

ANODIC PERFORMANCES AND INSERTION MECHANISM OF HARD CARBONS PREPARED FROM SYNTHETIC ISOTROPIC PITCHES

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Introduction

Recently, hard carbons, which are prepared from various thermosetting polymers, stabilized pitches, and oxygenated organic compounds, have attracted a lot of attentions because of their larger capacity than that of graphite. However, its insertion mechanism for lithium ion is not clear yet.

In the present study, the structure and electrochemical characteristics of hard carbons prepared from synthetic isotropic pitches through solid phase oxidation were investigated to find the correlation between capacity and structure.

Experimental

Two kinds of synthetic isotropic pitches supplied by Mitsubishi Gas Chemical Co were cross-linked by the following three kinds of methods to convert the pitches into thermosetting. (i) air oxidation of pitch particle (220°C, 24h, 0.5°C/min), (ii) acid oxidation of dispersed particle in aqueous nitric acid (stirred at 50°C, 2h), and (iii) dehydrogenation with sulfur (the pitch : sulfur ratio 1:1 by weight) at 600°C (heating rate: 1°C/min) for 1h under N₂ flow. In the case of method (iii), the pitch was once fused during the carbonization, however, the product showed complete isotropic texture.

Precursor pitches oxidized by the methods (i) and (ii) were carbonized at 600°C (heating rate: 1°C/min) for 1h under N₂ flow, and further calcined at 1000°C (heating rate: 10°C/min) for 1h under Ar flow.

Constant current (25mA/g) was applied to every discharge (lithium de-insertion) step. In contrast, constant potential charging (at 0V vs. Li/Li⁺ for 40h) was applied after constant current charging (25mAh/g) to obtain the maximum charge.

Results

Figure 1 shows 1st (constant current charge: CC) and 2nd (CC+constant potential charges at 0V for 40h: CCCP) charge-discharge potential profiles of (a) soft and (b) hard carbons, both prepared at 700°C from the naphthalene isotropic pitch. The precursor of the latter carbon was obtained by oxidizing the pitch with nitric acid. The 1st charge of the soft carbon showed a plateau at around 0.8V, which has been ascribed to the formation of solid

electrolyte interface (SEI) film by the decomposition of electrolyte, and another at around 0V for 150mAh/g. The discharge potential increased monotonously to show a step at around 1V, giving a total capacity of 400mAh/g, which is much smaller than that of charge. The 2nd charge profile was much more simple and monotonous. No plateau at around 0.8V was observed any more. However, it showed a very large capacity of 550mAh/g by continuing the constant potential charge at 0V. Although the discharge profile was similar to 1st one, very large increase in capacity at around 1V and a little increase at the potential region of 0 - 0.25V were observed in the 2nd discharge, achieving a capacity of 850mAh/g. Charge/discharge profile hardly showed a hysteresis at 0.1 - 0.8V while the discharge plateau at around 1V was proved to reflect the charge at 0V.

The 1st and 2nd charge/discharge profiles of the hard carbon were much the same to those of the soft carbon except shorter discharge plateau at around 1.0V. Hence, the discharge capacity was smaller than that of the soft carbon. Figure 2 shows charge/discharge voltage profiles of soft and hard carbons heat-treated at 1000°C. The soft carbon showed the basically same profile to that heat-treated at 700°C, although its capacity was much smaller, because of the smaller plateau at around 1V. The constant current and constant potential charge allowed discharge capacity of 350mAh/g to 2.0V.

The hard carbon also showed a monotonous charge profile to allow 420mAh/g in the 1st charge (CC) and 220mAh/g in the following discharge with monotonously increasing potential. 200mAh/g of irreversible charge should be noted. The 2nd charge (CC+CP) showed a capacity of 250mAh/g by the constant current charge at a very reduced potential and further large capacity of 500mAh/g by constant potential one.

The 2nd discharge took place in the potential region of 0 - 2V, giving a large capacity 482mAh/g with the potential plateau at around 0.1V by 203mAh/g. The discharge at this low potential region is unique for the hard carbon calcined at around 1000°C.

Figure 3 shows the voltage profiles of heteroatom containing hard carbons, which were prepared from isotropic naphthalene precursor pitch by dehydrogenation with sulfur (NIP-S1000) or oxidizing with nitric acid (NIP-NA1000) and isotropic quinoline precursor pitch (QIP-AIR1000) oxidized with air-blowing method. Comparing to NIP-AIR1000 (isotropic naphthalene precursor pitch

oxidized by air blowing), the heteroatom containing carbons showed commonly unique discharge at a high potential region (0.5 – 2.0V). The precursor pitches of QIP-AIR1000 and NIP-NA1000 carried 10 and 8wt% N, respectively. It decreased to 6 and 4 wt%, respectively, by the heat-treatment at 1000 °C. NIP-S1000 also lost its sulfur content 19wt% to 5 wt% by heat-treatment at 1000°C. Such a carbon showed the largest capacity in this potential region.

Discussion

Five types of lithium insertion may take place at their respective sites of the hard carbon as shown in Figure 4. Sites of Type I to III are charged at 0.8 – 0.25V, 0.25 – 0.1V and 0.1 – 0V, respectively, as postulated with the soft carbon in a previous paper. The site for Type IV is a void of certain size as postulated at intercluster positions. It must be emphasized that the void of very definite size is responsible for this insertion. Too large or too small cavity cannot accommodate the lithium ion at this particular potential. Many of lithium charged in this cavity is quite near to its metallic state, and probably in a cluster form without any crystal regularity because of rapid exchange with lithium charge-transferred to the hexagon surface as illustrated above. The cavity may define the distance among the charged lithium ions to be exchanged. The major difference with capacity of the present carbon is ascribed to the sites of Type IV and V. The former site may increase with smaller crystallographic size, which introduces more voids. This is a guideline to prepare a hard carbon of higher capacity.

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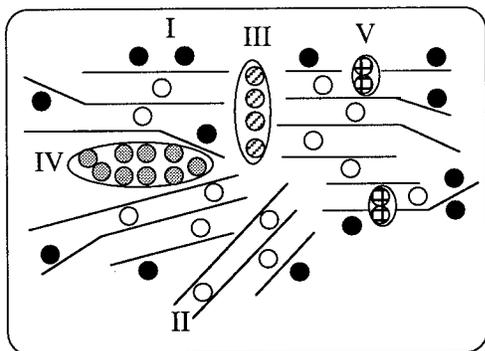


Figure 4. Lithium insertion model for heteroatom-containing hard carbon prepared from synthetic isotropic pitches.

References

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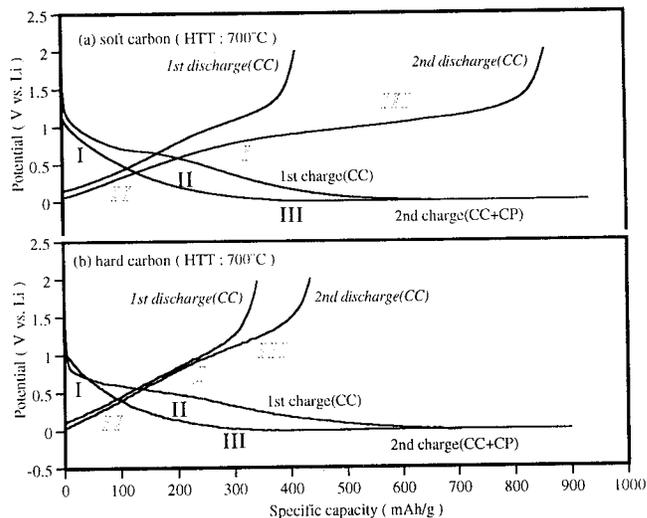


Figure 1. Charge-discharge profiles of (a) soft and (b) hard carbon prepared at 700°C from the naphthalene isotropic pitch

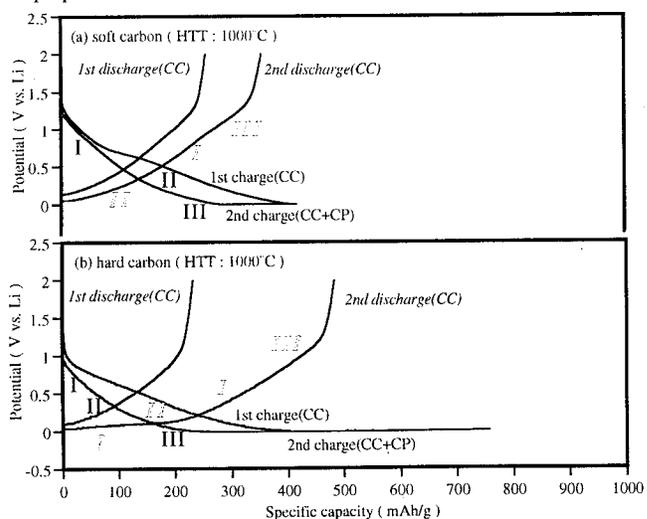


Figure 2. Charge-discharge profiles of (a) soft and (b) hard carbon prepared at 1000°C from the naphthalene isotropic pitch

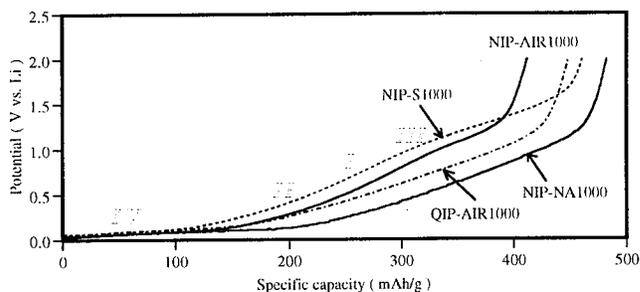


Figure 3. Discharge profiles of heteroatom-containing hard carbons