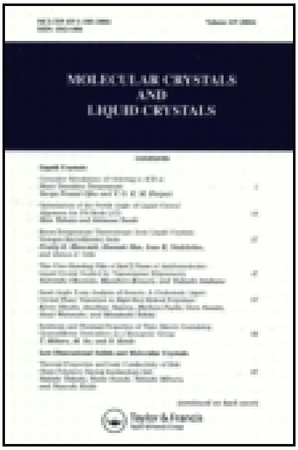

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ELECTROCHEMICAL CHARACTERISTICS OF POLYPARAPHENYLENE-BASED CARBON

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Polyparaphenylene (PPP)-based carbon is expected for a high-performance material of a negative electrode of lithium (Li) ion secondary battery, but the details of relationship between characteristics and heat treatment have not been known. In this report, electrochemical and electrical properties of heat-treated PPP-based carbon powder were investigated and the possibility of the use as the negative electrode of Li ion secondary batteries was shown.

Keywords: polyparaphenylene; Li ion secondary battery; heat treatment temperature; charge and discharge capacities; Resistivity

INTRODUCTION

Lithium (Li) ion secondary battery is expected as the high performance power sources for portable electric products. Polyparaphenylene (PPP)-based carbon is thought to be one of the most suitable materials for the negative electrode, which is a key to improve the performance of Li ion secondary batteries. In previous study, it was shown that PPP-based carbon with heat treatment at a temperature around 700°C has high charge-discharge performance as the negative electrode [1].

The electrochemical characteristics of negative electrode consisting of PPP-based carbon are affected significantly by heat treatment process of the raw material PPP. In order to realize the high performance negative electrode by using PPP-based carbon, it is important to establish the suitable treatment process of PPP as the electrode material. In the present time, there are significant issues to have been investigated; "Why the electrical resistivities of PPP powders are strongly depended on the heat-treatment temperature (HTT)?", "What changes in the structure of PPP powders by heat treatment?", and "How the electrical properties are affected by the change of structure?".

In this study, the properties of PPP-based carbon powders heat-treated at temperatures between 650 and 800°C are discussed.

EXPERIMENTALS

Kovacic method and Yamamoto method are known as the typical preparation methods of PPP [2]. In this study, we use PPP powder made by the former method because the heat-treated materials have suitable charge and discharge properties compared to that made by the latter method.

The electrochemical and electrical characteristics of PPP samples were studied after heat-treatment at the temperatures between 650 and 800°C in pure argon flow for one hour. Li ion charge and discharge capacities for the PPP-based carbon as the negative electrode was measured under the constant applied current of 30 mA/g.

The resistivity of carbon powders was measured as follows. About 100 mg of sample powder was charged into an apparatus with a small volume cylindrical sample chamber. The chamber and upper electrode with pushing rod are made of brass and the inner cylinder was made of the insulating material (Teflon). The sample powder and metal electrodes were contacted only top and bottom. The voltage drop through the sample was measured at constant applied current of 100 mA and applied pressure up to 64 MPa by compressed air. The volume change of the sample was measured using a dial gauge in order to determine the packing density at each applied pressures [3].

The thermogravimetric properties of PPP were observed by using a simultaneous TG/DTA instrument (SHIMADZU, DTG-60).

RESULTS

Li Ion Charge and Discharge Capacity of Negative Carbon Electrode

Figure 1 shows the second cycle of Li ion charge and discharge curves of the samples heat-treated at the various temperatures of 700, 800 and 900°C. The charge and discharge capacity values obtained from Figure 1 are summarized in Table 1. When the sample with HTT of 700°C was used as the negative electrode, a large charge capacity value of 434 mAh/g was obtained. The capacity values were decrease with the increase of HTT. It was hard to measure the capacity of the sample with HTT of 600°C, because of its high resistivity.

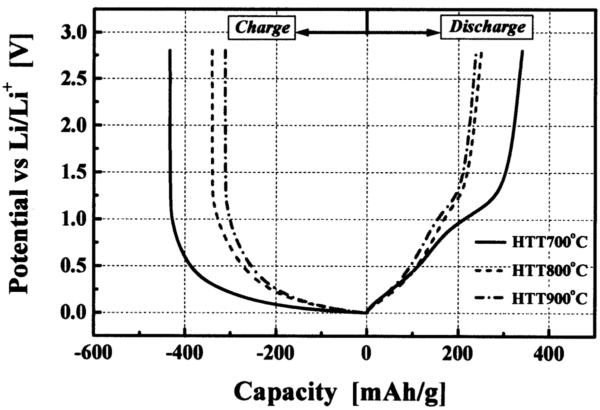

FIGURE 1 Li ion charge and discharge property of second cycle for PPP-based carbon heat-treated in Ar gas flow (current density 30 mA/g).

Resistivity of PPP Powder

Figure 2 shows the relation between HTT of the PPP-based carbon powder and the resistivity of them. The resistivity decreased from the order of 100 Ωcm to the order of 0.1 Ωcm with the increase of HTT from 670 to 800°C. The resistivity of the samples with HTT lower than 660°C was hard to be measured and was estimated to be 10^6 Ωcm from the internal impedance of the voltmeter.

The lowest resistivity value of PPP-based carbon with HTT of 800°C is still more than one order higher than that of vapor grown carbon fibers (VGCF's).

Thermogravimetric Measurement of PPP

Figure 3 shows the results of thermogravimetric analysis in the temperature range between 20 and 1000°C. The weight loss increases rapidly from 600°C, which indicates the decomposition and evaporation of the components in PPP in this temperature range. A valley in the curve is observed

TABLE 1 Charge and Discharge Capacity of Second Cycle

HTT (°C)	Charge capacity (mAh/g)	Discharge capacity (mAh/g)
700	434	340
800	341	250
900	312	239

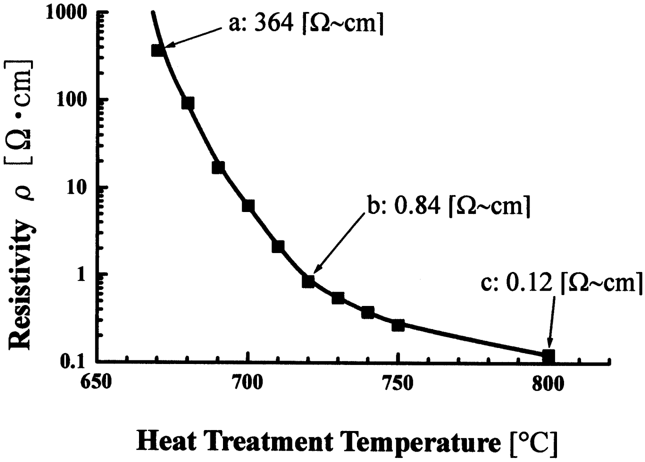

FIGURE 2 Relation between resistivity and HTT of PPP-based carbon powders under pressure of 64 Mpa.

around 550°C in Figure 4, the result of the differential thermal analysis, which is thought to show the release of hydrogen from PPP by heart-treatment.

DISCUSSION

The measured resistivity curve in Figure 2 is thought to consist of 2 parts which are separated at the temperature around 720°C. The resistivity of

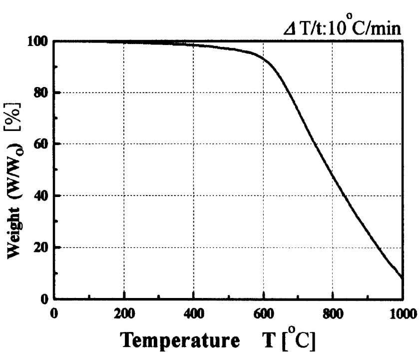

FIGURE 3 Thermogravimetry analysis for the conditon of the temperature from 20 to 1000°C in Ar gas flow.

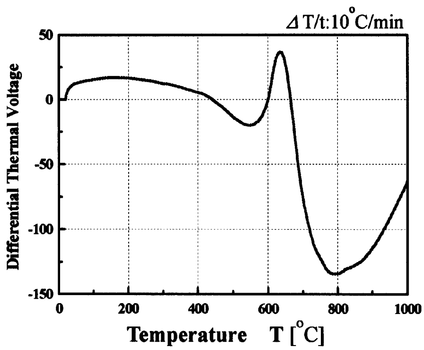

FIGURE 4 Differential thermal analysis for the condition of the temperature from 20 to 1000°C in Ar gas flow.

the sample was decrease gradually in HTT range higher than 720°C, though the rapid change in the resistivity in HTT range lower than 720°C. It is thought that there are at least two reasons why the resistivity of PPP changes by heat treatment. One is the surface cleaning effect of the sample particles by thermal treatment. If the surface of the PPP particle is covered with any insulating components, the surface cleaning is effective to make the electrical current path among the particles. The other effect is the structural change of inside carbon atoms which are ordered by the heat treatment. The latter effect is observed by HRTEM analysis, that is, hexagonal carbon layers grow at a higher HTT [4]. The surface cleaning effect is dominant in the change of resistivity in the lower HTT range. On the other hand, the surface cleaning has been done and the gradual crystal growth effect governs the change of resistivity in the higher HTT range. This conjecture is supported by the results of thermogravimetric analysis shown in Figures 3 and 4.

A large charge capacity value was observed when the sample was heat-treated at appropriate temperature of around 700°C, partly because of the existence of disorder in the structure of PPP-based carbon. However, their resistivities are significantly higher than that of VGCF, which may prevent charge and discharge of Li. In order to further improvement of the charge capacity, PPP-based carbon powders mixture with the lower resistivity carbon materials, such as VGCFs, must be considered.

SUMMARY

Electrochemical and electrical properties of heat-treated PPP-based carbon powder were investigated as a function of heat-treatment temperature between 650 and 800°C, and the possibility of PPP-based carbon as the negative electrode of Li ion secondary batteries was shown. The obtained results are summarized below.

- A large charge capacity value of 434 mA/g was obtained when PPP was heat-treated at 700°C.
- The resistivity of the powder was decreased with the increase of HTT.
- It was considered that there are two kinds of mechanisms for the change of resistivity. One was the powder surface cleaning effect by heat treatment, and the other was the structural ordering effect in the inside of carbon powder by heat treatment.
- The decomposition of PPP was observed by means of the thermogravimetric analysis in the temperature range between 600 and 1000°C.

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