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Anode Performance of Periodic Nanoporous Carbon in Secondary Lithium-ion Batteries

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Carbon materials have been used as electrodes in a lithium ion battery for use as negative electrode active materials. Many reports have shown that the charge-discharge capacity of non-graphitizable carbon heat-treated at low temperatures such as below 1100°C exceed the theoretical capacity [1-6]. The performance of lithium ion secondary batteries, such as the charge-discharge capacity, speed, voltage profile and cyclic stability depend on mainly heat treatment process and carbon nanostructures. The size of surface area and the dynamic behavior of the ions responsible for the characteristics of the devices are markedly influenced by material porosity [5,7].

On the other hand, the periodic nanoporous materials which consists of the material containing air-filled spheres instead of the silica spheres has been made by using the synthetic opal as the template [8]. These materials are expected to have unique and useful properties as electrical and optical devices because it has the periodic porous nano-structure with the periodicity of the order of optical wavelengths.

In this study, we investigated the electrochemical characteristics of periodic nanoporous carbon materials with various heat treatment temperatures (HTTs) for Li ion secondary battery applications. Periodic nanoporous carbons with three-dimensional periodicity at optical wavelengths were prepared using the method that the pristine products infiltrating starting materials into the voids in synthetic opals pyrolyze in a high-purity Ar atmosphere for carbonization of samples and subsequently removing the SiO₂ spheres by immersing into the aqueous solution of hydrofluoric acid. These samples were pyrolyzed at various temperatures for 1h in a high-purity Ar atmosphere again. In this experiment,

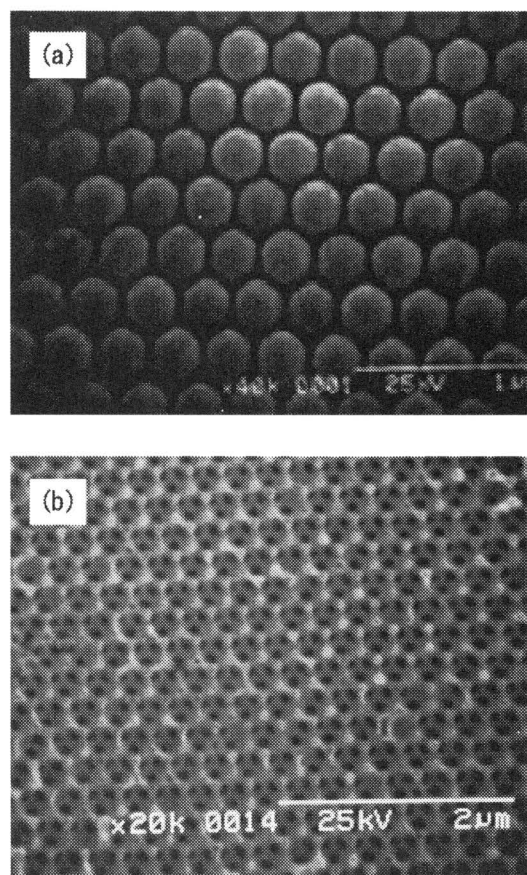


Fig. 1. SEM images of (a) synthetic opal made of SiO₂ spheres 300nm in diameter (b) periodic nanoporous carbon pyrolyzed at HTT of 700°C

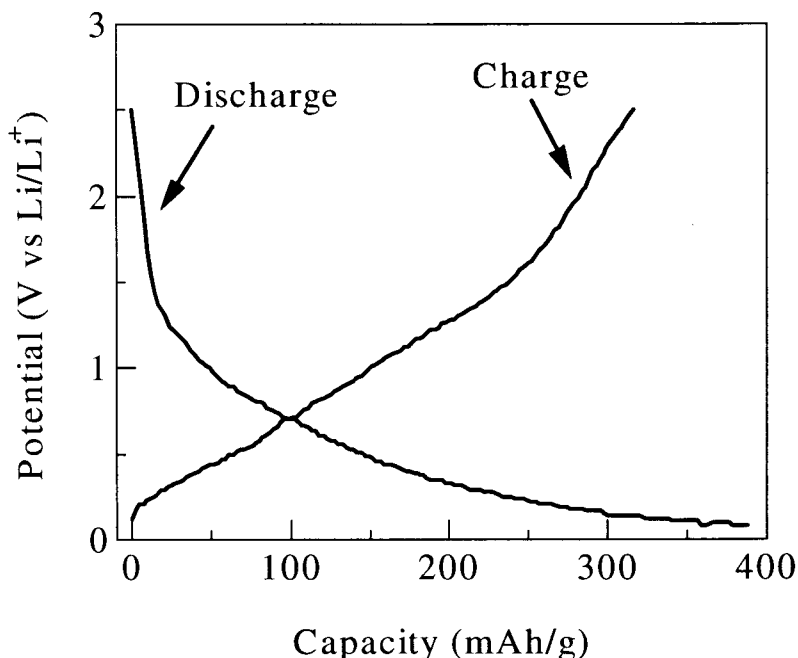


Fig. 2. Plots of the third charge-discharge profiles of a pyrolyzed periodic nanoporous carbon with a HTT of 690°C. The charge-discharge test was conducted under constant current corresponding to 300mA/g.

we use the samples made by infiltrating a phenolic resin as starting materials into voids of synthetic opal made of SiO₂ spheres of 300nm in diameter.

For preparation of a pellet-type electrode, periodic nanoporous carbons were held with Ni mesh. A lithium metal plate served as the counter and reference electrodes. Therefore, Li ion intercalation to a sample corresponds to a discharge process, while the deintercalation is a charge process. The electrolytes used in this study were 1M solution of LiClO₄ in a propylene carbonate (PC). Electrochemical measurements were carried out using beaker type cell at room temperature in an argon-filled glove box (MDB-1-B+MS80, Miwa). The cell was discharged to 0.03V vs (Li/Li⁺) at a constant current and then charged to 2.5 V at a constant current using a charge-discharge unit (HJ-201B, HOKUTO DENKO).

Figure 1 (a) shows the SEM image of synthetic opal made by SiO₂ spheres of 300nm in diameter, and Fig. 1 (b) shows periodic nanoporous carbon pyrolyzed at HTT of 700°C. These figures revealed the perfection of the replication process and that the periodicity and therefore the size of voids were approximately consistent with the diameter of spheres of synthetic opals. From fig. 1 (b), the three channels communicating with the underlying layer also can be seen.

Next, we have investigated the electrochemical properties of pyrolyzed periodic nanoporous carbons. Figure 2 shows the third charge-discharge profiles of a pyrolyzed periodic nanoporous carbon at HTT of 690°C. The charge-discharge test was conducted under the constant current corresponding to 300 mA/g. The carbon electrode cell showed reversible capacity of about 315

mAh/g, and indicate characteristic plateau in discharge/charge properties at about 1.0 V, as well as hysteresis in voltage profile about 0.0 V [9-11]. From these results, it appears that the electrode made of pyrolyzed periodic nanoporous carbon shows the good stability and relatively high Coulombic efficiency.

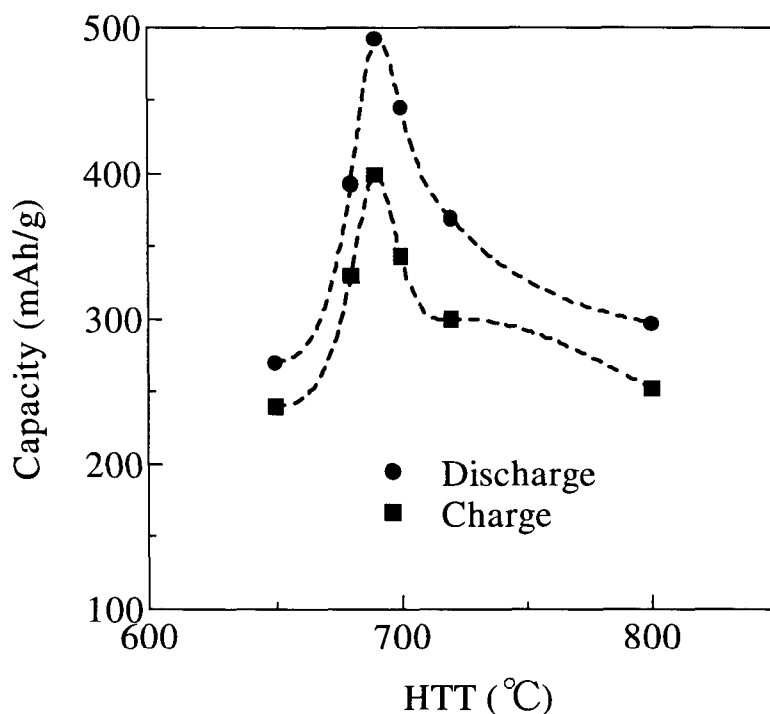


Fig. 3. Dependence of charge and discharge capacities on HTTs of periodic nanoporous carbons. The charge and discharge current was 300mA/g.

Figure 3 shows the dependence of the third charge-discharge capacities of pyrolyzed samples on HTTs. The reversible capacity of pyrolyzed sample with a HTT of about 700°C is the highest. That is, the charge-discharge capacity of samples can be improved by pyrolysis.

In conclusion, we prepared periodic nanoporous carbon using synthetic opal as a template. Then, we examined the electrochemical characteristics of periodic nanoporous carbon and indicated that the sample can be used as a electrode active materials in rechargeable batteries.

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