Characteristics of Hydrogen Adsorption on Chemical Activated Electrospun Carbon Nanofibers

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Abstract

Widely different hydrogen adsorption capacities have been reported for a variety of carbon materials which have attracted attention for hydrogen storage. In this paper, electrospinning was used for manufacturing carbon nanofibers (CNFs) and chemical activation was experienced for getting high surface area and pore volume. Two kinds of chemically activated CNFs were prepared. Zinc chloride activated CNFs were prepared by using electrospinning and thermal treatment with various zinc chloride weight in polymer solutions. For potassium hydroxide activation, electrospun CNFs were immersed in various concentration of KOH solutions. Wet electrospun CNFs were thermal treated for activation. The surface morphology of activated CNFs was observed by SEM. In case of zinc chloride activation, the diameter of activated CNFs was increased but in case of potassium hydroxide, the diameter of activated CNFs was decreased. According to the increment of chemical agents, the specific surface area and pore volume of zinc chloride and potassium hydroxide activated CNFs were increased. But the most effective factor which can affect the hydrogen adsorption capacity is pore volume in the range of pore width from 0.6 to 0.7 nm as shown zinc chloride activated sample.
Keywords : Carbon nanofibers, Chemically modified carbons, Activation, Adsorption.

Instruction

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 storing hydrogen are gas bombs, refrigerated (at 77 K) tanks and adsorbed in solids such as metal hydrides. Hydrogen storage in the solid matrices like metals, intermetallic compounds, porous solids and carbon materials appears to be appropriate option. Even though there are many arguments about hydrogen adsorption capacity, many reports agree with Monte-Carlo simulation predict that optimal pore size for adsorption should be close to 0.6 nm at room temperature.

Experimental

Two kinds of chemically activated CNFs were prepared. First kind is obtained by using zinc chloride as a agent. The other kind is made by potassium hydroxide activation of CNFs. These samples were named at Table 1 with various conditions of preparation.

Preparation of zinc chloride activated CNFs

PAN(polyacrylonitrile, d = 1.184, 181315, Aldrich) and DMF(N,N-Dimethyl formade, d = 133, 766137, Fisher) were used to make polymer solution and zinc chloride was used as a chemical agent to activate CNFs during carbonization. Four polymer solutions were prepared with various weight ratio [PAN : DMF : $ZnCl_2$ = 3 : 30 : 0, 3 : 40 : 2, 3 : 50 : 4, and 3 : 60 : 6]. The preparing conditions of samples are listed in Table 1 in detail. The polymer solution was injected into a 30 cm^3 syringe having a capillary tip which has 18 gauge needle (inner diameter : 0.84 mm) diameter. In order to avoid the collapse of the

structure of electrospun materials during carbonization, oxidation step was carried out at 250 ℃ for 8 h under air. Oxidized materials were carbonized at 1050 ℃ for 2 h to remove zinc chloride. These carbonized and activated samples were named A, B, C, and D in the order, according to the preparation of polymer solutions with following conditions [PAN : DMF : $ZnCl_2$ = 3 : 30 : 0, 3 : 40 : 2, 3 : 50 : 4, and 3 : 60 : 6].

Preparation of KOH activated CNFs

Sample A (0.3g) was immersed in each KOH solution (4, 6, and 8 M, 200ml) over night and placed in steel pipe at alumina boat for KOH activation. KOH activation was experienced at 750 ℃ during 3 h in nitrogen atmosphere with following conditions [heating rate : 5 ℃/min, nitrogen rate : cc/min]. KOH activated CNFs were washed with distilled water several times and dried at 110 ℃ over night.

Results and discussion

SEM images of $ZnCl_2$ activated CNFs are shown in Figure 1. As it can be seen in Figure 1(a), the fiber diameter of sample A is 200 ~ 300 nm uniformly. Even though zinc chloride was removed in carbonation and activation process step, the surface roughness of sample A is smooth. In Figure 1 (b) ~ (d), the fiber diameters of samples (B, C, and D) were ranged from 1 to 1.8 μm according to increment of zinc chloride weight in polymer solution. It can be seen that the fiber diameters of samples (B, C, and D) increased compared to diameter of A. It is suggested from different concentrations and conductivities of polymer solutions according to the contents of polymer solution. So the condition of electrospinning would be different each other.

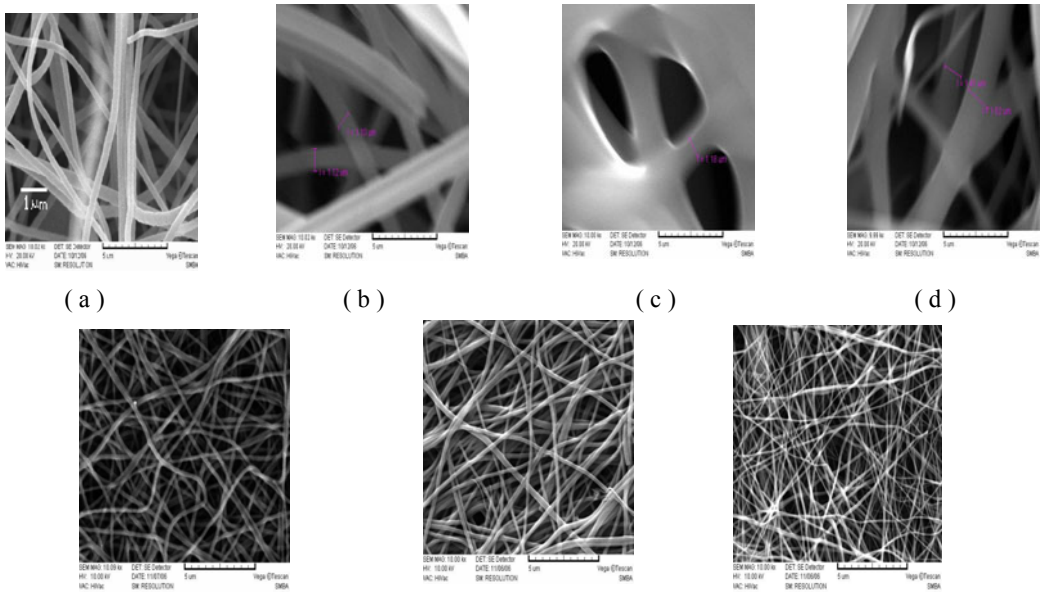

Figure 1. SEM images of CNFs : (a);A, (b);B, (c);C, (d);D, (e);E, (f);F, (g);G.

Figure 1(e) ~ (g) show SEM images of KOH activated CNFs. The surface roughness of KOH activated CNFs was smooth and the diameter of activated CNFs was uniform in same condition of activation. But comparing with Figure 1(a), the diameter of KOH activated CNFs decreased according to increment of KOH solution mole from 250 to 80 nm. It is supposed because oxygen made dioxide carbon and monoxide carbon from outside to inside during KOH activation on the surface.

The BET specific surface area analysis was summarized in Table 1. The BET specific surface area was increased about 56 times by the addition of zinc chloride from 17 to 944 m^2/g in case of samples (A, B, C, and D). The total pore volume was also increased from 0.032 to 0.9606 cc/g about 30 times.

Table 1. Textual properties and Hydrogen adsorption of CNFs.

	A	B	C	D	E	F	G
PAN (g)	3	3	3	3	3	3	3
DMF (g)	30	40	50	60	30	30	30
$ZnCl_2$ (g)	-	2	4	6	-	-	-
Immersing KOH solution (M)	-	-	-	-	4	6	8
BET specific surface area(m^2/g)	17	334	777	944	1410	2006	2420
Total pore volume (cc/g)	0.032	0.4304	0.5296	0.9606	0.748	1.784	2.391
HK micro pore volume (cc/g)	0.003	0.14	0.32	0.40	0.57	0.86	1.04
pore volume (0.6-0.7nm) (cc/g)	0.00397	0.01488	0.05698	0.08438	0.00923	0.01843	0.03544
The amount of hydrogen adsorption (∑wt%)	0.4345	0.5331	0.713	1.54	0.672	0.911	1.03

The micropore volumes was calculated by HK equation. The HK micropore volume was increased from 0.003 to 0.4 cc/g about 133 times. It indicates that zinc chloride was volatilized and chemically work for activation of CNFs during carbonization which provides very high specific surface area and pore volume on CNFs. In case of KOH activated CNFs, BET specific surface area was increased form 17 to 2420 m^2/g about 142 times. The total pore volume was increased from 0.032 to 2.391 cc/g about 74 times. HK micropore volume was increased from 0.003 to 1.04 cc/g. Regarding the micropore volume which has pore diameter from 0.6 to 0.7 nm, sample D has lager pore volume than any other sample. From Table 1, It is sure that KOH activation is more effective to increase specific surface area and pore volume than $ZnCl_2$ activation. Whereas in case of the micropore volume which has pore diameter from 0.6 to 0.7 nm, $ZnCl_2$ activation is more effective than KOH activation.

Figure 2 shows nitrogen adsorption isotherms of activated CNFs. Every curve was classified as a Type Ⅱ by IUPAC classification. Each graph has a point of inflection which is called 'knee' at P/P_0 (0 ~ 0.2). This point indicates that chemical adsorption is finished. So, it is possible to calculate specific surface area at this point using BET equation. Over 0.2 P/P_0, the adsorbed volume against to P/P_0 was increased, which means that they have also mesoporous on CNFs. In case of zinc chloride activation, the adsorbed quantity of sample D approached to 600 cc/g. But in case of potassium hydroxide activation, the adsorbed quantity of sample G reached 1600 cc/g.

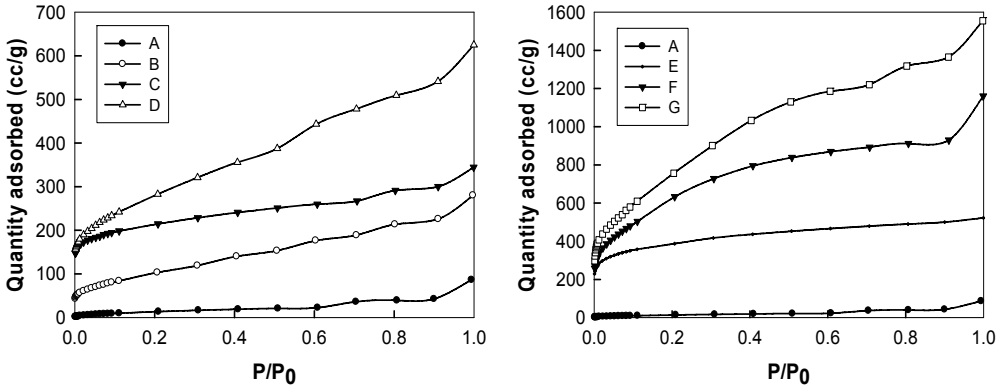

Figure 2. Nitrogen Isotherms of CNFs : (a); A, B, C and D, (b);A, E, F and G.

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Figure 3 shows the hydrogen adsorption capacity of two kinds of chemically activated CNFs. Hydrogen adsorption capacity was experienced from 0 to 40 atm at room temperature. Even though hydrogen adsorption capacity is increased with the increment of specific surface area and pore volume, as it is predicted by Monte-Carlo simulation, sample D has the highest hydrogen adsorption capacity because sample D has the highest pore volume in the range of pore width from 0.6 to 0.7 nm. In case of sample A, hydrogen adsorption capacity is 0.43 wt%. The hydrogen adsorption capacity of sample G which is KOH activated is 1.03 and the hydrogen adsorption capacity of ZnCl2 activated sample D is 1.54 wt% showing the highest hydrogen adsorption in Table 1.

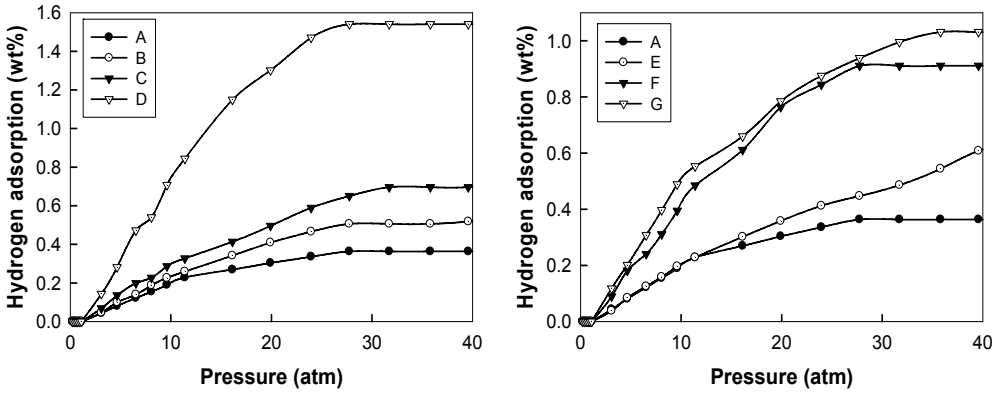

Figure 3. Hydrogen adsorption of CNFs : (a); A, B, C and D (b);A, E, F and G.

Conclusions

Two kinds of chemically activated CNFs were prepared. Zinc chloride activated CNFs were prepared by using electrospinning and thermal treatment with various zinc chloride weight in polymer solutions. For potassium hydroxide activation, electrospun CNFs were immersed in various concentration of KOH solutions. Wet electrospun CNFs were thermal treated for activation. The surface morphology of activated CNFs was observed by SEM. In case of zinc chloride activation, the diameter of activated CNFs was increased but in case of potassium hydroxide, the diameter of activated CNFs was decreased. According to the increment of chemical agents, the specific surface area and pore volume of zinc chloride and potassium hydroxide activated CNFs were increased. But the most effective factor which can affect the hydrogen adsorption capacity is pore volume in the range of pore width from 0.6 to 0.7 nm as shown zinc chloride activated sample D.

Acknowledgement

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