Available online at www.sciencedirect.com
ScienceDirect
Journal of Colloid and Interface Science 318 (2008) 42–49
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

The study of controlling pore size on electrospun carbon nanofibers for hydrogen adsorption

Ji Sun Im [a], Soo-Jin Park [b], Tae Jin Kim [c], Young Ho Kim [d], Young-Seak Lee [a,d,*]

[a] *Department of Nano Technology, BK21-E²M, Chungnam National University, Daejeon 305-764, Republic of Korea*
[b] *Department of Chemistry, Inha University, Incheon 402-751, Republic of Korea*
[c] *Core Technology Research Center for Fuel Cell, Jeonbuk Techno-park, Jeonbuk-do 561-350, Republic of Korea*
[d] *Department of Fine Chemical Engineering and Applied Chemistry, BK21-E²M, Chungnam National University, Daejeon 305-764, Republic of Korea*

Received 12 July 2007; accepted 16 October 2007

Available online 22 October 2007

Abstract

Polyacrylonitrile (PAN)-based carbon nanofibers (CNFs) were prepared by using electrospinning method and heat treatment to get the media for hydrogen adsorption storage. Potassium hydroxide and zinc chloride activations were conducted to increase specific surface area and pore volume of CNFs. To investigate the relation between pore structure and the capacity of hydrogen adsorption, textural properties of activated CNFs were studied with micropore size distribution, specific surface area, and total pore volume by using BET (Brunauer–Emmett–Teller) surface analyzer apparatus and the capacity of hydrogen adsorption was evaluated by PCT (pressure–composition–temperature) hydrogen adsorption analyzer apparatus with volumetric method. The surface morphology of activated CNFs was observed by SEM (scanning electron microscope) images to investigate the surface change through activation. Even though specific surface area and total pore volume were important factors for increasing the capacity of hydrogen adsorption, the pore volume which has pore width (0.6–0.7 nm) was a much more effective factor than specific surface area and pore volume in PAN-based electrospun activated CNFs.

Keywords: Hydrogen adsorption; Carbon fiber; Electrospinning; Chemical activation; Physical activation

1. Instruction

Hydrogen is considered as an ideal energy medium for replacing fossil fuels. An efficient hydrogen storage medium is an inevitable component for the adsorption of hydrogen as an energy carrier. Hydrogen storage in the solid matrices like metals, intermetallic compounds, porous solids and carbon materials appears to be appropriate option. In case of metals and intermetallic compounds, the negative factors for hydrogen storage are either the limitation of storage capacity or the reversibility of stored hydrogen under favor experimental conditions [1–3]. Many researchers have paid much attention on hydrogen adsorption in nanostructured carbon base materials, such as activated carbons [4–8], carbon nanotubes [9–11], carbon nanofibers [12–15]. Although a significant amount of research work has dealt with the hydrogen adsorption in carbon-based materials, the search for more suitable hydrogen adsorbents materials and for understanding of the adsorption mechanism of H_2 has increased considerably. It is still believed that microporous materials like activated carbon fibers (ACFs) are considered one of the most promising materials for practical way of hydrogen storage.

ACFs are non-hazardous, processed, and carbonaceous materials, having a porous structure, a high adsorption capacity and rate, and a large specific surface area. The advantages of ACFs are smaller fiber diameter, more concentrated pore size distribution and excellent adsorption capacity at low concentration of adsorbates compared with conventional activated carbons. The porosity of ACFs is developed during activation and it is influenced by many factors, such as the degree of activation and the conditions used for carbonization. Since variables

* Corresponding author. Fax: +82 42 822 6637.
E-mail address: youngslee@cnu.ac.kr (Y.-S. Lee).

0021-9797/$ – see front matter
doi:10.1016/j.jcis.2007.10.024

Table 1
Constituent mass ratios of the used mixtures in this study

Sample name	As-received	ZC-W2	ZC-W4	ZC-W6	PH-M4	PH-M6	PH-M8
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

such as temperatures, heating rate, and pressure do not seem to have an important role in influencing the micropore distribution [16–18], the alternative use of well-controlled chemical activation is interesting because of the development of porosity is substantially modified.

Furthermore, the electrospinning method is a very simple and efficient way for the fabrication of nano- to microscale fibers which has much smaller diameter than that of conventional carbon fibers. In a typical process, an electrical potential is applied between a droplet of polymer solution or melt held at the end of a capillary and a grounded collector. Recently, we have successfully prepared a carbon nanofiber web, which has meso- and macropores and [19] through the electrospinning technique with inorganic compound as template for the creation of porosity, that can accelerate the application of these materials to electrical energy storage systems.

Generally, there are two ways to evaluate the capacity of hydrogen adsorption with different temperature (cryogenic or room temperature) [20–22]. If the capacity of hydrogen adsorption is measured at 77 K, the result has much higher value comparing with the result which is measured at room temperature. But one of disadvantages is that it costs too much to keep low temperature (77 K) with regarding of application filed and economic effect. So in this paper, our point about hydrogen adsorption is how we can develop the capacity of hydrogen adsorption at room temperature with economic consideration for a practical usage.

In this present study, since microporous materials are considered the most promissory materials for a practical way of hydrogen storage, chemical agents such as zinc chloride and potassium hydroxide were used on electrospun-submicron fibers to obtain nanoporous carbons of optimum size for hydrogen adsorption. Subsequently, the effects of those pore size prepared by the chemical agents on the hydrogen adsorption capacity of electrospun ACFs were investigated.

2. Experimental

Zinc chloride and potassium hydroxide activation were conducted for activating CNFs.

2.1. Preparation of zinc chloride activated CNFs

PAN ($d = 1.184$, 181315, Aldrich) and DMF (N,N-dimethyl formamide, $d = 133$, 766137, Fisher) were used for getting polymer solution. To select a proper physical activation agent, two major conditions were considered in this paper. The first thing is that it must be soluble in solvent for electrospinning. The second is that the ion size (Zn^{2+}: 0.43 nm [23], Cl^{-1}: 0.362 nm [24]) should be smaller than wanted pore size, because zinc chloride will be volatilized as an ion state during carbonization. So $ZnCl_2$ (zinc chloride, 208086, m.p. = 586 K) was used to activate CNFs during carbonization. Four polymer solutions were prepared with various weight ratios (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 with final product names.

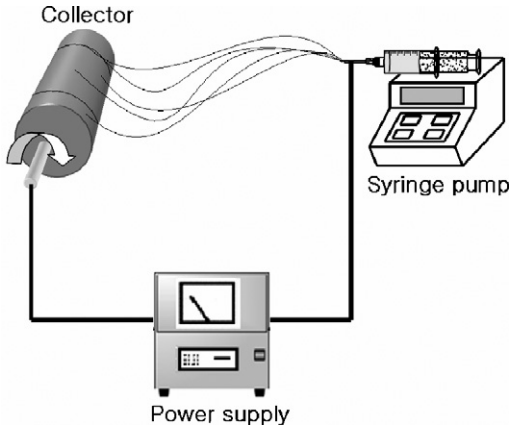

Fig. 1. Schematic diagram of the electrospinning set-up used for producing nanofibers.

Each polymer solution was heated at 383 K for 1 h. The polymer solution was injected into a 30 cm^3 syringe having a capillary tip which has 18 gauge needle (inner diameter: 1.27 mm). Each solution was electrospun into a fiber web using an electrospinning system equipped with power supply (NT-PS-25K, NTSEE Co., Korea). The schematic diagram of electrospinning system is shown in Fig. 1. Polymer solutions were electrospun with following conditions [voltage: 15 kV, syringe rate: 1.5 cc/h, collector rotation speed: 300 rpm, and TCD (tip to collector distance): 10 cm] [19]. Before carbonizing the electrospun fibers, oxidation process is necessary to change the thermoplastic character into thermosetting one. Because electrospun materials cannot keep their fiber form at high temperature because they would be soften and melt [25]. Oxidation of the electrospun fibers was carried out by heating to 523 K at a rate of 1 K/min and maintained for 8 h under the natural flow of air. In this research, carbonization step and zinc chloride activation step have carried out simultaneously. In case of sample As-received, oxidized materials were carbonized at 1323 K for 1 h in nitrogen atmosphere. But in case of sample ZC-W2, ZC-W4, and ZC-W6, oxidized materials were carbonized at 1323 K for 2 h to remove zinc chloride sufficiently with low melting point (586 K) of zinc chloride.