폴리비닐리덴 풀루오라이드로부터 제조된 다공성 탄소나노섬유

정혜진**, 조성무†*, 김동영*, 진병두*, 이도원**
*한국과학기술연구원 광전자 재료연구센터, **서울시립대 화학공학과

Poly(vinylidene fluoride)-based Porous Carbon Nanofibers

H. J. Chung**, S. M. Jo†*, D. Y. Kim*, and B. D. Chin*, and. D. W. Lee**

*Optoelectronic Materials Research Center, Korea Institute of Science and Technology,
39-1, Hawolgok dong, Seongbuk-gu, Seoul 136-791, Republic of Korea
**Department of Chemical Engineering, University of Seoul,
Jeonnong-Dong, Dongdeamun-Gu, Seoul 130-743, Republic of Korea

ABSTRACT

200-300 nm 직경을 지닌 폴리비닐리덴 플루오라이드 초극세 섬유를 전기방사법으로 제조하였다. 이들을 불융화시킨 후, 800-1800 ℃ 온도에서 탄화시켜 PVdF 계 탄소나노섬유를 제조하여 구조 및 기공분석을 하였다. 이들은 20-30 nm 크기의 탄소입자로 이루어져 있으며 탄소나노입자는 1 nm이하의 슬릿형 나노기공을 지니고 있었다. 탄화온도가 증가함에 따라 비표면적은 1500 ℃에서 414 m^2/g로 감소하였으나, 1800 ℃에서는 1300 m^2/g로 급격히 다시 증가하였으며 1 nm 이하의 나노기공만을 지닌 탄소섬유가 얻어졌다. 비표면적 및 기공특성과 수소저장특성을 관계를 조사하기 위하여 Magnetic Syspension Balance(MSB)를 사용한 중량법으로 평가한 이들의 수소저장능은 0.04-0.4wt%이었다.

주요기술용어 ·: Electrospinning(전기방사), Ply(vinylidene fluoride)(폴리비닐리덴 플루오라이드), PVdF nanofiber(PVdF 나노섬유), Prous carbon nanofiber(다공성 탄소나노섬유), Hydrogen storage(수소저장)

1. INTRODUCTION

Since the physical adsorption of hydrogen gas at the interface of carbon materials will be higher than the bulk due to the Van der Waals interactions, much researches on hydrogen storage using single wall nanotubes (SWNT), multi-wall nanotubes (MWNT), graphite nanofibers (GNF), active carbon, active carbon fiber, graphite powder, etc., have been done. Since Dillon first reported the excellent 6 to 8 wt% hydrogen storage capacity of SWNT at

---

† Corresponding author : smjo@kist.re.kr

room temperature and with atmospheric pressure[1], Liu observed the hydrogen adsorption of 4.2 wt% (0.5 H/C) at 100 bars and at room temperature using SWNT synthesized through the arc electric discharge method[2]. Zhu et al., reported a hydrogen adsorption of about 3 wt% at 3-100 MPa and at room temperature, using a well- aligned SWNT bundle[3]. On the other hand, purified SWNT (285 m^2/g) and saran carbon (1600 m^2/g) with a high BET surface area were also reported to have a hydrogen adsorption of about 0.04 H/C and 0.28H/C at 0.32 MPa, 80 K, respectively[4]. Nijkamp et al[5]. also discovered a large hydrogen adsorption by a microporous zeolite and active carbons at 77K and at atmospheric pressure. Chahine et al[6]. reported a very high hydrogen adsorption of 5.3 wt% (0.64 H/C) at 77K and at 1 MPa, in the highly porous carbon (AX-21 carbon). Despite the large volume of data from studies conducted on SWNT, MWNT, GNF, etc., as potent hydrogen storage materials, these data are scattered, and are thus inconclusive. Active carbon materials with very high surface areas have very low capacities at room temperature. This may be due to the very low levels of the effective pore size for hydrogen storage in spite of their high surface areas. The hydrogen storage capacity of saran carbon is higher than those of other active carbon materials[4]. The micropore in porous carbon materials is thought to be more effective for hydrogen storage when compared to the hydrogen molecule size of about 0.29 nm. PVdF and sarane polymers are polymers that can be used in obtaining mesoporous carbon[7]. The carbonization of PVdF can also produce a polyacetylene or carbyne structure. Its pore size may be smaller than that of saran carbon due to the small size of the fluorine atom.

The recent electrospinning process of polymer solution is a powerful method of producing ultrafine polymer fibers within the range of a few nanometers to a few hundred nanometers in diameter, which cannot be easily obtained using traditional methods. The process will be helpful in obtaining carbon materials with well-defined pore structure compared to the carbonization of microsized polymer fiber. In this study, microporous carbon nanofibers with high surface areas were prepared through the carbonization of electrospun PVdF nanofibers with an average fiber diameter of 200-300 nm. Their structural property, morphology, and hydrogen storage capacity were investigated.

2. EXPERIMENTAL

PVdF nanofibers were prepared using a PVdF solution (Kynar 761, Elf AtoChem) in an acetone/dimethylacetamide(=7/3 by weight) mixture, using the typical electrospinning method. They were slightly dehydrofluorinated (DHF) in the mixture of methanol/dimethyl-formamide(=9/1) containing 10 ml of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) at 50 °C for 5 hours. They were also highly DHF-treated in the mixture of methanol/DBU (=1/2). The DHF-treated PVdF nanofibers were carbonized at 800-1800 °C to induce micropore structures without a further activation process (Scheme 1).

The surface morphology of carbon nanofibers was observed using a SEM, an AFM, and a TEM. WAXS patterns were scanned using an X-ray diffractometer with CuKα radiation, within the range of 2θ =10-90°. Raman spectra were obtained using Micro Raman with argon

정혜진 · 조성무 · 김동영 · 진병두 · 이도원

laser. The nitrogen gas adsorption- desorption isotherms of the carbon nanofibers were measured at 77K using an automatic gas adsorption apparatus (Themo, Sorptomatic 1990). The BET surface area was calculated from the adsorption isotherms. The pore size distribution was obtained by applying the Horvath Kawazoe Poresizes for microporous samples and the B.J.H. Pore sizes for meso-porous samples.

The hydrogen storage capacity of carbon nanofibers was evaluated through the gravimetric method using magnetic suspension balance (MSB, Rubotherm). First, the blank test chamber containing samples was evacuated, to remove the impurities and water, at 150 °C/10^{-6} torr for 6 hours. The weights of the sample basket and samples were then measured at 10^{-6} torr/25 °C (±0.5 °C) and at an He gas atmosphere of 10 bars, respectively. It was assumed that He gas was not adsorbed by the carbon nanofiber samples in this condition. The weight difference between the vacuum and the 10 bar He gas, which indicates buoyancy due to the He gas, was used to determine the volume of the carbon nanofiber samples, as follows:

$$Vs = \Delta W_1/d_{He}, \qquad eq.(1)$$

, where Vs is the volume of the samples, ΔW_1 is the weight difference of the samples between the vacuum and the 10 bar He gas atmosphere, and d_{He} is the density of He at a specific pressure and temperature. The weights of the samples were measured under different H_2 pressures (10-100 bars) at 25 °C (± 0.5 °C). The weights of the absorbed hydrogen were determined after the correction of the buoyancy due to the hydrogen gas atmosphere, using the sample volume (Vs), as follows:

The weight of the adsorbed H_2
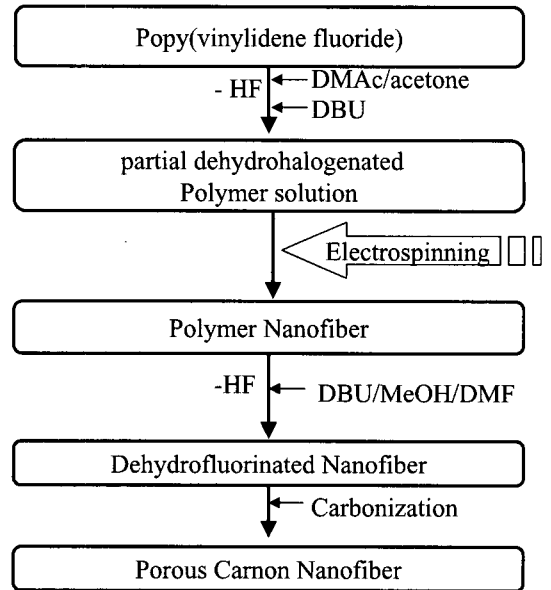
Scheme 1. Preparation process of PVdF-based carbon nanofibers.

$$= \Delta W_2 + Vs\ d_{H2}, \qquad eq.(2)$$

, where ΔW_2 is the weight difference of the samples between the vacuum and the specific H_2 pressure, Vs is the volume of the samples, d_{H2} is the density of H_2 at a specific pressure and temperature. The densities of He and H_2 gas for buoyancy correction were calculated from a real gas equation using the Thermodynamic and Transport Properties of Pure Fluid Program (NIST-supported).

3. RESULTS and DISCUSSION

PVdF and saran polymers formed the meso porous or microporous carbon materials during the carbonization. The ultrafine structure of the electrospun PVdF nanofibers is expected to be good for the formation of pores, which are effective for hydrogen adsorption, compared to PVdF films or microfibers. In this study, microporous carbon nanofibers were obtained
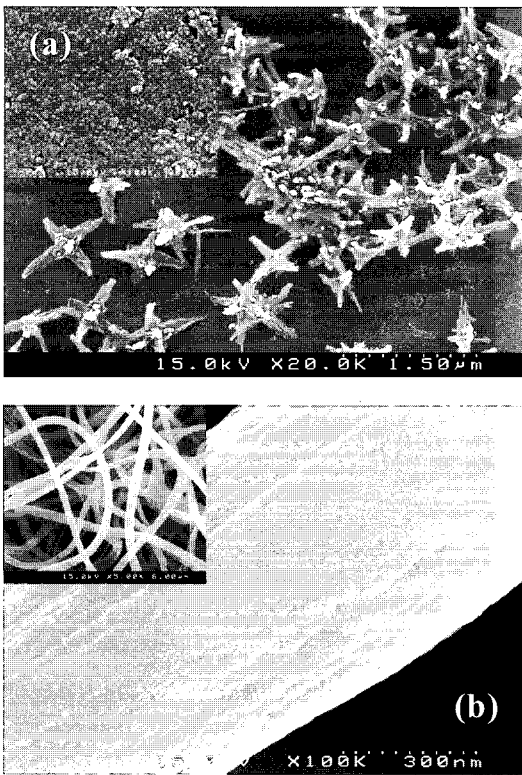
Fig. 1. SEM images of the electrospun PVdF nanofibers after carbonization at 1300 ℃ : (a) without DHF-treatment and after high DHF- treatment, using MeOH/DBU=1/2 mixture at 100 ℃ for 4hr.

Fig. 2. FT-IR spectra of the electrospun PVdF nanofiber after DHF-treatment.

through the carbonization of PVdF nanofibers without further activation. It is necessary to make the PVdF-based nano- fibers infusible to maintain their fibrous shape during the carbonization. If the PVdF fibers were to be heated without applying dehydro- fluorination (DHF) treatment for infusibility, they would melt at about 165 ℃, and only granular carbons would be produced at a high temperature, as shown in Fig. 1(a). Therefore, the structure of the PVdF-based carbon greatly depends on the extent of the DHF treatment before carbonization. First, the DHF treatment of the
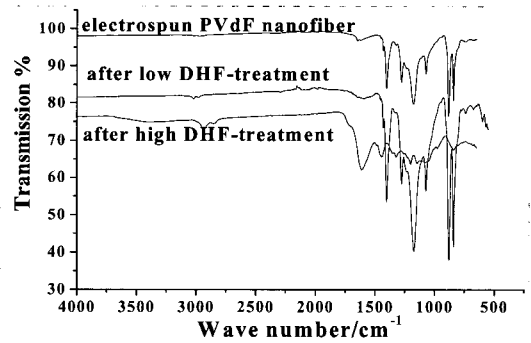
electrospun PVdF nanofiber was carried in the mixture of MeOH/DBU= 1/2 at 100 ℃ for 4hr. FT-IR spectrum of the resulting fiber showed the development of intensive -C=C- bond at about 1610 cm^{-1} due to DHF (Fig. 2). Fig. 1(b) showed the carbon nanofibers obtained from carbonization of high DHF-treated fiber, having very smooth surfaces and dense, nonporous structures. Fig. 3 showed disordered crystal structure of this carbon nanofiber even though carbon nanofiber with d_{002} =0.34 nm was sometimes obtained at the high DHF condition.

In the case of the PVdF fibers that were slightly dehydrofluorinated in the mixture of MeOH/DMF=9/1 containing 10 ml of DBU at 50 ℃, the resulting fiber shows only weak -C=C- bond due to dehydrofluorination of polymer solution for electrospinning (Fig. 2 and Scheme 1). The carbonization of this fiber at above 800 ℃, however, successfully produced the carbon nanofiber without melt, having mesoporous carbon nanofiber structure consisting of 20- to 30-nm carbon granules, as shown in Fig. 4. Fig. 4 shows porous carbon nanofibers with granular-shaped surfaces, and with an internal structure composed of carbon granules. The pore structure became dense with the increase
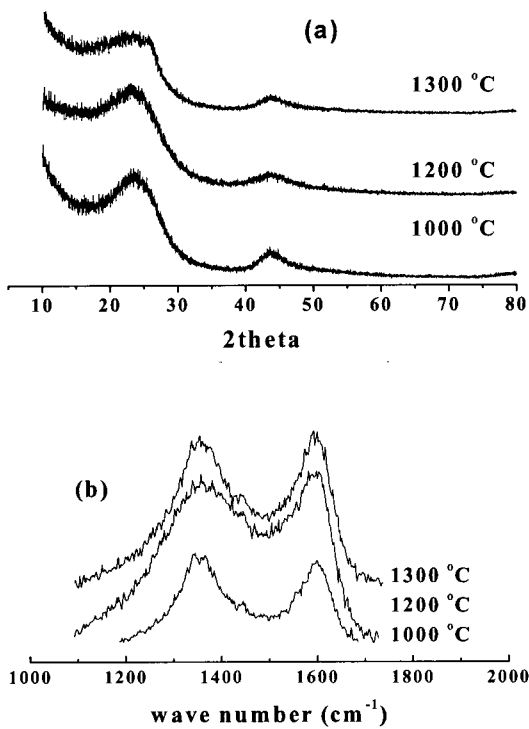
정혜진 · 조성무 · 김동영 · 진병두 · 이도원

Fig. 3. (a) XRD and (b) Raman spectra of PVdF based carbon nanofibers prepared after high DHF-treatment.

of carbonization temperature, indicating the formation of micropores at the higher carbonization temperature. The effect of DHF-treatment in the carbonization of PVdF polymer has been reported in previous studies[7]. The slight DHF treatment of PVdF nanofibers induced inhomogeneous structures consisting of the DHF-treated, amophorous region and the unreacted, crystalline region. The crystalline region melted at a high temperature while the dehydrofluorinated region maintained its fibrous shape during the carbonization. The onset temperature and the amount of volume reduction during carbonization differed between the unreacted and reacted regions. Thus, relatively large pores were produced between
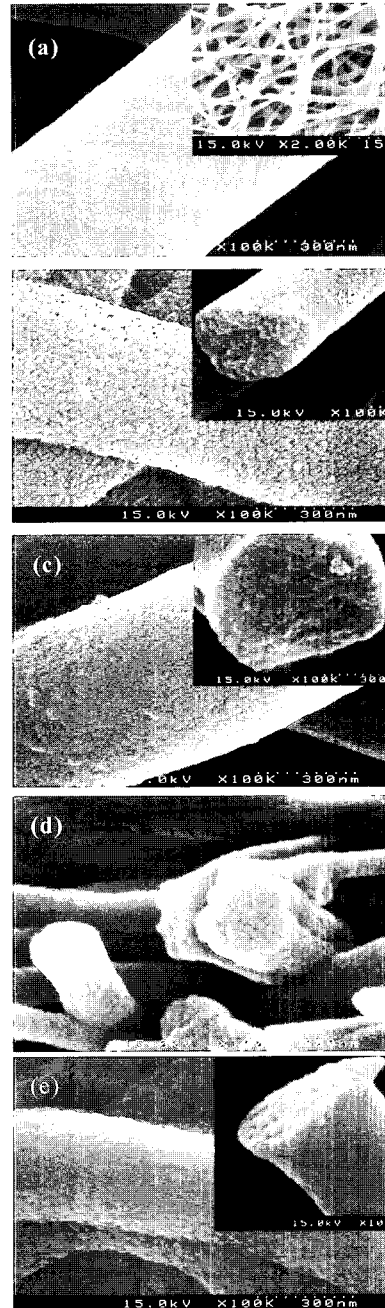

Fig. 4. SEM images of PVdF-based carbon nanofibers prepared after low DHF-treatment, using MeOH/DMF(=9/1) containing 10 ml DBU at 50 °C for 5hrs; Carbonization temperature : (a) 800 °C; (b) 1000 °C; (c) 1300 °C; (d) 1500 °C and (e) 1800 °C.
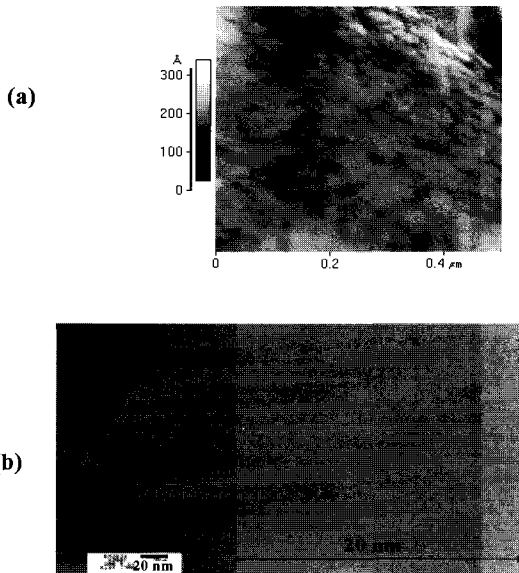
Fig. 5. AFM and TEM images of PVdF based carbon nanofibers prepared from carbonization at 1300 ℃ after slightly DHF-treatment.

Fig. 6. XRD and Raman spectras of PVdF based carbon nanofibers prepared after low DHF-treatment.

these regions. On the other hand, the structures of the highly dehydrofluorinated PVdF nanofibers were homogeneous, and large pores were not produced during carbonization. Therefore, the carbonization of PVdF nanofibers after low DHF treatment induced porous carbon nano-fibers with high surface areas due to their porous granular surfaces, as shown in Fig. 4 and Fig. 5(a). This does not indicate high hydrogen storage capacity because micropores are thought to be much more effective for hydrogen storage when compared to hydrogen molecule sizes of about 0.29 nm. TEM images of these 20- to 30-nm carbon granules, however, showed slit nanopore structures with a width of below 1 nm and a length of a few tens nm, as shown in Fig. 5(b). Therefore, these slit pores may contribute to the adsorption of hydrogen gas. As shown in Fig. 6, all
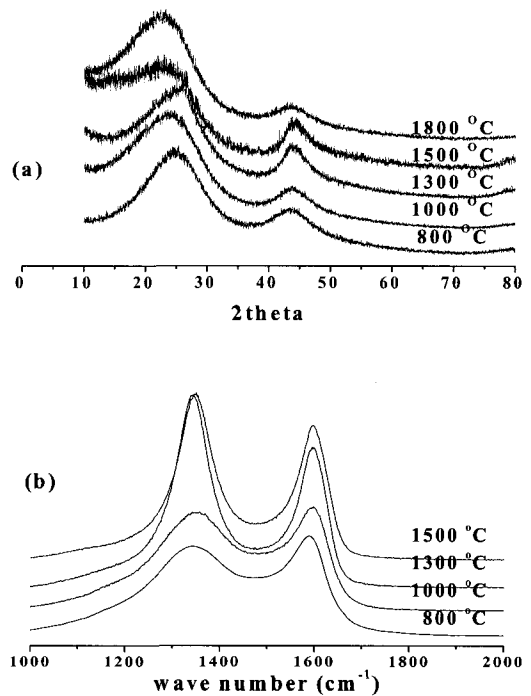
PVdF-based carbon nanofibers showed disordered carbon structures in the XRD and raman spectra regardless of the carbonization temperature.

The carbon nanofibers prepared under low DHF treatment were expected to have higher surface areas than those nanofibers prepared after a slight DHF-treatment showed typical curves of microporous carbon in the nitrogen gas adsorption-desorption isotherms while that of high DHF-treatment showed nonporous carbon, as shown in Fig. 7. BET surface area rapidly decreased with increase of carbonization temperature but remarkably increased at 1800 ℃ due to great increase of micropore with a diameter of below 1 nm, as listed in Table 1.

정혜진 · 조성무 · 김동영 · 진병두 · 이도원

Table 1. Surface Areas and Pore Size Analysis of PVdF based Carbon Nanofibers

Temperature (°C)		Surface area(m^2/g)	Pore size distribution (cm^3/g)			
			<1 nm	1-2nm	2-4nm	4-10nm
Low DHF	800	967	0.146	0.052	0.075	0.070
	1000	921	0.166	0.056	0.084	0.101
	1300	865	0.249	0.065	0.092	0.094
	1500	414	0.057	0.072	0.103	0.094
	1800	1300	1.767	-	-	-
high DHF	1000	33	-	-	0.017	0.014
	1300	16	-	-	0.006	0.004
	1500	26	-	-	0.012	0.010

* Pore size distribution was obtained by applying the Horvath Kawazoe Poresizes for microporous samples and the B.J.H. Pore sizes for mesoporous samples.

Increase of micropore volume is thought to be due to the densing effect of porous structure with increase of carbonization temperature. Sample at 1800 °C showed only micropore with a diameter of below 1 nm and high surface

Fig. 7. The nitrogen gas adsorption- desorption isotherms curves of PVdF-based carbon nanofibers.

area.

Carbon nanofibers prepared after high DHF-treatment did not observed the micropores. They showed very low surface area and adsorption curves similar to those of nonporous carbon in nitrogen gas adsorption-desorption isotherms.

Fig. 8 shows hydrogen storage capacities of PVdF-based carbon nanofibers. The hydrogen adsorption of the PVdF-based porous carbon nanofibers increased with the increase of hydrogen pressure and carbonization temperature. The sample at 1500 °C showed the maximum value of about 0.39 wt% inspite of its lowest surface area and lowest micropore volume. The sample at 1800 °C, however, showed similar storage capacity compared to that at 1500 °C even though it had highest surface area and highest micropore volume.

In the case of high DHF treatment, the resulting carbon nanofibers also showed some hydrogen storage although they had no micropores. Although the hydrogen storage capacities of them did not show large
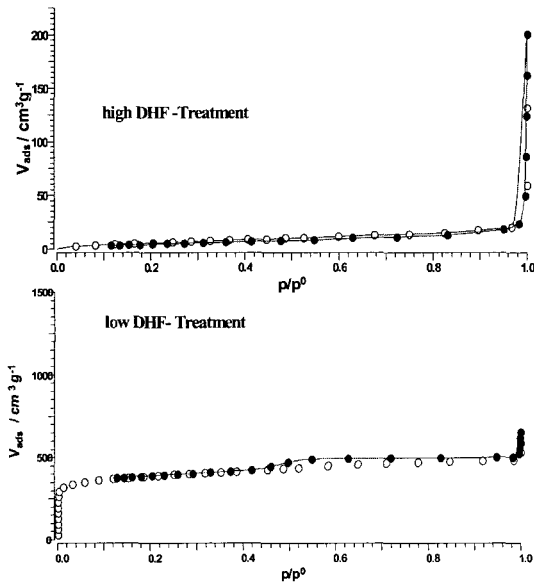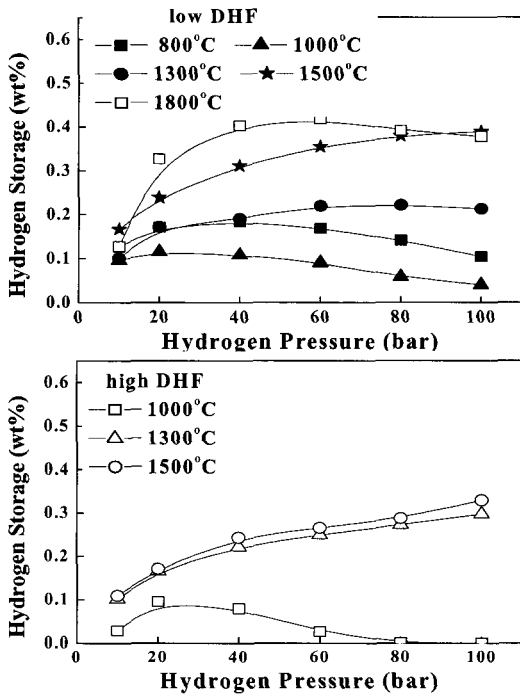
Fig. 8. The hydrogen storages capacities of PVdF-based carbon nanofibers.

difference, this may be due to the presence of ultra nanopore that can not detect by using nitrogen gas adsorption-desorption isotherms.

4. CONCLUSIONS

Carbon nanofibers were prepared through the carbonization after low and high DHF treatment of the electrospun PVdF-based nanofibers without further activation. Microporous carbon nanofibers with high surface area were obtained at low DHF treatment. At high DHF treatment nonporous carbon nanofibers with very low surface areas were prepared. The increase of the carbonization temperature rapidly resulted in the decrease of the BET surface areas. Their hydrogen storage capacities were 0.04-0.4 wt%,

and increased as the carbonization temperature increased. Hydrogen storage capacity may be affected by the pore size, pore shape rather than surface area. Carbon nanofibers without micropore also showed some hydrogen storage compared to those with high micropore volume. This may be due to the presence of ultra nanopore that can not detect by using nitrogen gas adsorption-desorption isotherms.

ACKNOWLEDGMENTS

REFERENCES

1) A.C. Dillon, K.M. Jones, T.A. Bekke-dahl, H. Kiang, D.S. Bethune, and M.J. Heben : "Storage of hydrogen in single walled carbon nanotubes", Nature, Vol. 386, 1997, pp. 377-379.

2) C. Liu, Y.Y. Fan, M. Lyu, H.T. Cong, H. M. Cheng, and M.S. Dresselhaus : "Hydrogen storage in single-walled carbon nanotubes at room temperature", Science, Vol. 286, 1999, pp. 1127-1129.

3) H. Zhu, A. Cao, X. Li, C. Xu, Z.Mao, D.Ruan, J. Liang, D. Wu : "Hydrogen adsorption in bundles of well-alligned carbon nanotubes at room temperature", Applied Surface Science, Vol. 178, 2001, pp. 50-55.

4) Y. Ye, C.C.Ahn, C. Witham, B. Fultz,J. Liu, A.G. Rinzler, D. Colbert, K.A.Smith, and R. E. Smalley: "Hydrogen adsorption and cohesive energy of single-walled carbon nanotubes", Appl. Phys. Lett., Vol. 74, No. 16, 1999, pp. 2307-2309.

5) M.G. Nijkamp, J.E.M.J. Raaymakers, A.J. van

Dillen, K.P. de Jong: "Hydrogen storage using physisorption-materials demands", Appl. Phys. A, Vol. 72, 2001, pp. 619-623.

6) R. Chahine and T. K. Bose :"Low-pressure adsorption storage of hydrogen", Int. J. Hydrogene Energy, 19, 1994, pp. 161-164.

7) J. Yamashita, M. Shioya, T. Kikutani, and T. hashimoto : "Activated carbon fibers and films derived from poly(vinylidene fluoride)", Carbon, Vol. 39, 2001, pp. 207-214.