

Chemical activation and hydrogenation of mesophase pitch-based carbon fibers

Yong-Jung Kim, Yohei Horie, Shinya Ozaki, Yutaka Matsuzawa, Byung-Ju Lee, Goro Nakao, Morinobu Endo*

¹Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano, 380-8553, Japan

Corresponding author e-mail address: endo@endomoribu.shinshu-u.ac.jp

Introduction

During the past decades, various types of carbon materials have been investigated as electrode materials for supercapacitor (high performance Electric Double-Layer Capacitor (EDLC)) which has adopted a porous carbon material with high specific surface area as an active material for an electrode [1-4]. Among them, the mesophase pitch-based carbon materials have a characteristic property in an activation process. Although they have no sufficient porosity by the physical activation methods (i.e., with steam, CO₂, etc.), a sufficient specific surface area with exceeding 2000m²/g can be obtained by chemical activation. Recently, in terms of the practical availability of commercial capacitors, it has been considered that the deterioration of the capacitance performance is attributed to the chemical reaction on the surface of carbon active materials in continuous charge/discharge cycles [5]. Furthermore, the resultant gas evolution causes the burst of capacitor cell. With regard to specific capacitance with high current density, therefore, it is important to enhance the cell performance and coulombic efficiency (cell stability) and remove the gas evolution by repetition of the charge/discharge cycle. To realize this, activated-milled mesophase pitch-based carbon fibers (AC-mMPCFs) were heat-treated under hydrogen atmosphere to exhibit superior performance of capacitance on stability and high current property. In this study, the effect of the chemical activation of milled mesophase pitch-based carbon fibers and the hydrogenation of AC-mMPCFs when used as a capacitor electrode are clarified.

Experimental

The mesophase pitch based carbon fibers (the average diameter is 14 μm) were obtained by a melt-blown method from a mesophase pitch with a softening point of 290 °C. After stabilization under air, the carbonization was performed at 650 °C. Moreover, these carbon fibers were milled mechanically and their mean length was selected to be about 25 μm. Then, the fibers were mixed well with potassium hydroxide (KOH) as an activator. The temperature ramp-up for the activation was carried out at a fixed rate of 5 °C/min in a nitrogen flow, and each sample was maintained for 2 h at 700 °C. After activation, the sample was cooled in a nitrogen flow. The samples obtained were washed with deionized distilled water to eliminate the remaining KOH, and finally they were dried at room temperature. In order to clarify the hydrogenation effect, the AC-mMPCF (mixing

ratio 4) with the largest specific surface area was adopted. Hydrogenation was carried out in a 30ml/min hydrogen flow at the same temperature, 700°C, as that of the heat-treatment for activation in order to prevent structural development caused by the heat-treatment at higher temperature.

The nitrogen adsorption isotherms were measured at liquid-nitrogen temperature using ASAP 2010 (Micromeritics, USA). The specific surface area was determined by the multi-point Brunauer-Emmett-Teller (BET) method. Moreover, pore volume, pore diameter, and pore size distribution were obtained by diverse methods.

The difference surface composition and surface structure of the hydrogenated and the AC-mMPCF were examined by X-ray photoelectron spectroscopy (XPS) with ESCA-850 electron spectrometer (Shimadzu). The measurement was performed with MgK α under a vacuum pressure $<10^{-6}$ Pa at room temperature. The acceleration tension and emission current of the nonmonochromatized X-ray source are 7kV and 30mA, respectively. The XPS spectra of two samples which hydrogenated and non-hydrogenated were calibrated using the C1s peak (284.6 eV). The measured peak areas (count s^{-1}) were corrected using the corresponding sensitivity factors in order to get quantitative data.

Results and Discussion

Figure 1 shows the N₂ adsorption-desorption isotherms of AC-mMPCF using 400wt. % KOH addition (400-mMPCF) and the sample obtained by heat treatment under a hydrogen atmosphere at 700°C (400-mMPCF-H2). Here, the abscissas are expressed by linear (a) and logarithm (b) of the relative pressure (P/P_0). The nitrogen adsorption isotherms obtained from the both are of the type I with no hysteresis and it shows no considerable difference, suggesting the preservation of uniform microporosity after the hydrogenation accompanying an additional heat treatment. In order to elucidate the micropore structure of the samples, the adsorption data in an extremely low region of relative pressure P/P_0 should be considered in detail. Fig. 1(b) presents well the details of the adsorption behavior in the low relative pressure, clearly showing that the beginning point of N₂ adsorption is in the vicinity of $P/P_0 = 10^{-6}$. Although there is a slight difference near unity, adsorption behavior of the both samples is almost the same. Thus, it can be concluded that the microporosity of the samples is independent of the hydrogenation, even though there is a possibility that the pore in the range of macro is affected by the additional heat-treatment. In Table 1, the results obtained from nitrogen adsorption were summarized in detail.

The surface nature is of great importance to prevent the side reaction which causes deterioration such as gas evolution, increase in the internal resistance and reduction of stability. In order to examine the chemical state on the surface, the XPS analysis was performed for both 400-mMPCF and 400-mMPCF-H2. The resultant XPS C1s and O1s spectra are shown in Fig. 2. Both of the samples exhibited large peak around 284.6 eV, which are attributed to the sp² carbon atoms of their lattice structure (Fig. 2 (a)). However, there is a clear difference in the range of 287 ~ 290eV. The peaks in this range are attributed to functional groups containing carbon and oxygen atoms, such as O=C-O (~288.6 eV), C=O (~286.8 eV), and C-O (~286.0 eV) [6]. It is considered that the disappearance of the peak in the range would be resulted from the reduction of the functional groups by hydrogenation. To confirm this, the O1s spectrum was examined ar-

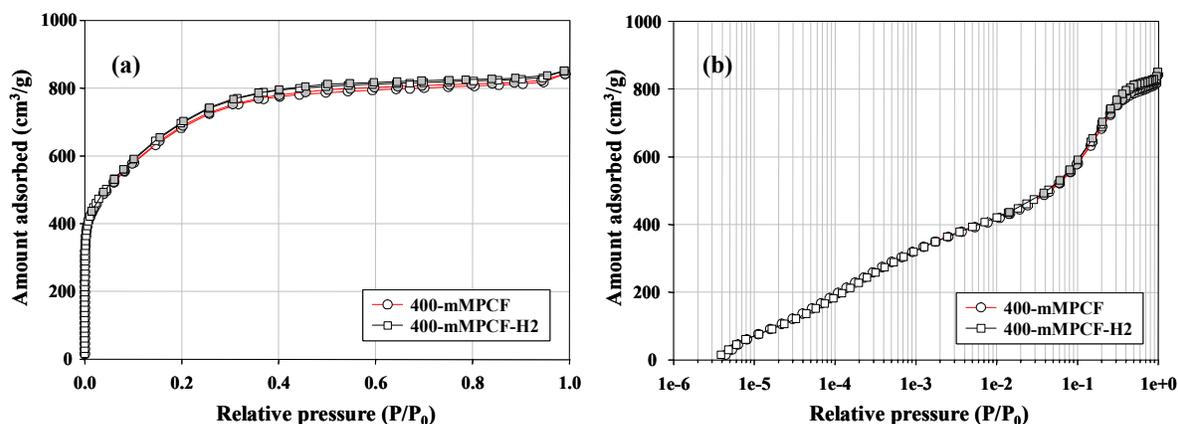


Fig. 1. N₂ adsorption-desorption isotherms of milled MPCF activated with 400wt. % KOH addition (400-mMPCF) and the sample obtained by heat treatment under a hydrogen atmosphere at 700 °C (400-mMPCF-H2). The abscissa is expressed by linear (a) and the logarithm (b) of the relative pressure (P/P₀).

Table 1. The results obtained from nitrogen adsorption at 77K.

Sample ID	SSA ¹⁾	Total pore volume ²⁾	Micropore volume ³⁾	Average pore diameter ⁴⁾
400-mMPCF	2300	1.302	0.082	22.6
400-mMPCF-H2	2353	1.316	0.059	22.3

1) SSA; Specific surface area (m²/g), 2) at the relative pressure of 0.9907, cm³/g, 3) cm³/g, 4) Å

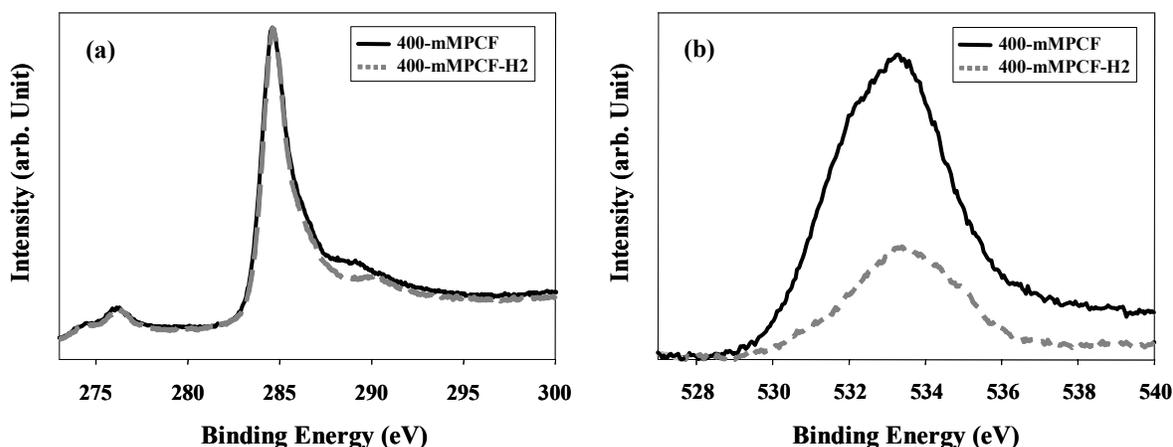


Fig. 2. XPS spectra of the hydrogenated and the non-hydrogenated. (a) C1s, (b) O1s.

und 532.8 eV. As shown in Fig. 6(b), and C-O (~286.0 eV) [6]. It is considered that the disappearance of the peak in the range would be resulted from the reduction of the

functional groups by hydrogenation. To confirm this, the O1s spectrum was examined around 532.8 eV. As shown in Fig. 6(b), the peak intensity of the O1s spectrum was drastically reduced, indicating the removal of oxygen atoms from the surface by hydrogenation. It is therefore concluded that the distinction between the surface compositions of 400-mMPCF and 400-mMPCF-H₂ is ascribed to reductive removal of oxygen atoms from the functional groups by hydrogenation. Alternatively, hydrogenation is an effective approach for the elimination of oxygen-containing functional groups.

Conclusions

The effects of the chemical activation and the subsequent hydrogenation of milled mesophase pitch-based carbon fibers on the performance of the capacitor electrodes prepared from them are clarified. As a result, it turned out that potassium hydroxide (KOH) is fairly effective as an activator to obtain enough porosity on mesophase pitch-based carbon fiber. A high activation reaction yield and a high specific surface area could be obtained. Moreover, the hydrogenation effect on the capacitance behavior of 400-mMPCF, i.e., milled mesophase pitch-based carbon fiber activated with 400wt. % of KOH addition, was confirmed. Hydrogenation did not affect pore structure of the samples, but changed only surface chemical structure. For the purpose of the enhancement of cell performance regarding specific capacitance at high current-density and coulombic efficiency (cell stability) on repeating charge/discharge cycles, hydrogenation is an extremely valuable approach, and the sample hydrogenated shows excellent properties on capacitance uptake. From the practical viewpoint of manufacturing the commercial products, consideration to control the functional group suggest one of the tailoring method to obtain the final target.

References

- [1] I. Tanahashi, A. Yoshida, A. Nishino, *J. Electrochem. Soc.* **137** (1990) 3052-3057.
- [2] I. Tanahashi, A. Yoshida, A. Nishino, *Carbon* **28** (1990) 477-482.
- [3] K. H. An, W. S. Kim, Y. S. Park, J. M. Moon, D. J. Bae, S. C. Lim, Y. S. Lee, Y. H. Lee, *Adv. Funct. Mater.* **11** (2001) 387-392.
- [4] B. Zhang, J. Liang, C. L. Xu, B. Q. Wei, D. B. Ruan, D. H. Wu, *Materials Letters* **51** (2001) 539-542.
- [5] B. E. Conway, *Electrochemical Super Capacitor; Scientific fundamentals and technological applications*, Kluwer Academic/Plenum Publishers (1999)
- [6] Soo-Jin Park, Joong-Seong Jin, *J. Colloidal and Interface Science* **236** (2001)155-160