CVI 法によるリチウムイオン電池負極用低結晶性炭素繊維の表面修飾
Surface-modification of low crystalline carbon fiber for anode of lithium-ion battery using chemical vapor infiltration technique

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Abstract　To reduce the high irreversible capacity of the low crystalline carbon fiber for the anode material of lithium-ion battery, pyrolytic carbon (pyrocarbon) was coated at 950℃ from C_3H_8(30%)-H_2 gas system using pressure-pulsed chemical vapor infiltration. Carbon fiber was coated with the dense pyrocarbon film having the laminar texture and the low surface area of 1.9 $m^2 g^{-1}$. It was revealed from XRD and Raman spectroscopy that the crystallinity of pyrocarbon is higher than that of the core carbon. Electrochemical properties were measured in ethylene carbonate (EC) and propylene carbonate (PC) base electrolytes. Irreversible capacity was reduced in EC-based electrolyte by coating with 8 mass% pyrocarbon, which would be attributed to the high crystallinity, laminar structure and low surface area of pyrocarbon. Irreversible capacity was also decreased in PC-based electrolyte. The crystallinity of pyrocarbon was not so high as PC-based electrolyte was decomposed in the case of the high crystalline graphite.

1. Introduction

Low crystalline carbon such as non-graphitizing carbon (hard carbon) has received the attention for its high reversible capacity, which exceeds the theoretical capacity of graphite (372 $mA h g^{-1}$) for the anode of lithium ion battery. Low crystalline carbons prepared from natural materials such as paper and wood also have the large reversible capacity, however, irreversible capacity is often high for these disordered structure [1].

Pyrocarbon-coating by CVD was recently applied to graphite-based anodes of lithium-ion secondary battery to improve the anode performance, especially in propylene carbonate (PC) containing solvent [2-4], which was continuously decomposed by the high crystalline graphite. Among the CVD technique, pressure-pulsed chemical vapor deposition (PCVD) / infiltration (PCVI) allows homogeneous coating with the relatively high crystalline pyrocarbon through the thickness of the porous substrate under the suitable conditions [5-8], resulting in high first coulombic efficiency of

pyrocarbon-based anode [9]. However, the increase of the surface crystallinity may cause the PC solvent to decompose.

In present study, the relation between surface structure and electrochemical properties was investigated for the low crystalline carbon fiber and the samples coated with pyrocarbon using PCVI methods in both ethylene carbonate (EC) and PC base electrolytes

2. Experimental

The carbon fiber substrate was prepared by the carbonization of the commercial filter paper (ADVANTECH MFS) at 1000℃ in Ar for 4 h.

Coating with pyrocarbon was performed using the typical PCVI apparatus [5]. The source gas mixture of C_3H_8 (30%) - H_2 was allowed to flow into a reservoir. It was instantaneously introduced (within 0.1 s) into the reaction vessel up to 0.1 MPa, and the pressure was held under the same condition to allow matrix deposition for 1.0 s (holding time). Then, the reacted gas was evacuated to below 0.7 kPa within 1.5 s. This cycle of the

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sequential steps was defined as one pulse, and repeated to the desired number of times. The temperature for PCVI treatment was kept at 950 ℃.

The morphology of the samples was observed using scanning electron microscope (SEM, JEOL, JSM820). Structure of pyrocarbon was examined by X-ray diffraction (XRD) measurement (Shimazu, XD-610 with Cu Ka radiation) and Raman spectroscopy (Jasco, NRS1000 with Nd:YVO$_4$ laser of 532 nm). The Brunauer-Emmett-Teller (BET) surface area and mesopore volume distribution were measured using nitrogen gas (Micromeritics, Gemini 2375).

Charge/discharge cycling was made at 25 ℃, using a three electrode cell with metallic lithium as counter and reference electrodes, in 1 mol L^{-1} LiClO$_4$ EC/DEC (1:1) or PC solution. Discharging and charging were performed under the condition of constant current of 30 mA g^{-1} followed at constant potential of 3mV vs. Li/Li$^+$ for 48 h (CCCV method) and constant current of 30 mA g^{-1} (CC method), respectively. The samples were dried at 150℃ for 15 h under vacuum, before using as working electrodes

Fig. 1. SEM images of original carbon fiber (a) and pyrocarbon-coated sample (b) obtained by PCVI treatment with 20000 pulses.

3. Results and discussion

Fig. 1 shows the typical SEM images of the original carbon fiber (a) and the pyrocarbon-coated sample obtained after 20000 pulses in PCVI treatment. It can be observed that the relatively rough surface of the original carbon fiber became smooth in submicron scale. It appears that pyrocarbon film adheres tightly to the carbonized fiber. It can be also observed that pyrocarbon has the laminar texture oriented parallel to the surface of the carbonized fiber. This laminar structure is effective in reducing the irreversible reaction such as the decomposition of the electrolytes because the basal planes of carbon crystallites with low reactivity are mainly exposed to the electrolyte solution.

Structural properties are shown in Table 1 for the original and pyrocarbon-coated carbon fibers. The d$_{002}$ of the pyrocarbon-coated samples are below 0.358 nm, which are lower than that of the original carbon, however, are much higher than that of graphite (0.3354 nm). R value (I$_D$/I$_G$) calculated from Raman spectrum of original carbon fiber is slightly decreased by coating with pyrocarbon. From these results by XRD and Raman spectroscopy, it is considered that the crystallinity of pyrocarbon film is higher than that of core carbon. However, the crystallinity of pyrocarbon is low in comparison with that of high crystalline graphite. The BET surface area is decreased from 223 m^{2}g^{-1} of the original carbon fiber to 1.89 m^{2}g^{-1} after coating with 8.3 mass% pyrocarbon.
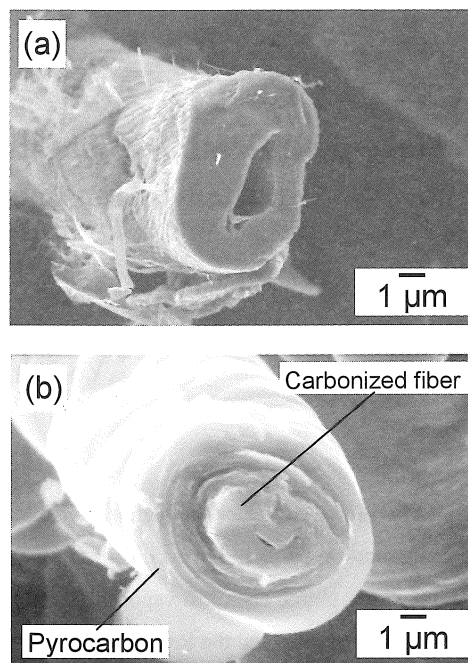
Surface area is further reduced with the increase of mass fraction and film thickness of pyrocarbon. From pore volume distribution analysis, it was found that the pores with the diameter of 1.5–5 nm were extremely decreased by pyrocarbon coating.

Fig. 2 shows the first charge-discharge curves of original {(a) and (c)} and pyrocarbon-coated carbon fibers {(b) and (d)} in 1 mol L^{-1} LiClO$_4$ EC/DEC (1:1) electrolyte {(a) and (b)} and 1 mol L^{-1} LiClO$_4$ PC electrolyte {(c) and (d)}. The charge-discharge profiles of the sample coated with 5-20 wt% pyrocarbon were similar to that observed in typical non-graphitizing carbon having the disordered structure. Charge capacity (Li de-intercalation) of the coating sample is 450-500 mA h g^{-1} in each electrolyte, which is nearly close to that of the original carbon fiber. High irreversible capacities of 180 and 132 mA h g^{-1} are observed in EC and PC-based electrolyte for the original carbon fiber, respectively, reflecting the disordered structure and high surface area of original carbon. Irreversible capacity is reduced from 180 to 132 mA h g^{-1} in EC-based electrolyte by coating with 8 mass% pyrocarbon. As mentioned above, the pyrocarbon film has higher crystallinity and lower surface area than those of the core carbon. In addition, pyrocarbon has the laminar texture, in which the basal planes of the crystallites are oriented parallel to the surface of the core carbon fiber. These structural features of pyrocarbon would

Table 1
Structural properties of original carbon fiber substrate and pyrolytic carbon (pyro-C) coated samples.

Number of pulses	Mass fraction of pyro-C / %	Average thickness of pyro-C / μm	XRD d_{002} / nm	Raman R value	BET surface area / $m^2 g^{-1}$
Original	0	0	0.386	1.8	223
500	8.3	-	0.358	1.4	1.89
1000	19.8	0.11	0.355	1.4	1.46
5000	59.7	0.52	0.353	1.3	0.81

cause the decrease of irreversible reactions such as decomposing the electrolytes and trapping lithium ions. Irreversible capacity can be also decreased in PC-based electrolyte. The crystallinity of pyrocarbon is low compared with high crystalline graphite, on which PC-based electrolyte is decomposed.
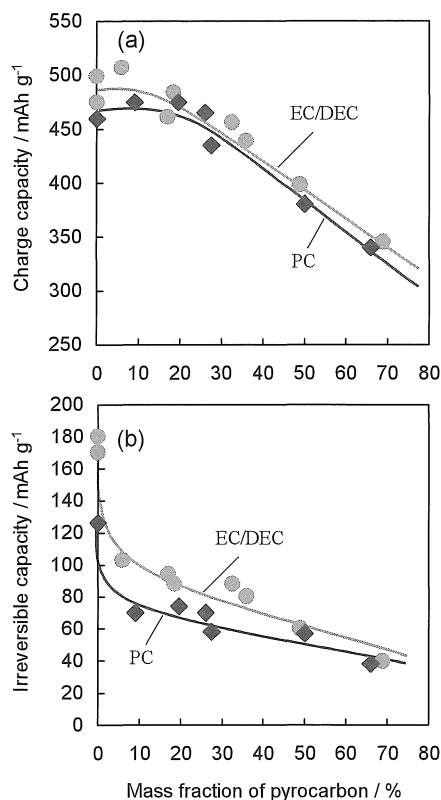
Fig. 3 shows the dependence of charge capacity (a) and irreversible capacity (b) of pyrocarbon-coated samples on mass fraction of pyrocarbon. Charge capacity (Li de-intercalation) of the pyrocarbon-coated sample is nearly close to that of the original carbon up to around 20 mass% of pyrocarbon in each electrolyte. Above 20 mass%, however, capacity is decreased with mass fraction of pyrocarbon. Pyrocarbon coated in present study is considered to be the graphitizable carbon (i.e. soft carbon). Therefore, the reversible capacity of the pyrocarbon

would be lower than that of the core carbon fiber regarded as non-graphitizable carbon, resulting in the decrease of capacity with mass fraction of pyrocarbon [10]. In fig. 3 (b), it is found that irreversible capacity is rapidly reduced by coating with 8-10 mass% pyrocarbon, reflecting the change of the nano-scaled surface structure as mentioned above. Irreversible capacity can be slightly decreased with increasing the mass fraction of pyrocarbon in both electrolytes, which would be attributed to the small reduction of the BET surface area with the thickness of pyrocarbon film as shown in Table 1. From the results of fig. 3 (a) and (b), it is considered that thin pyrocarbon film with uniform thickness is desired in order to achieve high coulombic efficiency at first cycle without reducing the reversible capacity. Irreversible capacity in PC-based electrolyte is slightly lower
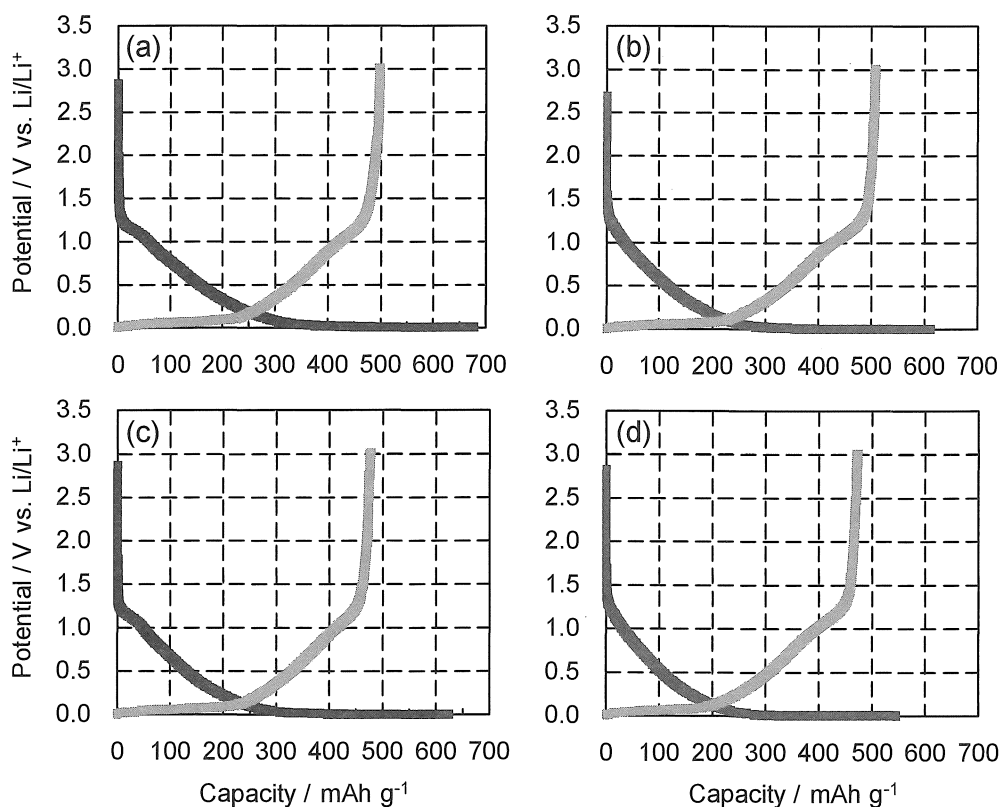
Fig. 2. First charge-discharge curves of original {(a) and (c)} and pyrocarbon-coated carbon fibers {(b) and (d)} in 1 mol L^{-1} $LiClO_4$ EC/DEC (1:1) electrolyte {(a) and (b)} and 1 mol L^{-1} $LiClO_4$ PC electrolyte {(c) and (d)}. Mass fraction of pyrocarbon; (b) 8 mass% and (d) 10 mass %.

than that in EC-based electrolyte in the region below 30 mass% of pyrocarbon as shown in fig. 3 (b). Because PC molecule is bulkier than EC molecule, the surface area of the pore in which PC molecule is accessible would be small in comparison with the area for EC molecule. It is supposed that the small effective surface area for PC electrolyte results in the decrease of the electrolyte decomposition to reduce the irreversible capacity. However, the details are open to further investigation.

Fig. 3. Dependence of charge capacity (a) and irreversible capacity (b) of pyrocarbon-coated sample on mass fraction of pyrocarbon.

3. Conclusion

In present study, the relation between surface structure and electrochemical properties was investigated in ethylene carbonate (EC) and PC base electrolytes for the low crystalline carbon fiber coated with pyrocarbon using PCVI methods. Carbon fibers were coated with the dense pyrocarbon films having the laminar texture oriented parallel to the surface of the carbon fiber. It was revealed from XRD and Raman spectroscopy that the crystallinity of pyrocarbon is higher than that of the carbon fiber. BET surface area was decreased from 223 m^2 g^{-1} of original substrate to 1.9 m^2 g^{-1} of the pyrocarbon-infiltrated sample. Reversible capacity of the sample coated with pyrocarbon up to 20 mass% was 450-500 mA h g^{-1} in each electrolyte, which was nearly close to that of the original carbonized paper. High irreversible capacity was observed in the original carbonized paper, reflecting the disordered structure and high surface area. Irreversible capacity was reduced in EC-based electrolyte by coating with 8 mass% pyrocarbon, which would be attributed to the high crystallinity, laminar structure and low surface area of pyrocarbon. Irreversible capacity was also decreased in PC-based electrolyte. The crystallinity of pyrocarbon was low compared with high crystalline graphite, on which PC-based electrolyte was decomposed. Irreversible capacity can be slightly decreased with increasing the mass fraction of pyrocarbon in both electrolytes, however, reversible capacity is also decreased with mass fraction of pyrocarbon.

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