Electroconductivity of Softwood and Hardwood Carbons Prepared by Nickel- and Iron-catalyzed Carbonizations

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Crystallized mesoporous carbon (CMC) prepared by carbonization of softwood (S) and hardwood (H) with 2 wt % nickel and 3 wt % iron were washed with acid, mixed with cornstarch as matrix, and then molded into disk specimens for evaluating electroconductivity. H-derived CMC had higher filler ability than the corresponding S-derived one irrespective of metal species. This can be understood by higher mesoporosity with probably better dispersion in the matrix for the former. CMC derived from iron-loaded H was comparable to Ketjenblack, excellent conductive carbon in the filler ability. Thus combination of H with iron was the most favorable for this purpose.

Key words: crystallized mesoporous wood carbon, iron-catalyzed carbonization, electroconductivity

1. INTRODUCTION

Because of the most abundant biomass of high quality, wood is expected to replace fossil resources as fluid fuels, chemicals, and materials in future. For achieving this goal, highly advanced and innovative technologies of wood utilization are required, as is also needless to say. A primarily important recognition relating to the problem is classification of this resource in two broad categories: softwood (abbreviated as S) and hardwood (H). This is because both wood species differ from one another in (1) cell tissue and size, (2) chemical composition, (3) the nuclear structure of lignin, etc., as noted in Table 1, to result in different distribution and quality of products when treated in chemical and thermochemical processes. For example, it is widely known in usual carbonization at 400-500°C that H affords harder charcoal in a lower yield than does S on account of generally denser cell tissue with thicker secondary wall containing a smaller amount of lignin having lower thermal degradability than hemicelluloses for the former. Such knowledge will notify us that both wood species should be used properly in accordance with their aptitude and the purpose.

As reported in our preceding papers, carbonization of S loaded with nickel at 900°C [1-4] and with iron at 850°C [5,6], respectively, produced crystallized mesoporous carbon (CMC) to exhibit high electroconductivity, or more correctly, filler ability [5,7] and adequate liquid phase adsorption capacity for macromolecules [6,8] through pulverization followed by washing with acid as practical post-treatment. Appearance of the dual function can be elucidated by efficient formation of unique crystal carbon in morphology, denominated graphitic nano shell chain (GNSC) to be displayed below, within the cell wall

Table 1 Main differences for softwood (S) and hardwood (H)

(1) <u>Cell tissue and the size</u> : H comprises a complex tissue of cells with generally smaller size and thicker wall compared to S.
(2) <u>Chemical composition</u> : Approximate proportions of lignin and hemicelluloses are usually 30 % + 20 % and 20 % and 30 % for S and H, respectively.
(3) <u>Nuclear structure of lignin</u> : About 90% of S lignin is guaiacyl (G) type, while H lignin is composed of about 50% G type and 50% syringyl type.

[7,9]. However, the corresponding H-chars are still not produced to check the aptitude for CMC and GNSC.

In the present study, our attention was paid to filler ability of S- and H-derived CMC after washing with acid to clarify what combination of wood and metal species was favorable. For making highly conductive material by blending CMC into a proper matrix, the followings are particularly required for the starting carbon [1]: (i) small elementary particles, (ii) high mesoporosity, and (iii) high crystallinity. Important for the resulting blend is (iv) high dispersion of carbon particles in the matrix. Thus discussion was centered on difference in these factors for the relevant S- and H-chars by considering the relation to points (1), (2), and (3) of Table 1.

2. EXPERIMENTAL

2.1 Raw wood

Raw S was previously employed powder of larch with diameter of 0.5-1.4 mm [4,9]. Raw H was prepared by crushing birch chips to powder with the same diameter as that of raw S.

2.2 Loading of metal precursors

$(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{OH})(\text{CH}_3\text{COO})_2$ as nickel and iron catalyst precursors, respectively, were added to both raw S and H by aqueous impregnation. The amount was adjusted to 2 wt % for nickel and 3 wt % for iron as metal in wood, according to previous results [5-9].

2.3 Carbonization

After vacuum drying, nickel-loaded (Ni-) S and H were carbonized in a downdraft stainless steel tube reactor at 900°C for 1 h in a flow of nitrogen. Carbonization of iron-loaded (Fe-) S and H was performed at 850°C for 1 h. Raw S and H also were carbonized at 900°C for 1 h to obtain control chars, No-SC and No-HC. Char yield was all calculated on a dry ash-free, metal-free basis.

2.4 Washing with acid

Obtained Ni- and Fe-chars were soaked in 1 M HNO_3 with stirring for 24 h at room temperature to remove the metal. After washing with distilled water and drying at 105°C, acid-treated chars, denoted as ANi-SC, ANi-HC, AFe-SC, and AFe-HC, were recovered.

2.5 Properties and morphology of wood chars

For characterizing the crystallinity of carbon and pore structure, X-ray diffraction (XRD) profile and adsorption and desorption isotherms of nitrogen were measured, respectively, in addition to quantification of residual nickel or iron. The details are given elsewhere [2-4]. These measurements were likewise made with two commercial conductive carbons for comparison, Denka black (DB) and Ketjenblack EC (KB) with good and excellent capacities, respectively. Thermogravimetric (TG) curves of wood chars were additionally measured under a flow of the synthetic air up to 800°C to examine their thermochemical stability (ULVAC TGD 9600). The flow rate, the heating rate, and sample weight were fixed at 20 mLSTP·min⁻¹, 2.5°C·min⁻¹, and 20 mg, respectively. The morphology and surface state were observed by FESEM (JOEL JSM-T2000). The SEM observation was furthermore made on atmospherically oxidized chars, OANi-SC, OANi-HC, OAFE-SC, and OAFE-HC, to check the morphological and aggregative feature of each crystal carbon. The atmospheric oxidation for selectively eliminating amorphous carbon was carried out under the same conditions as those described in previous paper [9].

2.6 Pulverization with matrix and molding

All of wood chars and commercial carbons were mixed with cornstarch as matrix and a small amount of water, and then pulverized in a planetary ball mill (FRITSH P-7). The blending of char or carbon and the matrix was made for two sets: 3.0 g and 1.0 g (25 % blend) and 2.5 g and 1.5 g (37.5 % blend). The pulverization conditions were described previously [9]. The pulverized mixtures were subsequently molded in a stainless steel vessel by hot press at 140°C and 200 kgf·cm⁻² for 20 min. The resulting disk specimens were 30 mm and 1.6 ± 0.1 mm in diameter and thickness, respectively, for both blends.

2.7 Measurement of volume resistivity

For obtained disk specimens, volume resistivity that is equivalent to the reciprocal of electroconductivity was measured with a four-point probe (Dia Instruments, Loresta-GP). The resistivity was determined as the average of at least 15 places.

3. RESULTS AND DISCUSSION

3.1 Crystallinity, thermochemical stability, pore structure,

and morphology

Figure 1 illustrates XRD profiles for all of specimens. Although peak appeared at about 26° is assigned to crystallized carbon, the presence of nickel or iron, even if the amount was slight, would diminish the intensity [5,9]. It was thus difficult to establish the whole order in the crystallinity from the peak intensity. Conveniently, TG curves depicted in Fig. 2, where small fluctuation of the weight change involved by oxidation of residual metal at 550-580°C was corrected for relevant chars, indicated that thermochemical stability became high in the order of No-HC, No-SC, AFe-HC, AFe-SC, ANi-HC, and ANi-SC. This situation with no serious influence of coexisting metals disclosed that the stability of carbon itself was compatible with the crystallinity, hereby allowing application of the above order to the relevant purpose. Lower crystallinity for H-chars than for the corresponding S-chars would have relation to point (2) of Table 1, whereas higher crystallinity for Ni-chars than for Fe-chars can be explained by synergy of larger activity of the former metal and higher temperature of carbonization. Table 2 summarizes yield and pore properties together with the content of nickel or iron. Lower yield for H-chars than for S-chars with and without metal would be likewise related to point (2). Pore structure was developed to a greater extent for H-chars than for S-chars in the presence of both metals, as indicated by larger SBET, S_m, and V_m for the former. This trend found in

Fig. 1 XRD profiles for various wood chars and commercial carbons.

Fig. 2 TG curves for wood chars measured in a flow of the synthetic air.

Table 2 Yield and pore properties for various wood chars and commercial carbons.

Specimen	Yield ^{a)} (%)	Fe or Ni (wt %)	SBET ^{c)} (m ² ·g ⁻¹)	Sm ^{d)} (m ² ·g ⁻¹)	Vi ^{e)} (cm ³ ·g ⁻¹)	Vm ^{f)} (cm ³ ·g ⁻¹)	Va ^{g)} (cm ³ ·g ⁻¹)	Vt ^{h)} (cm ³ ·g ⁻¹)	Rm,s ⁱ⁾ (%)
No-SC	23.8	< 0.1	237	29	0.018	0.015	0.015	0.048	31.3
No-HC	21.4	< 0.1	262	78	0.022	0.036	0.023	0.081	44.4
AFc-SC	27.5 ^{b)}	0.80	224	260	0.001	0.252	0.288	0.541	46.6
AFc-HC	26.5 ^{b)}	0.67	279	298	0.002	0.283	0.214	0.499	56.7
ANi-SC	27.2 ^{b)}	0.31	132	181	0.001	0.228	0.253	0.482	47.3
ANi-HC	26.3 ^{b)}	0.29	140	199	0.002	0.246	0.226	0.474	51.9
DB	----	< 0.1	225	17	0.011	0.013	0.036	0.060	21.7
KB	----	< 0.1	816	590	0.110	0.703	0.224	1.037	67.8

^{a)} Dry ash-free, catalyst metal-free basis. ^{b)} Values before washing with acid, ^{c)} BET surface area, ^{d)} BJH mesopore surface area, ^{e)} BJH micropore volume, ^{f)} BJH mesopore volume, ^{g)} BJH macropore volume, ^{h)} Total pore volume = $V_i + V_m + V_a$, ⁱ⁾ Selectivity of mesopore, defined as V_m/V_t [1].

Fig. 3 SEM images of (a) AFe-SC, (b) AFe-HC, (c) ANi-SC, and (d) ANi-HC. Note: granules were seen in the encircled area with white dotted line for (d).

the absence of metal implied that either point (1) or both points (1) and (2) of Table 1 would take part in the situation. As noted for preceding S-chars [9], the filler ability was strongly dependent rather on mesoporosity expressed by S_m and V_m than on SBET. The general order drawn for meso-porosity in this connection was $DB < No-SC < No-HC < ANi-SC < ANi-HC < AFe-SC < AFe-HC < KB$. Figure 3 displays typical SEM images of four CMC. Neither cell tissues of AFe-SC and AFe-HC were appreciably injured, so that the individual morphologies resembled those of No-SC and No-HC, not shown here, respectively, with original wood cell structure retaining intact. To the contrary, the inside and the vertical cross section of ANi-SC cell were uneven and ANi-HC was collapsed to yield several granules, identical to GNSC, in the lumen. It is thus probable that metal-loaded H-chars are easier to be crushed into fine particles than the corresponding S-chars, though greater destructibility of nickel-catalyzed carbonization was undoubted. The probably different crushability for S- and H-chars in which point (1) would chiefly participate did not conflict with the aforesaid difference in the crystallinity or thermochemical stability between the two chars.

3.2 Electroconductivity and morphology of GNSC

In Fig. 4, volume resistivity is represented for two kinds of disk specimens. As is evident from the result, the

Fig. 4 Volume resistivity of disk specimens prepared from wood chars and commercial carbons.

general conductivity was $No-SC < No-HC \ll ANi-SC < AFe-SC \leq DB < ANi-HC < AFe-HC < KB$. The order of wood chars enabled the judgment that the most favorable was the combination of H with iron loading, and its complete agreement with that in mesoporosity ensured predominance of factor (ii) over factors (i) and (iii), aside from factor (iv), described at the end of INTRODUCTION in determining the capacity. It should be emphasized for AFe-HC from a practical viewpoint that in the ability, this acid-treated CMC was superior to DB for both blends and was almost equal to KB at the higher blend. Another noticeable aspect, although common to other wood chars, was larger effectiveness of increasing the blending from 25 % to 37.5 % for enhancing the conductivity compared to DB and KB. This feature attributable to dense but compressible constitution was a striking contrast to fluffy and bulky commercial carbons with well-developed 'structure' [10]. Figure 5 shows SEM images of four oxidized CMC observed at high magnification. Obviously both Ni-chars and both Fe-chars had their own similar morphologies of GNSC that is the conductive body. This verified no great difference in respect of factor (i) between S and H for the same metal, and thus reconfirmed the predominance of factor (ii). It is also ascertained that regardless of wood species, iron could afford longer and narrower GNSC to leave

Fig. 5 SEM images of (a') OAFc-SC, (b') OAFc-HC, (c') OANi-SC, and (d') OANi-HC

Fig. 6 SEM images at lower magnification for (c') OANi-SC and (d') OANi-HC.

larger S_m and V_m in the crystal region than nickel [7]. In consequence, none of points (1), (2), and (3) of Table 1 but metal species were crucial for the essential formation of GNSC. However, the aggregation of H-derived GNSC was apt to loose and separate in comparison with that of S-derived one, as exemplified by lower magnification images of OANi-SC and OANi-HC (Fig. 6). It is point (1) that allowed the different aptitude to expose, similarly to the probably different crushability for both wood chars. Such loosen and separate aggregation for metal-loaded H-chars will promote crush into fine particles.

3.3 Influence of the crushability of CMC on dispersion in the matrix

Dissimilarly to such factors (i), (ii), and (iii) described in INTRODUCTION as inherent characteristics of carbon, factor (iv), namely, dispersion is the parameter that varies with direct contact and/or mutual contiguity among the particles in the matrix [11]. This parameter, although usually has close correlation with factors (i) and (ii), can basically reach the utmost level by packing as many and fine particles as possible in the composite on an equal weight. For CMC composed of easily crushable amorphous carbon and sufficiently hard GNSC, fine particles produced from the former by pulverization are likely to enter the space and void of the latter on compression and molding with matrix, hereby making the construction denser. This is nothing but better

dispersion leading to enhancement in the filler ability. As crushability is assumed to be proportional to amorphous carbon fraction, this character will be more favorable for H-chars than for S-chars regardless of metal loading. This explanation is consistent with the aforesaid thermochemical stability and SEM observation. Therefore, crushability should be accepted as a potential factor dominating the filler ability.

4. CONCLUSIONS

The present study was made to examine the filler ability of acid-washed CMC prepared from S and H loaded with nickel and iron. The result clarified that Fe-CMC derived from H was more favorable than others and comparable to KB, excellent commercial conductive carbon, in the ability. It was also affirmed that iron-catalyzed carbonization at 850°C was more effective than nickel-catalyzed one at 900°C for both S and H, and mesoporosity was the predominant factor in determining the ability. It was inferred that crushability was a potential dominant factor. Although influence of the nuclear structure of lignin was obscure, difference in mesoporosity and crushability between S- and H-chars was probable to have relation to different cell structure and chemical composition for H and S, independently of metal species.

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