

Structure and electrochemical property of pyrocarbon-based negative electrode prepared from carbonized wood by chemical vapor infiltration

Y. Ohzawa, M. Mitani, T. Nakajima

Department of Applied Chemistry, Aichi Institute of Technology

Yachigusa 1247, Yakusa-cho, Toyota 570-0392, Japan

The plate-type negative electrodes for lithium-ion secondary battery containing the three-dimensionally continuous current paths can be prepared by chemical vapor infiltration (CVI) technique. This preparation process consists of the infiltration of pyrolytic carbon (pyrocarbon) from gas phase into the electro-conductive porous preforms as the conductive fillers and/or current collectors. In this study, pyrocarbon was infiltrated into two sorts of conductive porous preforms, that is, the carbonized wood (A) and the TiN-coated wood (B) from C_3H_8 (30%) - H_2 at 950 °C by pressure-pulsed CVI (PCVI) methods, and the relation between structure and electrochemical behavior of the infiltrated pyrocarbon was investigated.

Fig. 1 shows the SEM images of the samples after infiltration of pyrocarbon into carbonized wood (A) and TiN-coated wood (B) preforms. It can be found that both samples have the honeycomb-shaped cellular structure, and the dense films of pyrocarbon with a thickness of 3 - 5 μm are deposited into the pores with the cross-section of rectangle. It is also found that pyrocarbon has the laminar texture oriented parallel to the cell surface of the carbonized wood. The laminar structure appears remarkably in pyrocarbon deposited directly on the carbonized wood as shown in photograph (A).

Fig. 2 shows the XRD patterns from the external surface of the carbonized wood preform and the samples (A) and (B) infiltrated with pyrocarbon. A (002) peak of sample (A) appears at higher angle of 25.4° ($d_{002} = 3.59$ nm) than that of original carbonized wood. This result indicates that the crystallinity of pyrocarbon is much higher than that of the substrate carbon. Intensity of (10) diffraction peak is relatively strong as compared with (002) diffraction peak, which results from the orientation of the pyrocarbon films perpendicular to the surface of the plate-like sample as shown in Fig. 1. On the other hand, the intensity of (10) diffraction line for sample (B) is significantly weak, which indicates that the degree of structural disordering in pyrocarbon of sample (B) is high compared with pyrocarbon of sample (A).

The BET surface area of sample (B) is higher than that of sample (A) as shown in Table 1. From this result and pore volume distribution analysis, it is supposed that pyrocarbon deposited on TiN in sample (B) is porous in nanometer size in comparison with pyrocarbon deposited directly on carbonized fiber in sample (A).

Sample (B) shows the charge capacity (Li de-intercalation) of 442 $mAhg^{-1}$ per mass of pyrocarbon at a current density of 30 $mA g^{-1}$, and 80 % of the capacity is maintained even at 960 $mA g^{-1}$. However, the capacity per total electrode mass is reduced to 115 $mA g^{-1}$ due to little capacity of TiN-coated wood. The capacity per total electrode mass of sample (A) is 298 $mAhg^{-1}$, which is larger than that of sample (B) because the carbonized wood could act as not only the conductive filler but also the host material for lithium intercalation/de-intercalation. Sample (A) demonstrates higher coulombic efficiency at first cycle (i.e. 87 %) than that of sample (B) because of the high crystallinity, laminar structure and low surface

area of pyrocarbon in sample (A). These structural features of pyrocarbon would cause the decrease of irreversible reaction such as the decomposition of electrolytes, resulting in the high coulombic efficiency at the first cycle in sample (B).

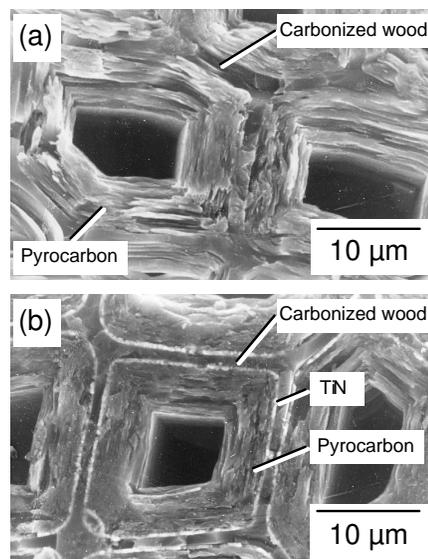


Fig. 1. SEM images of carbonized wood/pyrocarbon (A) and TiN-coated wood/pyrocarbon (B); number of pulses, 40000.

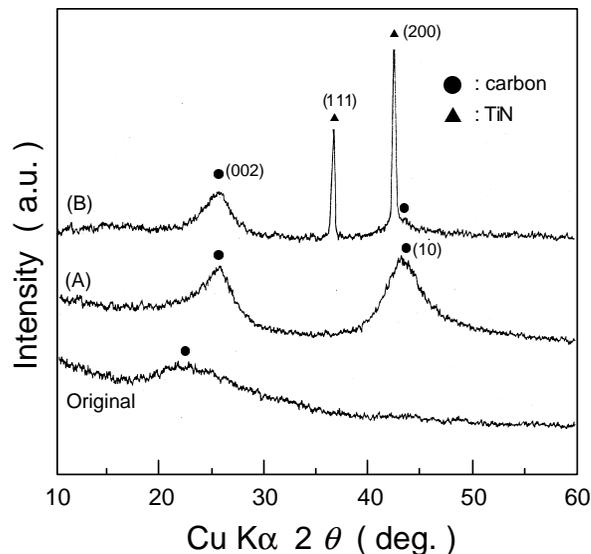


Fig. 2. XRD patterns of original carbonized wood, carbonized wood/pyrocarbon (A) and TiN-coated wood/pyrocarbon (B) samples; number of pulses, 4000.

Table 1. BET surface area, charge capacity and first coulombic efficiency data of carbonized wood / pyrocarbon (A) and TiN-coated wood/pyrocarbon (B) samples.

Sample	Surface area ($m^2 g^{-1}$)	Capacity ^{a)} ($mAhg^{-1}$)	Capacity ^{b)} ($mAhg^{-1}$)	Coulombic efficiency (%)
(A)	0.58	-	290	87
(B)	42	442	115	68

Current density, 0.2 $mA cm^{-2}$; number of pulses, 2500.

a): charge capacity per mass of pyrocarbon.

b): charge capacity per total mass of sample.