ANODIC PERFORMANCES OF CARBON PREPARED FROM SYNTHETIC MESOPHASE PITCHES

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Introduction

There are a number of carbon candidates for the anode of lithium ion secondary battery[1-3]. These can be classified into three groups according to their anodic performances[4], i.e. graphite, hard carbon and soft carbons, last two of which are heattreated at 700°C - 1200°C. Among them, soft carbons have been known that their reversible capacity is 2 - 3 times higher than theoretical capacity of graphite, 372mAh/g. However, there are three problems, high discharge potential plateau of 1 V and relatively high irreversible capacity, and slow charging rate.

In this study, anodic performances of carbon electrode prepared from synthetic mesophase pitches at the temperature of 500 - 1200°C were investigated to classify the structural factors for high capacity, discharge potential, and irreversible capacity.

Experimental

Synthetic mesophase naphthalene pitch(NP) was heattreated at the range of 500 - 1200°C. Their structure was investigated by element analysis, XRD, and raman spectroscopy. Their electrochmical characteristics were measured by charge/discharge tester in the dry box filled with Ar gas. The three electrode cell consists of carbon working electrode, lithium metal as counter and reference electrode, repectively. The electrolyte was 1M $LiPF_6$/EC+DMC(vol. ratio 1:1).

Charging methods examined were as follows. One was constant current method(current density : $0.2mA/cm^2$) , and the other was limited potential method, where first constant current charging (current density : $0.2mA/cm^2$) to 0 V followed by constant potential charging(40h at 0V vs. Li/Li^+) were applied to obtain the maximum capacity.

Results

Figure 1 shows the charge and discharge capacity of NP600-1 and NP700-1 measured by differnt charging methods. Discharge capacities of each carbons charged by method I were about 450mAh/g. The charging method II increased discharge capacities by expanding the potential plateau at 1 V. The discharge capacities of carbons prepared at lower temperatures depend on the charging method. The capacity at 0V during constant potential charging provided discharge at 1V. The method II allowed larger capacity of carbons prepared at lower temperature. NP500-1 did not allow charge and discharge regardless of charging methods.

Figure 2 shows the discharge capacities of NP-based carbons mesured by method II. They increased to 900mAh/g, 760mAh/g by the heattreat at 600°C and 700°C, respectively, and then decreased 300mAh/g at 1200°C. The longer heattreating increased the capacity to 930mAh/g at 600°C by 40h while decreased to 652mAh/g at 700°C by 10h.

Figure 3 shows a fair correlation between irreversible capacities and H/C ratio, where irreversible capacities were obtained from differences between charging capacities during constant potential region and increased capacities by constant potential charging.

Figure 4 correlates between discharge and irreversible capacities of the carbons heattreated under same conditions. Raising the heattreatment temperature upto 600°C sharply increased discharge capacity and reduced the irreversible capacity. The longer heattreatment upto 40h at this temperature increased the discharge capacity and reduced the irreversible capacity. Higher temperature than 600°C reduced both discharge and irreversible capacities. Longer heattreatment reduced both capacities.

Discussion

Carbons prepared from mesophase pitch at 500 -

1200°C exhibited a large discharge capacity while their irreversible capacity is also large. The maximum discharge capacity is obtained by the heattreatment at 600°C for 40h, where the growth of hexagonal plane and void are balance. In contrast, irreversible capacity decreased with severity of heattreatment, being ralated to the H/C ratio. Hence further reduction of H/C ratio without changing arrangement of hexagonal plane may give better performance.

The carbons heattreated in the present range suffer slow charging rate and discharge potential about 1 V. Both are caused by overpotential. Surface C-H groups appears responsible because the carbon heattreated above 700°C obtained considerable electric conductivity.

References

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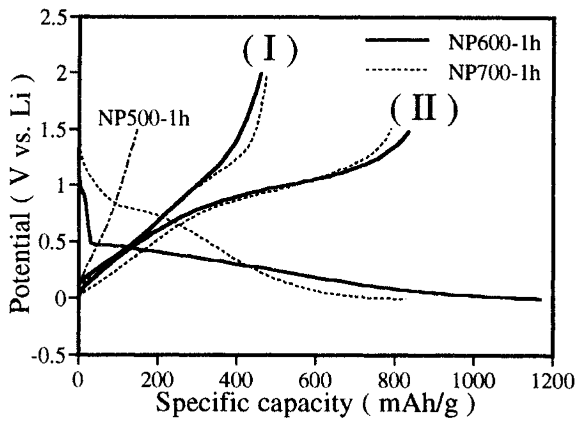

Figure 1. The charge/discharge characteristics of carbons derived from naphthalene mesophase pitch

I : constant current charging($0.2mA/cm^2$)
II : limited potential charging
(constant current + constant potential at 0V for 40h)

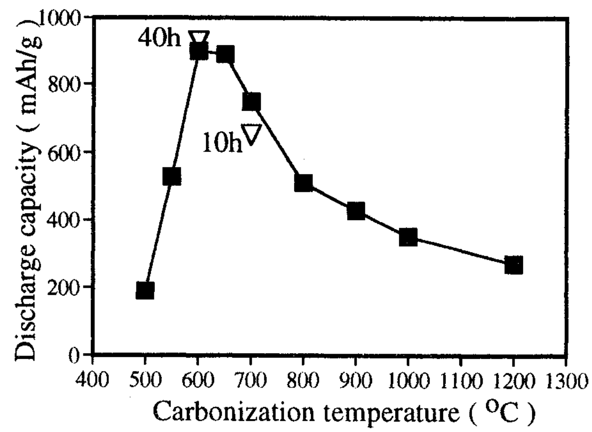

Figure 2. Discharge capacities vs. carbonization temp. plots for carbons derived from naphthalene mesophase pitch (holding time:1h, heating rate:10°C/min.)

* charging method : limited potential method (constant current ($0.2mA/cm^2$) + constant potential(40h at 0V vs. Li/Li^+))

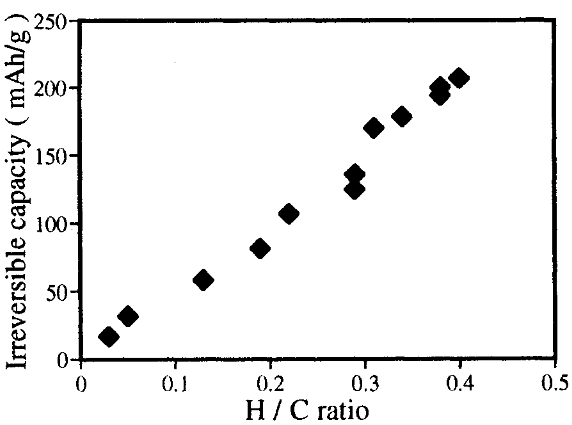

Figure 3. Irreversible capacities vs. H/C ratio plots for carbons derived from naphthalene mesophase pitch(Irreversible capacity : charge capacity during constant potential charging - increased capacity by constant potential charging)

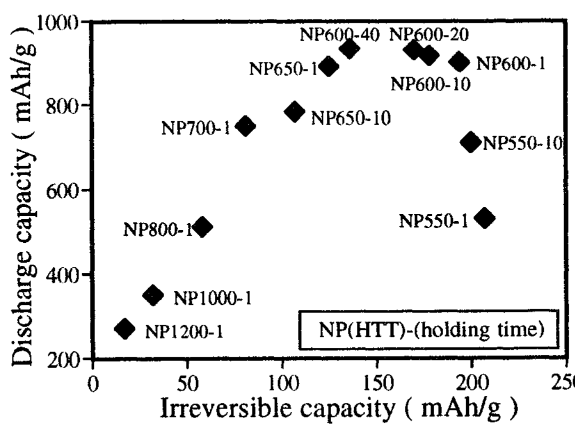

Figure 4. Discharge capacities vs. irreversible capacities plots for NP-based carbons

-.discharge capacity:charged by limited potential method
-.irreversible capacity:charge capacity during constant potential charging - increased capacity by constant potential charging