

Short communication

Relation between composition of the positive electrode and cell performance and safety of lithium-ion PTC batteries

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Available online 3 July 2007

Abstract

To improve the safety of lithium-ion batteries, a new type of positive electrode, which contains a positive temperature coefficient (PTC) compound consisting of a carbon black/polyethylene composite as the conductive material, was fabricated. The relation between the positive electrode composition and both the discharge characteristics and safety was investigated. The discharge capacity of PTC cells increased as the PTC compound ratio decreased or the acetylene black (AB) ratio increased. In an external short-circuit test, the maximum short-circuit current decreased with an increase in the PTC compound ratio, or with a decrease in the AB ratio. Moreover, in an overcharge test, the voltage of the PTC cells with any composition increased earlier than that in a conventional cell and a cell with a high PTC compound ratio showed high overcharge tolerance. Based on the results of X-ray diffraction (XRD) measurements for the positive electrodes of PTC cells, it was clear that there was inadequate oxidation of the active material, since the Li^+ extraction reaction from Li_xCoO_2 hardly progress at the part of the active material which contacts the PTC compound due to an increase in the resistance of the PTC compound at the high temperature.

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Keywords: Positive temperature coefficient; Overcharge test; Safety; Lithium-ion batteries

1. Introduction

Lithium-ion batteries (LIBs) are expected to be one of the main power-storage devices for hybrid electric vehicles and fuel cell vehicles because of their high energy density and high power density [1–3].

For LIBs to be used as such power-storage devices, battery safety is an important issue. To improve LIB safety, many safety devices have been installed in LIBs. One of these is a positive temperature coefficient (PTC) device that responds to an increase in current flow. If an enormous large current flows across the PTC element, its temperature increases due to Joule heat evolution. Concurrently, the resistivity of the PTC element drastically increases, and this prevents the current flow. However, since this PTC device is generally connected in series with one of the terminal leads in a cell, it cannot prevent current that flows via an internal short-circuit between the electrodes.

Thus, we have proposed a new concept for a positive electrode, as shown in Fig. 1, which contains a PTC compound consisting of a carbon black/polyethylene composite. The resis-

tivity of the PTC positive electrode increases nonlinearly at 130–140 °C, since the polyethylene in the PTC compound expands due to a phase change at a temperature around the melting point and cuts off the conductive network of the carbon black. When a large current flows across the PTC positive electrode or the temperature of the PTC positive electrode increases, the resistivity of the electrode increases and the current flow is restricted. Therefore, a PTC positive electrode may be effective for controlling current flow between electrodes since the electrode itself can limit current flow.

The PTC compound has greater resistivity than conventional conductive materials for the positive electrode of LIBs, such as graphite and carbon black, and therefore, battery performance is not so good. Therefore, to improve the discharge capacity, a small amount of secondary conductive material (acetylene black; AB) is added to support current collection in the electrode. Cells that incorporate PTC positive electrodes containing AB had better discharge characteristics and a longer cycle life than those with a PTC electrode without AB [4–6].

In this study, the relation between the composition of the positive electrode and both cell performance and safety of lithium-ion PTC cells was evaluated. Furthermore, we performed an overcharge test and analyzed the positive electrode of PTC cells to better understand the safety mechanism of PTC cells.

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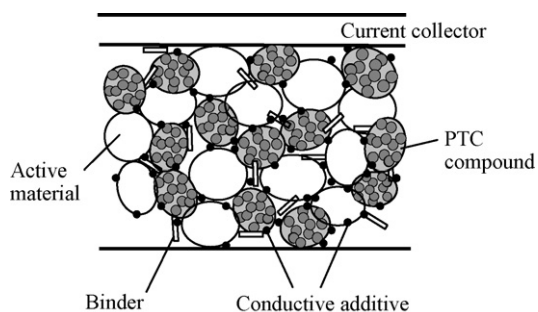


Fig. 1. Conceptual illustration of a PTC positive electrode.

Table 1

Composition of PTC positive electrodes of card-size cells in this study

PTC (wt.%)	AB (wt.%)	Cell
12	0.5	A
12	1	
10	1.5	
9	1.5	B
8	1	
7	1	
6	1	C
4	2	
3	3	

2. Experimental

As a PTC compound, high-density polyethylene resin (melting point: 136 °C) and carbon black (particle size: 95 nm) were mixed and kneaded in a vessel, and a carbon black/polyethylene composite pellet was fabricated. This pellet was pulverized and ground to a powder that had an average particle diameter of about 15 μm . The PTC positive electrode was made by coating a mixture of the active material (LiCoO_2) (particle size: 7.3 μm), the conductive material (PTC compound), AB (particle size: 42 nm), and binder (poly(vinylidene difluoride)) (PVDF) with *N*-methyl-2-pyrrolidinone (NMP) on an aluminum foil. The contents of the PTC compound and AB in the PTC positive electrodes were 3–12 wt.% and 0.5–4 wt.%, respectively, of the total mass of the electrode mixture. In addition, a reference positive electrode that incorporated only AB as a conductive material was prepared by the same process.

Card-size (48 mAh) cells and prismatic cells (500 mAh) were fabricated to investigate electrochemical and safety performance. For both sizes of cells, the negative electrode was prepared by coating a mixture of mesophase carbon microbead graphite, carbon black and PVDF with NMP on a copper foil. A polypropylene porous film or a polyethylene porous film was used as a separator. For the card-size cell, a positive electrode, a polypropylene separator, and a negative electrode were assembled. As the prismatic cell, a negative electrode, which was combined with a polyethylene separator to prevent misalignment during winding, and a positive electrode were wound together to make a battery element. These two kinds of cells were sealed in a laminated pack. A 1.2 M solution of LiPF_6 in a mixture of ethylene carbonate and diethyl carbonate was used as an electrolyte.

AC impedance measurements were carried out using a frequency analyzer (Solartron 1255) and a potentiostat (Solartron 1287) in a frequency range of 100 kHz to 10 mHz with an ac signal amplitude of 10 mV under open circuit conditions. The discharge characteristics were measured at constant discharge rates of 0.25, 1, 2, and 3 C at 20 °C. The charge condition was a constant current (1 C)–constant voltage (CC–CV) mode and the upper-limit voltage was 4.1 or 4.2 V. The discharge condition was constant-current (CC) mode and the cut-off voltage was 2.75 V.

To evaluate battery safety, an external short-circuit test and an overcharge test were carried out. During the external short-

circuit test, the card-size cells were charged at 1 C to 4.2 V, and the current was measured by the voltage drop at both ends of shunt resistance (10 m Ω), where the positive and negative electrode terminals of the cell were short-circuited at 140 °C. The overcharge test was performed for prismatic PTC cells. Before overcharging, the test cell was discharged at 1 C to 2.75 V, and then charged at different current rates to 10 V in the CC–CV mode in a chamber. The cell temperature was measured by thermocouples that had been attached to the surface of the cell.

X-ray diffraction (XRD, Rint-2000, Rigaku Co.) using a Cu $\text{K}\alpha$ radiation was used to characterize the active material of the positive electrode at different states of charge (SOCs). XRD samples were prepared by charging each cell up to the prescribed SOC, and dismantling the reference and PTC cells in an argon-filled glove box (dew point: –60 °C). The positive electrode samples that were removed were covered with polyethylene film and sealed to prevent the influence of air.

3. Results and discussion

3.1. Discharge properties

The composition of the PTC positive electrodes of card-size cells, in this study, is shown in Table 1. The discharge curves of cells A–C under a discharge rate of 2 C are shown in Fig. 2. The cell with a higher PTC compound ratio shows a lower cell voltage

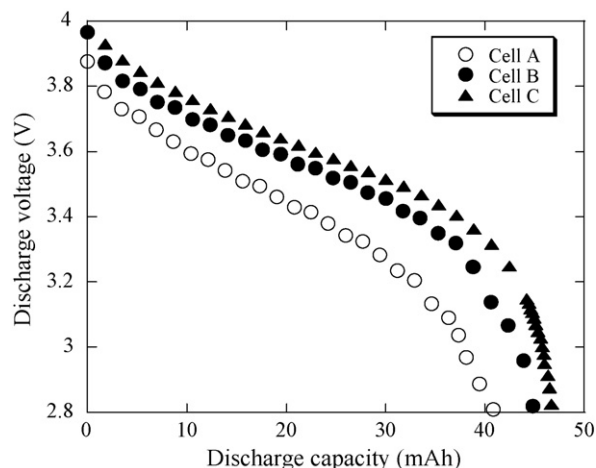


Fig. 2. Discharge curves of cells A–C under a discharge rate of 2 C.

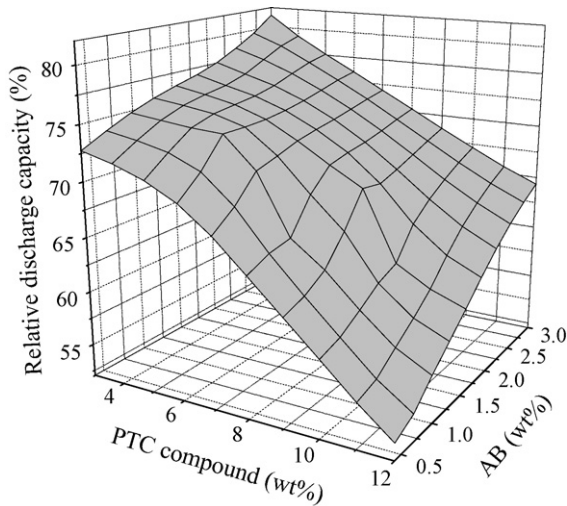


Fig. 3. Correlation between the PTC compound ratio, AB ratio, and relative discharge capacity at a discharge rate of 3 C.

and a lower discharge capacity, due to the high cell impedance. The discharge capacity also depends on the AB ratio. Fig. 3 shows the correlation between the PTC compound ratio, the AB ratio, and the relative discharge capacity at a discharge rate of 3 C for the PTC cells shown in Table 1. The relative discharge capacity values are shown as a percentage of the capacity at a rate of 0.25 C. As shown in Fig. 3, the relative discharge capacity of PTC cells increases with an increase in the AB ratio, due to an increase in the current-collecting channels from the active material [6].

Fig. 4 shows the external short-circuit current of PTC cells at 140 °C, where the electric resistance of a PTC positive electrode increases due to a drastic increase in the resistivity of the PTC compound. A cell with a low PTC compound ratio showed a high short-circuit current, since the cell impedance at 140 °C is less than that of a cell with a high PTC compound ratio. The dependence of the maximum short-circuit current (MSC) of PTC cells on the PTC compound ratio and the AB ratio is shown in Fig. 5. The MSC decreases as the PTC compound ratio increases

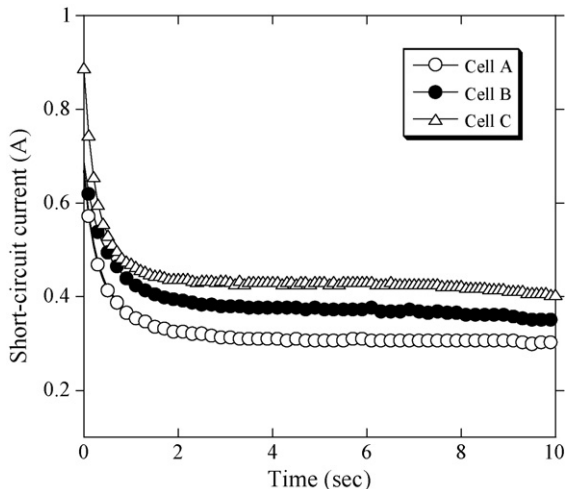


Fig. 4. External short-circuit current of PTC cells at 140 °C.

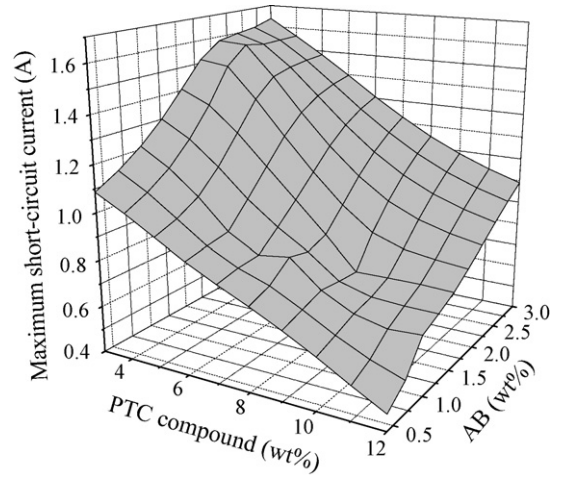


Fig. 5. Dependence of the maximum short-circuit current (MSC) of PTC cells on the PTC compound ratio and AB ratio.

or the AB ratio decreases. The MSC of the cell with 3 wt.% of the PTC compound and 3 wt.% of AB (cell D in Table 1) was 1.6 A. The MSC of the cell that contained only AB without PTC compound was 9.5 A [6], which is almost six times greater than the MSC of cell D, indicating that only 3 wt.% of the PTC compound is effective for reducing the short-circuit current.

3.2. Overcharge test

To evaluate the dependence of overcharge tolerance on the PTC electrode composition, prismatic PTC cells with various compositions were fabricated. For comparison, a reference cell in which the positive electrode contained only AB as a conductive material was also prepared by the same process. The positive electrode composition of fabricated prismatic cells is shown in Table 2. Fig. 6 shows discharge profiles of PTC and reference cells under a discharge rate of 2 C. PTC-6 wt.% and reference cells showed discharge capacities of more than 500 mAh and PTC-9 and -12 wt.% cells had capacities of 479 and 478 mAh, respectively, which were more than 90% of the value for the reference cell. The prismatic cells also show a pattern similar to the discharge characteristics of card-size cells (Fig. 2), in that a cell with a high PTC compound ratio shows a low discharge capacity.

The results of an overcharge test for the PTC and reference cells are shown in Table 3. The PTC-12 wt.% cell did not ignite or explode under any of the charge conditions. The cell with a high

Table 2
Positive electrode composition of fabricated prismatic cells

Cell	Positive electrode composition			
	LiCoO ₂ (wt.%)	PTC (wt.%)	AB (wt.%)	PVDF (wt.%)
PTC-12 wt.%	82.5	12	1	4.5
PTC-9 wt.%	85	9	1.5	4.5
PTC-6 wt.%	86.5	6	2	5.5
Reference	91	0	3	6

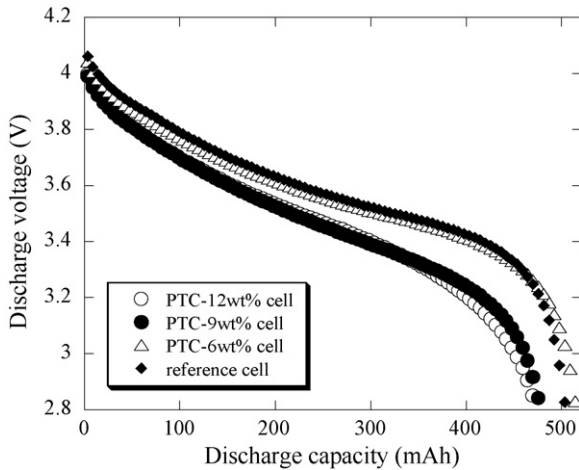


Fig. 6. Discharge profiles of PTC and reference cells under a discharge rate of 2C.

PTC compound ratio had high overcharge tolerance. Fig. 7(a and b), respectively, show the cell voltage and cell surface temperature for laminated prismatic PTC and reference cells that were overcharged to 10 V at CC–CV of 1.0 A (2C). The voltage of the reference cell gradually increased up to the first peak voltage of 5.3 V (3150 s) and then decreased slightly before it sharply increased to 10 V (3300 s). Almost all (95–100%) of the lithium was removed from the positive electrode in this stage [7]. The first peak voltage values of PTC-12, -9, and -6 wt.% cells are 6.9, 6.03, and 5.71 V, respectively, which increase with the PTC compound ratio, and all of the PTC cells show a greater peak voltage than the reference cell. The electric capacities charged up to 10 V for the PTC-12, -9, and -6 wt.%, and reference cells were 182, 183, 195, and 192% SOC, respectively. In the reference cells, the voltage reached 10 V at a temperature of almost 100 °C. Some reports have described a large difference between the surface and internal cell temperatures [7,8]. In addition, according to previously reported data [9], the internal temperature of a cell is more than 125 °C when the cell surface temperature is 100 °C under a charging rate of 1.5 C. Therefore, the rapid increase in voltage up to 10 V in the reference cell is likely caused by an increase in the cell impedance mainly due to electrolyte decomposition and a separator shutdown, since the internal temperature was more than 125 °C. By comparison, the temperatures at which the PTC-12, -9, and -6 wt.% cells reached 10 V were more than 85, 90, and 95 °C, respectively, corresponding to internal temperatures of 105, 110, and 120 °C. These values are lower than the temperature at which the voltage of the reference cell reached 10 V,

Table 3
Results of an overcharge test for the PTC and reference cells

Cell	Charging condition (CC–CV)			
	1.0 A to 10 V	1.5 A to 10 V	2.0 A to 10 V	3.0 A to 10 V
PTC-12 wt.%	○	○	○	○
PTC-9 wt.%	○	○	○	×
PTC-6 wt.%	○	○	×	
Reference	○	×		×

○: no fire, ×: fire.

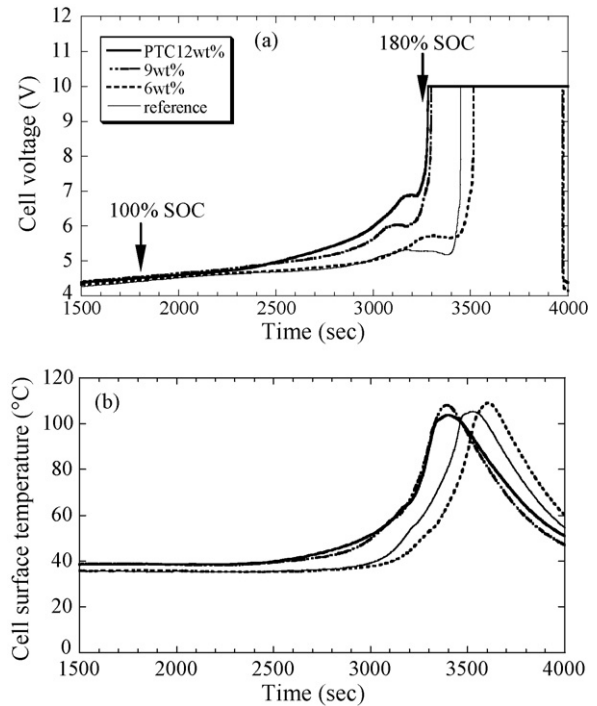


Fig. 7. (a) Cell voltage and (b) cell surface temperature for laminated prismatic PTC and reference cells overcharged to 10 V at CC–CV of 1.0 A (2C).

indicating that the increase in the PTC cell voltage to 10 V is caused by an increase in the resistance of the positive electrode. Fig. 8 shows the results of the overcharge test for the PTC-12 wt.% cell which was charged at rates of 2, 3, 4, and 6 C. As the charging rate increases, the cell surface temperature increases rapidly and the cell voltage quickly reaches the set voltage of 10 V. The electric capacities charged up to 10 V decrease as the charging rate increases, namely the electric capacities of PTC cells, when charged at 6 C are 659 mAh, correspond to 132% SOC. This result suggests that a large charge current causes rapid self-heating of the PTC positive electrode due to a Joule heat evolution of the PTC compound. Accordingly, the resistance of the PTC positive electrode increased and the cell voltage reaches the set voltage early, since the polarization voltage increased rapidly.

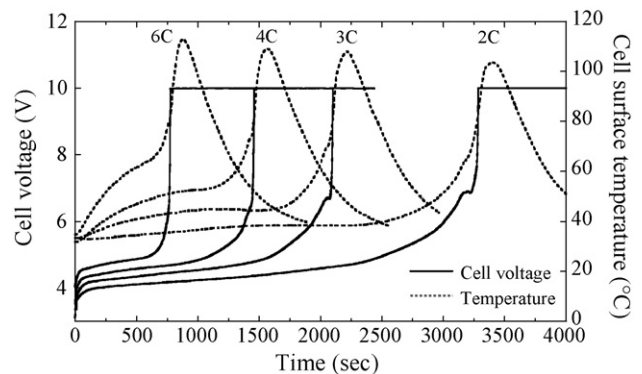


Fig. 8. Results of an overcharge test for the PTC-12 wt.% cells at charging rates of 2, 3, 4, and 6 C.

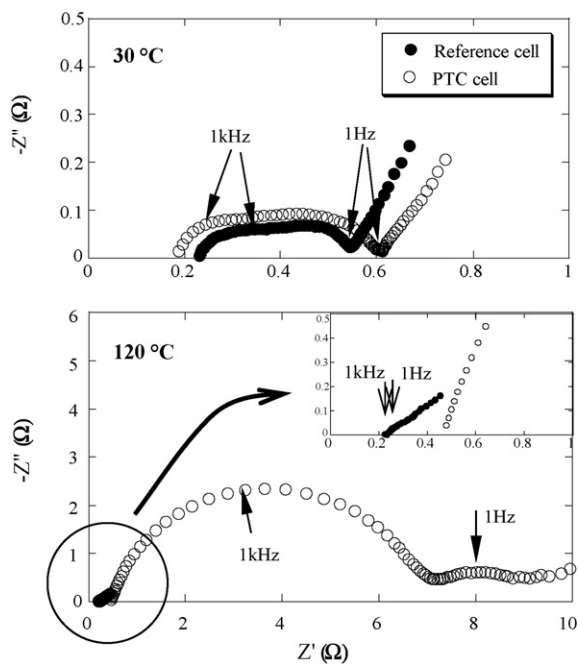


Fig. 9. Nyquist impedance spectra of the reference and PTC-12 wt.% cells at 30 and 120 °C.

3.3. Ac impedance measurements

To confirm the increase in the impedance of the PTC cell, ac impedance measurements were performed. The Nyquist impedance spectra of the reference and PTC-12 wt.% cells at 30 and 120 °C are shown in Fig. 9. Based on the results in Fig. 9, both semicircles of the reference and PTC measurement spectra at 30 °C overlap in the two capacitive semicircles without a large difference between the reference and PTC spectra. The semicircle of the PTC cell at 120 °C is more than 15 times larger than that at 30 °C, while the semicircle of the reference cell at 120 °C is less than 100th the size of that at 30 °C. This enormous increase in the impedance of the PTC cell indicates that polarization of the PTC cell greatly increases at high temperature. Moreover, we have reported that the impedance of the PTC cell begins to increase at 80 °C [9]. Therefore, considering that the cell internal temperature is higher than the cell surface temperature, the increase in the PTC cell voltage to 10 V in Fig. 7(a) is caused by an increase in cell impedance due to an increase in the resistance of the PTC compound.

3.4. XRD results

To understand the mechanism of the PTC electrode in the overcharge state, XRD analysis was performed for the positive electrodes of reference and PTC cells at 100 and 180% SOC which are indicated in Fig. 7(a). With an XRD analysis, we can investigate the change in the LiCoO_2 active material during the overcharge process. A monoclinic phase is observed near $x=0.5$ in Li_xCoO_2 after charging up to a 100% SOC. When the cells are overcharged, lithium ions are removed from the $\text{Li}_{0.5}\text{CoO}_2$ and supplied to the negative electrode, and finally

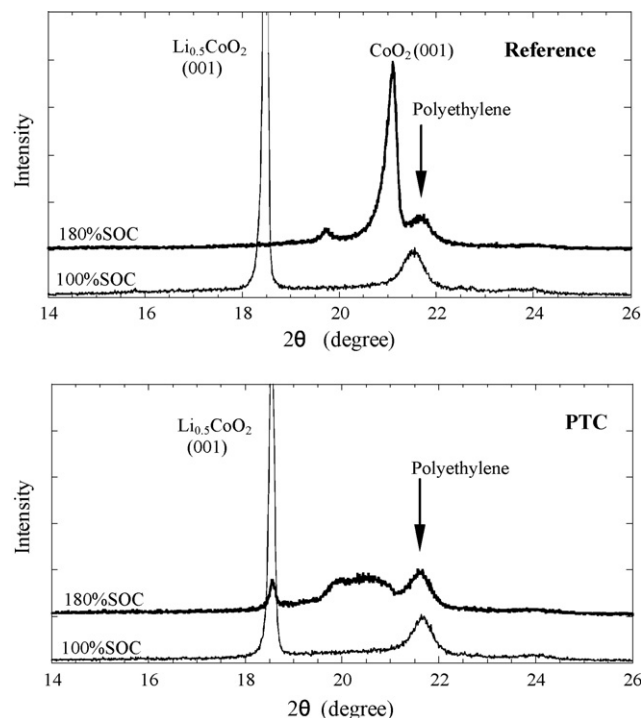
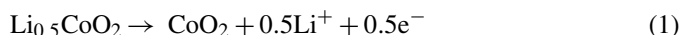


Fig. 10. XRD patterns of the reference and PTC-12 wt.% positive electrodes charged up to 100 and 180% SOC.

CoO_2 is produced. This electrochemical oxidation process can be expressed as follows:



When lithium ions are removed from $\text{Li}_{0.5}\text{CoO}_2$, a two-phase region is observed that consists of monoclinic and hexagonal phases corresponding to $x=0.21\text{--}0.18$ in Li_xCoO_2 . When lithium extraction progresses further, a hexagonal CoO_2 phase is observed [10–12]. Fig. 10 shows the XRD patterns of the reference and PTC positive electrodes. The peak at $2\theta = 21.7^\circ$ is the peak of polyethylene that sealed the sample electrode. At 100% SOC, the (001) peak of monoclinic $\text{Li}_{0.5}\text{CoO}_2$ is observed in both the reference and PTC positive electrodes. At 180% SOC, the peak at $2\theta = 21^\circ$ is observed in the reference electrode that corresponds to the (001) peak of hexagonal CoO_2 . The small peak at $2\theta = 19.8^\circ$ approximately corresponds to $x=0.3\text{--}0.2$ in Li_xCoO_2 . Meanwhile, in the XRD pattern of the PTC electrode at 180% SOC, the $\text{Li}_{0.5}\text{CoO}_2$ peak remained, and other transition states between $\text{Li}_{0.5}\text{CoO}_2$ and CoO_2 were found.

This result suggests that there are many charged states in the active material in the PTC positive electrode. In the PTC electrode, both the PTC compound and AB are in contact with the active material. When the cell temperature increases, the charge current preferentially flows through the AB due to an increase in the resistance of the PTC compound. Accordingly, the current density in AB increases rapidly, and lithium ion is intensively extracted at the part of the active materials that contacts AB. On the other hand, at the part of the active material that contacts the PTC compound, the reaction hardly progresses. Therefore, the Li^+ extraction reaction from Li_xCoO_2 was inhomogeneous and there were many different charge states at the surface of the

active material. The reactive area of the active material in the PTC electrode decreases, and the electrode reaction is restricted compared to that in the reference cell. These results indicate that a PTC cell remains safe at high temperature because there is inadequate oxidation of the active material, and therefore, the cell is more stable than the reference cell.

4. Conclusion

The relationships between the positive electrode composition and the discharge characteristics and safety were evaluated for lithium-ion cells using a PTC positive electrode. A cell's discharge capacity increased with a decrease in the PTC compound ratio and with an increase in the AB ratio in the positive electrode. Meanwhile, a reverse tendency was observed between the battery safety and the PTC compound ratio and AB ratio. The maximum current that flowed in the external short-circuit test increased with a decrease in the PTC compound ratio, or with an increase in the AB ratio. Moreover, in the overcharge test, overcharge tolerance was improved with an increase in the PTC compound ratio. The Overcharge tolerance of PTC cells is caused by an increase in the impedance of PTC cells due to an increase in the electrical resistivity of the PTC compound. In the XRD pattern of a PTC electrode at 180% SOC, $\text{Li}_{0.5}\text{CoO}_2$ peak remained, and other transition states between $\text{Li}_{0.5}\text{CoO}_2$ and CoO_2 were found. This result indicates that the reaction became inhomogeneous at the surface of the active material in the PTC electrode, since the resistivity of the PTC compound increases

at high temperature. Therefore, the PTC cell voltage increased early, which led to less stored energy than in the reference cell, and the PTC cell has good overcharge tolerance.

Acknowledgement

This work is supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan.

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