EFFECTS OF CROSS-LINKING CONDITIONS OF PRECURSOR PITCH ON THE CHARGE-DISCHARGE PERFORMANCE OF HARD CARBON FOR LITHIUM ION BATTERY

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Introduction

Now, several kinds of graphitic materials are being used as an anode of lithium ion secondary battery because of their excellent performances such as high capacity per volume, high discharge voltage, and long cycle life. However, it is very difficult that they overcome the theoretical capacity (LiC_6, 372mAh/g). Therefore, a lot of researches on carbon materials have been conducted extensively to enlarge the capacity. Hard carbons prepared from various thermosetting polymers, stabilized pitches, and oxygenated organic compound, have attracted many attentions because of its larger capacity than that of graphite. Synthetic isotropic pitches can be a precursor of hard carbon by cross-linking them with various methods.

In the present study, hard carbons were prepared from cross-linked isotropic pitches under various conditions, and their anodic performances were investigated to find the optimum structure of precursor pitch and cross-linking conditions.

Experimental

In the present study, 5 kinds of synthetic isotropic pitches, which were provided from Mitsubishi Gas Chemical Co, were cross-linked to convert into thermosetting precursor of hard carbon with (i) air blowing oxidation, (ii) nitric acid treatment, and (iii) dehydrogenation with sulfur. Precursor pitches oxidized by the methods (i) and (ii) were carbonized at 600°C(heating rate: 1°C/min) for 1h under N_2 flow, and further calcined at 1000°C(heating rate: 10°C/min) for 1h under Ar flow.

Anodic performances of the obtained hard carbons were measured with charge-discharge test unit. Each carbon was charged by constant current (25mA/g) and constant potential (0V, 40h) method, and its discharge capacity was obtained with constant current method.

Results

Figure 1 shows discharge potential profiles of hard carbons prepared from naphthalene isotropic pitch with air blowing under different conditions. Although, the profiles of the carbon were much the same regardless the oxidation conditions, the discharge capacity varied with oxidation conditions, especially in the low potential region of 0 – 0.13V. Oxidation at higher temperature and for longer oxidation time allows more oxygen contents, which means higher degree of cross-linkage of the pitch. Hence, hard carbon, which was oxidized under more severe conditions, showed higher capacity.

Figure 2 illustrates discharge profiles of hard carbons prepared from the naphthalene pitch by varying cross-linking procedures. All profiles were very similar, although the capacities at 0 – 0.13V and 0.5 – 2.0V depended on the cross-linking procedures. The largest capacity at 0 – 0.13V was observed with the carbon prepared from the precursor pitch oxidized with nitric acid (NIP-NA1000). Air oxidation (NIP-AIR1000) gave the similar profile. However, the carbon obtained by dehydrogenation with S (NIP-S1000) showed a large terrace at 0.8 – 2.0V region.

Figure 3 shows discharge potential profiles of hard carbons prepared from oxidized synthetic isotropic pitches, which were synthesized from different aromatic hydrocarbons, with nitric acid treatment. The hard carbon from naphthalene pitch shows the highest capacity in the low potential region, although the oxygen content of the precursor pitches were much the same. The structure of hard carbon from isotropic pitch is strongly affected by that of the precursor pitch, showing the structure depending capacity.

Discussion

In the present study, oxidation process was introduced to convert isotropic pitch into thermosetting, and to maintain isotropic structure through carbonization step. Therefore, the structure of precursor pitches determines that of hard carbon prepared from isotropic pitches. In air blowing oxidation, oxygen diffuses into pitch particles, and then cross-links molecules to give them thermal stability. Therefore, severe conditions are necessary to make pitch perfectly infusible during carbonization, because the diffusivity of oxygen into pitch particle is limited. However, it is very difficult to determine the oxidation conditions of pitch having low softening point, because the pitch fuses at higher temperature than softening point, and the oxidation reaction is very slow at low temperature.

Nitric acid treatment is very effective to cross-link all kinds of the pitch by maintaining the aromatic alignment in the pitch, because the oxidation is conducted at lower temperature (50°C) than softening point. The capacity of hard carbon prepared from oxidized precursor pitches with nitric acid treatment varies, reflecting the structure of the precursor pitches.

Acknowledgements - This study was supported by the Proposal-Based New Industry Creative Type Technology R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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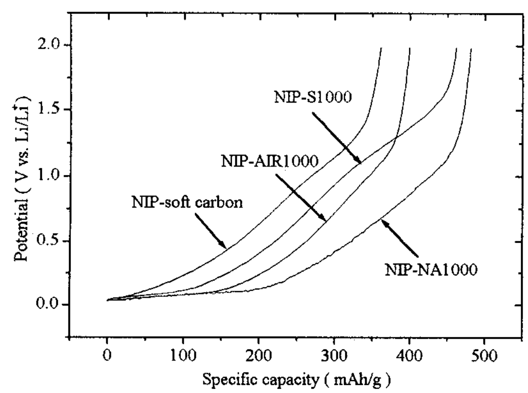

Figure 2. Discharge profiles of hard carbons prepared from the naphthalene pitch by different cross-linking methods.

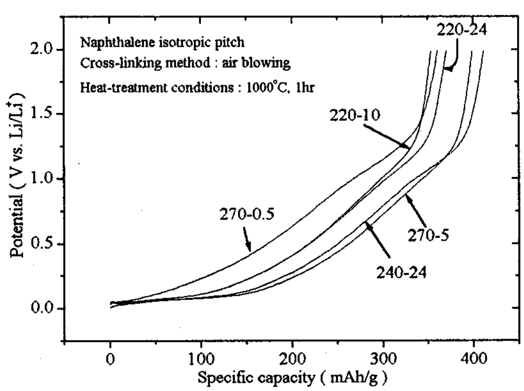

Figure 1. Discharge potential profiles of hard carbons prepared from naphthalene isotropic pitch with air blowing under different conditions.

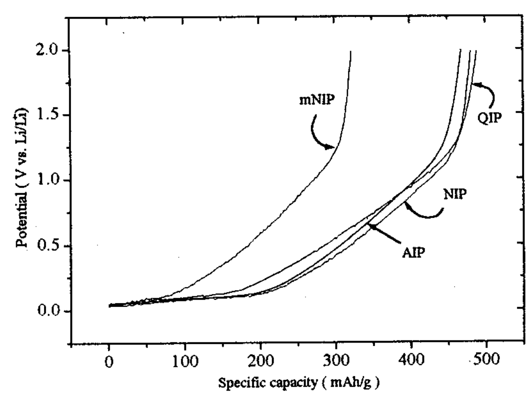

Figure 3. Discharge profiles of hard carbons prepared from oxidized synthetic isotropic pitches with nitric acid treatment.