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Thermal behaviors of lithium-ion cells during overcharge

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Abstract

The heat generation behavior in the overcharge has been investigated experimentally for various lithium-ion cells. Generated heat flow was examined by calorimetric measurement for different charging rates as a parameter and discussed. It is clarified that the heat generation during the overcharge is almost proportional to charging current. It is considered that if the cooling system can remove the equivalent heat to electrical input, it is possible to prevent the thermal-runaway which originates from the overcharge.

Keywords: Heat generation; Overcharge; Lithium-ion cell; Thermal-runaway

1. Introduction

With enlargement and higher energy density of the lithium-ion cell, more advanced safety technology becomes necessary. There are many tests in the evaluation of the safety of cells for various abuses. The overcharge, which is caused by failure and malfunctions of the cell charger, etc. leads to the thermal-runaway in bad cases, and sufficient countermeasure is required. It is important to well understand the heat generation behavior in the overcharge, because the thermal-runaway is closely related to the temperature rise in the cell [1,2]. Though, there are several reports on thermal behavior and temperature rise in the overcharge in lithium cells [1–5], the report that quantitatively examined the heat generation behavior seems to have not been published. In this study, the heat generation behavior in the overcharge has been examined quantitatively by calorimetric measurement for various lithium-ion cells at various charging rates. The change of open-circuit voltage in the overcharge was also examined by an intermittent charging.

2. Experimental

Five kinds of cells shown in Table 1 were tested. All cells except for sample E were commercial lithium-ion cells of 18650 size, and $LiCoO_2$-based materials were used in their cathodes. Sample E was a trial manufactured cell of 14500 size, which used $LiMn_2O_4$ in the cathode. PTC element included in the head of commercial cells was short-circuited by a metallic screw in order to avoid the effect, and also the safety vent lost the function of current breaker by the screw.

The heat generation in the cells was measured by a twin-type heat conduction calorimeter (Setaram, C80-22) in constant current charging with a compliance voltage limit of 6.0 or 7.0 V. The furnace temperature of the calorimeter was held constant at 303 K. Since the maximum range of the calorimeter was about 3 W, heat flow over the range was estimated from the inner temperature difference between the sample vessel and the reference vessel. Using specially designed sample vessels with a groove for a thermocouple, temperature in the vessels was measured.

The charge/discharge current was determined from the charge/discharge rate with the nominal capacity. Standard conditions of charge and discharge were defined as 0.2 C constant current followed by 4.2 V constant voltage charging, and 0.2 C constant current discharging with the termination voltage of 2.7 V, respectively. Charge and discharge of 5–10 cycles were initially carried out in the standard conditions, then the overcharge test was conducted at a certain charging rate between 0.1 and 1 C from the entirely discharged state until charged electricity came over 300 or 400% of the initial discharge capacity.

3. Results and discussion

Variations of the generated heat flow and the cell voltage in the overcharge at various charge rates in sample A are

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Table 1
Samples of lithium-ion cell for overcharge test[a]

Sample	Size	Cathode/anode	Electrolyte[b]	Nominal capacity (mAh)	Initial capacity (mAh)	Comment
A	18650	$LiCoMO_2$/graphite	EC, EMC	1500	1629 ± 11	A & T battery
B	18650	$LiCoO_2$/graphite	EC, DMC, DEC, EMC	1250	1342 ± 36	Panasonic
C	18650	$LiCoO_2$/graphite	EC, DMC, DEC	1500	1610 ± 13	Sanyo
D	18650	$LiCoO_2$/hard carbon	PC, DMC, EMC	1350	1303 ± 28	Sony
E	14500	$LiMn_2O_4$/graphite	EC, DMC, PC, EMC	250	254 ± 20	Trial manufactured

[a] Electrolyte for the samples without E was referenced from [6].
[b] EC: ethylene carbonate; EMC: ethyl methyl carbonate; DEC: diethyl carbonate; DMC: dimethyl carbonate; PC: propylene carbonate.

shown in Fig. 1. In each charging current, the generated heat flow and the cell voltage increase with time, after the overcharge begins, and the heat flow begins to increase rapidly when the voltage reaches about 4.6 V. In the cases of 0.5 and 1.0 C, there were some discontinuous changes in the voltage after the maximum heat flow. In the cases of 0.2 C or less, discontinuous changes in the voltage and the heat flow were observed a little before the stop of charge. It seemed that this was owing to the discharge of contents from the cell, of which the trace was observed after the test. When the charge was terminated, the generated heat lowered rapidly, but continued a comparatively high level. While, the cell voltage lowered rapidly to about 1.5–3.5 V below the full charge voltage. These facts indicate that the cell deteriorates by the overcharge.

Noticing the relationship between the heat flow and the charging current, the heat flow seems to be almost proportional to the current in the overcharge. Variations of the cell voltage and the ratio of the heat flow to the electrical input, which is called as generated heat ratio in latter, in sample A and D are shown in Fig. 2 against the ratio of the charged electricity to the initial cell capacity, which is called as

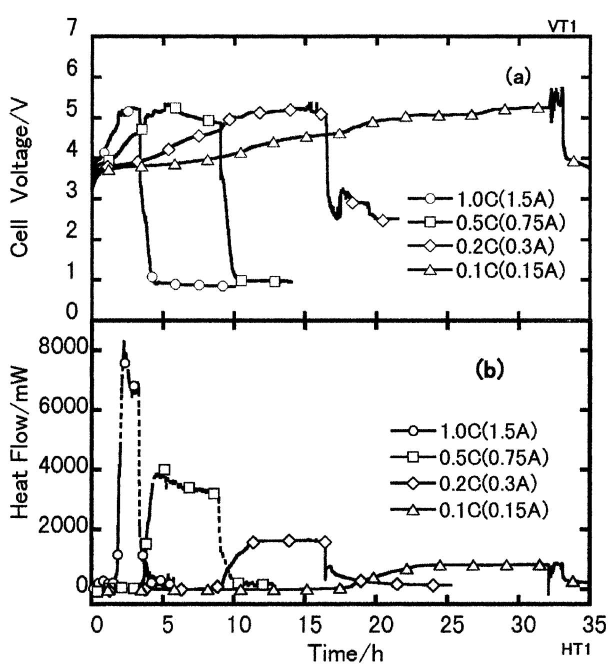

Fig. 1. Variations of cell voltage (a) and heat flow (b) during the overcharge in a commercial lithium-ion cell, sample A.

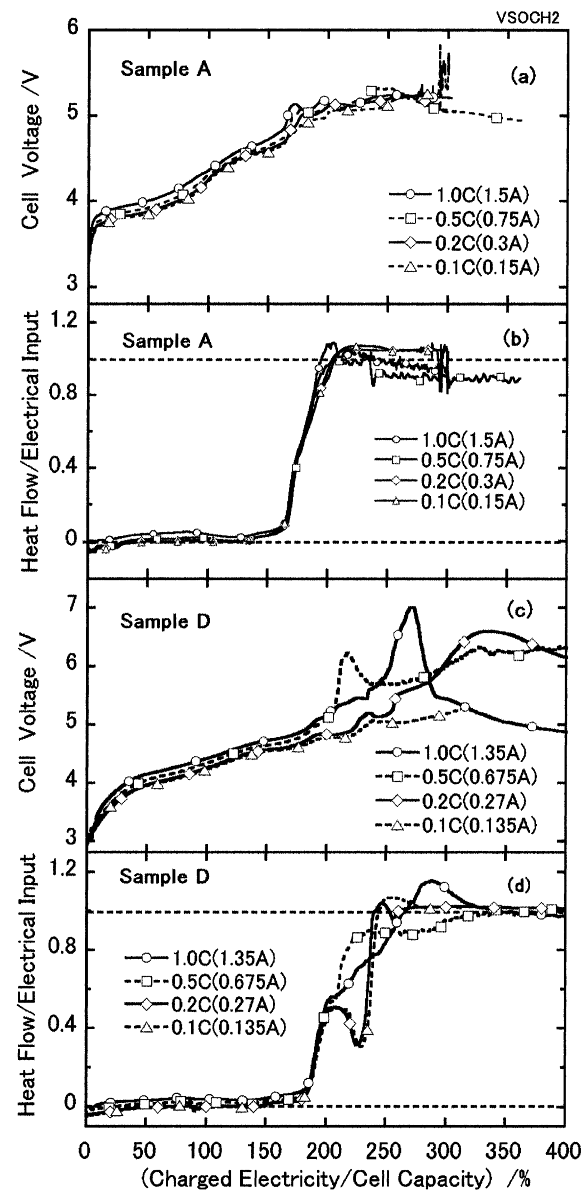

Fig. 2. Cell voltage (a), (c) and the ratio of heat flow to electrical input (b), (d) vs. the ratio of charged electricity to cell capacity during overcharge in sample A and D for different charging currents.

charged ratio. In sample A, the curve of the generated heat ratio to the charged ratio hardly changes by the charging current. Though, the generated heat ratio is small until about 160% at charged ratio, it rapidly increases when 160% is exceeded. The generated heat ratio becomes about 1 when 200% is exceeded, i.e. the generated heat flow agrees with the electrical input. Until the charged ratio 160% where the generated heat begins to increase rapidly, the voltage monotonously increases by the increase in the current, but small quantity. However, the relation with the current is complex at the charged ratio beyond 160% because the voltage fluctuates with charging.

In sample D, the curve of generated heat ratio to charged ratio hardly changes due to the current in 0.2 C or less. However, it changes due to the current above 0.5 C in the charged ratio over 200%. The voltage shows the similar change by the current with the generated heat ratio. And, the generated heat ratio becomes about 1.0, when the overcharge sufficiently advances. As above shown in sample A and D, in the low current of 0.2 C or less, the curves of the generated heat in five kinds of cell hardly changed by the current. However, the change in the curves became larger by the higher current in the large charged ratio. It was speculated that such change in the curves related with the temperature rise in the cell due to the higher current and with the discharge of contents.

Variations of the generated heat ratio and the cell voltage during the overcharge at 0.2 C are shown in Fig. 3 for five kinds of cell (sample A, B, C, D, and E). In all cells, the generated heat flow gradually increases with the charged electricity when the overcharge begins, and it begins to increase rapidly when the charged ratio reaches a certain value of 110–180%. Then, the generated heat ratio becomes about 1 after the maximum value, when the overcharge advances. The charged ratio in which the heat generation begins to increase rapidly is different by the cell type, and it is about 110% in sample E of $LiMn_2O_4$ cathode. It is between 160 and 180% in the cells of $LiCoO_2$-based cathode, when the unique change near 125% of sample C is ignored. These charged ratios seem to be related to the lithium content in the cathode active materials at the fully charged state, because $LiCoO_2$-based cathodes contain much more lithium at the fully charged state than $LiMn_2O_4$-based one.

As mentioned above, in all cells, the generated heat ratio showed the maximum value, and then it became close to unit, when the overcharge advanced. In the charge of 0.2 C or less, the maximum value was at most 1.2. This fact suggests that the thermal-runaway which originates from the temperature rise in the cell can suppress, if a cooling system can sufficiently remove the equivalent heat to the electrical input.

Fig. 4 shows the result of the intermittent charging test conducted with 1 h charging at 0.1 C and 1 h open-circuit

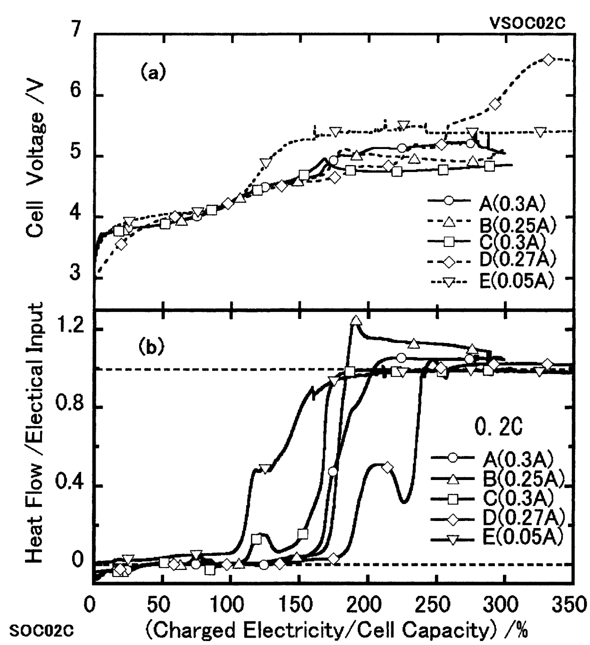

Fig. 3. Cell voltage (a) and the ratio of heat flow to electrical input (b) vs. the ratio of charged electricity to cell capacity during overcharge at 0.2 C of charging rate for five kinds of cell.

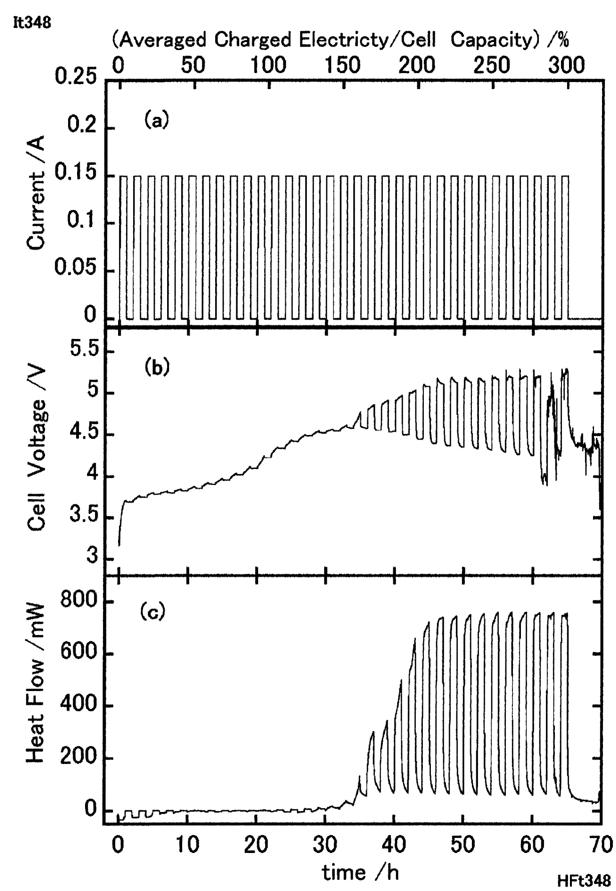

Fig. 4. Variations of charging current (a) cell voltage (b) and heat flow (c) during overcharge at an intermittent charging with 1 h charging at 0.1 C and 1 h open-circuit in sample A.

in sample A. Both variations of the voltage and the heat flow during the charging period agree approximately with them in the continuous charging, respectively. Though, the difference between charging voltage and OCV is small until 150% at charged ratio, it becomes larger when 160% is exceeded. This change is similar to the change in the heat flow. OCV is about 4.6 V near 150% at charged ratio, and it gradually decreases with charging in contrast with the increase in the charging voltage after 160% is exceeded. The heat flow estimated from the over-voltage that is defined as difference between charging voltage and OCV is about 1/5 of measured value at most, when the overcharge advanced. The heat generation cannot be explained with simple ohmic heat generation, because it is approximately proportional to charging current. From these results, it is speculated that the decomposition of the electrolyte becomes remarkable when the charging voltage exceeds 4.6 V, and that the reaction between the cathode material and the decomposition products occurs with large heat generation, resulting in the gradual degradation of the cell.

4. Conclusion

The generated heat flow during the overcharge was parametrically examined by the calorimetric measurement. It is clarified from the result that the heat generation during the overcharge is almost proportional to charging current. It is considered that if the cooling system can remove the equivalent heat to the electrical input, it is possible to prevent the thermal-runaway that originates from the overcharge.

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