PREPARATION OF NITROGEN-ENRICHED CARBON MATERIALS FROM PEPTIDES OF SILK FIBROINS AND THEIR APPLICATION TO SUPERCAPACITORS

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ABSTRACT

Nitrogen-containing carbon materials were prepared from *Bombyx mori* silk fibroins by simple heat treatment under inert atmosphere. The source of the nitrogen atoms originates from copious peptide bonds contained in the silk fibroin fibrils. The adequate temperature of the heat treatment turned over the nitrogen atoms of the peptide bonds to the silk-based carbons in the form of nitrogen-containing functionalities. Furthermore, the activation processes of the silk-based carbons with steam and potassium hydroxide provided nitrogen-containing activated carbons (ACs) with different pore-size distribution. In the application to an electric double layer capacitor, silk-based ACs activated by steam showed good volumetric capacitance which is comparable to phenol-based AC activated using KOH. Especially, it is suggestive that the functional groups including the nitrogen can withstand in the high voltage regime, that is, nitrogen containing carbon shows good stability on electro-oxidation reaction. Moreover, steam activation on silk fibroin is useful with high capacitance in terms of volumetric consideration, and it greatly contributes to reduce the production cost.

Keywords; *Activated carbon, Electrochemical properties, Electrodes*

1. INTRODUCTION

Most of the carbon materials, which are common active materials for EDLCs, have the functional groups containing many heteroatoms (such as oxygen, nitrogen, sulfur and halogen) with a certain fraction, due to the residual surface-valence of carbons. The presence of these functionalities gives carbon materials an acid-base character, which enhances their capacitance by the pseudo-capacitive effect. Recently, many research groups have focused on nitrogen-rich carbon materials due to their potential for wide applications such as electrodes for EDLCs [1-2], lithium secondary batteries [3-4], catalyst supports [5-6], and specific adsorbents for hydrogen sulfide [7]. The most common way of preparing nitrogen-rich carbon materials is the simple heat-treatment (HT) of suitable nitrogen-containing polymeric precursors.

The most important factor in the commercialization of certain device can be said as a proper cost, but the superior performance is also required to differentiate from conventional devices. Here we show the significance of a novel nitrogen-rich carbon material, 'silk carbon', prepared from silk fibroins as a starting material of nitrogen-containing activated carbons (ACs). With the steam activation, silk carbon shows remarkable capacitance in volumetric consideration. Furthermore, comparing with the activation process using KOH, steam activation can make it simple the process and reduce the cost.

In this work, four kinds of silk carbon-based ACs were prepared by two activation methods using steam and potassium hydroxide (KOH). All silk carbon-based ACs show a high volumetric capacitance and an excellent stability at the high voltage regime. These results are emphasized that steam-activated silk carbons are promising electrode materials of EDLCs for a next generation.

2. EXPERIMENTAL

Bombyx mori silk fibroin (Shinano Kenshi Co. Ltd., Japan) was used as a starting material for nitrogen-containing carbons. The silk carbon was further used for the preparation of activated carbons (ACs). To get a sufficient porosity on silk carbons, activation process has carried out using saturated steam and a chemical (KOH). After bleaching sericin (silk glue), silk fibroins were primarily heat-treated at 500 (sample SC-500) and 700 ^{o}C (sample SC-700) for 6 h under inert nitrogen (N_2) atmosphere using a pilot-plant scale furnace (0.7 m in dia. and 1.6 m in length, Tokai Konetsu Kougyo Co., Ltd., Japan). The resulting silk carbon was ground to fine powders by a ball-mill method to uniform the particle size (*ca.* 10 μm in diameter). In order to inspect the effect of the pre-heat treated temperature (HTT) on the evolution of porosity by activation steps, the sieved silk carbons, SC-500 and SC-700, were activated (0.6 m in dia. and 1.5 m in length, Tokai Denki Co., Ltd., Japan) under saturated steam at 850 ^{o}C (sample No. 1 and No. 2, respectively). The chemical activation using KOH

was carried out with a laboratory scale furnace (3 mm in dia. and 1m in length). The SC-700 samples were mechanically mixed with four-fold amounts of KOH (weight ratio, KOH/silk carbon = 4) and then heated individually at 700 ^{o}C (sample No. 3) and 800 ^{o}C (sample No. 4) for 2 h. The heating rate was 10 ^{o}C/min and all processes were conducted under an inert N_2 flow of 500 ml/min. The resulting activated product was cooled to room temperature under an ambient condition, and then washed repeatedly with deionized water (Iuchi, IP-315N2, Japan) to remove the KOH and organic/inorganic residues until the pH of the filtrate reached *ca*. 7. The obtained sample was dried under reduced pressure at 82 ^{o}C for 24 h. As a standard, a typical phenolic resin-based activated carbon (AC-phenol, Nisshinbo, Japan) with 2200 m^2/g of Braunauer-Emmet-Teller (BET) surface area was employed.

The sample amount for electrochemical measurement is fixed at 40 mg for one electrode. An electrode is consists of AC and binder (95:5). Teflon, PTFE, was used as a binder, and carbon black was not added. The mixture were pressed into disk shapes (diameter: 13 mm, thickness: *ca.* 0.4 mm) using a steel mold at 73.8 MPa. The capacitor consisted of a couple of electrodes which were arranged face to face and a separator (glass paper, Oribest Co. Ltd.) was inserted between the two electrodes. A glassy carbon was used as a current collector. The electrolyte used in this work was a non-aqueous electrolyte, *i.e.*, 1 M of tetraethylammonium tetrafluoroborate, $(C_2H_5)_4NBF_4$, mixed with propylene carbonate (PC). In order to inspect the stability in high voltage regime, charging voltages were limited to 3.0 V. The capacitance (C) of the electrodes was calculated by using galvano/potentiostat with constant current method, which follows equation (1) ;

$$C = (I \times \Delta t)/(W \times \Delta V) \text{---------- (1)}$$

,where I is the current at discharge, Δt is the time variation, ΔV is the voltage variation from the 40% to 60 % of its initial voltage, and W is the sum of the weight of both electrodes. Cyclic voltammograms (CVs) were recorded on Hokuto Denko HZ-3000 instrument. In order to confirm the stability of the electrolyte at high voltages, all CVs were scanned up to 4V in the vicinity of the decomposition of PC, after the previous cycle to obtain the stabilized cycle.

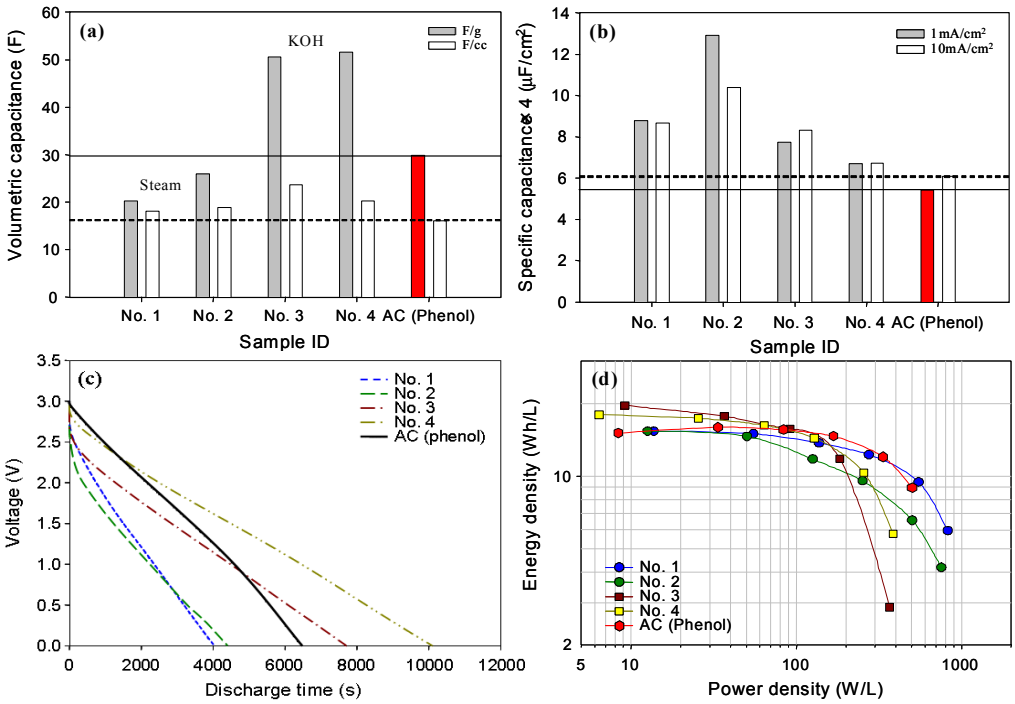

Figure 1. The capacitor properties of silk carbon-based ACs and the standard; the gravimetric and volumetric capacitances (F/g, F/cc) (a) and the capacitance per unit area (μF/cm^2) (b) at 1 and 10 mA/cm2 of the discharge current densities, the discharge profiles at the 1mA/cm^2 of the current density (c), and the Ragone plots based on the volumetric dimension (d). All data were obtained by charging up to 3.0 V.

3. RESULUTS AND DISCUSSION

Figure 1 shows the capacitor properties of the silk carbon-based ACs and the standard phenolic resin-based AC. The amounts of capacitive charge were shown in terms of gravimetric (Fig. 1(a)) and volumetric consideration (Fig. 1(b)). The voltage vs. time curves at 1mA/cm^2 have compared respectively. All measurements for the capacitive properties were performed after the stabilization which was conducted with the repeated cycles at 10 mA/cm^2. In appreciating the capacitor properties of the silk carbon-based ACs, the activation method becomes one of significant factors because it greatly contributes to the lowering of the cost in mass production. In this sense, the steam activation is a more profitable procedure due to the low operating cost, as well as its simplicity and safety. The histograms in Fig. 1 (a) represent the capacitance based on weight and volume at the discharge current density of 1 mA/cm^2, when it is charged up to 3.0V. In comparison with the standard (phenolic resin-based AC), which would be prepared by KOH activation, (its specific surface area is as high as 2200 m^2/g), the steam-activated silk carbons (No. 1 and No. 2) have smaller capacitance in gravimetric unit, whereas the KOH-activated silk carbons (No. 3 and No. 4) have the nearly doubled gravimetric capacitance (No. 3 and No. 4 samples: 51 and 52 F/g, respectively, the standard: 30 F/g). More importantly, all silk carbon-based ACs have shown larger volumetric capacitance than that of the standard, which is greatly advantageous in their application to the industrial products with limited space. It should be noticed that the samples No. 1 and 2 prepared by steam activation have higher values in volumetric capacitance which is advantageous to cut down the production cost. In order to examine the accessibility of ion penetration, capacitances per unit area (μF/cm^2) at 1 and 10 mA/cm^2 have been calculated on the basis of the specific surface area (b). The specific capacitances reported in many literatures have no consistency because of the difference in the measurement methods and the configuration of cells, *i.e.*, there are many methods such as electrochemical impedance spectroscopy (EIS), cyclicvoltammograms (CV), etc. Also, the configuration for the measurement, whether it is based on two- or three-compartment systems, is very important point in calculation of the capacitance. The data consistency between two- and three-electrode systems can be obtained by multiplying the capacitance in two-electrode system by 4. Thus, the specific capacitances obtained by using two-electrode system in this work are presented as the values multiplied by 4. In fact, the specific capacitance (*ca.* 5.5 μF/cm^2 at 1 mA/cm^2) of the standard is well consistent with the values reported in references. All the values of specific capacitance for the silk carbon-based ACs are superior to that for the standard (all values are beyond the dotted line). As for the steam-activated samples, the No. 2 prepared at the high pre-HTT exhibited the larger values of capacitance, compared with the No. 1 prepared at the low pre-HTT. In the KOH-activated samples, the lower activation temperature leads to the larger value of specific capacitance. Among all samples, the No. 2 shows the maximum

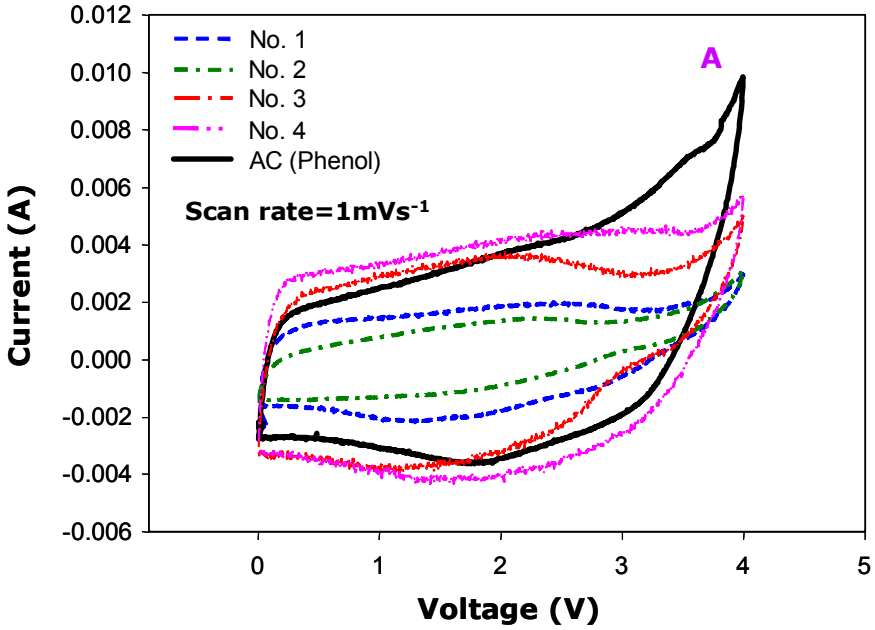

Fig. 2 Cyclic-voltammograms (CVs) of the silk carbon-based ACs and the phenolic resin-based AC as a standard at the sweep rate of 1 mV/s in the two-electrode system with symmetric configuration.

value of ion accessibility (specific capacitance per unit area can imply the accessibility of charged ion), which is twice higher than that of the standard.
Fig. 1 (c) shows the discharge profiles at 1mA/cm^2 of current density. All results show good linearity on discharge, whereas the standard is slightly curved. Furthermore, the Ragone plots based on the volumetric dimension are represented in Fig. 1 (d). The power density (P) and the energy density (E) were calculated by the following equations;

$$P = (V_1 + V_2)/2 \times I = V_0 I - (R + T/2C)I^2 \text{ ---------- (1)}$$

$$E = (V_1 + V_2)/2 \times I \times T/3600 = 1/2C(V_1^2 - V_2^2)/3600 \text{ ---------- (2)}$$

where, V_1 and V_2 represent the initial voltage after the IR drop (R) and the voltage at the end of discharge, respectively. As seen in Fig 1 (d), the KOH-activated sample No. 3 gives the highest value of maximum energy density (max. E = 19.6 Wh/L), whereas the maximum power density is the lowest value of all samples. On the other hand, the steam-activated sample No. 1 gives the highest value of maximum power density (max. P = 824 W/L) and the energy density comparable to that of the standard. It is quite significant that the No. 1 sample prepared by steam activation that is the low-cost, simple and safe exhibits the power property not less than the standard prepared by KOH activation.
Figure 2 shows the cyclic-voltammograms (CVs) of the silk carbon-based ACs and the standard sample at the sweep rate of 1 mV/s in the two-electrode system with symmetric configuration. While the CV profile of the standard sample gradually increases as the voltage increases, the silk carbon-based ACs clearly show better stability on the application of high voltages. To the best of our knowledge, this work has first confirmed the stability of nitrogen-containing carbons against electro-oxidation, although its mechanism is not clear. The observed slight tilt of the CV characteristics can be interpreted by some parasitic reactions, which are probably due to the heteroatoms in the silk carbon-based ACs.

4. References

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