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전이금속 함유 전기방사 된 탄소섬유 웹의 수소 흡장

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The hydrogen adsorption of electrospun carbon fibers web involving transition metal

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Key words : Electrospining(전기방사), Carbon(탄소), Hydrogen (수소), Adsorption (흡착)

Abstract : To increase the capacity of hydrogen adsorption, transition metals were adopted as catalyst. The PAN-based CNFs involving transition metal were obtained by electrospinning method and heat treatment. To study the surface of carbon fibers, SEM analysis was conducted. The mass of transition metals were spreaded or covered among CNFs. XRD and EDX analysis were used to confirm transition metals on the surface of carbon fibers. Volumetric method was used for studying the capacity of hydrogen adsorption on the carbon fibers involving transition metals. In this study, vanadium has the best characteristics among chromium, titanium, and copper for hydrogen adsorption.

subscrip

PAN : polyacrylonitrile
DMF : N,N-dimethyl formamide
TCD : tip to collector distance
CNF : carbon nano fiber

1. Introduction

The world is becoming more and more conscious about its consumption of fossil fuel and about consequent environmental problems. As a result, interest towards possible alternative sources of energy is rapidly increasing. Hydrogen is a desirable energy source because it is renewable and its use would reduce emission of pollution. The bottleneck of using hydrogen as a fuel is a safe, compact and economical technology of on-board storage. The current ways of saving hydrogen are gas bombs, refrigerated (at 77 K) tanks and adsorbed in solids such as metal hydrides [1, 2].

The study of composite of carbon and transition metal has drawn considerable interests following the observation that the hydrogen storage performance of carbon materials could be improved by adding transition metals [3].

2. Experiment

2.1 The preparation of polymer solutions

It is important to select a proper solvent to dissolve polymer completely when the polymer solution was electrospun. Especially, boiling point and conductivity of solution have to be considered. Generally, solvent is volatilized with formation of polymer jet. If the boiling point of solvent is too low, solvent would be volatilized before forming polymer jet. In case if it is too high, it is difficult to make solid nanofibers due to too low density of polymer solution. So far DMF is considered as the best

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solvent among various organic solvents due to proper boiling point (426 K) and excellent conductivity (conductivity = 10.90 μS/cm, dipole moment = 3.82 Debye) [4, 5]. In this study, PAN (d = 1.184, 181315, Aldrich) and DMF (d = 133, 766137, Fisher) were used to make polymer solution. Three kinds of transition metal oxide were prepared as a catalyst for hydrogen adsorption. As a control, polymer solution was prepared by dissolving PAN (3 g) in DMF (27 g).

Table 1. Mass ratios of the mixtures [Unit : g]

	PAN	DMF	Cr_2O_3	$TiOSO_4$	CuO
Sample A	3	27	–	–	–
Sample B	3	27	1	–	–
Sample C	3	27	–	1	–
Sample D	3	27	–	–	1

Other polymer solutions were made with PAN (3g), DMF (27g), and transition metal oxide (Cr_2O_3, $TiOSO_4$, CuO,1g) as shown in Tabel1.

2.2 Electrospinning

Every polymer sample was sonicated in bath at 50 ℃ for 3 h to disperse metal oxide in polymer solution. Polymer solutions were electrospun with following condition [voltage : 15 kV, syringe rate : 1.5 cc/h, collector rotation speed : 300 rpm and TCD(tip to collector distance) : 10 cm]. Oxidation step was carried out at 250 ℃ for 8 h under air. Because electospun materials can not keep their fiber form but soften and melt at high temperature. Generally before carbonization, oxidation is necessary to change the thermoplastic character into thermosetting character [6]. Finally oxidized materials were carbonized at 1050 ℃ for 1 h in nitrogen atmosphere.

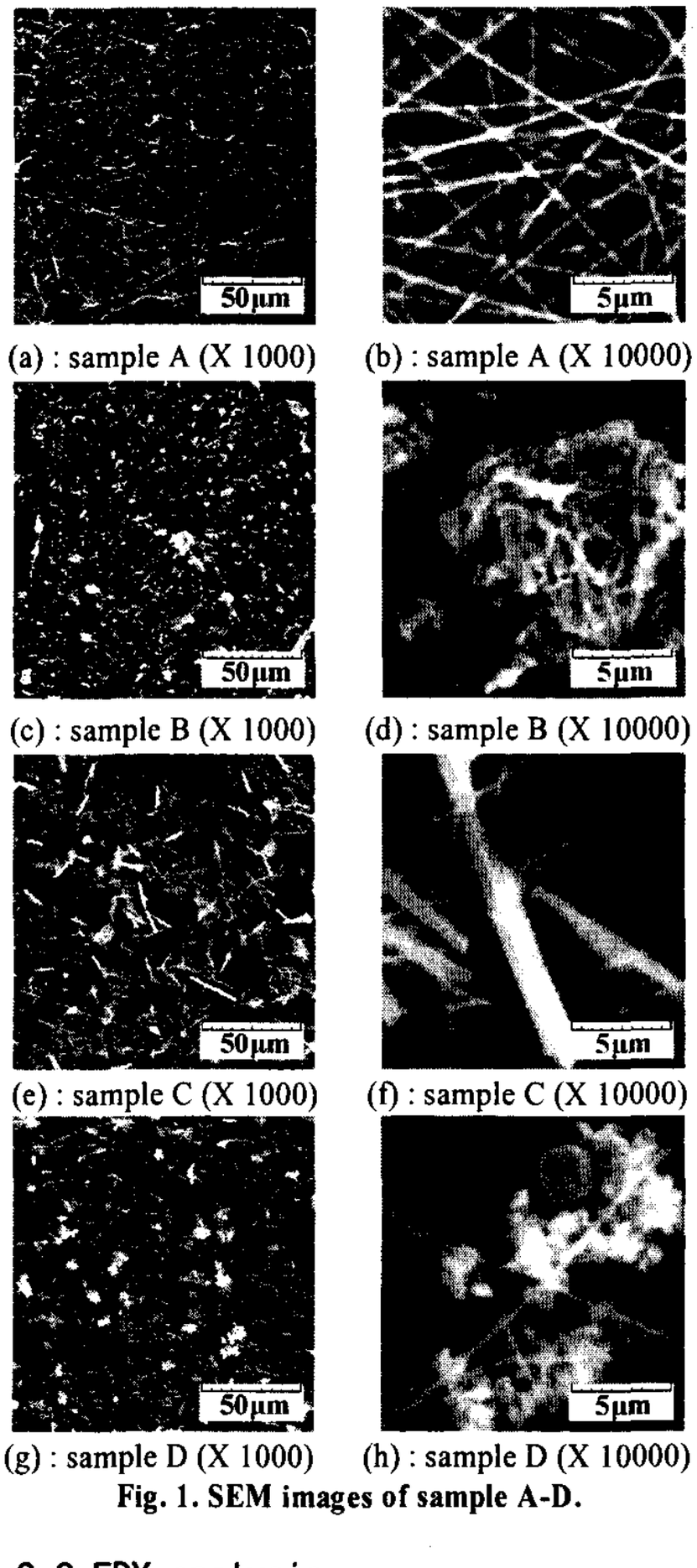
2.3 Characterization

To study the surface morphology of prepared carbon materials, specimens for microscopic examination were sputter coated with gold-palladium and examined using SEM apparatus (VEGAII LMU TESCAN Co., Korea).XRD and EDX analysis were conducted to confirm transition metals in carbon fibers. Volumetric method was used for an analysis of hydrogen adsorption with PCT apparatus at room temperature from 0 to 90 atm.

3. Results

3.1 SEM analysis

In Fig.1, SEM images of sample A-D are presented with two magnification (1000 and 10000). In case of sample A, the diameter of CNF is about 250 nm. In Fig. 1 (C) and (d), the mass of chromium exist among CNFs showing the spherical type. In case of CNFs involving titanium, the SEM images shows titanium coved CNFs showing stick shape as presented in Fig. 1 (e) and (f). The diameter of titanium coved CNFs is about 1.7 □m. The SEM images of CNFs involving copper are presented in Fig. 1 (g) and (h). The mass of copper is spreaded among CNFs. All metal are observed among CNFs. The size of CNFs and metal mass is measured by software program (VEGAII LMU TESCAN Co., Korea).



(a) : sample A (X 1000) (b) : sample A (X 10000)
(c) : sample B (X 1000) (d) : sample B (X 10000)
(e) : sample C (X 1000) (f) : sample C (X 10000)
(g) : sample D (X 1000) (h) : sample D (X 10000)

Fig. 1. SEM images of sample A-D.

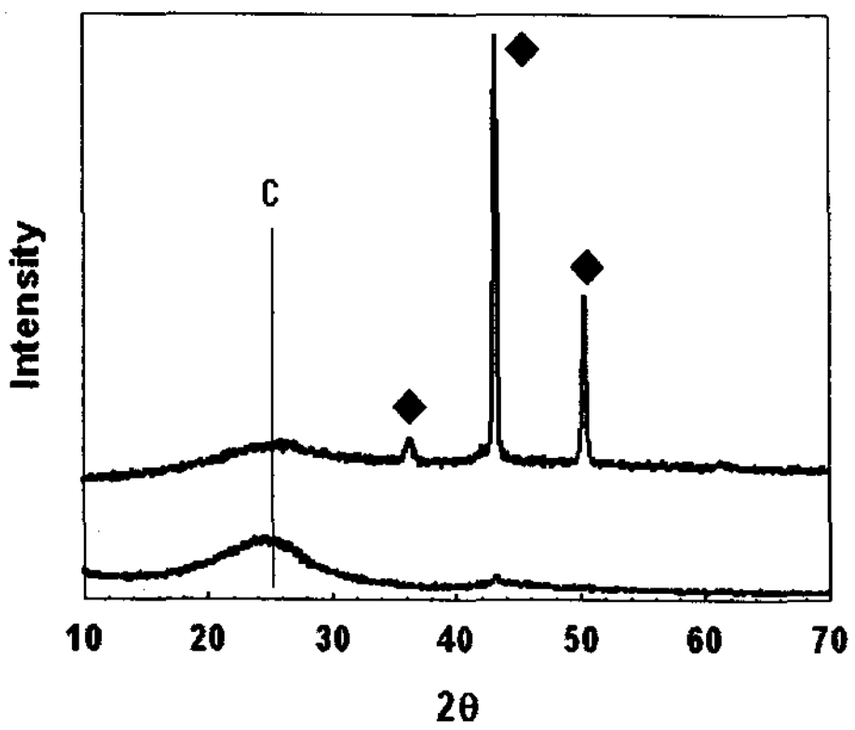
3.2 EDX analysis

Table 2. EDX data of sample A-D [Unit : %]

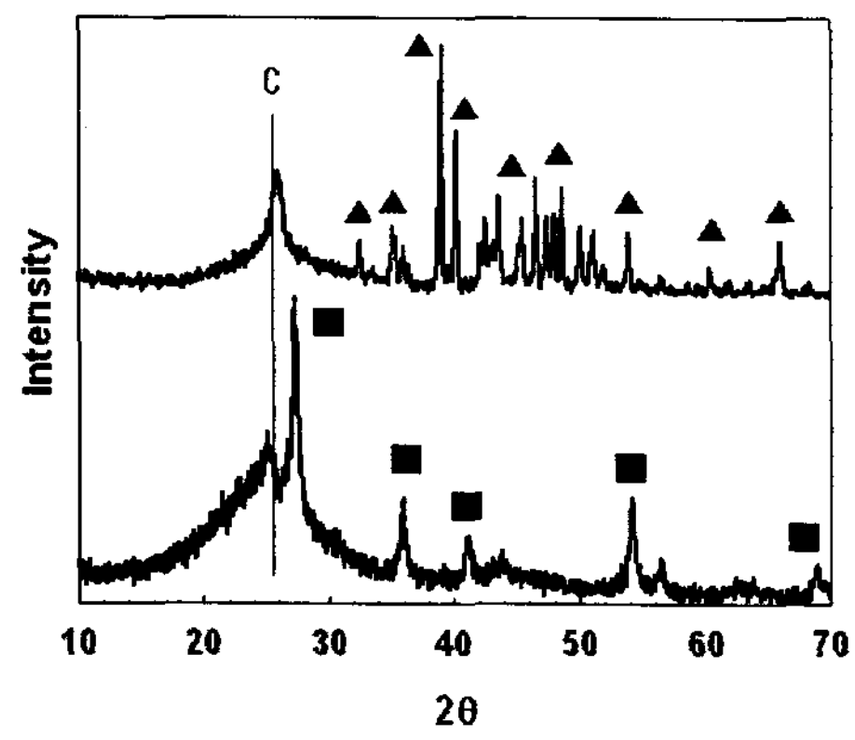
	C	Cr	Ti	Cu
Sample A	100	–	–	–
Sample B	74.86	25.14	–	–
Sample C	88.33	–	11.02	–
Sample D	84.43	–	–	15.57

EDX data of sample A-D is presented in Table 2. Chromium, titanium, and copper are detected showing 25.14, 11.02, and 15.57 wt% respectively. There is no oxygen content suggesting that oxygen was removed by making carbon monoxide and carbon dioxide during carbonization. It seems that sulfur was removed also as sulfur monoxide and sulfur dioxide during carbonization.

3.3 XRD analysis



(a)



(b)

Fig. 2. XRD data of sample A-D; (a) : sample A and B, (b) : sample C and D, (◆ : Cr, ▲ : Ti, ■ : Cu).

XRD data of sample A-D was obtained to detect metals in CNFs in Fig. 2. Carbon is confirmed around 2□(from 23 to 25. In Fig. 2 (a), chromium is detected showing three peaks at 2□= 36, 43, and 50. Titanium has many peaks in the range of 2□(from 32 to 65) in Fig. 2 (b). In case of sample D, the peaks of copper are presented at 2□= 35, 40, and 54.

3.4 PCT analysis

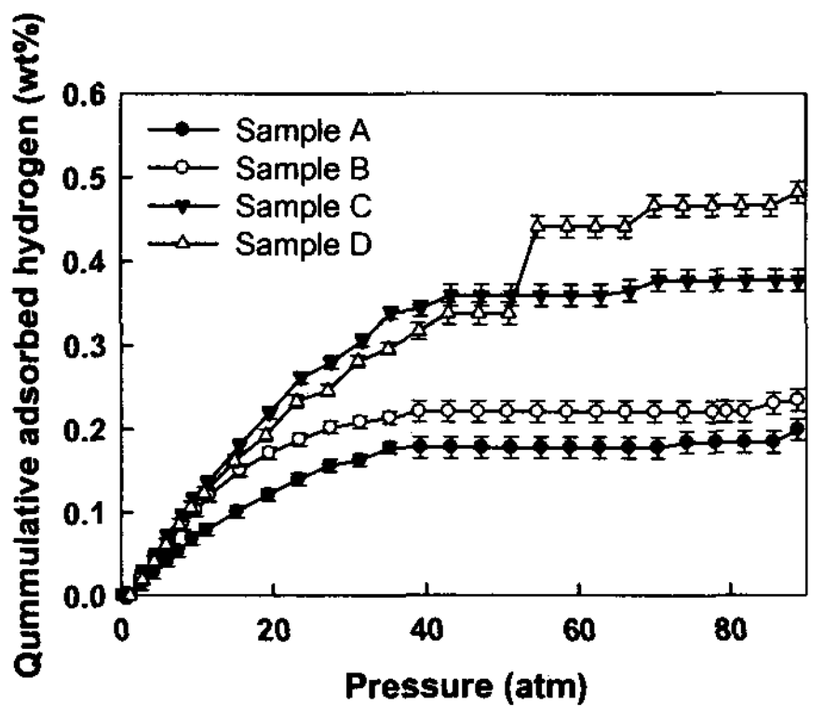


Fig. 3. The capacity of hydrogen adsorption of sample A-D.

Fig. 3 shows the capacity of hydrogen adsorption of CNFs involving transition metal. The amount of hydrogen adsorption was tested over three times for the accuracy of adsorption data. The error range was less than 0.013 wt%. Sample A which doesn't involve metal has the capacity of hydrogen adsorption showing 0.19 wt%. In cases of CNFs involving transition metal, the amount of adsorbed hydrogen was increased. Chromium and titanium lead to increase the amount of absorbed hydrogen up to 0.24 and 0.37 respectively. Copper has the best effect as a catalyst for the increment of hydrogen adsorption showing 0.48 wt%.

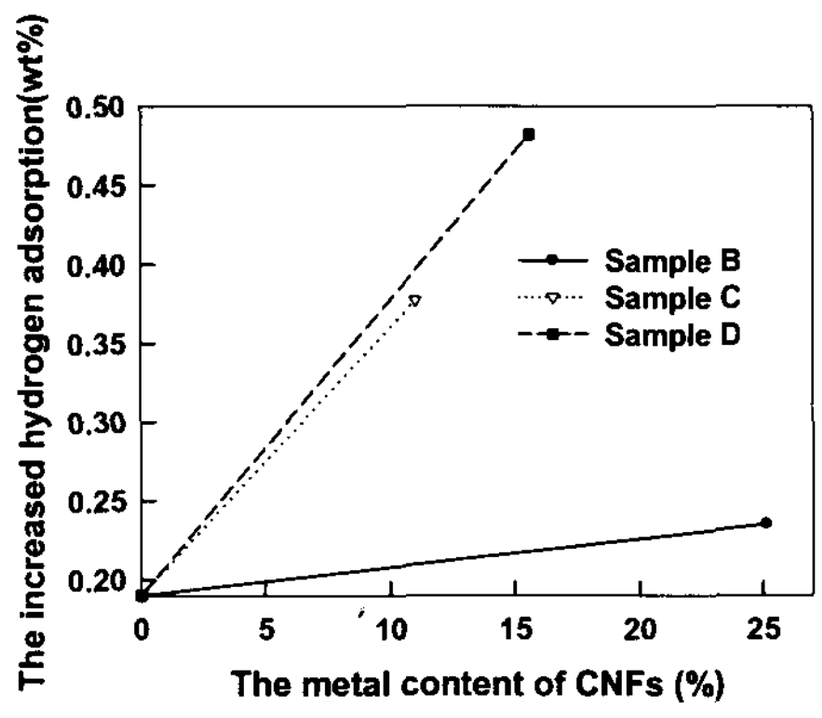


Fig. 4. The increased amount of hydrogen adsorption by the effect of transition metal as a catalyst.

Fig. 4 shows the effect of transition metal as a catalyst for hydrogen adsorption. The amount of hydrogen adsorption is 0.19 wt% without transition metal as mentioned in Fig. 3. Even though the content percentage of transition metal in sample B is the highest , the effect for hydrogen adsorption is the lowest. Regarding the effect for hydrogen adsorption and content percentage of transition metal together, copper and titanium have similar slope in Fig. 4 showing better effect than the effect of chromium.

3.5 Mechanism of hydrogen adsorption

It is suggested that transition metal in carbon fiber is attracting hydrogen molecule into the carbon fiber. The mechanism of hydrogen physical adsorption is shown in Fig. 5. This reaction seems to have charge attraction between metal and one side (-)charged hydrogen molecular. Even though there are some studies that hydrogen molecule is dissociated by transition metal and saved into the carbon fibers, many researchers are presenting there is no hysteresis when hydrogen molecule is absorbed and desorbed. In this experiment, it is sure that physisorption was occurred during hydrogen adsorption, because second and third hydrogen adsorption data is similar to first hydrogen adsorption data. It means the mechanism of hydrogen adsorption is physical adsorption [7].

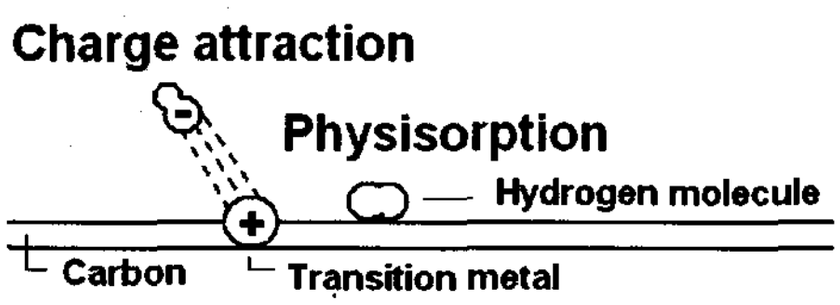


Fig. 5. The mechanism of hydrogen adsorption of carbon fibers involving transition metal.

4. Conclusions

The electrospun carbon fibers involving transition metals were prepared as a catalyst for hydrogen storage. The mass of transition metal existed among CNFs or covered CNFs having different shape according to the kind of transition metal. The capacity of hydrogen adsorption was increased by addition of transition metal. Copper shows the best ability as a catalyst for hydrogen adsorption showing 0.98 wt% among chromium, titanium, and copper. It seems that carbon fibers involving transition metal are attracting hydrogen molecule into the carbon fibers showing physical adsorption.

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