SiOC Anode Material Derived from Poly(phenyl carbosilane) for Lithium Ion Batteries

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ABSTRACT

Since SiOC was introduced as an anode material for lithium ion batteries, it has been studied with different chemical compositions and microstructures using various silicon based inorganic polymers. Poly(phenyl carbosilane) is a SiOC precursor with a high carbon supply in the form of the phenyl unit, and it has been investigated for film applications. Unlike any other siloxane-based polymers, oxygen atoms must be utilized in an oxidation process, and the amount of oxygen is controllable. In this study, SiOC anodes were prepared using poly(phenyl carbosilane) with different heat treatment conditions, and their electrochemical properties as an anode material for lithium ion batteries were studied. In detail, cyclic voltammetry and charge-discharge cycling behavior were evaluated using a half-cell. A SiOC anode which was prepared under a heat treatment condition at 1200ºC after an oxidation step showed stable cyclic performance with a reversible capacity of 360 mAh/g.

Key words : SiOC, Silicon oxycarbide, Poly(phenyl carbosilane), Lithium ion battery, Anode

1. Introduction

From the publication of Dahn’s study about the electrochemical properties of SiOC anodes for lithium ion batteries, various groups have been interested in SiOC materials. SiOC anodes show stable charge-discharge performances and long life cycles without mechanical defects, such as a volume expansion of the silicon anode. SiOC is a typical polymer-derived ceramic (PDC) material, and silicon based inorganic polymers, such as siloxane polymer, silazane polymer, carbosilane polymer, silicon resin and silica sol, are generally used as a precursor. Many researchers have described a reversible capacity with different polymers and with different organo-functional units, as by influencing the atomic ratio of Si/O/C and the microstructure of SiOC material, thus affecting the anode properties in the battery, as shown in the Gibbs triangle map with the electric capacity, as originally suggested by Dahn. Recently, Riedel et al. and Kanamura et al. studied the role of graphitized free carbon structures in a glassy SiOC network generated from a phenyl group in a precursor polymer, suggesting that carbon improved the anode properties of the SiOC material.

Poly(phenyl carbosilane) is a phenyl-containing carbosilane polymer that was developed in previous works as a precursor for SiOC film with several applications. The silicon atom in the carbosilane polymer bonds with four carbon atoms in its environment, and an oxygen atom must be introduced through a pyrolysis step. A new Si-O bond can be formed through the pyrolysis process, and the amount of oxygen can be controlled by the oxidation condition. Therefore, using carbosilane polymer makes it possible to control the Si-O-C structure and the amount of oxygen in the final SiOC material. Moreover, a rich amount of carbon, which is supplied from the phenyl functional unit, can be isolated from the SiOC network and graphitized. The aim of this study is to suggest the possibility of a SiOC material derived from poly(phenyl carbosilane) as an anode material for lithium ion batteries.

2. Experimental Procedure

2.1. Preparation of the anode materials

\[ M_w = 4,000 \] poly(phenyl carbosilane) was used. SiOC was prepared via a two-step heat treatment process involving an oxidation step and a pyrolysis step. Oxidation was done at 200ºC in air, and the pyrolysis process was then performed at 800 - 1200ºC under a nitrogen atmosphere. To compare the oxidation effects, a control sample was prepared without an oxidation step. It was labeled as SiC/C.

2.2. Preparation of the working electrode and a half cell

The hand-ground anode material was mixed with carbon black (Super P, MMM, Belgium) and PVDF (Kureha, Japan) at a ratio of 85 : 7.5 : 7.5. The working electrode was prepared by pasting the slurry onto Cu foil using a hand blade, and this was dried at 60ºC. Then, a coin cell was fab-
ricated with a PE separator and a lithium counter electrode and was packed in stainless steel cells. 10M LiPF$_6$ in EC/EMC (1/2, v/v) (PANAX StarLyte, Ukseung Chemical Ltd., Korea) was used as an electrolyte.

2.3. Electrochemical measurements

A cyclic performance test was performed at a constant current of 0.2 mA/cm$^2$ under a cut-off of 0.02/2.0V (vs. Li/Li$^+$. The cyclic voltammogram was scanned for 20 cycles at a scanning rate of 0.2 mV/s in the potential range from 0 to 2.0 V (vs. Li/Li$^+$).

3. Results and Discussion

3.1. Characterization of SiOC

Poly(phenyl carbosilane) is pyrolyzed at a temperature over 600ºC, after which Si, O and C atoms are rearranged into the SiOC glassy structure. During the rearrangement process, the excess carbon which originated from the phenyl unit is isolated from the glassy phase and is graphitized. Moreover, Si and C atoms crystallize into beta-phase SiC crystal when the heat treatment temperature increases to 1200ºC. Thus, SiOC material derived from poly(phenyl carbosilane) is initially formed as a glassy phase when the pyrolysis process is completed. It is converted into a composite structure which is composed of glassy SiOC, SiC crystal and graphitized carbon at a high temperature. SiC is considered as an inert material for lithium ion batteries, whereas this type of graphitized carbon can effectively improve the electrochemical behavior. Therefore, in this study, the SiOC materials were prepared in the heat treatment range of 800-1200ºC to minimize the crystallization of SiC after complete pyrolysis.

The glassy structure of SiOC as the matrix was confirmed by the $^{29}$Si-NMR technique because the silicon atom in the SiOC structure exists in the $\text{SiC}_3\text{O}$ state. From Fig. 1, the chemical shift of silicon appeared at $-5$, $-10$, $-32$, $-72$, and $-108$ ppm; these values correspond to $\text{Si}_3\text{C}_4\text{O}$, $\text{Si}_4\text{C}_4\text{O}_2$, $\text{Si}_2\text{O}_4\text{C}_3$ and $\text{Si}_4\text{O}_4$, respectively. When the pyrolysis temperature was increased, the peak intensity increased, especially in the range of $-10$ to $-30$ ppm, but the change was not distinguishable. Fig. 1(d) shows the $^{29}$Si-NMR spectrum of SiC/C, which was prepared at 1200 ºC without oxidation. From the figure, the chemical shift of $-10$ significantly appears as the strongest peak, whereas the peaks at $-32$ and $-72$ were observed to be small. Although the oxygen was not completely prevented, the content of the oxygen in the SiC/C was low compared to the SiOC prepared with the oxidation step (Fig. 1(c)).

The oxidation effect on the conversion process of poly(phenyl carbosilane) into SiOC can be confirmed by the $^{29}$Si-NMR technique because the silicon atom in the SiOC structure exists in the $\text{SiC}_3\text{O}_2$ state. From Fig. 1, the chemical shift of silicon appeared at $-5$, $-10$, $-32$, $-72$, and $-108$ ppm; these values correspond to $\text{SiC}_3\text{O}_2$, $\text{SiC}_4\text{O}_2$, $\text{Si}_2\text{O}_4\text{C}_3$ and $\text{Si}_4\text{O}_4$, respectively. When the pyrolysis temperature was increased, the peak intensity increased, especially in the range of $-10$ to $-30$ ppm, but the change was not distinguishable. Fig. 1(d) shows the $^{29}$Si-NMR spectrum of SiC/C, which was prepared at 1200 ºC without an oxidation step. From the figure, the chemical shift of $-10$ significantly appears as the strongest peak, whereas the peaks at $-32$ and $-72$ were observed to be small. Although the oxygen was not completely prevented, the content of the oxygen in the SiC/C was low compared to the SiOC prepared with the oxidation step (Fig. 1(c)).

The oxidation effect on the conversion process of poly(phenyl carbosilane) into SiOC can be confirmed by the XRD technique. The XRD spectra of SiC/C and SiOC, which were prepared at 1200ºC, are shown in Fig. 2. In this case, the SiC/C shows strong peaks at 35.7º, 42.2º, 56º, and 71.8º, which represent the beta phase of the SiC crystal, whereas only tiny peaks were observed in the SiOC material. It was
confirmed that the oxygen atoms introduced into the poly(phenyl carbosilane) network during the oxidation step cause the silicon atoms to participate in the formation of the SiOC structure and thus prevent the crystallization of SiC during the heat treatment step at 1200ºC.

TEM images of the SiC/C and SiOC materials are shown in Fig. 3. The dispersed graphitized carbon was observed in both SiC/C and SiOC, but there was a difference in the crystal domain. For SiC/C, the interconnected SiC crystals were dispersed and were observed everywhere. The primary crystal size of the SiC cluster was about 5 nm in diameter (Fig. 3(a)). However, for the SiOC which was prepared at 1200ºC after oxidation, the SiC crystals which formed were 2 - 3 nm in size, and they were not clustered.

3.2. Electrochemical performance

3.2.1 Cyclic Voltammetry (CV)

It is well known that SiC is an electrochemically inactive material for lithium ion batteries. To clarify the electrochemical properties of the SiC/C anode, CV and cycle performance tests were undertaken. In these tests, electrochemical activity was not noted despite the fact that carbon and a small number of Si-O bonds existed.

Cyclic voltammograms of the SiOC anode are shown in Fig. 4. For the SiOC anode prepared at 800ºC, it showed a broad and narrow cyclic pattern (Fig. 4(a)). However, when the heat treatment temperature was increased to 1000ºC and 1200ºC, as shown in Figs. 4(b) and (c), respectively, reduction and oxidation peaks were observed at 0.2 - 0.3 V and 0.4 - 0.5 V, respectively. The peak at 0.4 - 0.5 V in the oxidation direction was ascribed to the response of lithium ions to the Si-O network. Moreover, for the anode obtained at 1200ºC, the oxidation peak became sharp as the current increased, although the reduction peak was broader compared to the anode treated at 1000ºC. This implies that the SiOC anode treated at 1200ºC had greater ability and more beneficial behavior in terms of lithiation-delithiation cycling with a larger capacity.

3.2.2 Cyclic performance and voltage profile

Charge-discharge measurements were carried out using the SiOC anodes which were prepared at 800ºC and 1200ºC, as these two anodes can distinctly show the difference in the heat treatment effect. The initial discharge capacity of the SiOC anode which was prepared at 800ºC was 900 mAh/g, and the irreversible capacity of the first cycle was 470 mAh/g (Fig. 5(a)). The reversible capacity was then gradually decreased during the charge-discharge process from the sec-
ond cycle, despite the fact that the irreversible capacity was reduced during repeated cycling. Fig. 5(b) shows the voltage profile of the SiOC anode prepared at 1200°C. The first lithiation capacity was as high as 530 mAh/g, and the irreversible capacity was less than 150 mAh/g. These values are lower than the value recorded from the test of the 800°C anode. Moreover, the SiOC prepared at 1200°C showed better electrochemical behavior with a stable and relatively higher reversible capacity. The cycling performance is shown in Fig. 6. As observed in the voltage profile, the SiOC anode prepared at 1200°C showed a stable capacity for 10 cycles, whereas the capacity decreased in the 800°C condition.

4. Conclusion

A SiOC anode was prepared using poly(phenyl carbosilane) through an oxidation and pyrolysis process. Oxygen atoms in SiOC are introduced during the oxidation step, as the oxygen atoms not only create the Si-O-C network but also prevent the crystallization of SiC, an inert material used in lithium ion batteries. From an electrochemical performance test, the SiOC anode did not show electrochemical behavior despite the fact that it contains a graphitized network and a small number of Si-O bonds. SiOC anodes were prepared at a heat treatment temperature of 800 - 1200°C, showing good cyclic performance. In addition, the SiOC anode, which was prepared at 1200°C, showed stable cyclic performance with a reversible capacity of 360 mAh/g.

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REFERENCES