STUDIES ON THE IRREVERSIBLE CAPACITY OF ANODE MATERIALS FOR Li$^+$ BATTERIES SYNTHESIZED BY THE CO-CARBONIZATION OF PHENOLIC RESINS WITH POLYSILANE POLYMERS

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Introduction

Lithium ion batteries are rapidly dominating the market of portable secondary batteries due to their higher energy densities and longer shelf lives. In this battery system, various carbon materials are used as the anode material. However, as there is a limit in the lithium ion storage capacities of such materials, worldwide scale research is in progress to find alternative anode materials which possess higher capacities.

Silicon is known to have an ability to store up to 4.4 lithium ions per atom, and therefore is a potential candidate for the anode material of batteries of the next generation. However, elemental silicon is not suitable for usage in batteries, as the reversibility of its lithium ion store-release process is poor. This problem can be overcome by dispersing it in a carbon host material. Such materials have been produced by thermal CVD using organic silicon compounds [1,2], and the co-carbonization of carbon precursors with polymers containing silicon [3-6]. The latter method seems to be much feasible, as it can be conducted using simple equipment.

In this work, carbons containing silicon were produced by the co-carbonization of low cost phenolic resins with various polysilane polymers, and their lithium ion reversible and irreversible capacities were evaluated. Studies on the origin of the irreversible lithium ion capacity of the obtained materials were also conducted

Experimental

The polysilanes used in this work as the silicon source were polydimethylsilane (abbreviated to DMS hereafter), polyphenylmethylsilane (MPS), polydiphenyl silane (DPS) and polyphenylsilyne, a unique polysilane in which silicon atoms are connected to each other three-dimensionally. 3,5 xylenol derived phenolic resin (XN) was selected as the carbon source, as the influence of carbonization conditions on the pore structure of the resulting carbon is smaller compared to other phenolic resins. First, XN, a certain polysilane and hexamethylenetetramine (hardener) were ground and mixed together using a high speed mill. Next, this mixture was cured at 423 K. Carbons containing silicon were finally obtained by the carbonization of this material in an argon atmosphere at 1273 K. The amount of silicon in the material was adjusted by changing the ratio of XN to polysilanes.

The amount of silicon in the obtained samples was determined from the amount of residue which remained after oxidation, assuming it was silicon dioxide. The amount of carbon was measured by removing the silicon in the samples by hydrofluoric acid treatment. Hereafter the samples will be denoted as XN-[polysilane abbreviation](amount of silicon in wt%).

The porous properties of the obtained samples were evaluated by the molecular probe method. Adsorption isotherms of the probe molecules were measured at 298 K using an automatic adsorption apparatus (Bel Japan, Belsorp 28). The employed probe molecules were CO_2, C_2H_6, n-C_4H_{10} and i-C_4H_{10} (minimum molecular dimensions: 0.33, 0.40, 0.43 and 0.50 nm, respectively). Using the isotherms, the limiting micro-pore volume corresponding to the minimum size of the adsorbed molecules was determined using the Dubinin-Astakhov equation.

Electrochemical measurements of the samples were conducted using a two-electrode cell at a constant current
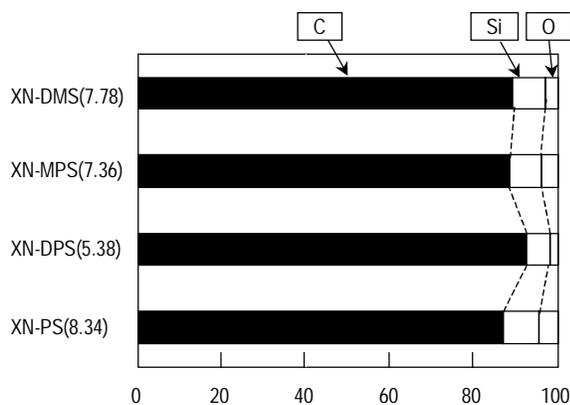
Fig. 1   Typical compositions of the obtained samples

Fig. 2   Si yield as a function of Si Content

Fig. 3   Li$^+$ reversible capacity as a function of Si content

of 25 mAg^{-1} and cut off voltages of 0 and 2.5 V.   Lithium metal was used as the counter (reference) electrode.   The carbon electrodes were constructed by supporting milled samples to copper foil using PVDF.   The electrolyte used was a 1 M LiClO$_4$-EC/DEC (1:1) solution (Mitsubishi Chemicals).   Celgard 2400 (Hoechst Celanese) was used as the separator.

Results and Discussion

Samples containing 4 to 18 wt% silicon were obtained by the co-carbonization of XN with various polysilanes. Figure 1 shows the composition of typical samples.   The samples were found to contain a significant amount of oxygen.   It is assumed that the silicon in the samples were partially oxidized by water which was generated through the carbonization of XN.

Figure 2 shows the silicon yield of the samples based on the amount of silicon in the starting material, as a function of the silicon content of the samples.   The silicon yields of XN-PS samples were extremely high, which reflects the unique structure of PS.   In the samples using other polysilanes, silicon yields decreased with the increase in the amount of silicon, but fairly high yields could be maintained by using temperature resistant polysilanes such as DPS.

Figure 3 shows the lithium ion reversible capacities of the samples, plotted as a function of silicon content of the
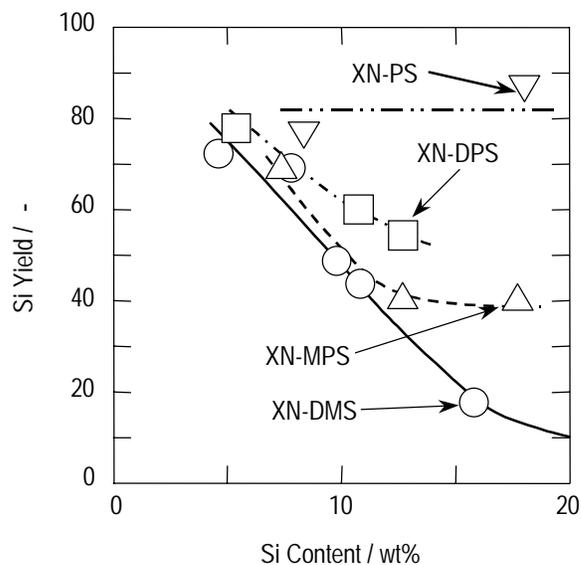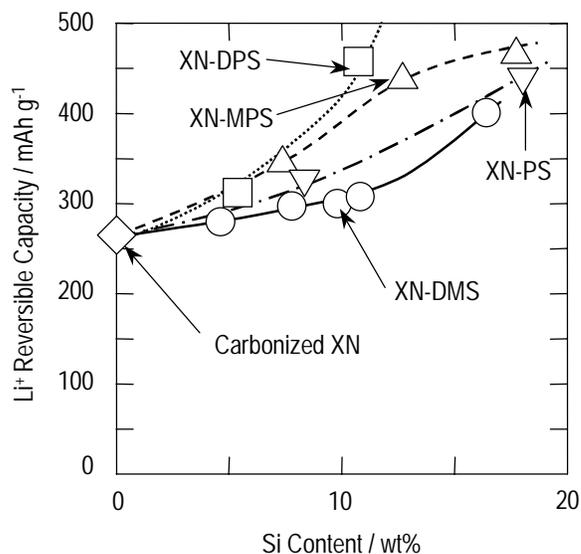
samples.   Not to mention, the capacities of the samples exceeded that of carbonized XN, and moreover, samples which possess capacities higher than the theoretical limit of graphite were also obtained.   The capacities increased with the increase in the amount of silicon, which trend was most significant in XN-DPS samples.
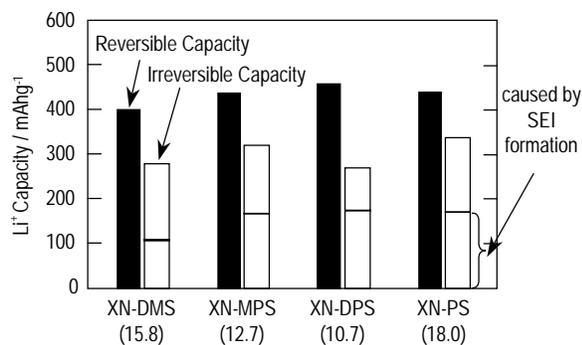
Fig. 4 Typical Li⁺ capacities of samples

Fig. 5 Irreversible capacity (measured -SEI derived) as a function of O content

Fig. 6 Number of Li+ stored per Si atom as a function of Si Content

The lithium ion reversible capacities of the samples were found to be fairly large, but their irreversible capacities were also large, as summarized in Fig. 4. Therefore, next the origin of the irreversible capacities of the samples was investigated.

In various carbons, the formation of solid electrolyte interface (SEI) layers is the main reason for the irreversible consumption of lithium ions. Previously, we showed that the lithium ion irreversible capacities of hard carbons can be estimated from the volume of pores accessible to carbon dioxide in the material. Therefore the volumes of such pores of the samples were measured and the irreversible capacities due to SEI formation were estimated. The results are also shown in Fig. 4. The results show that the irreversible capacities of the samples cannot be explained only by the formation of SEI layers.

It has been reported that oxygen in the samples traps lithium ions during insertion which also leads to the increase in irreversible capacity [4-6]. Therefore, the difference between the observed irreversible capacities and the estimated capacities due to SEI formation were calculated and were plotted against the amount of oxygen in the samples, which resulted in a fairly linear relationship (Fig. 5). The solid line in the figure is the irreversible capacity calculated assuming that LiO_2 is irreversibly formed, and well agrees with the data [5,6].

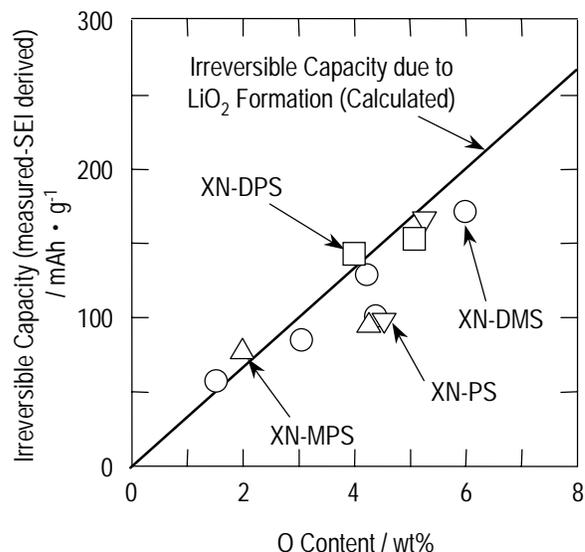From the above discussions, it can be concluded that the formation of SEI layers and the irreversible trapping of lithium ions by oxygen are the main origins of the irreversible capacities of silicon containing carbons, and this capacity can be quantitatively explained by these two factors. This implies that the amount of irreversible capacity mainly depends on the carbon precursor. In this work XN was selected as a model precursor due to its well known structure after carbonization. It should be noted

that XN contains a significant amount of oxygen, and that the reversible lithium ion capacity of carbonized XN is fairly small. Therefore, there is a high possibility that the reversible capacity can be significantly increased accompanied by the decrease in irreversible capacity, by selecting a proper carbon precursor for co-carbonization with polysilane.

Finally, the numbers of lithium ions reversibly stored per silicon atom in the samples were calculated and were plotted as a function of the silicon content of the samples (Fig. 6). The amount of lithium ions stored in the carbon of the materials were considered in calculations. The reported values of similar materials are in the range 0.7 to 1.5 [1,3,6]. The values of the samples obtained in this work were mostly in this range, but extremely high values could be obtained when DPS and MPS were used as the silicon source, which implies that reversible capacities can also be increased by controlling the manner of Si dispersion in the materials.

Conclusion

Carbons containing silicon were prepared by the co-carbonization of phenolic resins with various polysilanes. The obtained samples showed fairly high lithium ion reversible capacities. It was found that the lithium ion irreversible capacity originated from the formation of SEI layers and the oxygen contained it the samples. It is expected that a material with an extremely large reversible capacity and small irreversible capacity can be obtained by the co-carbonization of a proper combination of carbon precursor and polysilane.

Acknowledgement

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