Thermal behaviors of lithium-ion batteries during high-rate pulse cycling

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Abstract

Heat generation due to electrochemical side-reaction during high-rate pulse cycling has been studied. In order to measure the value, calorimetry was carried out. The excess heat was observed comparing with the electric energy loss for each cycle, which was thought to be caused by side-reactions. Some side-reactions affect the surface characteristics of the electrodes and enlarge the impedance of the battery resulting in more heat generation.
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1. Introduction

Lithium-ion batteries are expected as auxiliary power sources for fuel cell electric vehicles (FCEV). High-power batteries with long life are required for such purpose. Developing the estimation methods of life of the batteries is one of the subjects, and it is important to know the mechanism of the degradation of the battery performance in various conditions. One of the causes of the degradation is side-reaction in the batteries. When the side-reaction occurs, heat generation (exothermic reaction) or heat absorption (endothermic reaction) due to the reaction is observed. Calorimetry is an effective method to characterize the thermal behavior of batteries, and some research groups reported the characterization of self-discharge of batteries in open-circuit, which was due to chemical side-reaction [1]. In this work, we focus the characterization of electrochemical side-reaction occurring during charge and discharge, especially in high-rate pulse cycling, by calorimetric measurement.

2. Experimental

A twin-type heat-conduction calorimeter (C-80, SE-TARAM) was used for calorimetry. The sample battery which was trial manufactured was supplied from Matsushita Battery Industrial Co. Ltd. The shape of the battery was cylindrical and the size was 18 mm in diameter and 65 mm in length. The nominal capacity C was 420 mAh. The standard condition of charging and discharging was constant current of $C/3$ A (140 mA), and the cut-off voltage was 4.2 V in charging while 2.5 V in discharging. The active cathode material was $LiNiO_2$ containing Co and Al, and the active anode material was non-graphitizable carbon. The sample was inserted directly into the chamber of the calorimeter without using a sample holder because of limitation of the size. A battery of the same type was inserted into the reference chamber in the calorimeter in order to cancel the heat due to side-reaction except for the electrochemical side-reaction, and to level the specific heat capacity, the thermal conductivity, the weight, and the density between sample and reference. The sample battery was connected to a multichannel power source (R6741, ADVANTEST) by two lead wires to flow current. Two other wires also used to measure the terminal voltage of the sample. The value of the current and the voltage was recorded by a digital scope (DL708, YOKOGAWA) with a high-resoluble

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insulation module (701853HR), and a standard resistor of 0.1 Ω (TOKYO SEIDEN) was used as an external shunt for the current measurement. Although the lead wires were not connected to the reference battery, they were also inserted into inside the reference chamber to balance the heat flow from the inside to the outside of the calorimeter, which was heat loss, between sample and reference. The influence of heat generation by the resistance of the lead wires during charge and discharge could be ignored because the length of the wires in sample side was same as that in reference side.

The profile of the high-rate pulse cycling test for the sample battery was shown in Fig. 1 that was decided considering the application as a power assist for FCEV. That was simplified cycling referring to the *PNGV Battery Test Manual* [2], and proposed by research group of CRIEPI [3]. The temperature in the calorimeter was controlled to 313 K during the cycling test. The center of state of charge (SOC) of cycling range was 50% that was set by charge at constant voltage of 3.60 V. Discharged and charged quantity of electricity during cycling was only 3% for the nominal capacity. Discharging current and time was constant at $10C$ A (4.2 A) and 11 s, respectively. In charging, CC–CV profile was applied for 33 s. The charging current in CC period was $5C$ A (2.1 A), and the charging voltage was 3.62 V during the CV period. The rest time between charging and discharging was 60 s.

In every 5000 cycles, the sample battery was intermittently being characterized for several battery performances,

which were capacity in $C/3$ discharge, ac impedance (10 mHz–10 kHz), and dc resistance (*I–V* characteristics, where $1C$–$10C$ A discharge are applied to the sample and the voltage in 10 s was measured) at 298 K.

3. Results and discussion

The main factors of heat generation during charge and discharge are the electrochemical polarization and the battery reaction itself [4]. The latter is concerning with the entropy change of the reaction, and reversible between charging and discharging directions. If heat generation is observed in discharge, same value of heat is absorbed in charge. On the while, heat due to polarization is exothermic in both charging and discharging. Thus, only heat due to polarization was observed in the total amount of generated heat during cycling if there are no side-reactions.

Fig. 2 shows the typical calorimetric result of one cycle during the cycling test. The time constant of the calorimetric system was 340 s. Since the slow heat transfer from the battery to the detector in the calorimeter, it was difficult to evaluate the generated heat exactly in real time. However, it is effective to evaluate the mean value of the heat-flow P_{mean}, or to calculate the total amount of the generated heat W by integration of the heat-flow curve, for each cycle, in order to discuss the input/output energy balance. Fig. 3 shows the variation of the total amount of heat W in each cycle for the initial cycling test, where 5000 cycles were progressed continuously. The electric power loss, which was the difference in charged and discharged electric energies and was mainly caused by the overvoltage during cycling, was also plotted. Dissipated energy as heat was larger than the lost electric energy suggesting excess heat generation was occurred by side-reactions. Since the shift of baseline in the calorimetric result was −0.014 mW between before and after the test, the excess heat was related to the electrochemical phenomenon. In Fig. 4, charge/discharge
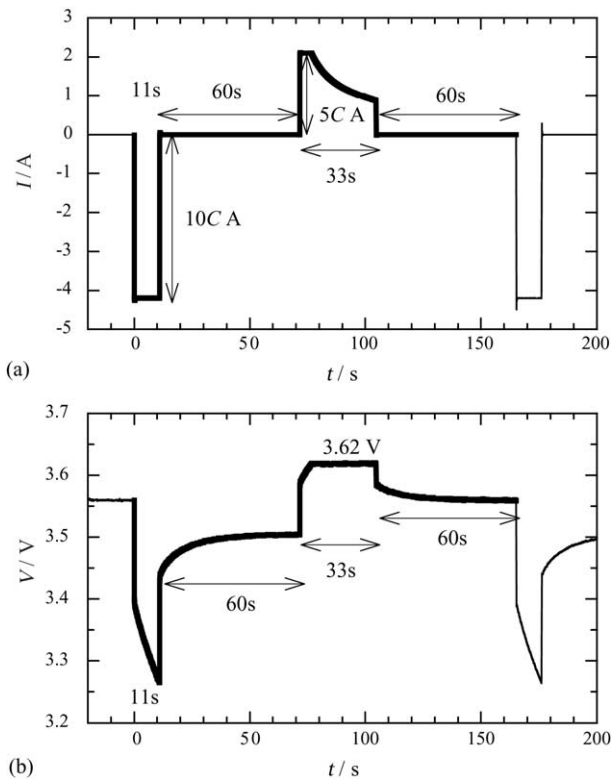

Fig. 1. The profile of high-rate pulse cycling test applied: (a) the current profile and (b) the voltage profile.
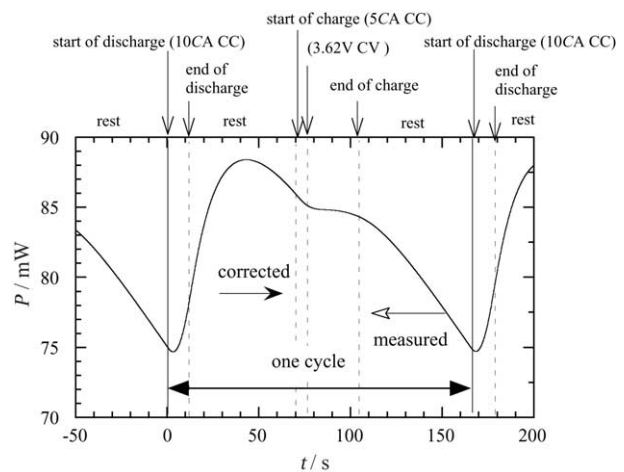

Fig. 2. Typical heat-generation curve of a lithium-ion battery for the high-rate pulse cycling test.
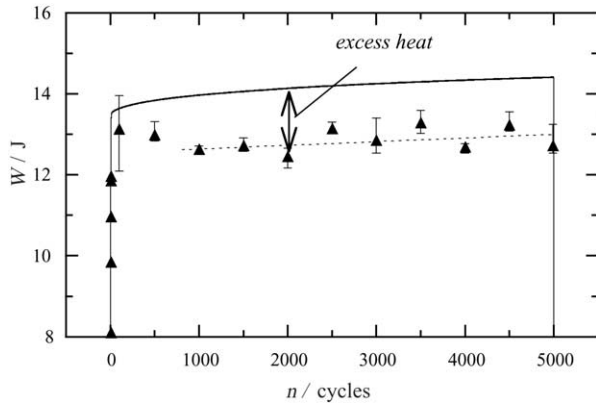
Fig. 3. Generated heat (—) and electric power loss (▲) for each cycle during the high-rate pulse cycling test for the battery as a function of cycle number, n.

efficiency ε for the quantity of electricity in every cycles was plotted. In the initial 10 cycles, charged quantity was less than discharged value, and SOC range was shifted to discharged state gradually. However, the electric quantities of discharge and charge were balanced after several decade cycles, where the efficiency was close to 100%. Even in the cycle, where discharge and charge balance was stabilized, the generated heat was larger than the electric loss as shown in Fig. 3. After the cycling test of 5000 cycles, the sample could discharge 187.1 mAh, while the charged electricity has been 196.7 mAh before the cycling test. The lost electricity was 9.6 mAh during the test that meant the shift of SOC was 2.3%. It was suggested that the excess heat was originated from the electrochemical side-reaction because it could not be explained only in the heat by discharge of 9.6 mAh. Considering the variation of ε shown in Fig. 4, the shift of SOC was thought to be occurred in initial stage of the cycling test. However, the excess heat was remarkable at the good efficiency term in the cycling test. The total integrated value of the quantity of electricity flowed in the sample battery with cycle progressing was evaluated to −74.3 mAh, where minus value means the charging electricity fell below the discharged electricity. Since the accuracy of the electricity of the measurement system is about ±0.5% and the total discharged electricity was
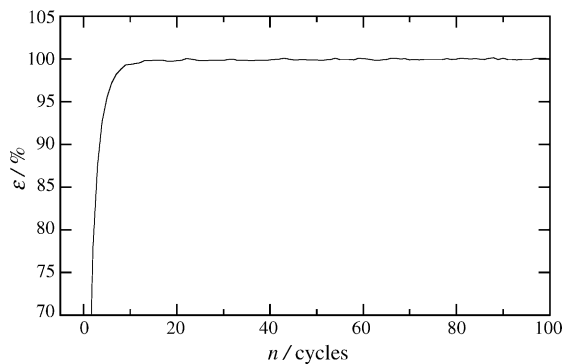
approximately 64.2 Ah in 5000 cycles, the value of 74.3 mAh was meaningless. Thus, it was difficult to discuss about the side-reaction in detail from the viewpoint of the cycle efficiency. However the side-reaction causes several joules of heat in one cycle as shown in Fig. 3. It is concluded that the calorimetry is an effective method to study the side-reaction.

In Fig. 5, the results of the calorimetric measurement of second cycling test for the same sample were plotted comparing with that of the first test. The heat was gradually increased with cycle in both tests. Since the value of the first cycle in the second test was not equal to that of last cycle in the first test, some factors of heat generation, which grew with cycle in the first test were initialized before the second test. However, in the results of the second test, larger heat generation was observed at the same cycle number that was counted from the start of the tests, and the difference was approximately 1 mW in mean value between two tests. This result suggests that there were some factors of heat generation, which were growing permanently with cycle. The same cycling test was repeated until total cycle number exceeded 50,000, and the heat flow gradually increased in the later tests actually. The mean value of heat at 5000th cycle that was the last cycle in each test was plotted in Fig. 6 for all cycling tests. The value shows linear relation with square root of total cycle number, and the coefficient was 0.036.
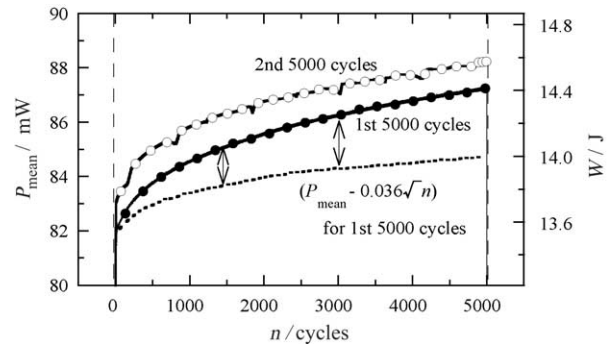

Fig. 5. Variation of the mean value of heat flow from the battery for each cycle. Initial 5000 cycles (●) and the next 5000 cycles (○).

Fig. 4. Charge/discharge efficiency ε for the quantity of electricity in each cycle.
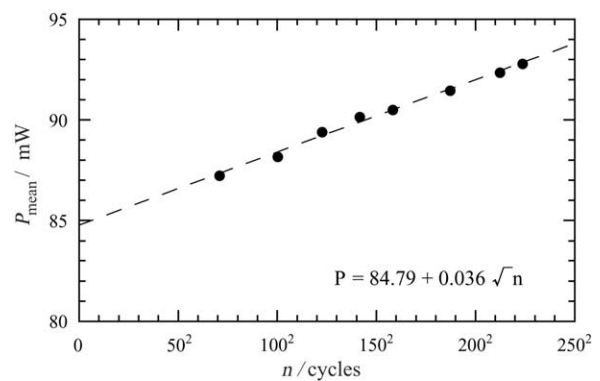

Fig. 6. The mean value of heat flow in 5000th cycle for each continuous cycling test as a function of total cycle number.
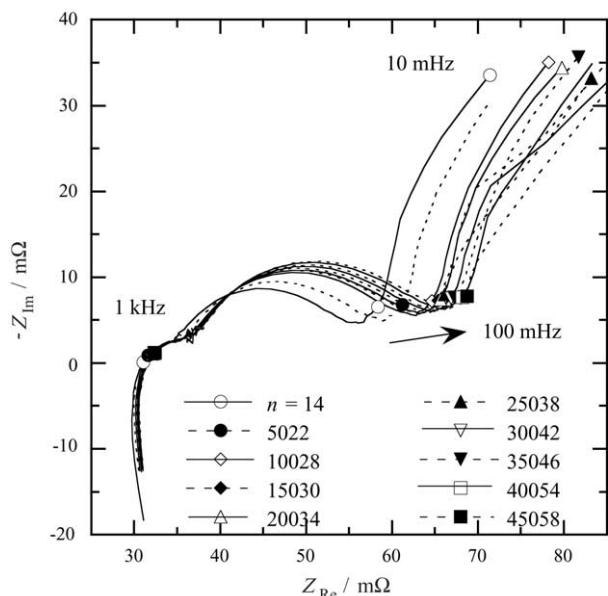
Fig. 7. The ac impedance of the battery at 298; SOC = 50%, i.e. charged state of 3.60 V.

Fig. 7 shows the variation of ac impedance of the sample battery of which SOC is 50% (3.60 V charged state) at 298 K. It is remarkable to increase the reaction resistance that is corresponding to the diameter of the semicircle. Since the larger resistance causes more heat when current flows through the battery, the increase of heat depending on cycle progressing might be originated in this enlargement of the impedance. The real component of the impedance at 100 mHz, which is close to larger end of the semicircle, is plotted in Fig. 9 as a function of total cycle number. It seems that the impedance also has a linear relation to square root of cycle number, suggesting the relation to the heat generation factors that grows permanently with cycles. The real component of the impedance at 1 kHz that is almost correspondent to the resistance of the electrolyte solution in the battery also shows similar relation with cycle number, though the variation is not so large, as shown in Fig. 8. Wright et al. reported similar result in which power fade of their lithium-ion batteries as a function of square root
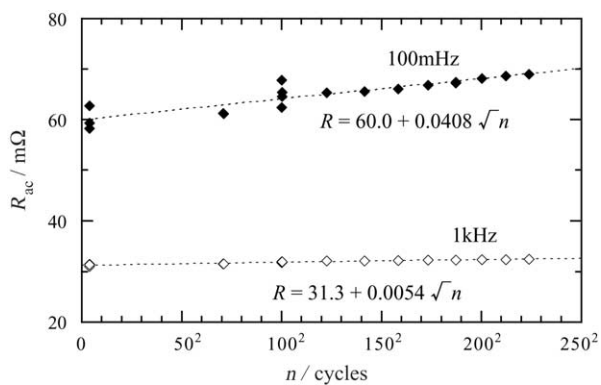

Fig. 8. Variation of real part in ac impedance with cycle progressing at the frequency of 100 mHz (♦) and 1 kHz (◊).
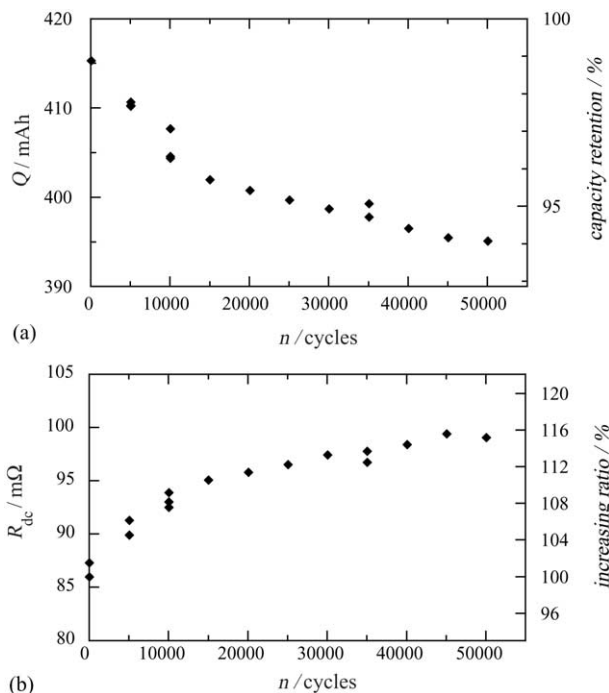

Fig. 9. Degradation of the battery performance at 298 K depending on cycle progressing: (a) capacity of the battery, $C/3$ A discharging and (b) dc resistance for discharge at SOC = 50%, which is the coefficient of relation between voltage in 10 s and current during constant current discharge.

of cycling time was described [5]. The tendency depending on cycle number (or time) is fitting in the mechanism of corrosion type reaction, where the rate is controlled by diffusion of the reactants. If there are side-reactions of which products affect the surface of the electrodes, e.g. formation of layers, they cause the increase in the impedance. Thus, it is concluded that the surface layers such as SEI is formed and grows up by the side-reactions resulting in increase of the impedance.

The dotted curve in Fig. 5 is the value that has been subtracted the heat due to impedance increasing with cycles from the mean value of the heat generation in each cycle for the first cycling test. This curve also increases with cycles. The electrochemical polarization might increase with cycle during the high-rate cycling test because of slow diffusion of lithium-ion both in the electrodes and in the electrolyte forming concentration distribution of lithium-ion widely. However, the concentration distribution is dissolved in the term of characterization of battery performances, which are carried out in every 5000 cycles. This is supposed to be one of causes of increase in heat generation with cycle, which is initialized between the cycling tests.

In Fig. 9, the capacity fade and the degradation of power characteristics, i.e. increase in dc resistance for discharge, of the sample battery were observed depending on cycle progressing. Side-reactions, which relate to the active electrode materials or lithium-ion are thought to be factors of the capacity fading. On the while, side-reactions that affect the surface of the electrode are not only causes of increase

of the impedance resulting in degradation of the power characteristics, but also causes of capacity fade because larger impedance produces larger overvoltage. More detailed studies such as the identification of the side-reactions and the determination of the reaction rate will be subjects in future work.

4. Conclusions

In order to evaluate the heat due to the electrochemical side-reaction, calorimetry was carried out for of a lithium-ion battery during high-rate cycling test. As the result, excess heat generation compared with the electric energy loss was observed. Although some causes of the heat during cycling was initialized during the characterization of battery performance, there were the other causes which grew up gradually with cycle progressing, and they were thought to be related to the enlargement of the impedance of the battery that was caused by side-reactions with producing surface layers on the electrodes.

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