IMPROVED HYDROGEN ADSORPTION OF ELECTROSPUN ACTIVATED CARBON FIBERS BY DIFFERENT ELECTRONEGATIVITY LEVELS OF TWO CATALYSTS

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Introduction

Recently, there has been much concern over finding new energy sources because of the increasing use of electric devices and the limited supplies of existing fuels. Hydrogen energy is a promising way to solve our energy problems because of its unlimited supply, clean cycle and efficiency [1]. There are, however, some obstacles to be overcome before hydrogen energy can be used in industrial fields. One important problem that must be solved is how to efficiently and safely store hydrogen gas [2,3].

In this paper, the metal-carbon-fluorine (MCF) system was introduced in order to maximize hydrogen storage capacity. In the MCF system, there is an electronegativity gap between the metal and fluorine because fluorine has the higher electronegativity. Because of this, the electron of the hydrogen molecule entering the carbon material is attracted to one side. Through this action, two additives can effectively guide hydrogen molecules into the carbon materials. In our experiment, carbon nanofibers were used as the storage media. The carbon nanofibers were prepared using electrospinning and heat treatment, and vanadium pentoxide was used as a precursor of vanadium. Finally, fluorine was introduced to the surface of the carbon nanofibers by using direct fluorine treatment.

Experimental

The polymer solution was prepared for electrospinning with the weight ratio (PAN : DMF : V_2O_5 = 1 : 9 : 1). The polymer solution was ejected from a syringe tip onto an aluminum foil covered collector using an electrospinning apparatus. The polymer solution was injected into a 30 ml syringe having a capillary tip (18G, inner diameter: 1.27 mm), and the syringe was placed in a KD scientific syringe pump (Model 100). Electric power was applied with a high voltage power supply (NT-PS-25K, NTSEE Co., Korea) using 18 kV. The details have been presented elsewhere [4].

Before carbonizing the electrospun fibers, a stabilization step (oxidation process) was necessary to prevent the electrospun materials from losing their fiber form softening or melting at high temperature. This stabilization step was carried out at 523 K for 8 h under air, with a heating rate of 1 K·min^{-1}. After the oxidation step, heat treatment was carried out to carbonize the oxidized fibers under an argon atmosphere with the following conditions: heating rate: 10 K/min, target temperature: 1323 K, holding time: 3 h, argon gas feeding rate: 100 ml/h.

A KOH solution (8 M, 200 ml) was prepared as a chemical activation agent. A 3 g sample of the carbonized fibers was immersed in the KOH solution. To immerse the sample uniformly, a shaker apparatus (SK-300, JEIO TECH, Korea) was used at 50 rpm for 3 h. The wet sample was placed on an alumina boat in a steel pipe to carry out the chemical activation. Activation was conducted at 1023 K for 3 h in an argon atmosphere. The heating rate was 5 K/min, and the feed rate of argon gas was 40 ml/min. After chemical activation, the activated electrospun carbon fibers (AECFs) were washed with distilled water several times to remove residual potassium. This sample was dried at 383 K over night. The resulting sample was labeled as MC. The MC sample was pretreated at 473 K for 2 h under a vacuum to remove water and impurities. Fluorination was carried out at 303 K and one bar for 10 min by introducing fluorine gas directly onto the carbon nanofibers in the reactor. This fluorinated sample was labeled as MCF.

Results and Discussion

The nitrogen isotherms of two samples are presented in Fig. 1. Generally, the change in the low pressure area means that the sample has micropores. From the significant change of curves in the relative pressure range of less than 0.01 bar, it is clear that both MC and MCF have micropores that can improve the hydrogen storage efficiency. It is suggested that fluorine treatment slightly decreased the surface area and pore volume because of the formation of bonds between carbon and fluorine.

The pore size distribution of samples was calculated by the Horvath-Kawazoe (HK) method in order to investigate the structure of the micropores, shown in Fig. 2. MC and MCF have a peak pore diameter at 0.63 and 0.66 nm, indicating they have the optimal pore size for hydrogen adsorption. Generally the pore size around 0.7 nm is predicted as an optimal pore size of carbon material for a hydrogen carrier by Monte-Carlo simulation and it is confirmed in our previous work. Both of them show the development of ultra-micropores, which came from the effect of dissociated oxygen during the carbonization step. When comparing the two samples, MC shows higher porosity. It is suggested that the pore was blocked or eliminated and that the pore size was also decreased by the formation of bonds between carbon and fluorine during the direct fluorination step.

The capacity of hydrogen adsorption is presented in Fig. 3. In the case of MC, the amount of adsorbed hydrogen is about 2.5 wt%. After fluorination treatment, the system of using metal and fluorine based on activated carbon nanofibers shows the improved performance of hydrogen storage. The amount of hydrogen adsorption approaches around 3.2 wt%. This improved capacity of hydrogen adsorption may come from the use of fluorine to produce the MCF system. The rule of fluorine is explained in the hydrogen adsorption mechanism.
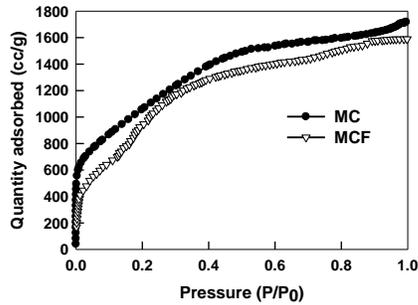
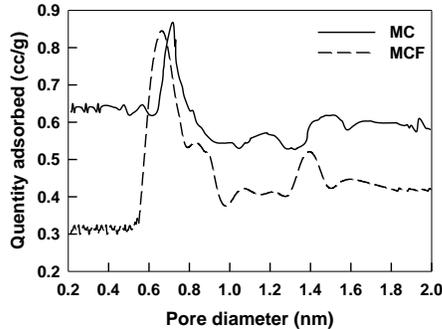**Fig. 1** Nitrogen isotherms of samples.

Fig. 2 HK micropore size distribution of samples.

The mechanism of hydrogen storage using the MCF system is suggested in Fig. 4. As the hydrogen molecule moves from outside to the surface of the carbon, the hydrogen molecule is affected by the electronegativity gap of the metal and fluorine. Fluorine has the highest electronegativity (4.0) among the elements, and the vanadium has lower electronegativity (1.63). And the electronegativity of carbon is 2.55 which the value is between fluorine and vanadium. Therefore, the fluorine exhibits electrically negative-charged characteristics (δ^-) on the surface, and the metal exhibits relatively positive-charged characteristics (δ^+). Consequently, this electronegativity difference will electrically attract the hydrogen molecule into the carbon fibers. This phenomenon can be described by the following equation (3), modifying Coulomb's law:

$$F = K \cdot |\ E_1\text{-}E_2\ |\ /\ R^2 \qquad (3)$$

F is the electric force between metal and fluorine, and E_1 and E_2 are the electronegativity of metal and fluorine, respectively. K is a constant, and R is the distance between metal and fluorine. The hydrogen molecule is affected by electric forces that vary with its position. As shown in Fig 6, when the hydrogen molecule is in position B, the hydrogen is affected by the same electric force in opposite directions, so the hydrogen molecule does not move in the horizontal direction. When the hydrogen molecule is in position A, the electric force on the hydrogen molecule can be determined from its distance from two additive elements, as in equation (4):

$$F = K \cdot [\ |\ r_1\text{-}r_2\ |\ /r_1^2 \cdot r_2^2] \cdot |\ E_1\text{-}E_2\ |\ /\ R^2 \qquad (4)$$

The electrons in the hydrogen molecule are attracted towards the surface by this force and can be adsorbed on the surface of the carbon more efficiently. The hydrogen storage would be improved by this effect.
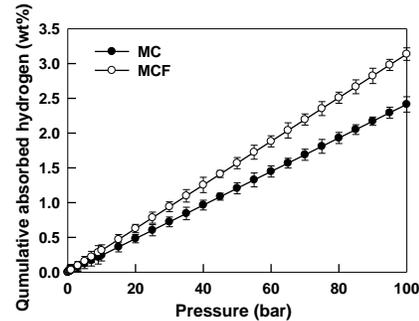

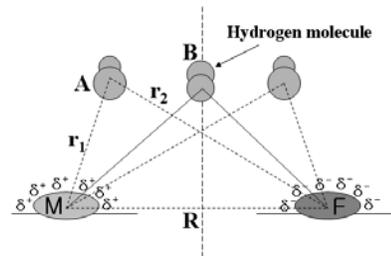**Fig. 3** Hydrogen storage capacity.

Fig. 4 The mechanism of hydrogen adsorption enhancement by the MCF system.

Conclusions

Electrospun activated carbon fibers were modified using vanadium and fluorine in order to improve the fibers' hydrogen storage capacity. The elemental contents of the MCF system were determined by XPS, successfully detecting carbon, vanadium and fluorine peaks. The pore structure was developed up to around 2800 m^2/g and 2.7 cc/g through KOH activation, and micropores in about 60 % of the samples. After investigating the micropore size distribution, it is concluded that the pores are developed at about 0.6 - 0.7 nm diameter, which is the optimal pore size for improving hydrogen adsorption. Even though the development of the pore structure decreased slightly after fluorination, the capacity of hydrogen adsorption improved. This increased hydrogen storage can be attributed to the effect of the electronegativity gap of the two elements present in the MCF system.

References

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