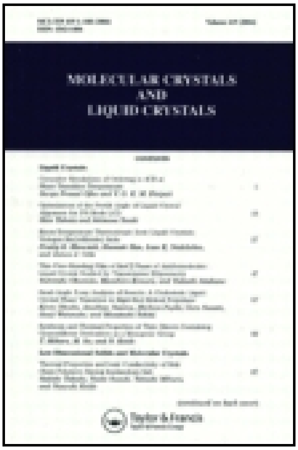

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Pressure-pulsed chemical vapor infiltration of pyrolytic carbon into fibrous tin prepared from carbonized paper preform

Yoshimi Ohzawa [a] , Masami Mitani [a] , Vinay Gupta [a] , Michio Inagaki [a] & Tsuyoshi Nakajima [a]
[a] Department of Applied Chemistry, Aichi Institute of Technology, Yachigusa 1247, Yakusa-cho, Toyota, 470-0392, Japan

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PRESSURE-PULSED CHEMICAL VAPOR INFILTRATION OF PYROLYTIC CARBON INTO FIBROUS TiN PREPARED FROM CARBONIZED PAPER PREFORM

Yoshimi Ohzawa, Masami Mitani, Vinay Gupta,
Michio Inagaki, and Tsuyoshi Nakajima
Department of Applied Chemistry, Aichi Institute
of Technology, Yachigusa 1247, Yakusa-cho,
Toyota 470-0392, Japan

The plate-type negative electrodes for Li-ion rechargeable battery were prepared by pressure-pulsed chemical vapor infiltration of pyrolytic carbon at 950°C from C_3H_8 (30%)-H_2 into the TiN-based electroconductive forms having the fibrous structure. The electrodes had the three-dimensional current paths in the layers of active materials without the organic binders and the conductive additives. The charge-discharge profiles were similar to that observed in non-graphitizable carbon having disordered structure. Reversible capacity of pyrolytic carbon at current density of 0.2 mA cm^{-2} and coulombic efficiency at the first cycle were ~500 mA h g^{-1} and ~72%, respectively. The capacity at current density of 8 mA cm^{-2} maintained 80% of that at 0.2 mA cm^{-2}.

Keywords: chemical vapor infiltration; pyrolytic carbon; lithium ion battery; porous material

INTRODUCTION

The chemical vapor infiltration (CVI) process has been developed for matrix filling into fiber preforms to prepare the fiber-reinforced ceramics [1,2]. Among the CVI processes, the pressure-pulsed CVI (PCVI) process consists of sequential steps of evacuation of reaction vessel, instantaneous introduction of source gas and holding to allow deposition [3,4]. Using the PCVI method, highly porous SiC shapes can be obtained by partially densification with SiC matrix into the biologically derived porous preforms such as the carbonized cotton and paper [5]. In this process, if electroconductive materials such as TiN and TiC were partially infiltrated instead

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of SiC matrix, highly porous electroconductive shapes would be obtained. Furthermore, to infiltrate the active materials for Li-ion rechargeable batteries from the gas phase into these porous bodies, the electrodes having the three-dimensional current paths in the layers of active materials would be prepared without the organic binders and the conductive additives. In this study, PCVI process with pyrolytic carbon as the active material was examined using fibrous TiN obtained from the carbonized paper preform.

EXPERIMENTAL

Highly porous carbon preforms were prepared as follows; Commercial filter paper was put between carbon plates, carbonized at 1000°C in Ar for 4 h, and cut to $10 \times 15 \times 0.5\,\mathrm{mm}^3$. The initial porosity of the carbonized paper preform was 92–94%. The porosity and pore volume were estimated from the bulk density, which was calculated from the weight and dimension of the sample.

Matrix filling into the preforms was performed using the typical PCVI apparatus [5]. The source gas mixture was allowed to flow into a reservoir. It was instantaneously introduced (within 0.1 s) into the reaction vessel at up to 0.1 MPa and pressure held under same condition to allow matrix deposition (holding time). Then, finally evacuated to below 0.7 kPa within 1.5 s. This cycle of the sequential steps was defined as one pulse and repeated to the desired number of times.

Galvanostatic charge/discharge cycling was made at 25°C, using a three electrode cell with metallic lithium as counter and reference electrodes, in $1\,\mathrm{mol\,L}^{-1}$ $LiClO_4$ EC/DEC (1:1) solution. As-infiltrated samples were dried at 150°C for 4 h under vacuum, before using as working electrode.

RESULTS AND DISCUSSION

TiN was partially infiltrated into carbonized paper performs at 900°C with holding time of 1.5 s from gas system of $TiCl_4$(1%)-N_2(10%)-H_2. After 10000 pulses of PCVI, Fibrous TiN-based forms were obtained, which had the porosity of 86–88%, the resistivity of $9 \times 10^{-4}\,\Omega\mathrm{cm}$ and the average pore sizes of $\sim 20\,\mu\mathrm{m}$. The geometric surface area per unit volume showed higher value than that of the conventional foil-type current collector for the Li-ion battery. Therefore, it was expected that contacting resistance between active materials and current collector was reduced when the fibrous TiN forms were used as current collector. Galvonostatic cycling was applied at apparent current density of $0.3\,\mathrm{mA\,cm}^{-2}$ in potential range from 0 to 3 V vs. Li/Li^+. Under the present condition, TiN was not active against the electrochemical reaction with Li ion or electrolyte.

Using the porous carbonized paper/TiN as current collector, pyrolytic carbon was infiltrated at 950°C with holding time of 1 s from gas system of C_3H_8 (30%)-H_2. The filling ratio of pyrolytic carbon, which is defined as the fraction of infiltrated matrix volume per initial pore volume in perform, increases almost linearly up to 50000 pulses. The filling ratio and the residual porosity after 50000 pulses were 70% and 28%, respectively. Further infiltration caused the film formation on a macrosurface of the porous preform, which would prevent the in-depth penetration of the electrolyte into the electrode. On the sample obtained after 35000 pulses of PCVI, mass fraction of pyrolytic carbon (i.e., active material) per unit volume of the electrode reached to the similar value with that of the electrode for the commercial lithium-ion battery.

Figure 1 shows the SEM images of the carbonized paper/TiN/pyrolytic carbon samples. From low-magnification micrograph (a), it can be observed that the fibers have a relatively random orientation and connect with each other's. From image (b), it can be found that TiN this films with a thickness of ~0.5 µm deposit on the carbonized fibers and the dense films of pyrolytic carbon with a thickness of ~3 µm are formed on TiN films. Those observations indicate that three-dimensional current paths having a relatively random orientation are formed in the active material layers of the negative electrodes. In micrograph (b), it appears that pyrolytic carbon films adhere tightly to TiN. From these results, it is expected that the contacting resistance between active material (pyrolytic carbon) and current collector (TiN) shows the relatively low value even if the organic binders and the conductive additives are not used.

Using as-infiltrated samples after 7000 pulses of PCVI as the electrodes, galvanostatic charge/discharge cycling was carried out. Figure 2 shows the charge-discharge curves at first cycle. On the discharge (i.e., lithium intercalation) profile, the potential gradually decreases up to 0.1 V, below which the long plateau appears. In the case of the charging process, the

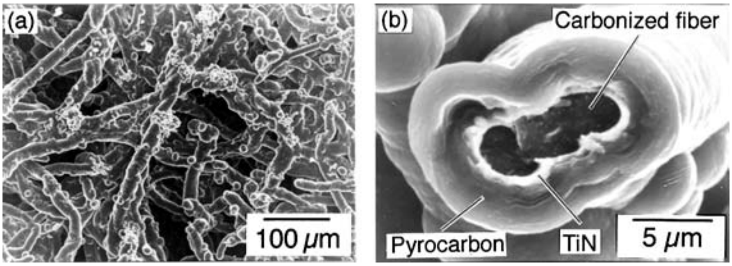

FIGURE 1 SEM images of the sample after infiltration of pyrolytic carbon into TiN-based form at 950°C with 32500 pulses.

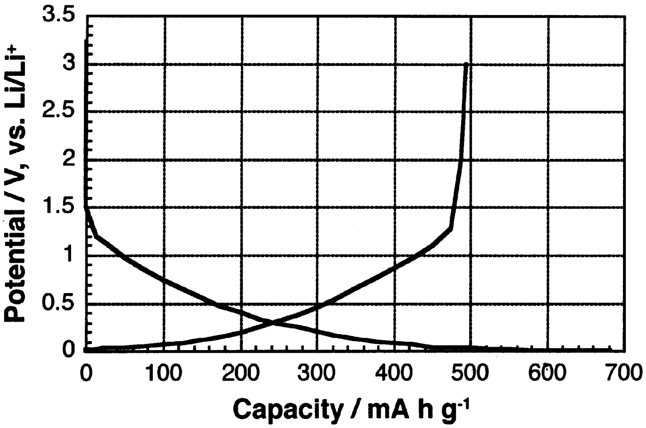

FIGURE 2 Charge-discharge curves of pyrolytic carbon infiltrated at 950°C with 7000 pulses at current density of 0.2 mA cm^{-2} (25 mA g^{-1}).

plateau is also observed at the potential below 0.2 V. Charge capacity and coulombic efficiency at the first cycle is 495 mA h g^{-1} and 72%, respectively. Those behavior is similar to that observed in some non-graphitizable carbon having the disordered structure. It is well known that two main types of pyrolytic carbon, laminar and isotropic (disordered) micro-

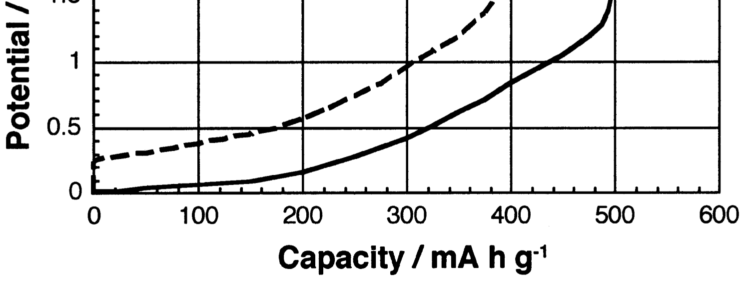

FIGURE 3 Charge curves of pyrolytic carbon infiltrated at 950°C with 7000 pulses at current density of 0.2 mA cm^{-2} (25 mA g^{-1}, solid line) and 8 mA cm^{-2} (1000 mA g^{-1}, broken line). Discharge current density is 0.2 mA cm^{-2}.

structure, could be deposited by CVD/CVI process [6,7]. In the SEM image of the cross-section of the pyrolytic carbon film as shown in Figure 1, the laminar texture oriented parallel to the surface of the fiber is not observed. On the other hand, the laminar texture appeared clearly in the films deposited at 1100°C [8]. It was supposed that the degree of disordering in structure increased with decrease of CVI temperature, however, the details is now open to further investigation. Figure 3 shows the charge curves of pyrolytic carbon under several current densities. The capacity at $1000\,\mathrm{mA\ g^{-1}}$ of current density is 80% of that at $25\,\mathrm{mA\ g^{-1}}$. It is supposed that the relatively high capacity at high charge rate results from the formation of three-dimensional current paths in the active material layers and the tight adhesion between pyrolytic carbon and TiN, which would be effective in reducing the internal resistance. Capacity of pyrolytic carbon maintained 92% of initial value even after the charge-discharge cycling of 60 times.

CONCLUSION

Using PCVI with pyrolytic carbon into fibrous TiN obtained from the carbonized paper preform, the negative electrodes for Li-ion rechargeable battery were prepared, which had the three-dimensional current paths in the layers of active materials without the organic binders and the conductive additives. Reversible capacity of pyrolytic carbon at current density of $0.2\,\mathrm{mA\ cm^{-2}}$ was $\sim 500\,\mathrm{mA\ h\ g^{-1}}$, and the capacity at current density of $8\,\mathrm{mA\ cm^{-2}}$ maintained 80% of that at $0.2\,\mathrm{mA\ cm^{-2}}$.

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