abstract

In order to characterize the reaction mechanism of lithium-ion cells during charge and discharge, two experimental methods, calorimetry and staircase voltage step coulometry (SVSC), are examined. As a result of calorimetry during charge and discharge, the influence of previous treatment applied to the cell is observed in the heat generation behavior. SVSC gives kinetic information of the rate-determining step in the cell reaction. It is found that there is a slow-rate reaction besides the main cell reaction during charge and discharge. It is suggested that the irreversibility of the slow-rate reaction causes the voltage hysteresis between charge and discharge. The cell reaction mechanism is discussed, mainly focusing the reaction at the hard carbon anode used in the test cell. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium-ion cell; Calorimetry; Staircase voltage step coulometry; Hard carbon

1. Introduction

Lithium-ion cells come onto the market by several companies for portable electronic applications in these days. We have been constructing electrical and thermal simulation models of these cells which can be also applied to large-scale batteries. In some commercial cells, e.g., US14500 (Sony Energytec), the cell performance is affected by previous charging or discharging condition. Since the mechanisms of these behaviors are not understood well, it is difficult to simulate the cell performance in detail. In our recent calorimetric study, unique heat generation behavior was observed during charge for a US14500 cell [1]. In order to explain the result, we proposed a reaction model in which there are three kinds of reaction sites in hard carbon used as the negative electrode material. In this study, we examined staircase voltage step coulometry (SVSC) to discuss the kinetic cell reaction mechanism of a lithium-ion cell.

2. Experimental

Cylindrical type lithium-ion cells (US14500, Sony Energytec) were used as test samples. The active electrode materials are LiCoO_2 in the positive electrode and hard carbon in the negative. The nominal cell voltage is 3.6 V and the nominal electric capacity is 500 mAh.

A twin-type heat conduction calorimeter (C-80, Setaram) was used for calorimetry. Experimental setup of the calorimetry was the same as that in previous works [1,2]. The test cell was charged and discharged under various conditions and the heat generation behavior was analyzed. In the following, the state of the cell is described as the quantity of electricity, Q (mAh), discharged from the fully charged state, which is defined by constant voltage charging of 4.20 V at a constant temperature of 303 K.

SVSC is a constant voltage charging or discharging technique where the cell voltage is changed periodically drawing a staircase-like voltage profile. In this study, the voltage was stepped up or down every 6 h, and the step of voltage was 0.1 V. The cell voltage was controlled by TR6143 (Advantest), and the current response was measured by DMM2001 (Keithley) through a standard resistor for every 0.61 s. The discharge was started from fully charged state and the charge was from 450 mAh dis-

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charged state. SVSC was carried out under three different temperature conditions (283, 303 and 323 K).

3. Results and discussion

3.1. Calorimetry

Fig. 1 is a typical result of calorimetry for the test cell. The positive and negative directions in the heat flow, P , are corresponding to heat generation and heat absorption, respectively. Heat absorption is observed during charge while heat generation during discharge, and these are the similar results observed by Kobayashi et al. [3] and Hong et al. [4]. Complex behavior observed in the region below about 120 mAh is reversible between charge and discharge. This is caused by crystal phase transitions of the positive electrode material, Li_xCoO_2 , around $x = 0.5$ [2]. Heat generation behavior during charge was affected by previous treatment for the cell [1]. That is, larger amount of heat was dissipated from the cell during charge after the cell had been discharged at higher temperature, after the cell had been discharged more deeply, or after longer rest time.

3.2. Staircase voltage step coulometry

SVSC gives an approximate profile of open circuit voltage (OCV) of the cell. This pseudo OCV curves of the

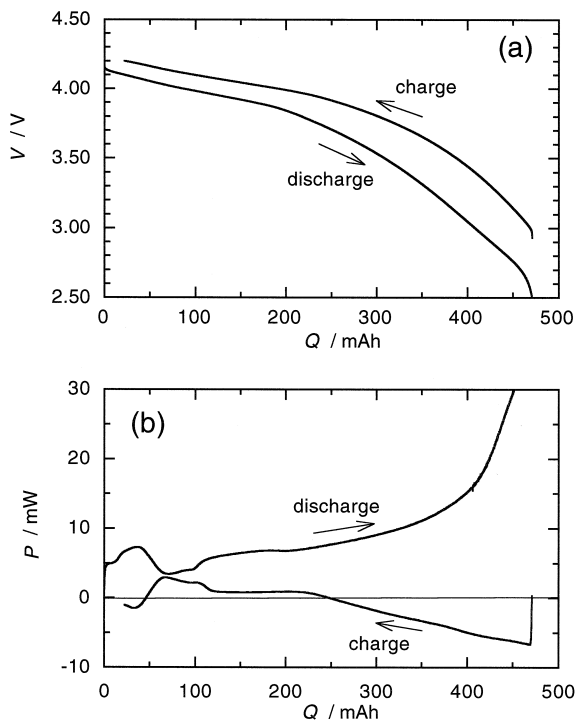


Fig. 1. (a) Terminal voltage, V , and (b) heat generation, P , curves of the lithium-ion cell during discharge and charge as a function of the discharged electricity from the fully charged state, Q . The charging and discharging currents are 50 mA. The temperature is 303 K.

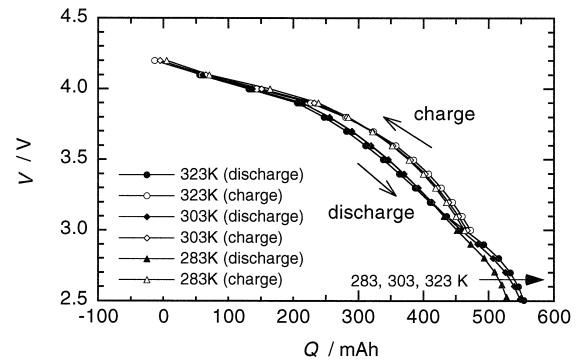


Fig. 2. Pseudo OCV profiles of the lithium-ion cell obtained from SVSC measurements.

test cell are shown in Fig. 2. Hysteresis is observed at about 3.9 V and below between discharge and charge. In Fig. 1a, the difference of discharging and charging voltages is large in the region that $Q > 200$ mAh, and this is essentially caused by the hysteresis of OCV. It is thought that the energy corresponding to the OCV hysteresis has to be compensated as heat dissipation when the cell is cycled. It is suggested that the unique heat generation behavior during charge have a relation to this energy compensation.

Electrode reaction of which rate is dominated by diffusion of electroactive species is a typical first-order reaction. At constant voltage condition, if the rate-determining step of the cell is first-order reaction, limiting current, i , is expressed as

$$i = i_0 \exp(-pt) \quad (1)$$

where t and p are time and reaction rate, respectively, and i_0 is current at $t = 0$. The differential coefficient of $\log i-t$ curve gives information about p . It is also useful to analyze the $i-Q_s$ curve from a relation described below [5],

$$\begin{aligned} \frac{d \log i}{dt} &= \frac{1}{i \ln 10} \frac{di}{dt} = \frac{1}{2.3} \left(\frac{dQ_s}{dt} \right)^{-1} \frac{di}{dt} \\ &= \frac{1}{2.3} \frac{di}{dQ_s} = -\frac{p}{2.3} \end{aligned} \quad (2)$$

where Q_s is charged or discharged electricity. Since p is also described as

$$p = \frac{DA}{\delta L} \quad (3)$$

where D , A , δ , L are the diffusion coefficient of the electroactive species, the surface area of the electrode, the thickness of the diffusion layer, and the volume of the bulk material containing the electroactive species, respectively, it is possible to discuss about the diffusion coefficient from the reaction rate [6].

Fig. 3 shows some $i-Q_s$ curves of SVSC discharge and charge at 303 K. It seems that there are several rate-de-

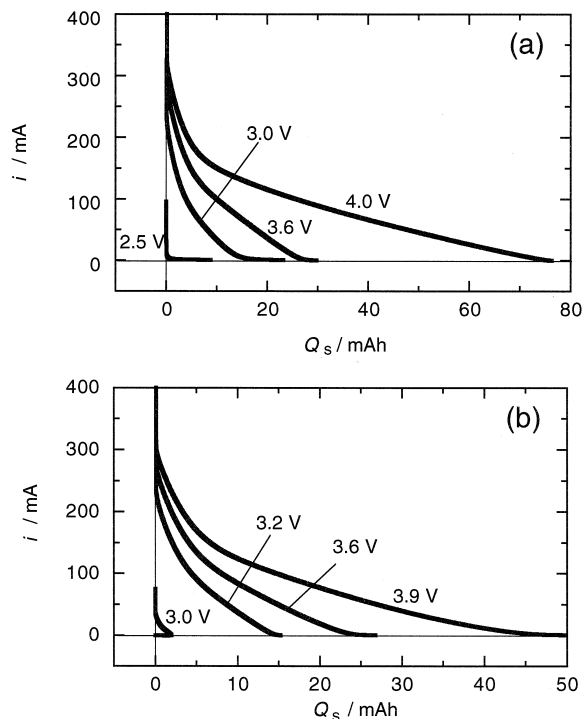


Fig. 3. Typical $i-Q_s$ curves of SVSC for the lithium-ion cell at 303 K; (a) discharging and (b) charging.

terminating processes at each voltage and that several reactions occur in parallel. The curves consist of initial processes where the current decreases rapidly and a main reaction where the current decreases linearly against Q_s . The initial processes are thought to be charging of the electrochemical double layers and charge transfer in short time range before mass transfer process becomes dominant. In the discharging direction, an extremely slow-rate reaction emerges under 3.9 V, and becomes more remarkable at lower voltage. On the contrary, the contribution of the main reaction decreases with the voltage. Almost all electricity is discharged through the slow reaction at 2.5 V. The slow reaction did not achieve the equilibrium within 6 h. In the charging process, the tendency of the main reaction as a function of voltage is similar with that in the discharging process. However, the slow reaction is more remarkable at higher voltage until 4.0 V. It is suggested that this irreversibility of the slow reaction causes the OCV hysteresis observed at the region of 3.9 V and below. It is noteworthy that discharging current owing to the slow reaction is observed finally during SVSC charging if the voltage is lower than 3.2 V. Same results were obtained from SVSC charging at the other temperatures.

It is difficult to attribute each rate-determining step in $i-Q_s$ curves to a specific electrode reaction from only the result of SVSC. However, since the voltage hysteresis is one of representative characteristics of hard carbon electrode [7], the slow reaction might be attributed to a reaction occurring at the hard carbon electrode used in the test cell. In our previous work, a reaction model of the hard

carbon electrode was proposed to explain the results of calorimetry [1], in which existence of three kinds of reaction sites (sites A, B and C) was discussed. In this model, lithium is inserted into and extracted from site A electrochemically in low voltage region of the cell. Similarly, electrochemical reaction occurs at site B in high voltage region. However, insertion and extraction reaction at site C was not electrochemical reaction, but chemical transfer from/to the other sites. Excess heat generation during charge was supposed to be caused by this chemical process [1]. This CE reaction (an electrochemical reaction with a preceding chemical reaction) during discharge and EC reaction (an electrochemical reaction with a following chemical reaction) during charge can also explain the concave $i-Q_s$ curves shown in Fig. 3 [6]. If the rate of electrochemical reaction at site A is faster than that of chemical reaction, the initial decay in the $i-Q_s$ curves governed by the rate of electrochemical reaction, and the limiting rate is determined by the rate of chemical reaction. The lowest energy level of lithium in the chemical reaction site is supposed to be located at about 3.2 V in the cell voltage. During SVSC charging, lithium is brought into the main reaction site from the electrolyte by an electrochemical reaction. However, if the cell voltage is lower than 3.2 V, lithium might be also brought from the chemical reaction site because the energy level of the lithium in the main site is lower. Thus, discharging behavior might be observed finally during SVSC charging as shown in the curve of 3.0 V in Fig. 3b. The slow chemical reaction might be corresponding to extremely slow lithium diffusion at the inside of the electrode materials. The identification of each rate-determining process will be accomplished in future work.

The rates of the main reaction and the slow reaction were analyzed from the slope of $i-Q_s$ curves. Figs. 4 and 5 show the rate of the main reaction and that of the slow reaction, respectively. In Fig. 4, the voltage dependence of the rate is similar in all results. The lower temperature, the smaller rate. The activation energy was estimated as about 31 kJ mol^{-1} . On the other hand, it is difficult to find the remarkable dependency on the temperature for the slow reaction as shown in Fig. 5. The order is 10^{-4} to 10^{-5} s^{-1} which is smaller about one order of magnitude than that of the main reaction. The irreversibility of the reaction rate also supports the view that the rate-determining step of the slow reaction is not an electrochemical reaction, but a chemical reaction.

Reciprocal of the differential capacity that is obtained from 50 mA constant current discharging or charging at 303 K is also plotted in Fig. 4b. It seems that the dV/dQ is proportional to the rate of the main reaction except low voltage region. This suggests that the voltage profile during discharge and charge of the cell is principally depending on the rate of the main reaction. In addition, this result gives one more important information. If the cell is simply considered as a series connection of a capacitor and a

resistor, the current flow for a step voltage change, ΔV , can be described as

$$i = \frac{\Delta V}{R} \exp\left(-\frac{t}{RC}\right) \quad (4)$$

where R and C are resistance and capacitance, respectively. Since C is corresponding to dQ/dV , comparison of Eqs. (1) and (4) gives

$$p = \frac{1}{RC} = \frac{1}{R} \left(\frac{dQ}{dV}\right)^{-1} = \frac{1}{R} \frac{dV}{dQ} \quad (5)$$

Thus, the result in Fig. 4b suggests that the resistance factor of the main reaction is almost constant and indepen-

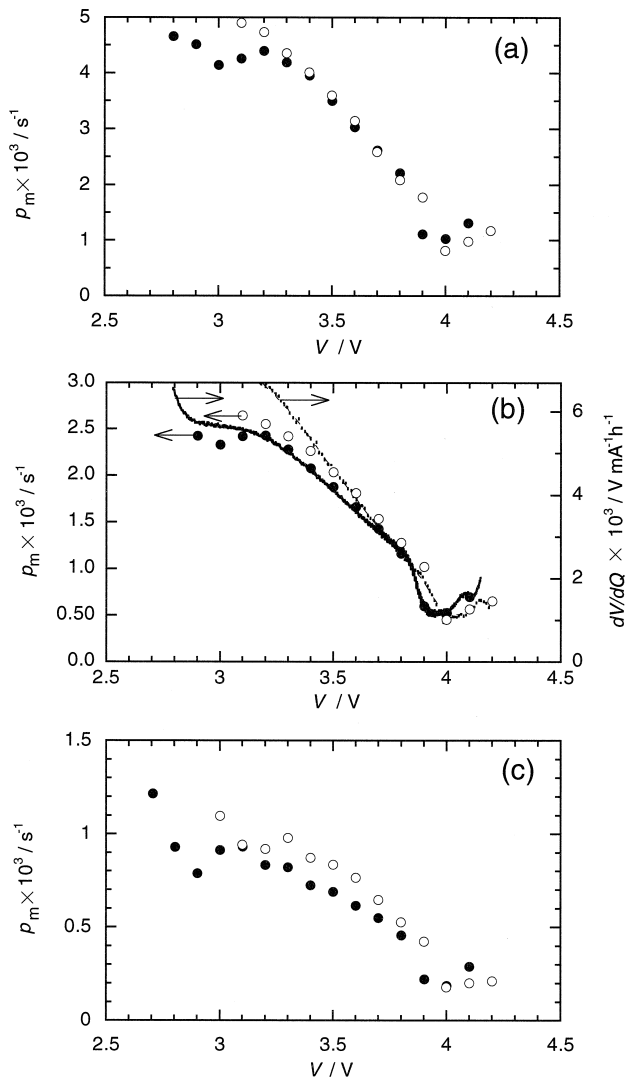


Fig. 4. The rate of the main reaction, p_m , in the lithium-ion cell at (a) 323 K, (b) 303 K and (c) 283 K: (●) discharge and (○) charge; and dV/dQ obtained from the results of 50 mA discharge (solid line) and charge (dotted line).

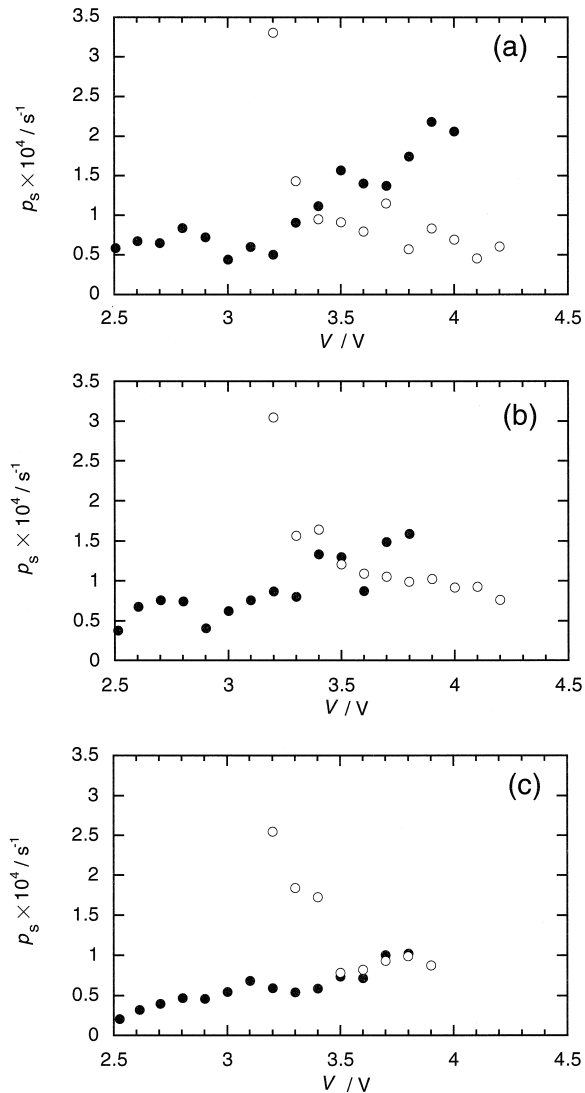


Fig. 5. The rate of the slow reaction, p_s , in the lithium-ion cell at (a) 323 K, (b) 303 K and (c) 283 K: (●) discharge and (○) charge.

dent on the state of charge, and that the profile of the reaction rate is not corresponding to that of diffusion coefficient of the rate-determining step, but merely determined by capacity distribution of the electrode materials for the main electrochemical reaction site as a function of voltage.

4. Conclusions

Several rate-determining processes were observed in $i-Q_s$ curves as the result of SVSC. It was found that at least two kinds of reactions occur during charge and discharge in the test lithium-ion cell and suggested that the behavior of the slower reaction causes the voltage hystere-

sis. A speculated model for the reaction at the hard carbon electrode can explain the both results of calorimetry and SVSC.

Acknowledgements

The authors would like to thank Mr. Kunio Ishi who had been a managing director of Sony Energytec for providing the lithium-ion secondary batteries.

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