

Thermal studies of a lithium-ion battery

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Abstract

In order to characterize the heat generation behavior of a lithium-ion secondary battery during discharge, calorimetry of the battery was carried out. The temperature dependency of the heat generation was studied between 283 and 333 K. An exothermic peak and an endothermic peak were observed around 4 V, except at 333 K. These peaks are caused by a phase transition of the positive electrode material, Li_xCoO_2 , between the hexagonal and monoclinic structures, which is observed at around $x=0.5$. The heat of discharge consists of mainly two factors, the battery reaction and the electrochemical polarization. In the temperature range between 283 to 333 K, if the battery is discharged at 50 mA, the least heat generation is observed at about 300 K owing to the temperature dependence of both factors. © 1997 Published by Elsevier Science S.A.

Keywords: Lithium-ion batteries; Calorimetry; Crystal-phase transition; Lithium cobalt oxide; Electrochemical polarization; Entropy change

1. Introduction

Lithium-ion secondary batteries have been of great interest among battery researchers as a candidate system for the dispersed storage of electric energy at user's site because of its excellent characteristics such as high energy density, long cycle life, etc. In recent years, small size lithium-ion batteries, i.e. coin-type, cylindrical-type, prismatic-type and card-type batteries, have been commercialized by some private companies for use in portable electronic products. However, the development of large size batteries for dispersed energy storage is still difficult because there are many complicated problems associated with electrical and thermal safety and reliability. During charging and discharging the battery, the temperature of the battery changes due to heat generation or absorption. It is very important to understand the heat-generation mechanism in view of the thermal design of the battery. Calorimetric study is one approach used to characterize the heat-generation behavior of batteries. In our past study, a twin-type heat conduction calorimeter was utilized for a commercial lithium-ion secondary battery to measure the heat of charge and discharge [1].

The main factors of heat generation were electrochemical polarization, electrical resistance, and the battery reaction. The last one was exothermic in the discharging process while endothermic in charging, and good reversibility of the battery

reaction was confirmed. In addition, thermal behaviors which were suggested to be caused by crystal-phase transitions of the positive electrode material were observed. In this work, calorimetry of the battery during discharge at various constant temperatures is carried out, and the temperature dependence of the heat generation by the discharge is discussed.

2. Experimental

A cylindrical type (diameter: 14 mm, thickness: 50 mm) lithium-ion battery (US14500, Sony Energytec) was used as a sample. The active electrode materials are LiCoO_2 in the positive electrode and hard carbon in the negative. The electrolyte solution is a mixed solvent of propylene carbonate and diethyl carbonate with LiPF_6 as the supporting electrolyte. The nominal battery voltage is 3.6 V, that is determined from an average value during 5 h discharge from 4.2 to 2.5 V, and the nominal electric capacity is 500 mAh. The battery, introduced into a twin-type heat conduction calorimeter (C-80, Setaram), was connected with outside instruments, a nanovoltmeter (Model 181, Keithley Instrument) to measure the voltage and a programmable d.c. source (Model 7651, Yokogawa Electric Corporation) to charge or discharge through two pairs of lead wires [1]. The heat loss through the wires is at most 1.5% of the heat generated. A brass rod dummy was used as a reference material. In the following, the battery charged at constant voltage of 4.30 V and constant temperature of 303 K is defined as in the full charged state, and the state of the battery is described as the quantity of

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electricity, Q , discharged from the full charged state. The temperature inside the calorimeter was controlled to some specified values between 283 and 333 K. The battery was discharged at a constant current of 50 mA until 2.75 V. The time constant of the delay due to heat transfer between the sample and the thermopile of the calorimeter is 341 s [1]. The influence of this delay was corrected before analysis of the results.

3. Results and discussion

Fig. 1 shows terminal voltage curves of the battery, V , and derivative curves of Q by V (dQ/dV) during discharge at several constant temperatures. The derivatives were calculated numerically. At lower temperatures, the battery voltage is also lower and less electricity is produced by the reaction if discharged to the same voltage. The voltage decreases during discharge with no plateaus, especially rapidly after about 170 mAh. In the former region, slight structures are observed in the derivative curves. Some complex behaviors are also observed around 100 mAh in Fig. 2 which are plots

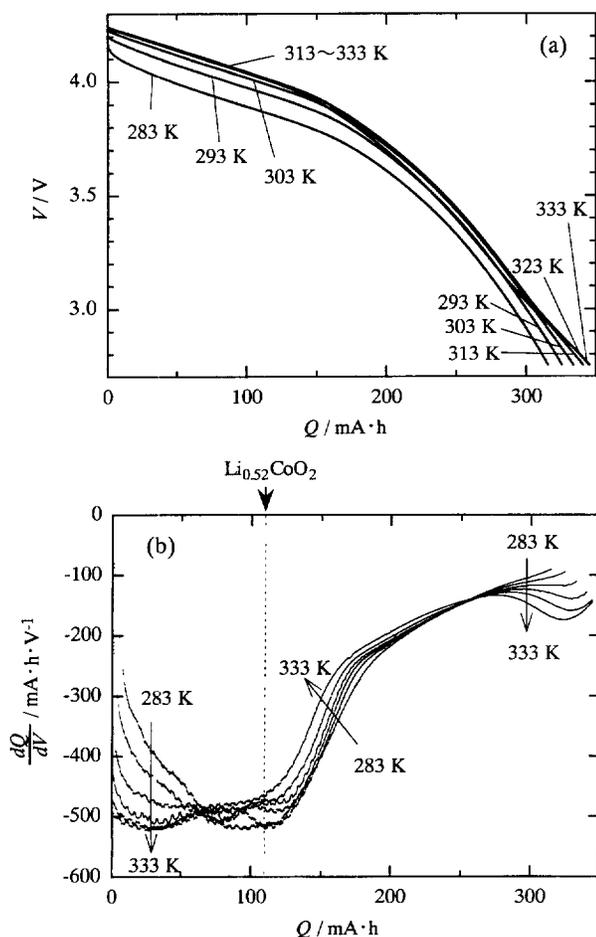


Fig. 1 (a) Terminal voltage, V , of the lithium-ion battery during discharge as a function of discharged quantity of electricity, Q , at various temperatures; discharging current = 50 mA. (b) The derivative of Q by V as a function of Q

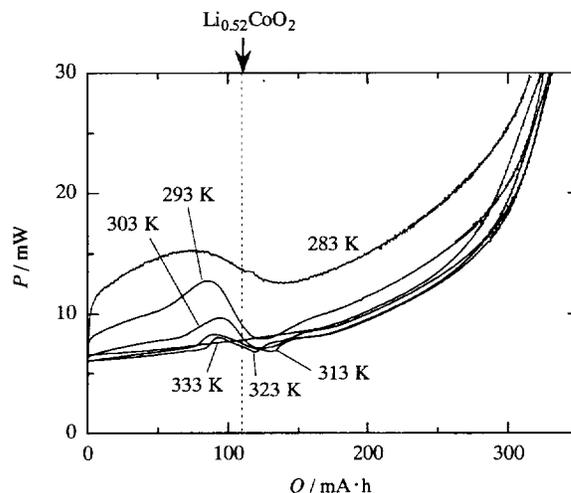


Fig. 2. Heat flow, P , from the lithium-ion battery during discharge at various temperatures.

of the heat flow, P , from the battery to a thermopile of the calorimeter during discharge as a function of Q . There is an exothermic peak and an endothermic peak during one discharge, and these become smaller with temperature increasing. No peaks are observed during discharge at 333 K. The measurements were carried out three times at each temperature, and good reproducibility was indicated except slight decreasing of the dischargeable capacity. It is difficult to imagine these behaviors of the voltage and the heat originated in the negative electrode material because of its low crystallinity. From comparison with Reimers and Dahn's results [2], it is suggested that they are caused by crystal-phase transitions of the positive electrode material, Li_xCoO_2 . In their derivative curves of the lithium concentration by the voltage, dx/dV , of an $\text{Li}_x\text{CoO}_2/\text{Li}$ cell, two slight peaks were observed around $x=0.5$. These are associated with order/disorder transitions of lithium ions in the CoO_2 framework and coupled to lattice distortions. The crystal-lattice structure is monoclinic at around $x=0.5$, while it is hexagonal in other composition range. The composition of the positive electrode material of the test battery was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The measurement was carried out for the positive electrode extracted from a battery which was discharged 110 mAh expecting the monoclinic structure because it located between the peaks in Fig. 2. The result indicated that the mole ratio of lithium to cobalt was 0.52. Thus, it is concluded that the electrical and thermal behaviors at around 100 mAh are caused by the phase transitions of Li_xCoO_2 . Fig. 3 shows differential thermal analysis (DTA) curves of the battery measured by the calorimeter during temperature scanning from 303 through 343 K [4]. The scanning rate was 0.1 K min^{-1} . An endothermic peak is observed at about 325 K when the discharged state of the battery, Q , is 130.1 or 160.1 mAh and Li_xCoO_2 is suggested to be monoclinic. This peak is caused by the transition from monoclinic to hexagonal. The transition is endothermic in this direction and exothermic in

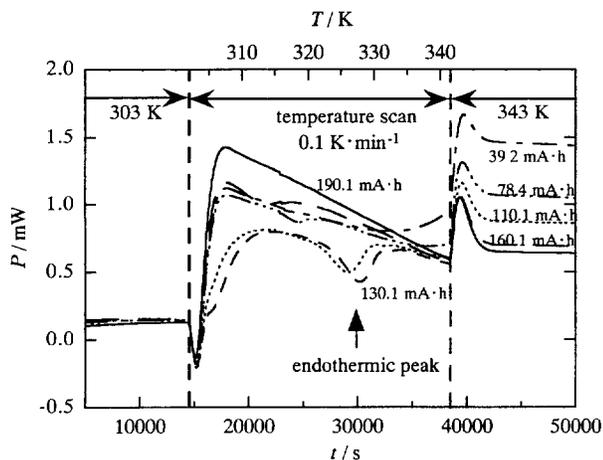


Fig. 3. DTA curves of the lithium-ion battery in the range of 303 and 343 K. The discharged quantities of electricity from the full charged state are (---) 39.2 mA·h; (- · - · -) 78.4 mA·h; (- - - -) 110.1 mA·h; (- - -) 130.1 mA·h; (—) 160.1 mA·h, and (—) 190.1 mA·h.

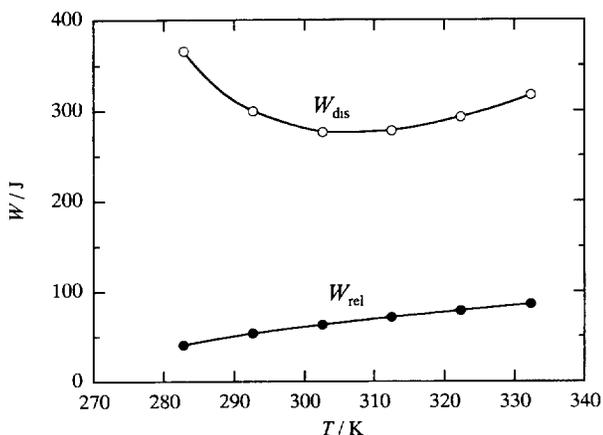


Fig. 4. Temperature dependence of heat generated by discharging the lithium-ion battery: (○) heat generated during discharge, W_{dis} , and (●) heat generated after the end of discharge, W_{rel} .

the reverse, and does not occur at 333 K and at higher temperatures.

It is known that there is a coexistence region of two hexagonal phases between $x = 0.75$ and $x = 1$ [2,3]. We believe

that the peaks observed around 300 mAh in Fig. 1(b) corresponds to the transition between the hexagonal I and II phases.

The results of the calorimetric studies indicates a long decay of the heat flow in addition to the delay due to heat transfer inside the calorimeter. The quantity of this delayed heat is larger at higher temperatures. This heat is thought to be caused by the relaxation phenomena inside the electrodes, such as the diffusion of lithium ions. The concentration gradients of lithium ions in the electrode materials are formed by charge or discharge, and are relaxed when resting. Fig. 4 shows the plots of the integration of the heat output during discharge, W_{dis} , and the delayed heat, W_{rel} , generated after the end of discharge. The heat generation of the relaxation is smaller at lower temperatures because the diffusion of lithium ions is probably more passive. In fact, when the battery discharged at room temperature is warmed until about 333 K, an exothermic behavior due to activation of the diffusion is observed. Although, when warming is carried out again, the heat generation is hardly observed [4]. It is due to the relaxation of the concentration gradients in the electrodes in the first warming treatment.

Energy efficiencies of the discharge reaction as a function of temperature were also studied. Fig. 5 shows output energy, W , of each discharge as a function of temperature, T . The total output energy is the sum of the electrical and the thermal outputs including the delayed heat, and corresponds to the change of the chemical energy in the battery by discharge because of the conservation of energy. While the battery generates more electric power at higher temperatures, the heat generated by discharge has a minimum in the range of 283 to 333 K. As seen in Fig. 2, more heat is generated at lower temperatures at the same Q on the whole. The heat during discharge is mainly caused by two factors: (i) the battery reaction, especially entropy change of the reaction, and (ii) the electric resistance, including the polarizations at the surface of the electrodes [1]. If the same reaction is progressing at the same discharged state at all temperatures, the former heat is larger at higher temperature because it is described as

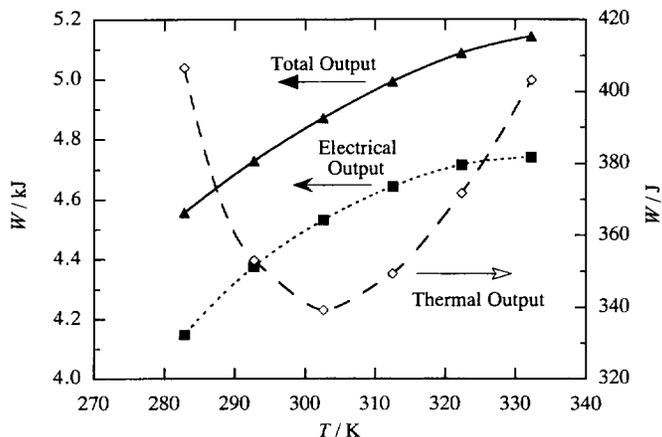


Fig 5 Temperature dependence of energies given off by discharging the lithium-ion battery: (○) thermal output as heat; (■) electrical output as electric power, and (▲) total output.

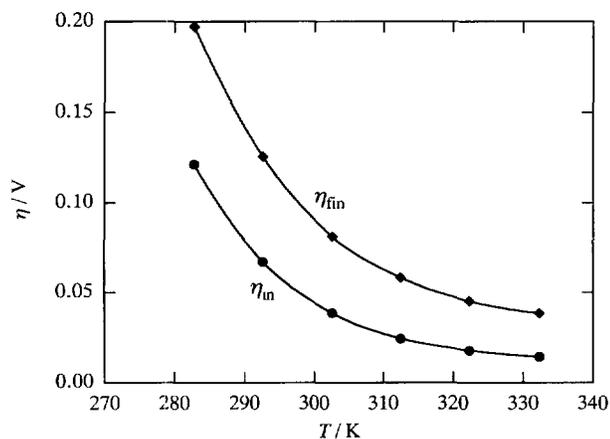


Fig. 6. Temperature dependence of overvoltage (●) at the beginning, η_{in} , and (◆) at the end, η_{fin} , of discharging the lithium-ion battery.

$T\Delta S$, where ΔS is the entropy change of the battery reaction. In addition, side-reactions such as a decomposition of the electrolyte are also activated at higher temperatures. On the other hand, the latter heat is larger at lower temperatures in this battery as seen in Fig. 6 which shows the overvoltage at the beginning, η_{in} and the end, η_{fin} of the discharge. This is a reason for the minimum in the heat generation. The temperature dependence of the overvoltage shown in Fig. 6 is probably caused by higher electric resistance of the electrode

materials, lower mobility of lithium ions in the electrolyte, and lower activity of battery reaction at lower temperature.

4. Conclusions

When a lithium-ion battery is discharged, thermal behaviors due to the crystal-phase transition of the active electrode materials are observed.

In the temperature range between 283 to 333 K, when the battery was discharged at 50 mA of constant voltage, the heat generation is least at about 300 K.

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