High Electroconductivity of Wood Char Obtained by Iron-catalyzed Carbonization

Tsutomu Suzuki,[1] Hiroshi Matsuzaki,[1] Kyoko Suzuki,[1] Yukie Saito,[2] Sei-ichi Yasui,[3]
Noriyasu Okazaki,[1] and Tetsuo Yamada[1]
[1]*Department of Applied and Environmental Chemistry, Kitami Institute of Technology,*
165 Koen-cho, Kitami, Hokkaido 090-8507
[2]*Graduate School of Agricultural and Life Sciences, The University of Tokyo,*
1 chome, Yayoi, Bunkyo-ku, Tokyo 113-8657
[3]*Agricultural Research Institute, Zukosha Co., Ltd.,*
Nishi 18 Kita 1-17, Obihiro, Hokkaido 080-0048

(Received April 15, 2008; CL-080394; E-mail: suzuki@serv.chem.kitami-it.ac.jp)

A disk specimen prepared from char obtained by carbonizing 3 wt % iron-loaded larch at 850 °C was superior and comparable to those from acetylene black and Ketjenblack, respectively, in electroconductivity. Subsequent soaking of the wood char in a diluted acid for removal of the metal led to improvement in the quality to surpass the level of Ketjenblack. Also, the carbonization with 3 wt % iron at 850 °C was more effective than that with 2 wt % nickel at 900 °C for enhancing the conductivity. The more favorable catalysis of iron can be elucidated by the formation of finer nanocarbon particles with higher mesoporosity to compensate for the less crystallinity.

As is well known, wood charcoal obtained by conventional carbonization at 400–500 °C is amorphous and poor in electroconductivity. Even with 1000 °C char, the conductivity is still low. For acquiring the capacity adequate for utilization as the filler, higher temperature than 1500 °C is probably required with a view to promoting the graphitization of char carbon.[1] On the other hand, carbonization of wood impregnated with 2 wt % nickel at temperature as low as 900 °C could serve the purpose.[2,3] This is because the catalytic activity of nickel was so high as to effectively produce crystallized carbon called T component. The easy production of such a value-added char has an important significance in advanced utilization of the typical carbon-offset resource. Nevertheless, the substitution of iron catalyst for nickel catalyst is industrially and environmentally desirable on account of generally lower cost and much less danger to human health for the former. Although the smaller effect of iron on the formation of T component may be handicapped, the crystallinity of carbon is not the only factor governing the conductivity: poorly crystallized Ketjenblack has a very high conductivity due to the unique structure composed of hollow-shell fine particles.[4] This motivated the present study examining the relevant property of iron-loaded char.

$Fe(OH)(CH_3COO)_2$ was added to powdered Japanese larch with diameter of 0.6–1.4 mm as the wood material by aqueous impregnation to adjust the content of iron as metal to 3 wt %. $Ni(CH_3COO)_2\cdot 4H_2O$ was also impregnated to make 2 wt % nickel contain. After vacuum drying, these metal-loaded woods, as well as raw wood, were carbonized at 850 and 900 °C for 1 h in a flow of N_2. Obtained chars were designated like U–Fe$_{850}$, U–Ni$_{900}$, U–None$_{900}$, etc. U–Fe and U–Ni were soaked in 1 M HNO_3 with stirring at room temperature for 12 h for removal of each metal, and the acid-treated chars were termed A–Fe and A–Ni. All of chars were then pulverized in a planetary ball mill (FRITSCH P-7) after mixing with smaller larch powder (0.3–0.6 mm in diameter) and distilled water to mold a disk, with 40 mm and 2.3 ± 0.1 mm in diameter and thickness, respectively, for measuring volume resistivity (Dia Instruments, Loresta-GP with a four point probe). In the pulverization, the mixture of 1.5 g of char, 2.5 g of wood powder, and 1–2 g of water were rotated together with agate balls of 15 mmϕ at 630 rpm and 2×10 min. Subsequent molding of the pulverized mixture into the disk was made in a stainless vessel by hot press at 140 °C and 200 kgf·cm^{-2} for 20 min. Similar pulverization and molding were applied to commercially available conductive carbon, Denka black (DB, a sort of acetylene black) and Ketjenblack EC (KB) having medium and excellent conductivities, respectively, for comparison. Prior to molding, 50% mean particle diameter (D_{50}) for each pulverized mixture was calculated from the size distribution measured by laser diffractometry (FRITSCH Particle Analysett 22). After molding, disk samples were weighed to check the density. All of carbon specimens were characterized in terms of the crystallinity evaluated by X-ray diffraction (XRD, Rigaku RINT 1200) and pore structure determined from adsorption and desorption isotherms of N_2 at −196 °C (ThermoQuest Sorptomatic 1990), in addition to the content of each metal before and after acid-soaking. The detailed manners and procedures of these measurements were given elsewhere.[5] Furthermore, fine structure was observed for U- and A-chars by TEM (JEOL Model 2000 EX).

Figure 1 illustrates XRD profiles of typical U- and A-chars, DB, and KB. As iron has a larger mass absorption coefficient

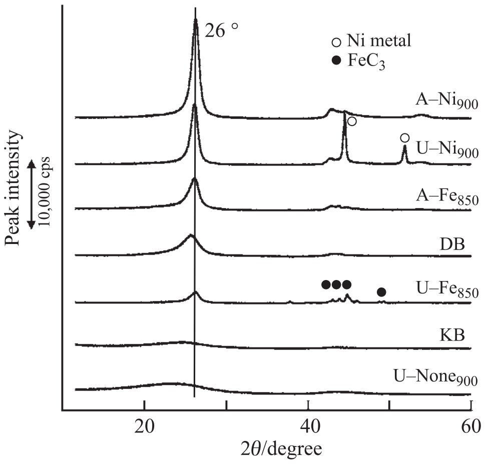

Figure 1. XRD profles of several U- and A-chars, DB, and KB.

Table 1. Pore properties of carbon specimens

Specimen	Fe or Ni /%	S_{BET}[a] /m^2·g^{-1}	S_m[b] /m^2·g^{-1}	V_m[c] /cm^3·g^{-1}	V_t[d] /cm^3·g^{-1}
U–None$_{900}$	0.0	237	29	0.011	0.069
U–Fe$_{850}$	3.2	274	256	0.245	0.425
A–Fe$_{850}$	0.6	250	248	0.237	0.406
U–Ni$_{900}$	2.1	148	165	0.196	0.318
A–Ni$_{900}$	0.1	151	181	0.206	0.442
DB	—	183	13	0.011	0.056
KB	—	777	574	0.702	1.022

[a]BET surface area, [b]BJH mesopore surface area, [c]BJH mesopore volume, [d]Total pore volume.

(308 cm^2·g^{-1}) than nickel (46 cm^2·g^{-1}), Fe-char usually gives much smaller peaks of carbon than Ni-char. However, the observed difference in the intensity of T component appeared at about 26° between U–Fe$_{850}$ and U–Ni$_{900}$ was larger than the difference predicted by taking the above problem into account. The catalytic activity of iron at 850 °C was thus considered to be smaller than that of nickel at 900 °C. A–Fe$_{850}$ and A–Ni$_{900}$ afforded larger intensity of T component than the corresponding U-chars. This was mainly due to increase in the content of carbon accompanied by the elimination of coexisting metal. The recovery of A-char relative to U-char was over 98% on an ash- and metal-free basis, and no serious loss took place even for disordered carbon. Thus, improvement of the crystallite in orientation cannot be denied as an additional reason for the increased intensity.[5] Consequently, the crystallinity of carbon was estimated to be U–None$_{900}$ and KB < DB < U–Fe$_{850}$ < U–Fe$_{900}$ (not shown, thereafter written as "ns") < A–Fe$_{850}$ < A–Fe$_{900}$ (ns) $\ll$ U–Ni$_{850}$ (ns) < U–Ni$_{900}$ $\fallingdotseq$ A–Ni$_{850}$ (ns) < A–Ni$_{900}$. Table 1 summarizes pore structural characteristics of the same specimens as those given in Figure 1, along with the content of iron or nickel. Mesoporosity represented by BJH[6] surface area (S_m) and volume (V_m) was DB < U–None$_{900}$ < U–Ni$_{900}$ < A–Ni$_{900}$ < A–Fe$_{850}$ < U–Fe$_{850}$ < KB. Therefore, iron at 850 °C developed the mesoporous structure to a greater extent than did nickel at 900 °C, although the influence of acid treatment differed for each U-char. The removal of iron was smaller than that of nickel. The inconvenience was probably ascribed to the formation of iron carbide, as recognized in Figure 1. Volume resistivity given in Figure 2 was obtained for disk samples composed of minute particles with 5 ± 1 μm as D$_{50}$ and having the density of 1.30 ± 0.5, 1.07, and 0.90 g·cm^{-3} for wood chars, DB, and KB, respectively, and the conductivity was U–None$_{900}$ $\ll$ DB < U–Ni$_{900}$ < A–Ni$_{900}$ < U–Fe$_{850}$ $\fallingdotseq$ KB < A–Fe$_{850}$. In addition, the following orders held: U–None$_{900}$ $\ll$ U–Ni$_{850}$ (ns) < A–Ni$_{850}$ (ns) < DB and KB $\fallingdotseq$ U–Fe$_{900}$ (ns) < A–Fe$_{850}$ < A–Fe$_{900}$ (ns). Although the conductivity was disadvantageous to DB and KB with lower density, their bulkier and so less compressive properties compared to wood char, responsible for the cause, should be regarded as drawbacks in use as the filler. It is to be noticed that A–Fe$_{850}$ exceeded KB and A–Ni$_{900}$ to have the higher aptitude, verifying that the iron-catalyzed 850 °C carbonization was entirely satisfactory. The difference between U- and A-chars and between 850 and 900 °C for both metals convinced the advantage of the higher crystallinity of carbon, while the difference for U–Fe$_{850}$ and U–Ni$_{900}$ signified a strong dependence on mesoporosity. In brief, the high quality of U–Fe$_{850}$ can be explained by the synergy of the moderate crystallization of carbon and the adequately developed mesoporosity. It is, however, ambiguous whether or not the latter was a much more predominant factor than the former in determining the conductivity. In connection with this, typical TEM images displayed in Figure 3 revealed that U–Fe$_{850}$ and U–Ni$_{900}$ were mainly composed of carbon particles with 30–40 nm and about 50 nm in diameter, respectively, whereas such elemental particles were not formed in None$_{900}$. The individual particle sizes were unchanged by varying the temperature and acid treatment. Because the constitution of fine carbon particles in principle favors the conductivity, the formation of finer nanocarbon with higher mesoporosity may be decisive for the superiority of U–Fe$_{850}$ to U–Ni$_{900}$, although the different catalysis for the two metals is still not fully clarified.

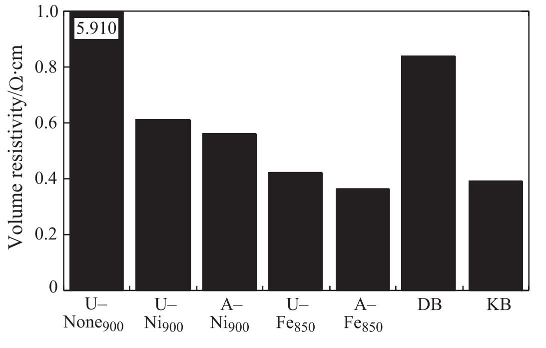

Figure 2. Conductivity of carbon specimens.

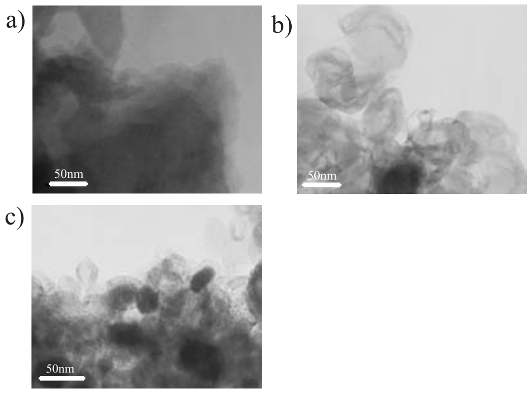

Figure 3. TEM images of a) U–None$_{900}$, b) U–Ni$_{900}$, and c) U–Fe$_{850}$.

This work was supported by a grant of Hatakeyama Foundation, as well as a Grant-in-Aid for Scientific Research (No. 18580159-00) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 S. Ishihara, *Mokuzai Gakkaishi* **1996**, *42*, 717; *J. Soc. Mater. Sci. Jpn.* **1999**, *48*, 473.
2 K. Suzuki, T. Suzuki, Y. Takahashi, M. Okimoto, T. Yamada, N. Okazaki, Y. Shimizu, M. Fujiwara, *Chem. Lett.* **2005**, *34*, 870.
3 T. Suzuki, K. Suzuki, Y. Takahashi, M. Okimoto, T. Yamada, N. Okazaki, Y. Shimizu, M. Fujiwara, *J. Wood Sci.* **2007**, *53*, 54.
4 S. Maeno, *Tanso* **2006**, 140.
5 K. Suzuki, T. Suzuki, N. Takazawa, M. Funaoka, *Holtzforshung* **2008**, *62*, 157.
6 E. P. Barrett, L. G. Joyner, P. P. Halenda, *J. Am. Chem. Soc.* **1951**, *73*, 373.