Electrochemical and Structural Properties of Polyparaphenylene (PPP)-based Carbon

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Introduction

Lithium (Li) ion secondary batteries are used as high performance power sources for portable electrical products. In future, enhancement of the battery capacity will be necessary not only for the portable equipments but also for electric energy storage systems. Polyparaphenylene (PPP)-based carbon is expected as a high performance material of a negative electrode of Li ion secondary battery. It is known that a large amount of Li ions get into PPP-based carbon prepared by the Kovacic method [1-2]. PPP samples were heat-treated at the temperatures between 680 and 760C in pure argon gas flow for one hour. The large discharge capacity value of 554mAh/g at second cycle was obtained for the negative electrode of 720C treated PPP-based carbon [3]. This capacity is larger than the theoretical value of 372mAh/g for graphite electrode. In order to obtain the higher performance electrode, the structural properties of the samples were observed by means of field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HRTEM) and image processing [4]. Carbonization of PPP samples was analyzed by means of weight loss measurement, thermo gravimetric analysis (TG), mass spectrometry (MS) and elemental analysis [5]. The relations between these results and the carbonization of PPP polymer were discussed.

Experimental

PPP prepared by Kovacic method shown in following chemical formula (1) was used in present experiments and heat-treated in an electric tubular furnace from 400 to 1000C under a

$$nC_6H_6 + 2nCuCl_2 \xrightarrow[H_2O]{AlCl_3} \left\{\!\!\left\langle \bigcirc \right\rangle\!\!\right\}_n + 2nCuCl + 2nHCl \qquad (1)$$

pure argon gas flow. The heating rate was 10C/min and the residence time was one hour.

Lithium (Li) ion charge-discharge capacity for PPP-based carbon electrode was measured by using three-electrode (Li electrode, carbon electrode and reference electrode) test cell under the constant current of 30mA/g [6].

In order to investigate the thermal behavior of PPP polymer, the weight loss were measured for heat-treated samples and the volatile components evaporated from PPP polymer were measured by using gas chromatography and mass spectrometry (GC-MS). PPP sample was heated up from 30 to 720C at a heating rate of 10C/min in pure helium gas flow of 300ml/min and the temperature of heating was retained at 720C. The atomic ratios of hydrogen

Figure 1. Charge and discharge capacities for PPP-based carbon electrode

Figure 2. Weight loss of PPP samples heat-treated from 400 to 1000C

Figure 3. CG-MS data of PPP heated up to 720C

to carbon in PPP heat-treated at various temperatures were calculated from the results of elemental analysis.

Results and Discussion

Figure 1 shows Li ion charge and discharge capacities of second cycle. The discharge capacity of 554mAh/g for PPP-based carbon heat-treated around 720C was obtained. If heat treatment temperature (HTT) is higher than 720C, the large discharge capacity can't be expected. In the region of HTT which is lower than 720C, the irreversible capacity (deference of charge capacity and discharge capacity) increase.

In order to investigate the reason why Li ion charge-discharge capacity for PPP-based carbon changed as shown in Fig.1, the resistivities of the samples were measured and the microtextures were observed by means of HRTEM and image processing. The resistivities drastically decreased in 5 orders to 6.6 ohm-cm with the increase of heat treatment temperature from 680 to 730C. And the microtextural and structural evolution of the samples was observed. This means that the microtextural evolution of PPP by heat treatment is responsible for the decrease of resistivity. The Li ion charge-discharge capacity is depended on the electrical resistivity and microtexture of PPP-based carbon [3] [5]. The microtexture of PPP-based carbon is influenced by the structure of starting PPP polymer and the heat treatment condition.

The weight loss of PPP samples heat-treated from 400 to 1000C with one-hour residence time is shown in Fig.2. The maximum volatiles release is between 600 and 680C.

Figure 3 shows CG-MS data of PPP polymer heated up to 720C with a heating rate of 10C/min and residence time such as (d). The number of detected molecules of volatiles per one sampling time are given in Fig.3 (a) to (c). They correspond to hydrocarbons such as benzene, biphenyl and terphenyl respectively. In this case the

Figure 4. Atomic ratios of H to C calculated from elemental analysis.

GC-MS data show that the molecules of small molecular mass, such as benzene and biphenyl, are released at first, and then heavier molecules, such as terphenyl, are volatilized all along the threshold at 720C.

From the results of elemental analysis, atomic ratios of hydrogen to (H/C) carbon in PPP heat-treated at various temperatures are shown in Fig.4. The value of H/C for PPP samples drastically changes in the region of the temperature from 600 to 700C. In the region, as a lot of volatile components, such as benzene and biphenyl, contained in PPP polymer evaporate by heat treatment, the value of H/C decreases and the conductivities are improved.

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