Method for Preparation of Copper-Coated Carbon Material

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Metallic copper-coated carbon fiber was prepared by applying a blending method. Raw isotropic coal pitch was blended with $CuBr_2$, and the obtained mixture was subjected to centrifugal spinning. In this way a copper salt-blended fiber with uniform distribution of copper was spun. The raw fiber was exposed to stabilization with air through heating to 330 °C and next to treatment with hydrogen at temperatures up to 770 °C. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electron probe microanalysis (EPMA) analyses clearly showed the presence of metallic copper in the resulted fiber. Additionally, presence of the metal was detected predominantly in peripheral regions of the obtained fiber. The mechanism of copper diffusion over carbon volume is proposed.

1. Introduction

Technology of carbon materials often requires addition of certain additives. Such a situation takes place during preparation of carbon-supported catalysts when various metals such as Mo, Pt, Pd, Cu, or metal oxides are deposited on an activated carbon support. Next, because of various requirements related to special properties such as increased strength or resistance, numerous materials such as composites or carbon fibers often have to be coated with a proper material.[1] There are a number of methods practically utilized for loading of additives or formation of coatings for carbon materials. Typically, coatings are formed by several procedures including laser techniques,[2] electroplating,[3] chemical vapor deposition (CVD),[4] and others. On the other hand, activated carbon-supported catalysts are usually obtained utilizing methods such as immersion, ion exchange, or physical deposition of vapors.[5] The common point of all the mentioned procedures is that either the catalyst or coating is formed by deposition or formation of proper material on the carbon surface from the surroundings. An alternative way to load additives into carbon material is the so-called blending method. Here, the additive is thoroughly mixed with carbon precursor prior to carbonization and then properly treated (carbonized and activated).[6] The product obtained in this way shows uniform distribution of the additive over the carbon matrix volume. However, normally both formation of coatings and catalysts supporting should result in deposition of the additive just on the surface of the final product. Considering these aspects we have already proposed a modified blending method to load additives in the structure of activated carbon fiber (ACF).[7] The method worked out by us allowed us to deposit K_2CO_3 in the peripheral regions of ACF. This material showed superior ability to remove H_2S from air. As a continuation of this idea we tried to extend the modified blending method to other chemicals. Because copper is an element that finds application as a coating[8] or catalyst in organic synthesis,[9] we attempted to deposit this metal preferentially close to peripheral regions of the carbon matrix. More precisely, we intended to get a high concentration of Cu close to the surface of the carbon fiber. This might be another way to produce Cu-coated carbon fiber or to load copper catalyst on those regions of carbon fiber most exposed to reagents. As will be shown in this paper, preliminary results indicate that the technique presented in this work seems to be a promising way to form coatings.

2. Experimental Section

2.1. Materials. The carbon precursor used in this work for preparation of carbon fiber was isotropic coal tar pitch with a softening point of 250 °C, supplied by Nippon Carbon Co. Ltd., Japan. The pitch was of 100 Poise of viscosity at 290 °C, with below 1 wt % quinoline-insoluble, and 62 wt % of xylene-insoluble fractions contents. $CuBr_2$ and solvents (quinoline and methanol) were of reagent grade and used without extra purification.

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2.2. Sample Preparation. The preparation procedure for the raw fiber containing copper was essentially based on an idea similar to that used for the preparation of K-loaded pitch fiber.[7] Hence, $CuBr_2$ (0.72 g) and the isotropic coal pitch (20 g) were dissolved in 100 cm^3 of methanol and 100 cm^3 of quinoline, respectively. The two solutions were mixed together thoroughly by stirring and simultaneous ultrasonification for 4 h. Next, the solvents were distilled under a lowered pressure and at temperature up to 190 °C using a rotary evaporator. Because traces of solvents seriously impair spinnability, the pitch was finely pulverized and put into a vacuum oven to remove any traces of them. To avoid eventual stabilization (oxidation) of the pitch material, air in the oven was exchanged with nitrogen prior to scrupulous drying. After those steps, the pitch powder thus obtained was evacuated ($8.0 \times 10^{-2} \sim 1.5 \times 10^{-1}$ Pa) for 3 days at 190 °C and then fused at 260 °C under N_2 atmosphere. After cooling, the resulting mass was crushed to small pieces of several mm in size. To get the fiber, the raw Cu-loaded pitch thus obtained was subjected to centrifugal spinning using an apparatus described elsewhere.[10] Afterwards, the raw pitch fiber (0.3 g) was placed into a ceramic tube (50 mm diam.) of a temperature-programmable horizontal furnace to continue the preparation. Hence, the raw fiber was stabilized by means of heating in air flow up to 330 °C (0.7 K·min^{-1}). Subsequently, without removing it from the furnace tube, the fiber was washed with flowing nitrogen gas for 15 min at increasing temperature. The purpose of introducing nitrogen after the stabilization step was to remove air from the tube to avoid both burnoff at elevated temperature and eventual reaction with hydrogen that was introduced to the tube as next medium. At 460 °C nitrogen flow was switched to hydrogen, and in this atmosphere the sample was continuously heated to 770 °C (3.0 K·min^{-1}). Hydrogen gas for the carbonization process was utilized to convert copper salt included in the stabilized fiber into metallic copper. The main part of the treatment under hydrogen flow was carried out at temperatures in the range where $CuBr_2$ (mp 498 °C) should be present in molten form and metallic copper (mp 1084.6 °C) remains in a solid state. Finally, the furnace was cooled to ambient temperature within ca. 90 min, and hydrogen was replaced from the tube by flowing nitrogen introduced into the tube. The flow rates for all the gases were set at 0.5 dm^3min^{-1}.

The Cu-containing pitch prepared according to the procedure described above showed a good ability for spinning. However, because the copper loading in the obtained fiber was too low, clear results from XRD patterns could not be obtained. Therefore, another powdered pitch highly loaded with $CuBr_2$ was prepared. In this case 4 g of $CuBr_2$ and 16 g of the isotropic coal pitch were used for the preparations. $CuBr_2$ was dissolved in 600 cm^3 of methanol, and the amount of quinoline was not changed. All the other preparation conditions remained unchanged, and the sample was treated according to the same procedure as applied for obtaining of pitch fiber. After completing the treatment, the processed material was pulverized. Unfortunately, this pitch powder highly loaded with $CuBr_2$ was not suitable for spinning. However, it was possible to take good XRD patterns.

2.3. Methods. The results of XRD measurements presented in this work were taken with a RAD-C apparatus (Rigaku, Japan) with Ni-filtered Cu Kα radiation. Maps of Cu distribution over prepared fiber were measured using an electron probe X-ray microanalyzer (EPMA-1400, Shimadzu, Japan) under acceleration voltage of 15 kV, sample current of 30 mA, and electron beam size of 1 μm. X-ray photoelectron spectroscopy (XPS) spectrum was collected with a Perkin-Elmer PHI ESCA-5600 apparatus with Mg Kα radiation

3. Results and Discussion

XRD measurements performed after three subsequent steps of preparation (raw pitch powder, after stabilization, and after treatment with hydrogen) resulted in obtaining of clear results. Changes in the state of copper-blended pitch material are illustrated by XRD patterns presented in Figure 1.

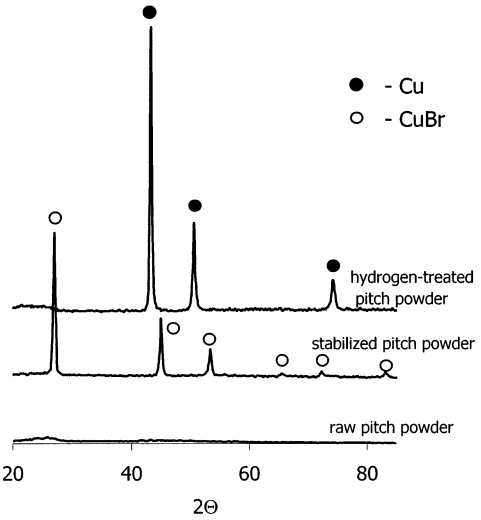

Figure 1. XRD patterns of the pitch powder: raw ($CuBr_2$-loaded) powder pitch; after stabilization; after treatment with hydrogen.

The X-ray diffraction pattern of the raw pitch powder was of low intensity and did not contain any stronger peak indicating presence of a copper compound. Seemingly, this was caused by an amorphous state of the introduced copper compound.

After completion of the stabilization stage, Cu-loaded pitch powder contained CuBr as it is evidently indicated by six peaks in the XRD pattern (Figure 1, open circles). Presence of CuBr at this stage of the preparation process indicates occurrence of a reduction reaction. Reduction of $CuBr_2$ must take place either during preparation of the raw material or during the stabilization step.

Another change in the state of loaded copper was caused by the treatment of stabilized pitch powder with hydrogen gas. Hence, the XRD pattern of the hydrogen-treated pitch powder clearly showed three peaks, surely indicating presence of metallic copper (Figure 1, closed circles).

Presence of metallic copper was also confirmed in the structure of the hydrogen-treated fibrous sample. As shown in Figure 2, the XPS spectrum contains a strong peak at binding energy of 932.7 eV. This value is attributed to the Cu2p region of metallic copper.[11]

Additionally, it should be pointed out that treatment with hydrogen gas caused another essential change. Namely, the reduced carbon fiber demonstrated a characteristic reddish color comparable to that of metallic copper. This visual observation seems to provide another confirmation of both XRD (taken for pitch powder highly loaded with Cu) and XPS (taken for Cu-loaded fiber) results indicating presence of metallic copper in the fiber after treatment with hydrogen.

Both EPMA maps showing distributions of copper throughout raw and hydrogen-treated fiber and adequate SEM images are presented in Figure 3. As can be seen in the figure, samples chosen for these observations were of ca. 30−50 μm diam.

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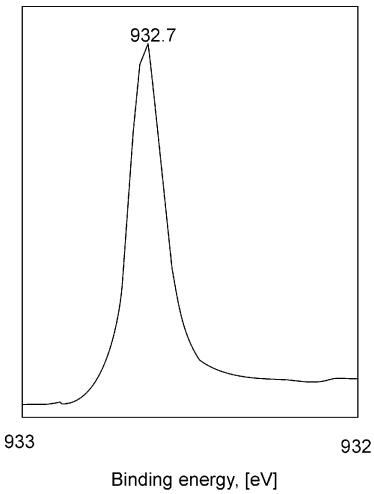

Figure 2. XPS spectrum (Cu2p region) of hydrogen-treated Cu-loaded carbon fiber.

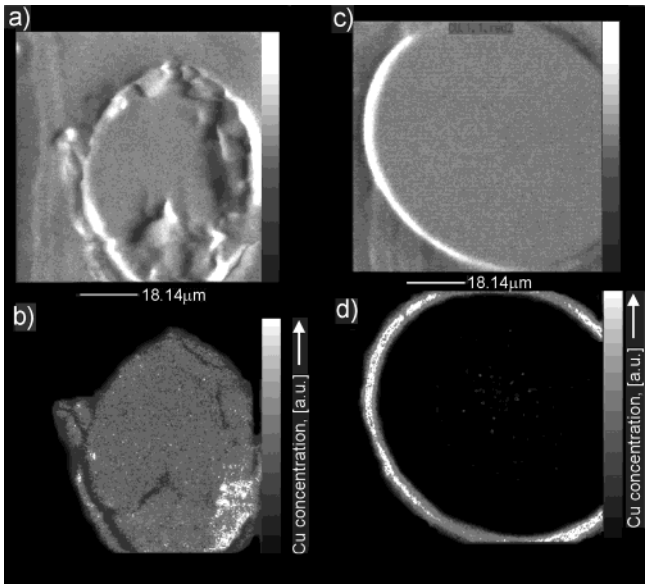

Figure 3. SEM images and EPMA maps showing distribution of copper over raw fiber (cross-section); a) SEM micrograph; b) EPMA map, hydrogen-treated fiber (cross-section); c) SEM micrograph; and d) EPMA map.

There is an essential difference in the distribution of copper throughout these two fibers. Hence, the raw fiber (Figure 3b) contains copper distributed uniformly over the fiber volume. In fact, some regions show somewhat higher concentration of the element, but it seems to be insignificant. On the other hand, the hydrogen-treated fiber exhibited very specific distribution of the element. Although regions of this fiber located close to its surface showed very high concentrations of copper, presence of only traces of the metal was observed in the inner regions.

Considering the results of measurements presented above, it can be concluded that the preparation procedure described above leads to diffusion of either CuBr or $CuBr_2$ through the fiber volume during the treatment with hydrogen gas. The diffusion proceeds from inner to outer regions of the processed fiber. In fact, all the conditions applied during the fiber treatment were carefully chosen to extort the concentration gradient of CuBr (or $CuBr_2$) in the space of the treated fiber. Both $CuBr_2$ and CuBr melt at relatively low temperatures close to 500 °C. Therefore, conditions of the stabilization step should not cause change in the state of aggregation of none from mentioned salts. Even reduction of $CuBr_2$ to CuBr should not have any impact on the state. On the other hand, treatment with hydrogen (temperature ranging from 460 to 770 °C) at some point must cause melting of CuBr present in the stabilized fiber. Apart from that, hydrogen gas flowing through the tube must also contact copper salt present in the structure of processed fiber. It seems to be natural that those particles of CuBr located close to the fiber surface are preferentially exposed to the reaction (reduction) with hydrogen. As seen from XRD (Figure 1), EPMA (Figure 3d), and visual observations results, such a situation takes place during treatment with hydrogen. As a consequence, the reduction with H_2 results in a progressive transformation of CuBr to metallic copper (melting point 1084.6 °C). By this reason, regions where the reaction mainly takes place must become poor in CuBr and rich in metallic copper. Temperature of the treatment (460−770 °C) is too low to melt the metal and at the same time keeps the copper salt in a liquid state. As the CuBr concentration gradient (driving force) over processed fiber volume occurs, the molten CuBr diffuses from the inner regions of the hydrogen-processed fiber to the surface to equalize its concentration over the fiber volume. This must be an explanation why the inner regions of the fiber become poor in Cu (CuBr) and the outer regions are abundant in the metal.

Apart from the reduction reaction caused by hydrogen, hydrogasification of carbon material must also take place during treatment with the gas. Earlier reports concerning the hydrogasification give a clue that reactivity of hydrogen toward coal is poor. As reported elsewhere,[12,13] during hydrogasification of coals at pressure of 2.5 MPa, small amounts of light hydrocarbons (mainly methane) started to evolve at temperature ca. 330 °C. The evolution rate increased at temperature of ca. 650 °C and tended to rise for higher temperatures. Whereas hydrogasification with evolution of methane proceeded with a higher rate for higher temperatures, production of other mentioned hydrocarbons ceased at temperatures 1000−1100 °C. According to another report,[14] demineralized wood-char loaded with Ni and Ca started to react with hydrogen at ca. 100 °C (0.1 MPa) and a significant increase in the rate of char consumption occurred at ca. 600−650 °C. Taking into account this information, some practical points may be concluded. Hence, to minimize consumption of carbon material during the treatment with hydrogen gas, duration of the process should be as short as possible. Moreover, because of presence of copper in processed fiber, hydrogasification may occur at different temperatures. However, this problem requires another extensive research.

4. Conclusions

As stated above, copper could be successfully deposited in the outer regions of pitch-based carbon fiber by use of the modified blending method. Hopefully, the

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procedure described in this work can be extended to other elements if proper combinations of additive precursor (not necessary halide), support, and treatment conditions would be ascertained. To some extent it seems to be possible to control the distribution of introduced additive over the fiber volume by a careful assortment of conditions applied during the treatment with hydrogen. Presumably, the rate of temperature increase and the point of hydrogen introduction are the factors that have the strongest impact on the final distribution of copper throughout the fiber. Further, we believe that it is worthwhile to consider the described technique as a potential way to also load other metals into carbon material in general. Additionally, the idea described in this work appears to be potentially expandable to other combinations of support/additive of various shapes to form coatings or deposit catalysts. However, appropriate selection of starting material, chemicals, and treatment must be achieved.

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