Preparation of Crystallized and Mesoporous Carbon by Nickel-catalyzed Carbonization of Wood

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Char composed of crystallized carbon (T component) and enriched with mesopore was obtained by carbonization of nickel-loaded wood at 850 and 900 °C for 1 h in a flow of nitrogen, although the corresponding treatment of wood without nickel gave amorphous and microporous carbon. This also disclosed a close relationship between the production of T component and the formation of mesopore. The crystallized and mesoporous wood carbon that can possess a double function of electroconductivity adequate for electromagnetic shielding and adsorption capacity comparable to that of coal-derived activated carbon is a promising high-quality carbon electrode material.

Wood char usually obtained by carbonization at 400–500 °C is lightweight, porous, and insulating. The former two properties are advantageous in the practical use, leading to such applications as soil improver, feed, moisture conditioner, deodorant, decolorant, etc.,[1] in addition to solid fuel. However, the pore structure is unsuitable for adsorbing macromolecules because of occupation by micropore with diameter of < 2 nm for the most part.[2] The porosity remains unchanged[2] with BET surface area (S_{BET}) decreasing[3] when increasing the temperature of carbonization up to 900 °C and above. Although the latter property is declined with raising the temperature, even the char obtained at 900–1000 °C does not have so large electroconductivity as metals[4] because it is still composed of amorphous carbon.[5] These situations imply little contribution of such a high temperature carbonization to wider utilization of wood char. In contrast, 900 °C-carbonization of wood impregnated with $(CH_3COO)_2Ni{\cdot}4H_2O$ can effectively produce electroconductive crystallized carbon (T component), thereby enabling the resulting char to have a practical capacity of electromagnetic shielding (abbreviated as EMS).[6] The high catalytic activity of nickel bringing about a large production of T component may also involve a great change of the porous structure by which adsorption performance can be improved. The circumstances that it is not examined yet motivated the present study to check pore characteristics of nickel-loaded wood chars prepared at relevant temperatures, together with the production of T component. The result disclosed the formation of mesopore (2–50 nm in diameter) in parallel with the crystallization of carbon and thus demonstrated the successful production of a highly value-added carbon with adequate electroconductivity and adsorption capacity in liquid phase by carbonization at 850–900 °C.

Powdered Japanese larch with diameter of 0.5–1.4 mm was employed as the raw wood material. To the wood the nickel precursor was added by wet impregnation in a previous manner.[6] The amount of nickel as metal was adjusted to 2 wt %. After vacuum drying at 50 °C, the nickel-loaded wood of 2 g was packed in a vertical quartz tube reactor to carbonize at 700–900 °C for 1 h in a flow of nitrogen (23.6 mLSTP/cm^2·min). The heating rate was 10 °C/min regardless of the temperature. For reference, raw (none-loaded) wood was heat-treated under the same conditions. All of chars prepared were weighed to obtain their yields on a dry, ash- and nickel-free basis, and then subjected to X-ray diffraction (XRD) with Cu Kα radiation (Rigaku RINT 2000) and measurement of adsorption and desorption isotherms of nitrogen at -196 °C (ThermoQuest, Sorptomatic 1990). For the former XRD, the average crystallite size of carbon corresponding to thickiness (L_c) and peak intensity relative to that of an artificial graphite, Lonza (PRI) were determined from the diffraction line at (002) plane. From the latter nitrogen isotherms, specific surface area and pore distribution were calculated by BET[7] and BJH[8] methods to obtain S_{BET}, BJH surface area (S_{BJH}), BJH total pore volume (V_t), and BJH mesopore volume (V_m). Two mesopore parameters represented by $R_{m,s}$ and $R_{m,v}$, which are defined as the ratio of S_{BJH} to S_{BET}[9] and that of V_m to V_t, respectively, also were evaluated.

Figure 1 illustrates XRD profiles of chars with nickel. It is obvious that a marked production of T component occurred at

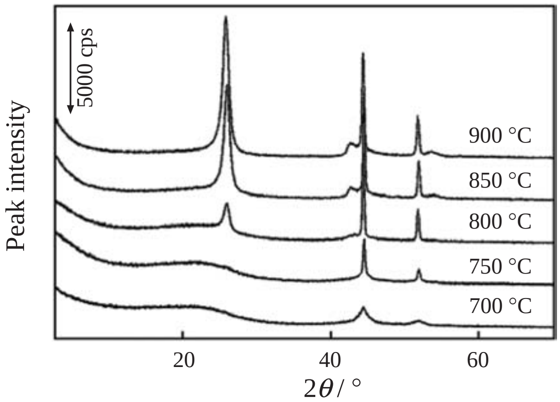

Figure 1. XRD profiles of nickel-loaded chars obtained at various temperatures.

Table 1. Yield, L_c, RPI, and estimated EMS capacity for nickel-loaded wood chars

Carbonization temp./°C	Yield[a] /%	L_c /Å	RPI[b]	EMS[c] capacity
700	24.7	<10	—	impractical
750	24.4	<10	—	impractical
800	24.2	79	4.33×10^{-2}	impractical
850	23.8	91	16.7×10^{-2}	practical
900	23.2	86	20.8×10^{-2}	practical

[a] Dry ash-free, nickel-free basis. [b] Relative peak intensity, see the text. [c] According to the criterion that $L_c > 85$ Å and RPI $> 15 \times 10^{-2}$ are required for practicability. See the text.

850 °C, as well as at 900 °C, as verified by a relatively sharp diffraction line appeared at 26°, whereas none-loading gave amorphous carbon even by 900 °C-carbonization, as is shown elsewhere.[6] For 850- and 900 °C-chars, a small peak was also observed at about 42°, indicating an increased width of carbon crystallite. As is usual, two peaks due to nickel metal at 44 and 51° became sharper for carbonization at higher temperatures. According to our criterion[10] based on L_c and RPI, which are summarized in Table 1 together with char yield, both nickel-loaded 850- and 900 °C-chars were judged to surpass a practical EMS standard of 30 dB in 50–800 MHz. Isotherms of nitrogen adsorption and desorption for nickel-loaded chars indicated that a gap between the two curves at about 0.5–0.9 of P/P_0 was wider for higher temperature. The aspect showed an increased proportion of mesopore with increasing the temperature, while it was not the case with none-loaded chars, as expected from literature.[2]

Figure 2 displays variations of S_{BET}, $R_{m,s}$, and $R_{m,v}$ with the temperature of carbonization. It becomes clear that either mesoporosity given by $R_{m,s}$ or $R_{m,v}$ had a tendency to enhance at the cost of S_{BET}. However, $R_{m,s}$ was inappropriate due to more than 100% for nickel-loaded 900 °C-char. As this ratio has been applied originally for coal chars,[9] its inaptitude may reflect different development of mesopore structure between coal and wood chars. On condition that $R_{m,v}$ is an acceptable parameter, a more noticeable point in this figure is that the value of 83 and 76% and S_{BET} of 188 and 157 m^2/g for nickel-loaded 850- and 900 °C-chars, respectively, were comparable to 89.7% as $R_{m,s}$ and 174 m^2/g for the uppermost mesopore carbon derived from coal with steam activation.[9] This demonstrates that without additional treatment, these nickel-catalyzed carbonization could realize a double function of adequate electroconductivity and high adsorption capacity like activated carbon. The production of such an industrially valuable wood carbon as can be a high-quality carbon electrode material will expand the utilization of wood that is a typical biomass to a greater extent. In Figure 3, V_m and RPI are plotted against carbonization temperature. For nickel loading, the increase of V_m accompanying the decrease of S_{BET} (Figure 2) with increasing the temperature implied coalescence of micropores into mesopores, thereby confirming the development of pore structure quite different from none-loading. It is more important to notice a close relationship between the crystallization of carbon and the generation of mesopore with this Figure. For such a scientifically interesting finding, the detailed mechanism is uncertain at the present stage. This problem is thus to be elucidated by further research.

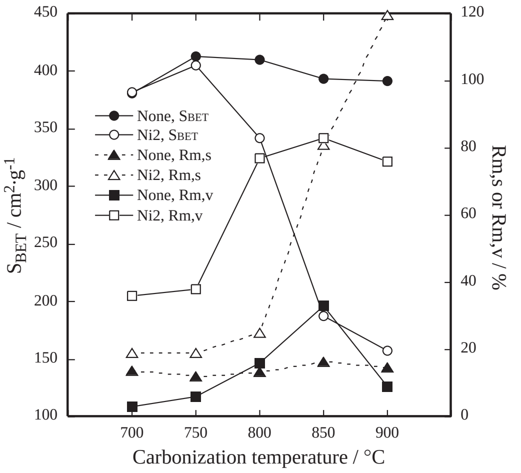

Figure 2. Changes of S_{BET}, $R_{m,s}$, and $R_{m,v}$ with carbonization temperature.

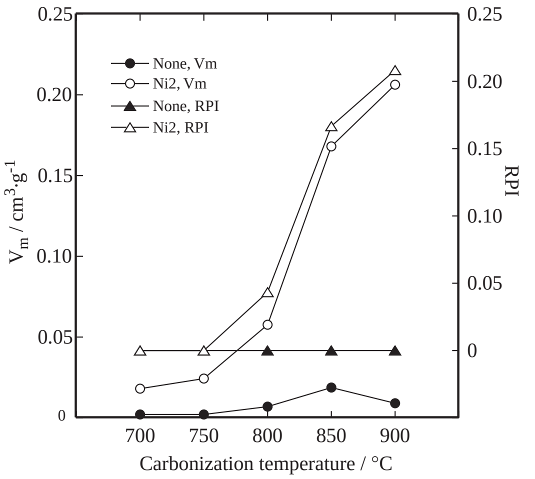

Figure 3. Changes of V_m and RPI with carbonization temperature.

References

1 T. Suzuki, in "Biomass Handbook," ed. by Japan Institute of Energy, Ohmu-sha, Tokyo (2002), p 116.
2 Y. Kurimoto, K. Kano, and O. Sawabe, *Mokuzai Gakkaishi*, **50**, 106 (2004).
3 T. Kitamura, T. Matsumoto, and H. Katayama, *Mokuzai Gakkaishi*, **45**, 171 (1999).
4 S. Ishihara, *J. Soc. Mater. Sci. Jpn.*, **48**, 473 (1999).
5 K. Nishimiya, T. Hata, Y. Imamura, and S. Ishihara, *J. Wood Sci.*, **44**, 56 (1998).
6 T. Suzuki, T. Yamada, N. Okazaki, A. Tada, M. Nakanishi, M. Futamata, and H.-T. Chen, *Mater. Sci. Res. Int.*, **7**, 206 (2001).
7 S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
8 E. P. Barrett, L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).
9 N. Yoshizawa, Y. Yamada, T. Furuta, and M. Shiraishi, *Energy Fuels*, **11**, 327 (1997).
10 T. Suzuki, *Wood Carbonization Res.*, **1**, 68 (2005).