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Development of new safe electrode for lithium rechargeable battery

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Abstract

A new concept cathode was proposed to improve the safety of lithium rechargeable batteries. The cathode contains a positive temperature coefficient (PTC) compound that can drastically increase resistivity at more than a specified temperature (PTC properties). A PTC cathode containing the PTC compound was fabricated and its resistivity was evaluated. The resistivity of PTC cathodes increased by several tens at 130–140 °C, which is the melting point of polyethylene. In lithium rechargeable batteries using these cathodes (PTC cell), a level nearly reaching the designed capacity is obtained at less than 1*C* rate. The discharge capacity of PTC cells became high as the content of PTC compound increases. Moreover, under 3*C* discharge condition, the voltage of PTC cell dropped at 138 °C where the resistivity of the PTC cathode drastically increased. Additionally, on the external short circuit test at 145 °C, the short circuit current of the PTC cell was almost 0 A. These results indicate that PTC cathodes will improve the battery safety.

Keywords: Positive temperature coefficient; Safety; Lithium rechargeable battery

1. Introduction

Lithium rechargeable batteries are widely used in portable equipment because of their high energy density. Uses for the power storage have been developed in such large scale applications as hybrid electric and fuel cell vehicles [1–4]. The application of lithium rechargeable batteries to such power storage devices increases concern about battery safety. To improve the safety of batteries, we propose a new concept electrode containing a positive temperature coefficient (PTC) compound as shown in Fig. 1. We expect that this electrode will increase resistivity drastically at higher than specified temperature, and that current collecting power will reduce when the cell temperature rises because of the short circuit, overcharging and so on. Therefore, this battery safety concept is useful not only for external short circuits but also internal short circuits.

We report here the development of the fabrication procedure of PTC cathodes, the electrical properties of PTC cathodes and the discharge properties of PTC cells. Furthermore, we evaluated the safety function of PTC cells.

2. Experimental

2.1. PTC plate sample

We selected a carbon black/polymer composite for the PTC compound because of its electrochemical stability and low resistivity. The resistivity of the PTC composite increases at the melting point of polymer since it expands and restricts the conductive flow of carbon black.

High-density polyethylene resin (melting point: 136 °C) and carbon black were mixed and kneaded in a vessel, and a carbon black/polyethylene composite pellet of 2 mm in diameter (PTC pellet) was fabricated. This PTC pellet was melted and shaped to a PTC plate of 2 mm in thickness. Furthermore,

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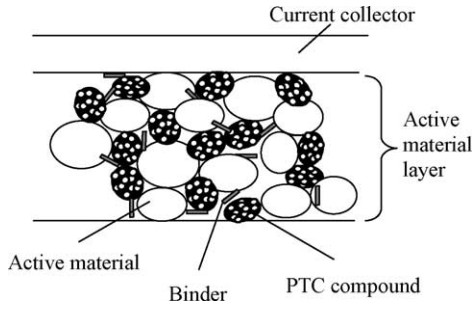

Fig. 1. Schematic illustration of cross-sectional proposed cathode.

a 10 mm × 10 mm square plate was cut from the PTC plate (PTC plate sample).

2.2. Cathodes

The PTC pellet was pulverized and ground to a powder whose average particle diameter was about 15 μm. The PTC cathodes were made by coating the mixture of the active material ($LiCoO_2$), electronic conductor (PTC compound), and binder (poly(vinylidene fluoride) (PVdF)) with *N*-methyl-2-pyrrolidinone (NMP) on an aluminum foil. PTC cathodes were fabricated that contained PTC compound of either 6 or 12 wt%. Moreover, for comparison with the PTC cathode, a reference cathode using graphite of 6 wt% as electronic conductor was prepared by the same process.

2.3. Electrochemical cells

Anode was prepared by coating the mixture of mesophase carbon micro-bead (MCMB) graphite and PVdF with NMP on a copper foil.

The cathode, polypropylene porous film as a separator, and anode were assembled, and card-size cells were fabricated. For the electrolyte, a 1 M solution of $LiPF_6$ in a mixture with ethylene carbonate and diethyl carbonate was used.

2.4. Evaluation of electrical properties

PTC properties were evaluated for PTC plate, PTC cathodes and reference cathode samples. These samples were sandwiched between metal electrodes with built-in heaters. Resistivity was calculated from the resistance, thickness and area of samples.

2.5. Evaluation of cell performance

The cell's discharge performance was measured at constant currents of 1/4, 1/2, 1, 1.5 and 2*C* discharge rates down to 2.75 V at 20 °C.

To evaluate the safety function of the PTC cells, the following two tests were performed after charging the batteries under 1.2*C* rate to 4.1 V. Firstly, as a discharge test, cell voltage was measured under 3*C* rate in a temperature range from 120 to 160 °C.

Secondly, during an external short circuit test, the current was found by measuring the voltage drop at both ends of shunt resistance (10 mΩ) when the cathode and anode terminals of cell were short-circuited at each temperature.

3. Results and discussion

3.1. Electrical properties

Fig. 2 shows the temperature dependence of resistivity for the fabricated PTC plate. The resistivity increased more than 100 times at about 130 °C, compared with 50 °C (initial resistivity). Initial resistivity was about 0.1 Ω cm, and it was 1000 times larger than graphite [5].

Fig. 3 shows the temperature dependence of resistivity for the PTC and reference cathodes. There was no resistivity change for the reference cathode, but the resistivity of the PTC cathodes increased several tens of times at 130–140 °C, the melting point of polyethylene. The PTC cathodes had higher initial resistivity than the reference cathode because the resistivity of the PTC compound is higher than graphite. Although the initial resistivity of the PTC-12 wt% electrode was lower than that of PTC-6 wt%, the resistivity change of

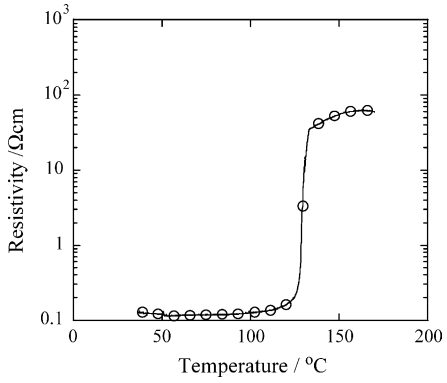

Fig. 2. Temperature dependence of resistivity for PTC compound.

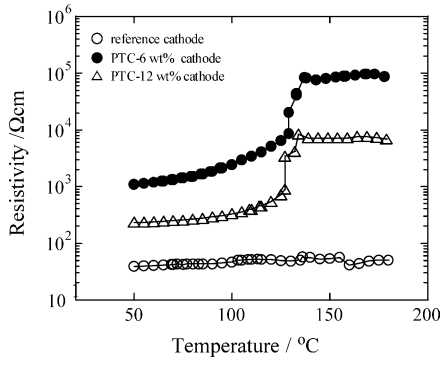

Fig. 3. Temperature dependence of resistivity for PTC and reference cathodes.

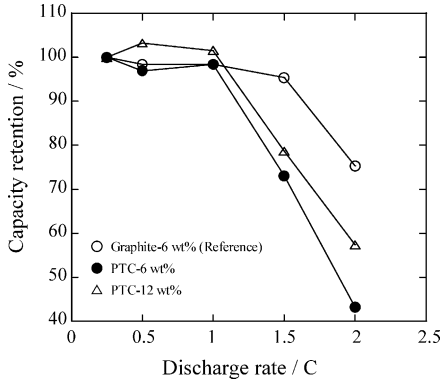

Fig. 4. Dependence of capacity retention on discharge rate for PTC and reference cells.

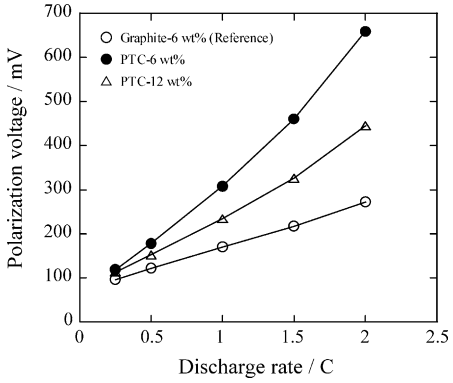

Fig. 5. Dependence of polarization voltage on discharge rate for PTC and reference cells.

both electrodes was the same. It is because initial resistivity depends on the content of PTC compound, while the resistivity change depends on the material property of PTC compound. These results show that PTC properties appeared at not only the PTC compound but also the cathode containing PTC compound.

3.2. Cell performance

Fig. 4 shows the discharge properties of the PTC and reference cells. The discharge capacity of the PTC cells almost achieved designed capacity at less than 1*C* rate. Compared with the reference cell, the discharge capacity of PTC cells drastically reduced at more than 1.5*C* rate. On the other hand, the capacity of the PTC-12 wt% cell was larger than the PTC-6 wt% cell. These results are caused by the high initial resistivity of PTC cathodes as shown in Fig. 3, and the cell using high resistivity cathode has low discharge capacity.

Fig. 5 shows the dependence of polarization voltage on the discharge rate for PTC and reference cells, where polarization voltage V_p is defined:

$$V_p = V_o - V_r \quad (1)$$

where V_o and V_r are the open circuit voltage and cell voltage at a 33% depth of discharge, respectively. The polarization voltage of reference cell increased linearly against the discharge rate, while that of PTC cells increased non-linearly.

To understand the results of the discharge capacity and polarization voltage, scanning electron microscope (SEM) observation was performed. Fig. 6 shows the SEM photographs for reference and PTC cathodes. In the reference cathode, there were many scale-like grains of graphite around the ac-

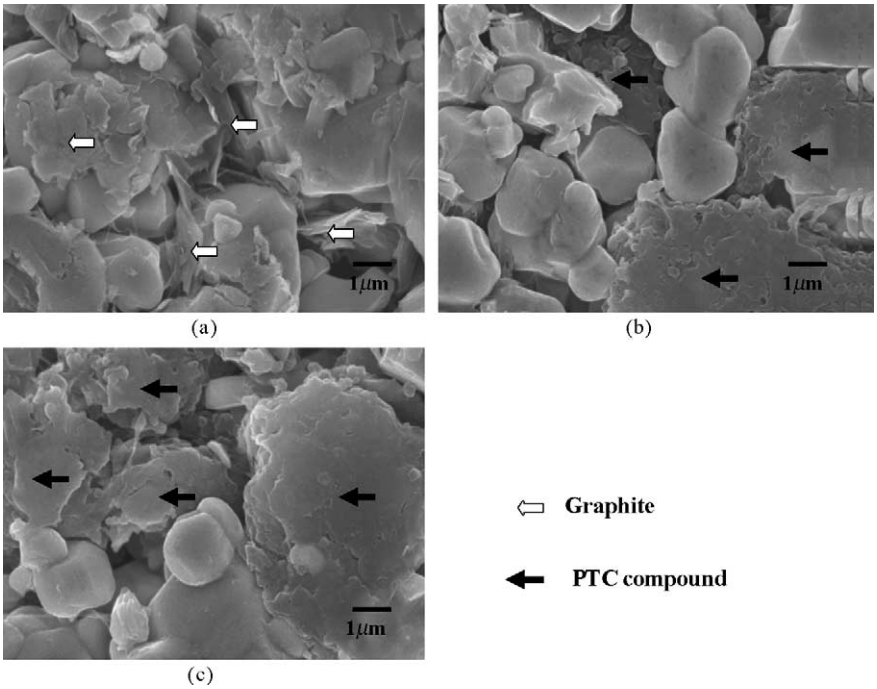

Fig. 6. SEM photographs of (a) reference, (b) PTC-6 wt% and (c) PTC-12 wt% cathodes.

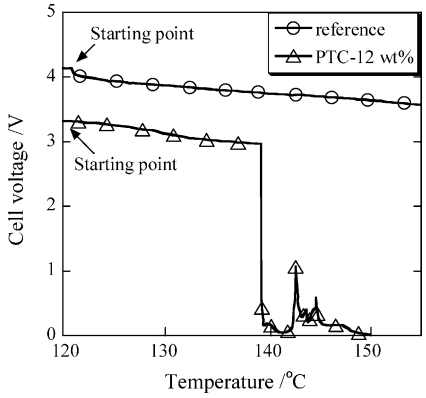

Fig. 7. Discharge voltage profiles of PTC-12 wt% and reference cells under 3*C* rate.

tive material shown in Fig. 6a. As shown in Fig. 6b and c, the grains of the PTC compound observed in the PTC cathodes were larger than those of graphite and hardly came in contact with the active materials. The current collecting power of the PTC cathodes was expected to be lower than the reference cathode. This result apparently causes an increase of the overpotential of the cell. Therefore, not only the Ohmic potential drop, but also overpotential was larger in the PTC cells, suggesting that this result caused the non-linear increase of polarization voltage and capacity drop at more than 1.5*C* discharge rate in PTC cells.

3.3. Basic evaluation of the safety function

To investigate the safety of the batteries using PTC cathodes, a discharge test and an external short circuit test were performed at a high temperature.

Fig. 7 shows the relationship between discharge voltage and cell temperature at 3*C* rate. The voltage of the reference cell gradually decreases as the cell temperature rises. On the other hand, the voltage of the PTC-12 wt% cell dropped at 138 °C, the same point at which the resistivity of the PTC-12 wt% cathode drastically increases, as shown in Fig. 3. This means that the resistivity of the PTC cathode drastically increased and electrode reaction was deactivated at this point.

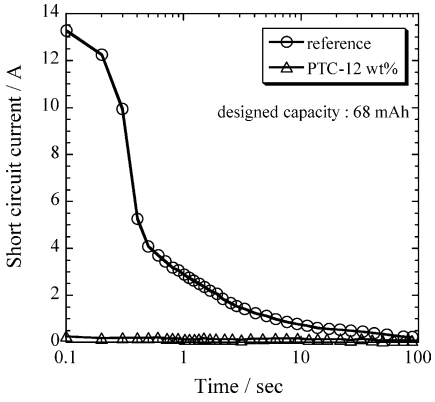

Fig. 8. Short circuit current of cells using PTC-12 wt% and reference cathode short circuited at 145 °C.

Fig. 8 shows the short circuit current for PTC-12 wt% and reference cells that short circuited at 145 °C. The maximum current of the reference cell was about 13 A. On the other hand, the current of the PTC-12 wt% cell was almost 0 A. This result means that the short circuit current was cut off when the PTC property appeared at 145 °C. From these results, we conclude that PTC cathodes have the safety function in lithium rechargeable batteries.

4. Conclusion

We proposed, fabricated and evaluated new concept PTC functional cathodes to improve battery safety. The resistivity of the PTC cathodes increases several tens of times at more than 130 °C. The discharge capacity of PTC cells achieved almost designed capacity at less than 1*C* rate.

Furthermore, as a result of the discharge test, the voltage of the PTC-12 wt% cell dropped at 138 °C. During the external short circuit test under the condition of 145 °C, the current was almost 0 A. These results indicate that, when PTC properties appeared at more than the melting point of polyethylene, the electrode reaction was aborted and the current was cut off. Therefore, we conclude that cells using PTC cathodes can improve battery safety.

Acknowledgement

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