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Electrochemical Capacitance of Nitrogen-Containing Nanocarbons Prepared Using Porous Anodic Alumina Template

M. Kiriū, K. Fushimi, H. Konno and H. Habazaki*

Graduate School of Engineering, Hokkaido University, N13-W8, Sapporo 060-8628, Japan

*Corresponding author: habazaki@eng.hokudai.ac.jp

Nanocarbons with test tube brush-type morphology have been prepared by liquid phase carbonization of poly(acrylamide) (PAA) or poly(vinylchloride) (PVC) in pores of template. The template used is dc etched aluminum foil that is further anodized in sulfuric acid electrolyte. The nanocarbons derived from PAA contain nitrogen, whose content decreases with increasing heat treatment temperature. At each heat treatment temperature, the specific surface area as well as pore structure is similar for both the nanocarbons derived from PAA and PVC. Nevertheless, the markedly large electrochemical capacitance, measured in 1 mol dm⁻³ sulphuric acid, is obtained for the PAA-derived nanocarbons, compared with that from PVC, due to pseudocapacitance arising from nitrogen species in the former nanocarbons. Despite the specific surface area of less than 250 m² g⁻¹, the PAA-derived nanocarbons reveal the capacitance as large as ~130 F g⁻¹. The capacitance per specific surface area is found to increase almost linearly with the content of nitrogen. It is also found that the capacitance of the nanocarbons with the test tube brush-type morphology is larger than that of the carbon nanofilaments prepared similarly using a template of porous anodic alumina on plain aluminum foil.

Keywords; nano-carbons, electrochemical capacitor, pseudo-capacitance, template synthesis

1. Introduction

In recent years supercapacitors are attracted considerable attention as energy storage devices with high power density and excellent durability. Activated carbon is the most frequently used electrode materials for supercapacitors. The charge storage is based on the charge separation taking place across a very small distance in an electric double layer. Large capacitance of the activated carbon is associated with the extremely high specific surface area of more than $2000 \text{ m}^2 \text{ g}^{-1}$, owing to the porous nature of the activated carbon. Since charging and discharging involves simply the movement of ions to and from the electrode surface, the process is inherently rapid. In addition, the supercapacitors reveal excellent cycle stability due to their simple charge storage mechanism.

Surface functional groups of carbon are known to influence largely its double layer properties, such as wettability, point of zero charge, electrical contact resistance, adsorption of ions and self-discharge characteristics ¹⁾. Recently, particular interest has been paid to nitrogen species, which enhance markedly the capacitance of carbon materials. Jurewicz et al. have reported the improved supercapacitor performance of activated carbon by ammoxidation ²⁻⁴⁾. The enhanced capacitance by nitrogen heteroatoms is often explained in terms of faradaic reactions, i.e., pseudocapacitance effect. Lota et al. have demonstrated a beneficial effect of nitrogen substituted for carbon on the capacitance behaviour of porous carbon in acidic and organic electrolytes. The importance of pore size as well as redox properties of nitrogen-containing nanocarbons prepared using mesoporous silica template for capacitance of the carbon materials is also clearly revealed ⁵⁾. Further, capacitive behaviour of carbon materials with high nitrogen contents of more than 20 mass%, which were prepared from melamine resins, has been examined in acidic electrolyte ⁶⁾ as well as in alkaline and organic electrolytes ⁷⁾. Despite the relatively low specific surface area of $400 \text{ m}^2 \text{ g}^{-1}$ or less, the

capacitance of $\sim 200 \text{ F g}^{-1}$ has been obtained in acidic electrolyte, although in an organic electrolyte, the capacitance is as low as $20\text{-}40 \text{ F g}^{-1}$. In this manner, nitrogen-substituted carbons are interesting electrode materials for supercapacitors. However, precise mechanism of the enhanced capacitance by nitrogen species has not yet been understood since no obvious redox reactions are observed in cyclic voltammograms.

The authors have prepared carbon nanofilaments (CNFs) using anodic porous alumina template by liquid phase carbonization of polymers^{8,9)}. Some of polymers, such as poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA) form liquefied pitch-like intermediate during heating in an inert atmosphere¹⁰⁾. Thus, by simply heating a mixture of such polymer powders and the porous template, the CNFs have been developed in the pore of the template. The diameters of the CNFs corresponded to the pore size of the template. Further, the CNFs thus formed have a platelet structure; the carbon layers developed are normal to the filament axis. The orientation of this type may be generated from the edge-on interaction of polyaromatic compounds in the liquid phase with the pore wall of the alumina template¹¹⁻¹³⁾. The platelet-type CNFs possess large edge surface. Thus, the materials are of interest as an electrode of electric double layer capacitors, since the capacitance of the edge plane of graphite is significantly larger than that of the basal plane¹⁴⁾.

Additionally, the template process is suitable to produce the carbon materials with controlled morphology and pore structure, which allow us to investigate the influence of nitrogen species on the electrochemical capacitance of the carbon materials precisely. In the present study, we have prepared nitrogen-containing nanocarbons from poly(acrylamide) (PAA) as well as nitrogen-free nanocarbons from PVC using porous anodic alumina template. The template used in this study has been developed by anodizing of etched aluminium foils, which are used in electrolytic capacitor industry. Thus, the nanocarbons developed have test tube brush-type morphology¹⁵⁾. The capacitance of the nanocarbons has been examined as a

function of nitrogen content in the nanocarbons.

2. Experimental

2.1 Preparation of nanocarbons

Template used in this study was prepared by anodizing of dc etched aluminum foils, approximately 100 μm thick, at 25 V in 0.1 mol dm^{-3} sulphuric acid electrolyte at 15°C for 1 h. The etched foil, provided from Japan Capacitor Industrial Co. Ltd., Tokyo, Japan, had tunnel pits, 0.2-0.5 μm square and more than 40 μm length. The porous anodic films grew from the pore wall of the etched foil. The anodizing converted almost entire aluminium foil to porous anodic alumina. After immersion of the anodized foil in 0.1 mol dm^{-3} phosphoric acid at 25°C for 30 min for slight pore widening, it was used as a template.

A mixture of PAA (Kishida Chemical Co. Ltd., molecular weight of approximately 16000000) or PVC (TS-500R, Sekisui Chemical Co. Ltd., degree of polymerization of 500) powders and the template was heated in an argon stream at 400 K h^{-1} to 300°C, then kept at this temperature for 30 min. Around this temperature, the polymers were converted to pitch-like liquefied intermediates, penetrating easily into mesopore channels, about 20 nm in diameter, of the template possibly by capillary flow. The mixture was further heated up to 600°C at 400 K h^{-1} and kept at this temperature for 1 h. Then, the template was dissolved in a 10% NaOH solution, and the nano-carbon materials were obtained. A part of the nanocarbons were further heat treated at 700 to 1000°C for 1 h in a stream of argon.

2.2 Characterisation of nanocarbons

Structure and morphology of the nanocarbons obtained were examined by a JEOL JSM-6500 field emission gun scanning electron microscope operating at 5 kV and a JEOL JEM-2000FX transmission electron microscope operated at 200kV. Nitrogen gas

adsorption/desorption isotherms were obtained at -196°C using Bel Japan, Belsorp Mini instrument. From the adsorption isotherms, BET surface areas of the nanocarbons were estimated. Elemental microanalysis was performed to determine the chemical composition of the nanocarbons. Further, X-ray photoelectron spectroscopy (XPS) measurements were carried out to identify the chemical state of nitrogen species. The photoelectron spectra were obtained using Shimadzu ESCA-3200 spectrometer with Mg $K\alpha$ radiation. The binding energies of individual species were calibrated using a method described elsewhere^{16, 17}.

2.3 Electrochemical measurements

The working electrodes for electrochemical measurements were prepared by coating a mixture of the nanocarbons, poly(tetrafluoroethylene) binder (PTFE, E.I. du Pont de Nemours and Company) and acetylene black (AB, DENKI KAGAKU KOGYO Co. Ltd.) on to titanium mesh current collector. The ratio of the nanocarbons, PTFE and AB was 70: 10: 20 mass%. Cyclic voltammograms were obtained in deaerated $1\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$ aqueous solution in the potential range of -0.2 to 0.8 V vs Ag/AgCl at a potential sweep rate of $5\text{-}50\text{ mV s}^{-1}$. Charge-discharge curves were also obtained in the same electrolyte and potential range at a current density of 0.5 A g^{-1} .

3 Results and Discussion

3.1 Preparation and characterisation of nanocarbons

Fig. 1 shows a cross-sectional scanning electron micrograph of the porous anodic alumina template used in this study. Vertical pits, $200\text{-}500\text{ nm}$ size, developed during dc etching of aluminium are visible in this micrograph. A number of cylindrical pores of $20\text{-}30\text{ nm}$ in diameter are grown from the wall of the pits to the approximately horizontal direction in this micrograph. Barrier layers, generally present beneath the pore bottom, are separating

pores developed from two adjacent tunnel pits.

Reflecting the pore structure of the template, the nanocarbons prepared from PVC (Fig. 2(a)) and PAA (Fig. 2(b)) reveal test tube brush-type morphology. A number of nanofilaments are disclosed in the scanning electron micrographs, and their diameter is 20-30 nm, corresponding to the size of pores developed by anodizing. The test tube brush-type morphology was more clearly visible from transmission electron micrographs. An example of the transmission electron micrograph of the PAA-derived nanocarbons heat treated at 1000°C is shown in Fig. 3. Presence of a core carbon rod of 300 nm width, which is formed in a tunnel pit of the template, is obvious in this micrograph. The length of CNFs extending from the core carbon rod is comparable to that of the nanopores in the template (Fig. 1). High resolution image of a CNF part (Fig. 3 (b)) demonstrates the platelet structure, i.e., the carbon layers are normal to the filament axis. Thus, similar to the PVC or PVA-derived CNFs^{9, 15)}, platelet-type CNFs are developed from a PAA precursor.

The specific surface areas of the nanocarbons prepared in this study are not as large as that of activated carbons ($>1500 \text{ m}^2 \text{ g}^{-1}$), which are often used as an electrode of capacitors. As shown in Fig. 4, the specific surface areas of the PAA- and PVC-derived nanocarbons decrease with an increase in the heat treatment temperature. Even at 600°C the specific surface areas are less than $250 \text{ m}^2 \text{ g}^{-1}$. The areas are similar for the PAA- and PVC-derived nanocarbons heat treated at each temperature. In addition, the adsorption and desorption isotherms for the PAA-derived nanocarbons are essentially the same as that of the PVC-derived one. Examples of the isotherms for the PAA-derived nanocarbons heat treated at 600 and 1000°C (Fig. 5) disclose the absence of a hysteresis loop, such that no mesopores are present in the nanocarbons. Slight rise in the adsorption volume at very low nitrogen pressure implies the presence of micropores⁸⁾.

Although morphology and pore structure for the PAA- and PVC-derived nanocarbons

are quite similar, the presence of nitrogen species in the PAA-derived nanocarbons has been confirmed by elemental analysis and XPS measurements. Fig. 6 shows the change in nitrogen content as well as hydrogen content, determined by elemental analysis, with heat treatment temperature. The nitrogen content is 10.4 mass% at 600°C, decreasing with heat treatment temperature. The increased heat treatment temperature also reduces the hydrogen content, since the carbonization proceeds with increasing the temperature.

In order to identify the nitrogen species in the nanocarbons, XPS measurements have been carried out. Fig. 7 shows the N 1s spectra of the PAA-derived nanocarbons heat treated at three different temperatures. The nanocarbons heat treated at 600°C reveal two main peaks at 398.0 and 400.0 eV. After heat treatment at higher temperatures, an additional peak at 401.9 eV appears, and the peak at 400.0 eV shifts 0.3 eV to higher binding energy with increasing heat treatment temperature. From the previous XPS studies¹⁸⁻²²⁾, the lowest binding energy peak of 398.0 ± 0.2 eV can be assigned for surface functional nitrogen species, such as imine, amine and amide. The peak at 400.0 - 400.3 eV is for pyrrolic nitrogen, and the highest binding energy peak at 401.9 ± 0.2 eV corresponds to the nitrogen substituents in aromatic graphene layers or quaternary nitrogen species. Thus, the nitrogen-substituted graphene layers appear to be developed at higher temperatures at and above 800°C. With increasing heat treatment temperature, the intensities of functional nitrogen species and pyrrolic nitrogen species decrease, in agreement with the results shown in Fig. 6. The reduction of the intensity with increased temperature is more significant for the surface functional nitrogen species than for the pyrrolic nitrogen. Further, from XPS analyses, it was found that the content of oxygen species associated with the carbon materials was negligible at all heat treatment temperatures.

3.2 Electrochemical characteristics

Cyclic voltammograms of the nanocarbons heat treated at each temperature (Fig. 8)

disclose clearly the higher capacitance of the PAA-derived nanocarbons compared with the PVC-derived ones. Since specific surface areas as well as pore structures are not largely different for both the nanocarbons at each heat treatment temperature, the enhanced capacitance of the PAA-derived nanocarbons should be attributed to the pseudocapacitance of nanocarbons. At all three temperatures, the rectangular voltammographs are obtained for the PVC-derived nanocarbons, while the voltammographs showing higher capacitance below 0.5 V vs Ag/AgCl are obtained for the PAA-derived nanocarbons heat treated at 600 and 800°C. Even for the PAA-derived nanocarbons, a voltammogram with fairly rectangular shape is developed after heat treatment at 1000°C.

The capacitances of the PAA- and PVC-derived nanocarbons are summarised in Table 1. From both the CV measurements and charge-discharge curves, similar capacitances were obtained. The PAA-derived nanocarbons heat treated at 600°C shows the highest capacitance among the nanocarbons examined. The capacitance value is as large as 130 F g^{-1} , being considerably larger than that of conventional activated carbon materials ($30\text{-}60 \text{ F g}^{-1}$)²³, despite the fact that the specific surface area of the nanocarbons prepared ($<250 \text{ m}^2 \text{ g}^{-1}$) is nearly one order of magnitude lower than that of typical activated carbon.

It is obvious from Fig. 8 and Table 1 that the capacitance decreases with increased heat treatment temperature, particularly for the PAA-derived nanocarbons. The reduced capacitance should be associated mainly with the decrease in the specific surface area (Fig. 4) for both the PAA- and PVC-derived nanocarbons, in addition to the reduced nitrogen content for the PAA-derived nanocarbons. In order to clarify the influence of nitrogen species on the capacitance, the capacitance per surface area is plotted as a function of the nitrogen content (Fig. 9). The capacitances of the PAA- and PVC-derived nanocarbons heat treated at the three different temperatures are all plotted in this figure. There is a good correlation between the capacitance and the nitrogen content for the PAA-derived nanocarbons; the capacitance

increases almost linearly with the nitrogen content. Extrapolation of the linear correlation to the nitrogen content of 0 mass% corresponds to those for the PVC-derived nanocarbons, confirming that the nitrogen species enhance the capacitance. The capacitance of the PVC-derived nanocarbons ($15\text{--}18\text{ }\mu\text{F cm}^{-2}$) is similar to that of typical activated carbons²³⁾. Thus, there is no beneficial effect of the high edge surface of the platelet structure nanocarbons, possibly due to low graphitisation degree of the carbon materials.

Although the PAA-derived nanocarbons heat treated at 600°C shows the highest capacitance, the capacitance decreases largely as the sweep rate increases in the CV measurements (Fig. 10). The reduction of the capacitance with sweep rate becomes less significant with increasing heat treatment temperature. One of the reasons may be increased electric conductivity of the nanocarbons heat treated at higher temperatures. This is partly supported by the fact that at higher sweep rates the cyclic voltammograms were no longer rectangular. The smaller change in the capacitance with sweep rate for the PVC-derived nanocarbons compared with the PAA-derived counterpart may be also due to different electrical conductivity, which arises from the different carbonization behaviour of the polymers²⁴⁾.

However, the PAA-derived nanocarbons heat treated at 600°C demonstrate the good cycle stability (Fig. 11). The high capacitance of $\sim 130\text{ F g}^{-1}$ is sustained up to 1000 cycles examined. The nitrogen functional species are stably present during the cycle examination, and Faradaic redox reactions occur repeatedly without degradation.

Finally, in order to confirm whether brush-type morphology is beneficial for capacitor characteristics, the CV measurements of simple CNFs prepared from PAA at 600°C were carried out. The CNFs were prepared using porous anodic alumina template developed on plain aluminium foils without tunnel pits. The capacitance per specific surface area for the CNFs was $39\text{ }\mu\text{F cm}^{-2}$, being lower than that of the brush-type ones formed at the same

temperature ($57 \mu\text{F cm}^{-2}$). Since the nitrogen contents of both the samples were similar, the higher capacitance of the brush-type nanocarbons may be originated from this unique morphology. A number of CNFs are connected to a carbon rod of 200-500 nm for the brush-type one. Such morphology should be beneficial for the electronic conduction compared with the separated carbon nanofilaments.

4 Conclusions

Using morphologically well-defined nanocarbons that are prepared by a template technique, influence of nitrogen species in the nanocarbons in electrochemical capacitance can be examined precisely. The capacitance per specific surface area of the nanocarbons, prepared from PAA, with test tube brush-type morphology increases approximately linearly with the nitrogen content. Surface functional nitrogen species and pyrrolic nitrogen are mainly present in the nanocarbons. The capacitance decreases with increasing heat treatment temperature, due to the reduced specific surface area as well as reduced nitrogen content, but the rate characteristics is improved at high heat treatment temperatures.

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Figure captions

Fig. 1 Scanning electron micrograph of a fractured cross-section of the dc etched aluminium foil after anodizing at 25 V in 0.1 mol dm^{-3} sulphuric acid electrolyte for 1 h.

Fig. 2 Scanning electron micrographs of the nanocarbons derived from (a) PVC and (b) PAA after heat treatment at 600°C .

Fig. 3 (a) Transmission electron micrograph of the nanocarbons derived from PAA after heat treatment at 1000°C . (b) High magnification image of the square region shown in (a).

Fig. 4 Change in specific surface area of the nanocarbons derived from PAA and PVC with heat treatment temperature.

Fig. 5 Nitrogen adsorption/desorption isotherms of the PAA-derived nanocarbons heat treated at 600 and 1000°C .

Fig. 6 Change in nitrogen and hydrogen contents in the PAA-derived nanocarbons with heat treatment temperature.

Fig. 7 N 1s X-ray photoelectron spectra of the PAA-derived nanocarbons heat treated at 600, 800 and 1000°C .

Fig. 8 Cyclic voltammograms of the PAA (solid line)- and PVC (dashed line)-derived nanocarbons heat treated at (a) 600, (b) 800 and (c) 1000°C , measured in 1 mol dm^{-3} sulphuric acid electrolyte.

Fig. 9 Change in the capacitance per specific surface area of the PAA- and PVC-derived nanocarbons with the content of nitrogen.

Fig. 10 Sweep rate dependence of the capacitance of the PAA-derived nanocarbons heat treated at 600 and 800°C and of the PVC-derived nanocarbons heat treated at 600°C .

Fig. 11 Cycle stability of the capacitance of the PAA-derived nanocarbons heat treated at

600°C. The capacitance was measured by repeated galvanostatic charge-discharge measurements in 1 mol dm⁻³ sulphuric acid electrolyte at a current density of 0.5 A g⁻¹.

Table 1 Capacitances of the nanocarbons prepared from PAA and PVC after heat treatment at three different temperatures.

Precursors	Heat treatment temperature (°C)	Capacitance (F g ⁻¹)*
PAA	600	123
	700	97
	800	78
	900	52
	1000	39
PVC	600	42
	800	23
	1000	18

* The values were obtained from CV curves with a sweep rate of 5 mV s⁻¹.

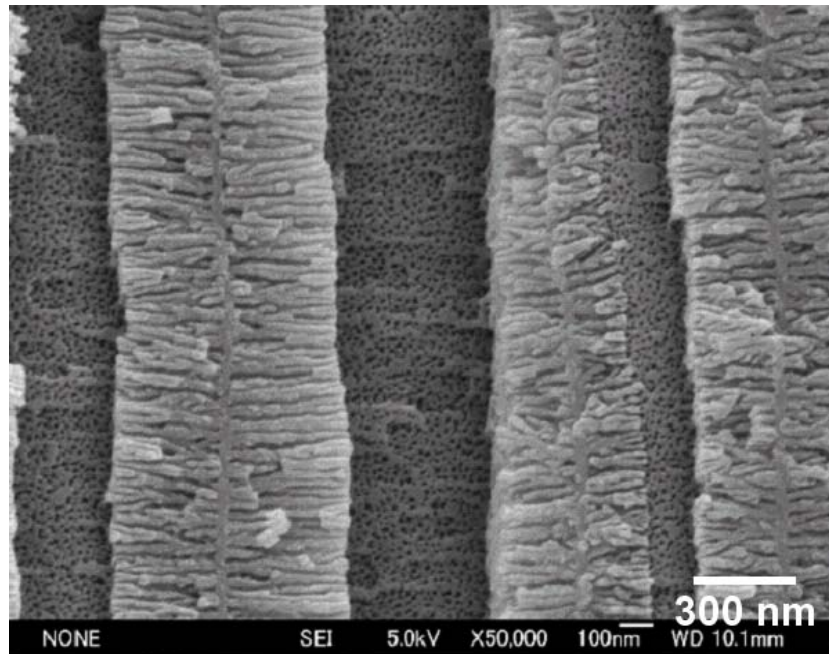


Fig. 1 Scanning electron micrograph of a fractured cross-section of the dc etched aluminium foil after anodizing at 25 V in 0.1 mol dm^{-3} sulphuric acid electrolyte for 1 h.

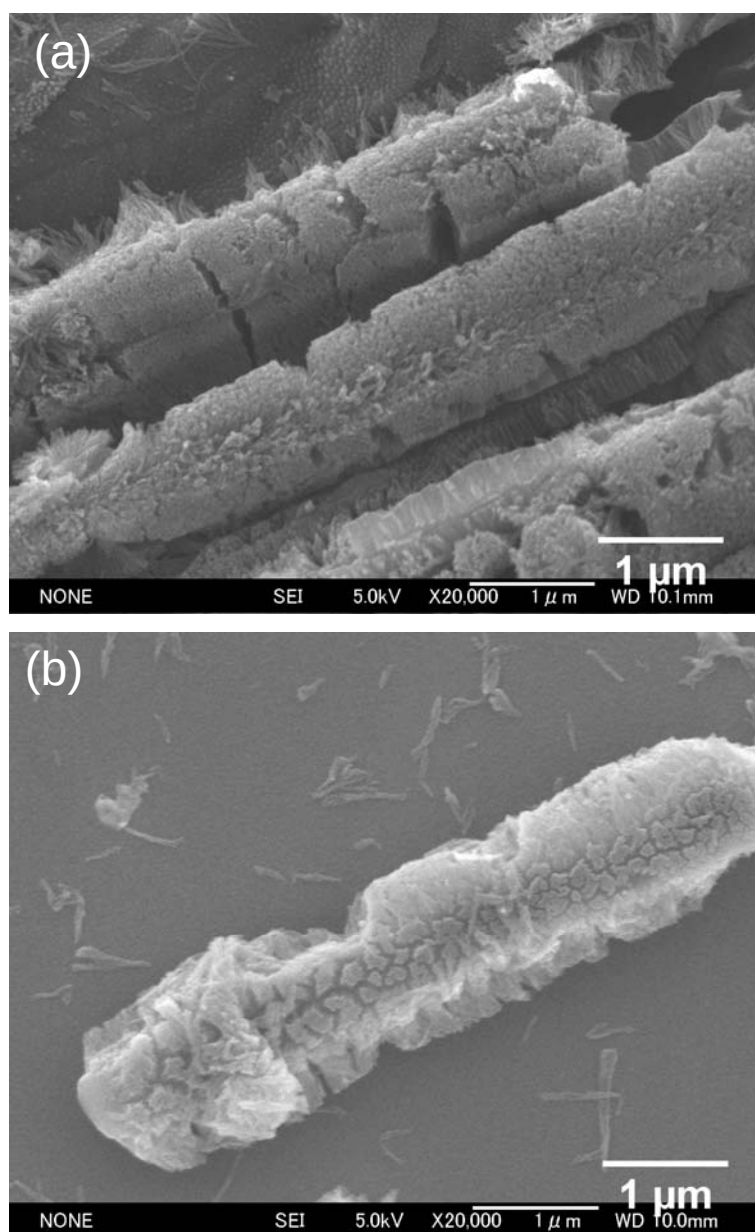


Fig. 2 Scanning electron micrographs of the nanocarbons derived from (a) PVC and (b) PAA after heat treatment at 600°C.

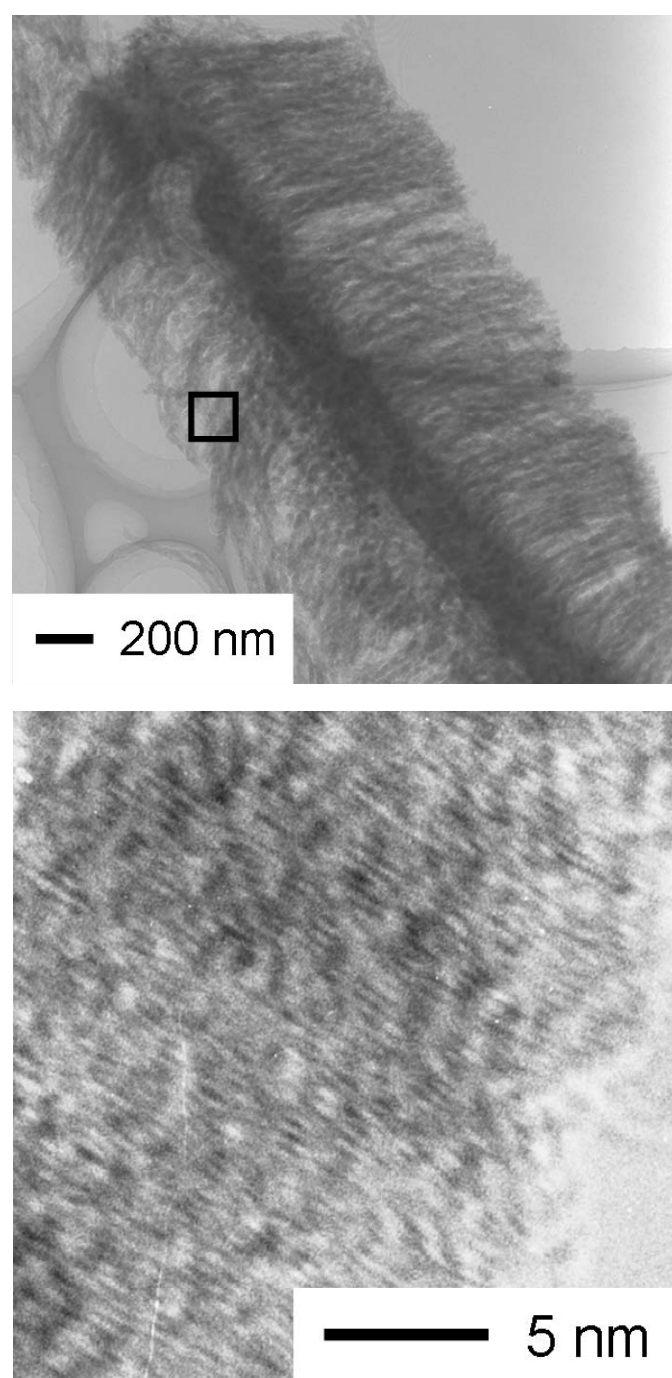


Fig. 3 (a) Transmission electron micrograph of the nanocarbons derived from PAA after heat treatment at 1000°C. (b) High magnification image of the square region shown in (a).

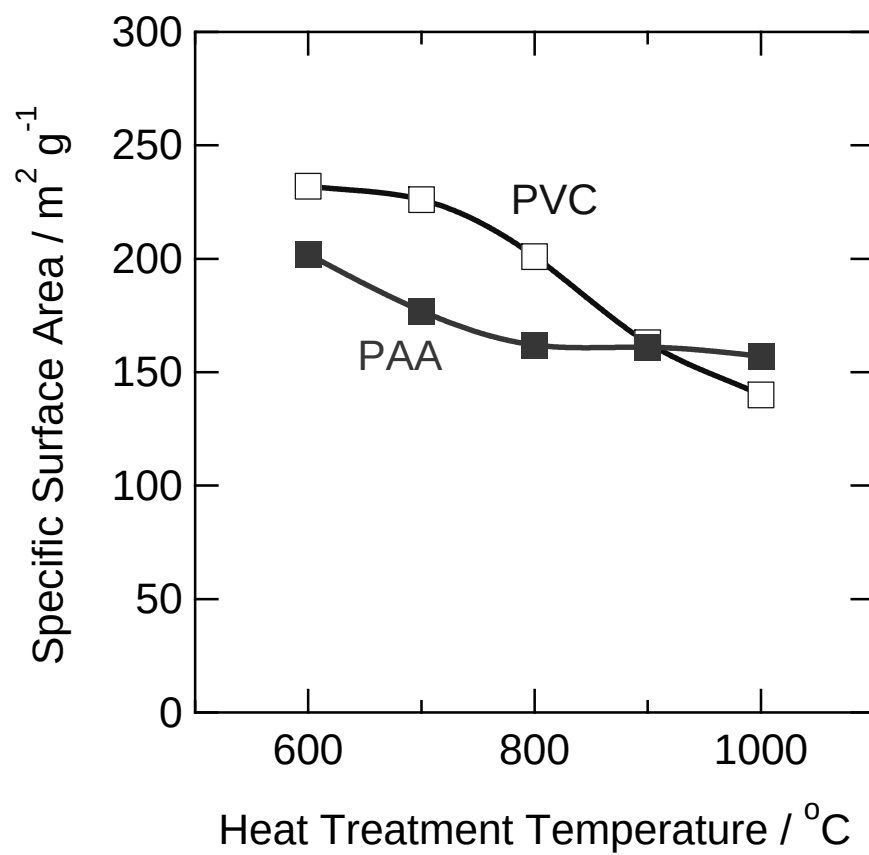


Fig. 4 Change in specific surface area of the nanocarbons derived from PAA and PVC with heat treatment temperature.

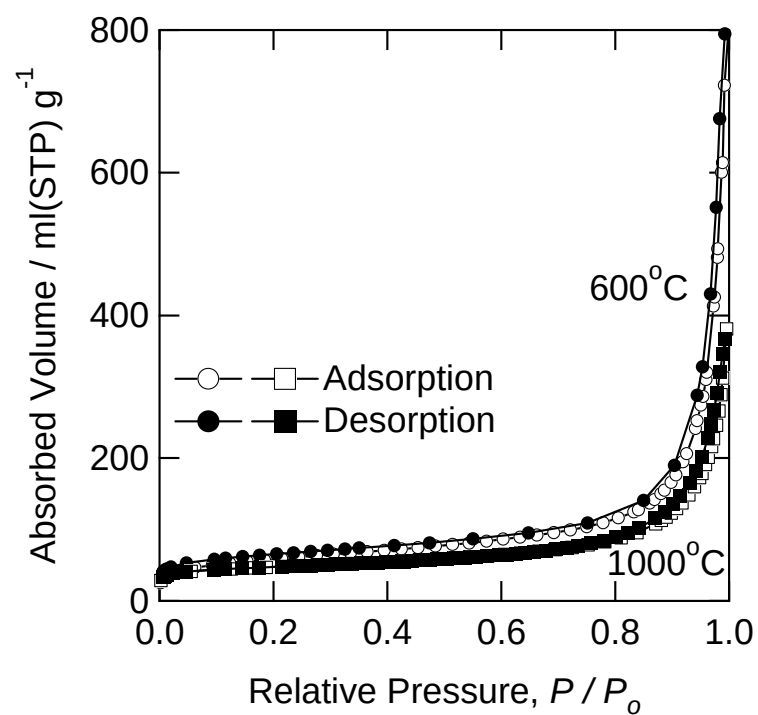


Fig. 5 Nitrogen adsorption/desorption isotherms of the PAA-derived nanocarbons heat treated at 600 and 1000°C.

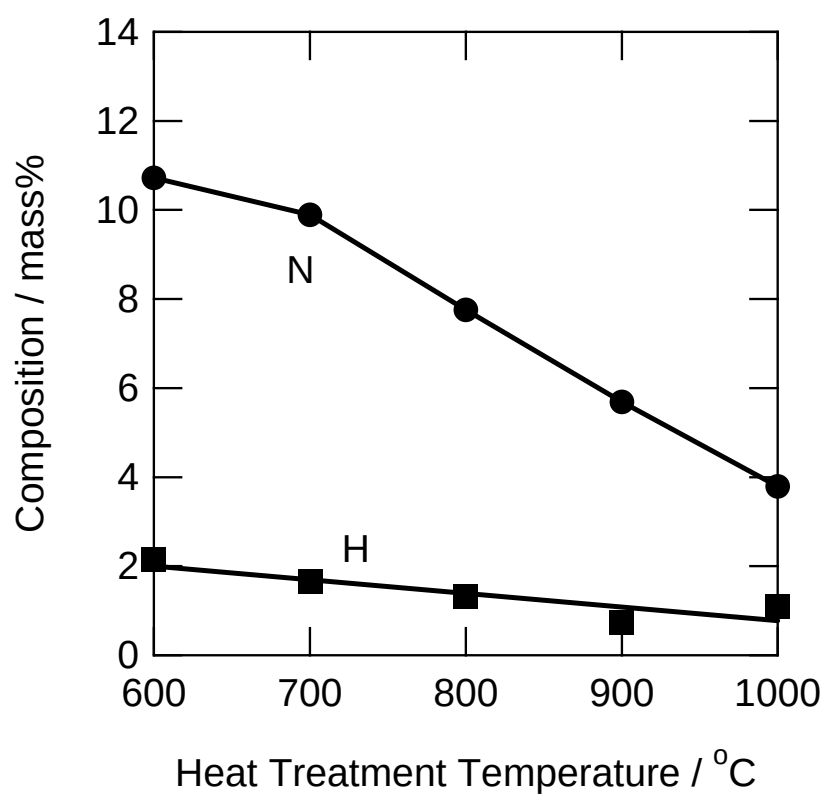


Fig. 6 Change in nitrogen and hydrogen contents in the PAA-derived nanocarbons with heat treatment temperature.

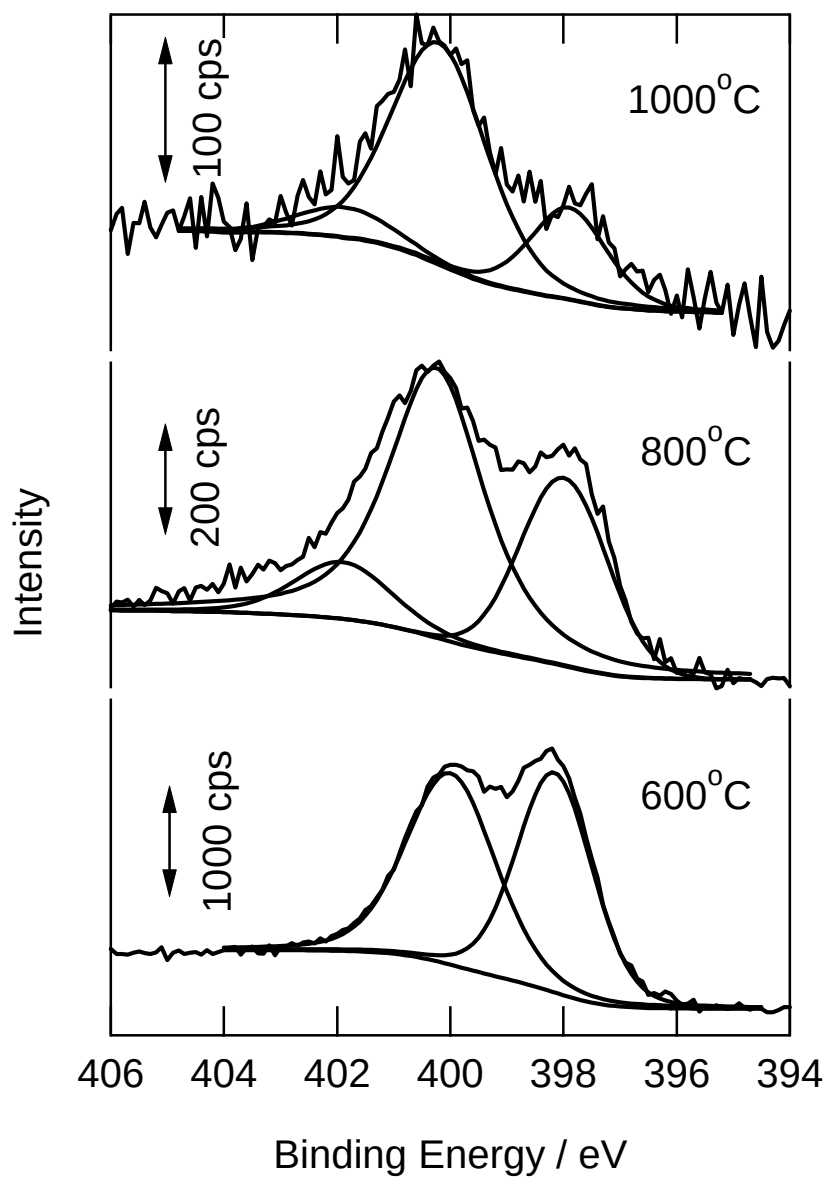


Fig. 7 N 1s X-ray photoelectron spectra of the PAA-derived nanocarbons heat treated at 600, 800 and 1000°C.

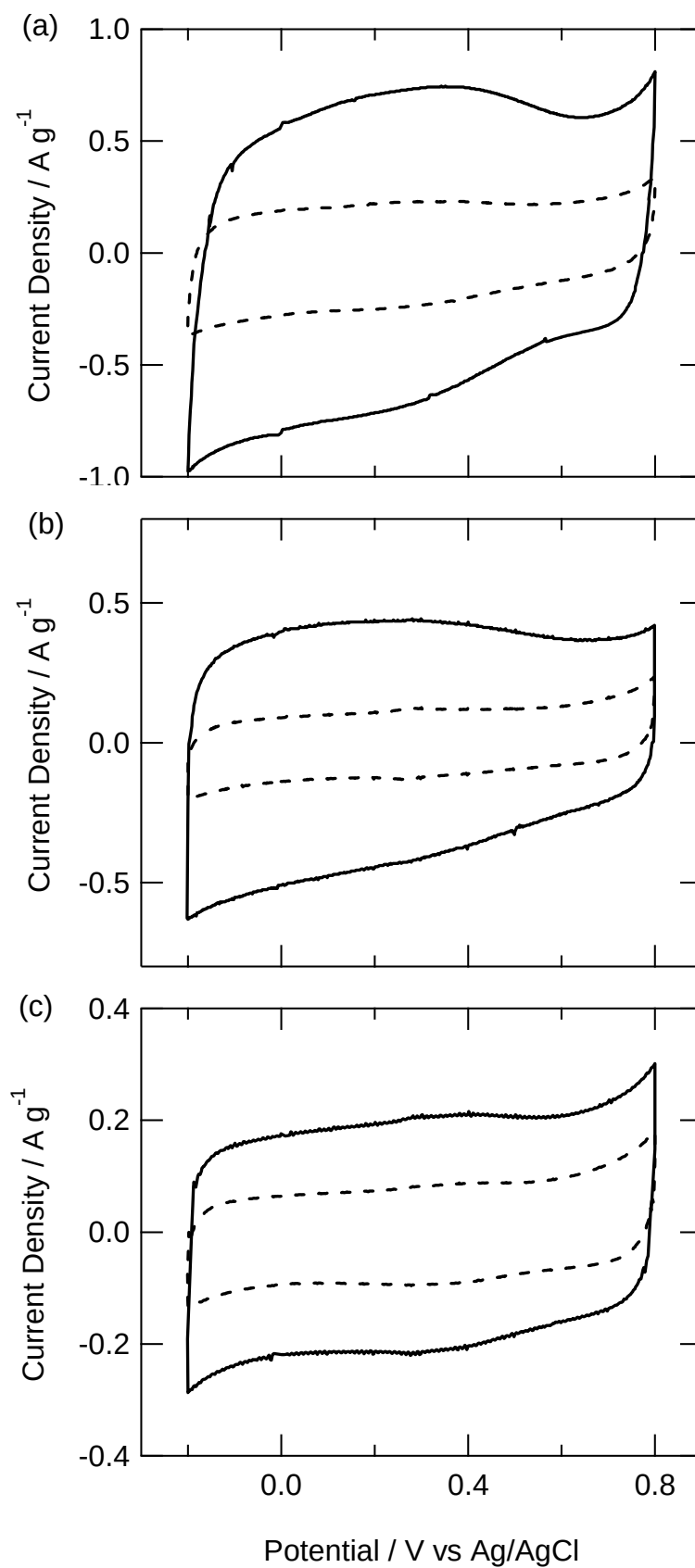


Fig. 8 Cyclic voltammograms of the PAA (solid line)- and PVC (dashed line)-derived nanocarbons heat treated at (a) 600, (b) 800 and (c) 1000°C, measured in 1 mol dm⁻³ sulphuric acid electrolyte.

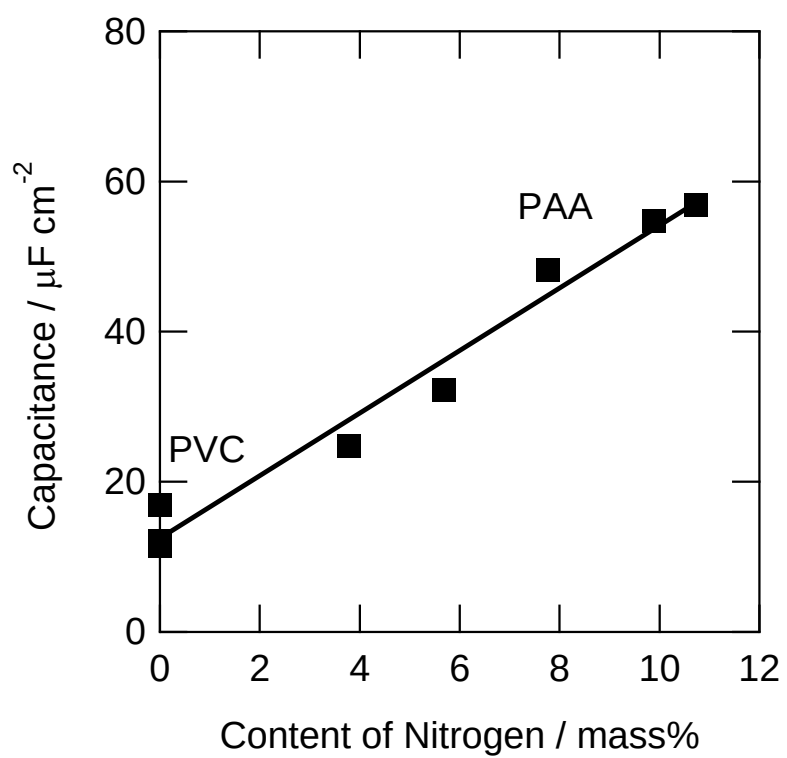


Fig. 9 Change in the capacitance per specific surface area of the PAA- and PVC-derived nanocarbons with the content of nitrogen.

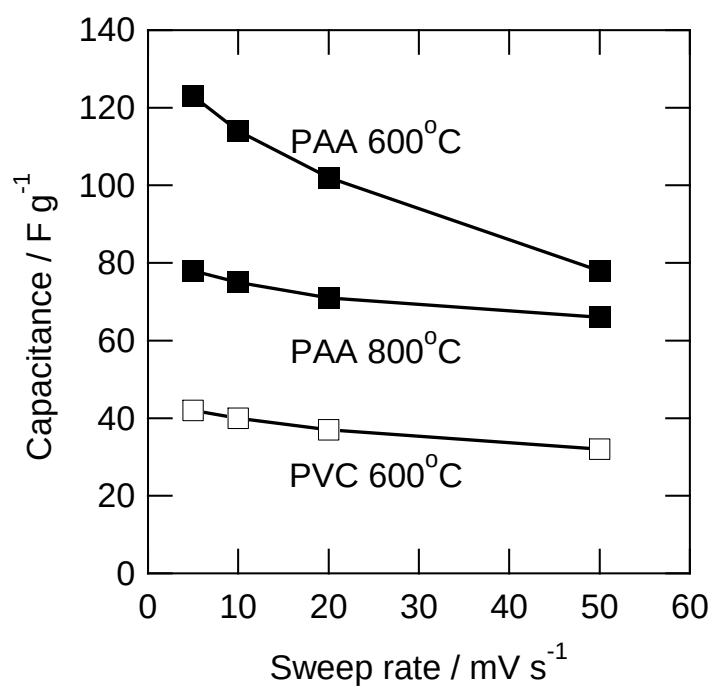


Fig. 10 Sweep rate dependence of the capacitance of the PAA-derived nanocarbons heat treated at 600 and 800°C and of the PVC-derived nanocarbons heat treated at 600°C.

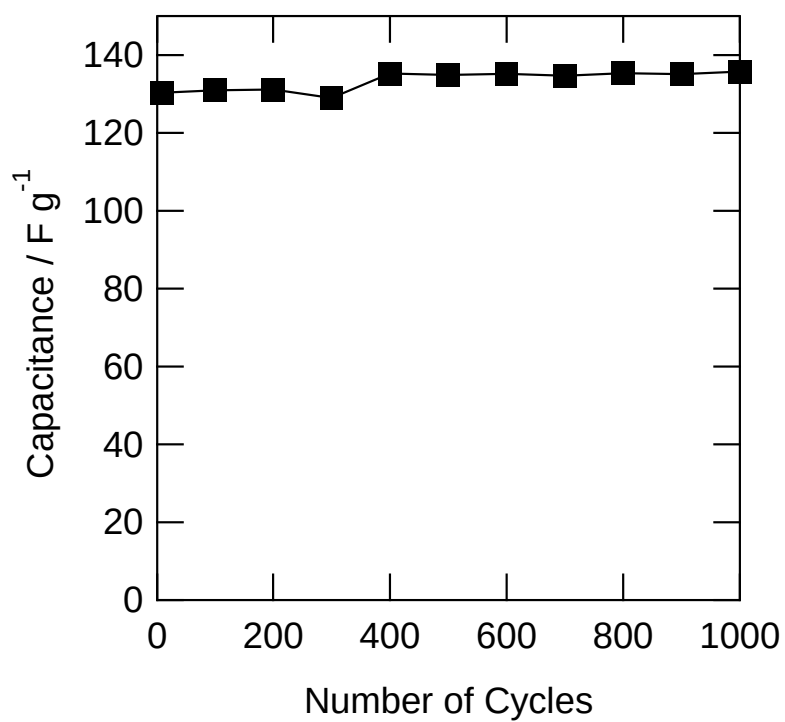


Fig. 11 Cycle stability of the capacitance of the PAA-derived nanocarbons heat treated at 600°C. The capacitance was measured by repeated galvanostatic charge-discharge measurements in 1 mol dm⁻³ sulphuric acid electrolyte at a current density of 0.5 A g⁻¹.