

Pore structure control of activated carbon fiber for CO gas sensor electrode

Byong Chol Bai^{1,2} and Tae-Sung Bae^{3,*}

¹Division of Green Chemistry & Engineering Research, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Korea

²Department of Applied Chemistry and Biological Engineering, Chungnam National University, Daejeon 34134, Korea

³Korea Basic Science Institute (KBSI), Jeonju 54907, Korea

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***Corresponding Author**

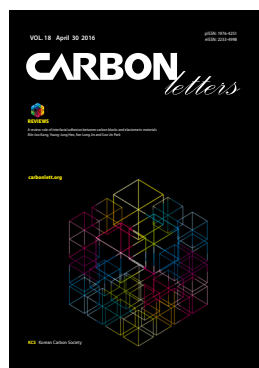
E-mail: chemipia@kbsi.re.kr

Tel: +82-63-711-4515

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Materials with porous structures developed in previous research have been used extensively in industrial purification and chemical recovery operations due to their large specific surface areas and pore volumes. Among a wide range of activation methods, chemical activation is an effective and simple method to prepare activated carbons with a high specific surface area. Depending on the chemical agents used, chemical activation can lead to unique pore structures [1-3].

CO gas detection has recently become a critical issue because CO is one of the most common air pollutants. Pollutant CO gas is produced by incomplete hydrocarbon burning and accompanies almost all combustion processes. CO is especially dangerous because it possesses no odor or color and is therefore undetectable by humans. CO gas also becomes explosive at concentrations above 12% and has a threshold limit value of 25 ppm. Vehicle exhaust is a major source of environmental CO emissions and contributes to smog formation. Thus, the development of highly selective and stable CO sensors is an important goal and will assist in the study of environmental impacts. Motivated by the increasingly strict laws for different pollutant sources, recently there has been rapid progress in the fabrication of sensors to detect and monitor the environment, and several types of gas sensors have been reported in the literature [4-9].

In this study, carbon based materials were used to fabricate a gas sensor matrix by electrospinning and heat treatment. To improve the sensitivity of the sensor by enhancing the gas adsorption, a porous structure was developed using chemical activation. The gas sensing mechanism was discussed based on the carbon pore structure.

A polymer solution was prepared by dissolving polyacrylonitrile (PAN; d = 1.184, 181315 Aldrich, USA) in N,N-dimethyl formamide (DMF; d = 133, 766137 Fisher, USA). Electrospun fibers were obtained from the polymer solution using the electrospinning method. The electrospinning process was carried out under the following conditions: 0.8 mL/h polymer solution feed rate, 13 kV supplied voltage, 12 cm tip to collector distance, and 120 rpm collector rotation. The electrospun materials were stabilized by heating up to 523 K in air at a heating rate of 3 K min⁻¹, followed by treatment of the samples at 523 K for 3 h. Carbonization of the stabilized electrospun materials was carried out under an argon atmosphere with the following conditions: 15 K/min heating rate, 1273 K reaction temperature, 1 h holding time, and a 50 mL/h argon feed rate. The prepared sample was named CF.

H₃PO₄ solutions (1, 2, 3, and 4 M) were prepared as chemical activation agents. The CF was placed in an alumina boat in a steel pipe at a ratio of 20 mL/g (H₃PO₄ solution/CF) to carry out the chemical activation. Activation was conducted at 1023 K for 2 h in an argon atmosphere. The heating rate was 5 K/min and the feed rate of the argon gas was 30 mL/min. Following the chemical activation, the obtained samples were washed several times with distilled water to remove residual potassium and were then dried at 383 K overnight. These activated samples are called ACF-HP1, ACF-HP2, ACF-HP3, and ACF-HP4, according to the molar concentrations (1, 2, 3, and, 4 M, respectively) of the H₃PO₄ solutions.

Table 1. Summary of textural characteristics of CNFs

	CF	ACF-HP1	ACF-HP2	ACF-HP3	ACF-HP4
V_T (cc/g)	0.006	0.149	0.296	0.279	0.398
V_M (cc/g)	0.001	0.066	0.121	0.115	0.099
$V_M/V_T \times 100$ (%)	16.67	44.19	40.72	41.31	25.08
S_T (m ² /g)	11.211	52.416	120.395	369.551	525.378
S_M (m ² /g)	2.312	20.464	56.472	162.616	132.848
$S_M/S_T \times 100$ (%)	20.54	39.04	46.91	44.01	25.28

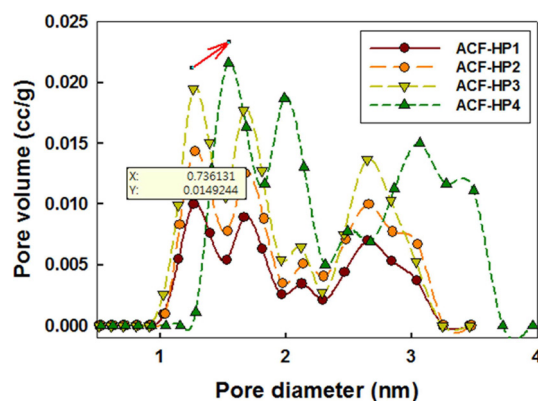
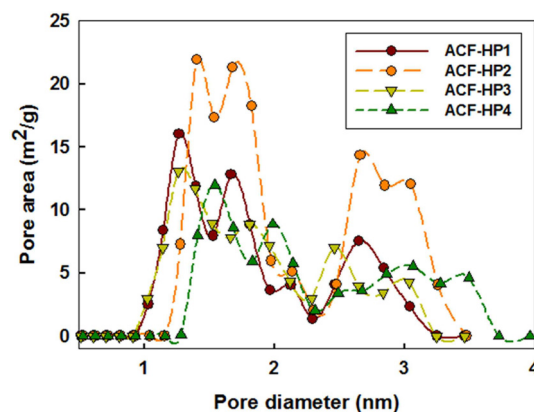
CNF, carbon nanofiber; CF, carbon fiber; V_T , total pore volume; V_M , micropore volume; S_T , Brunauer-Emmett-Teller total surface area; S_M , HK micropore surface area.

The textural properties of the prepared samples (CF, ACF-HP1, ACF-HP2, ACF-HP3, and ACF-HP4) were investigated. Samples were degassed at 423 K for 3 h, and nitrogen adsorption was then carried out at 77 K using a Brunauer-Emmett-Teller (BET) apparatus (ASAP 2020; Micromeritics, USA) to investigate the specific surface area, total pore volume, pore size distribution, and micropore fraction.

The electrical resistance was measured using a programmable electrometer (6514, Keithley, Cleveland, OH, USA) to evaluate the gas-sensing properties of the prepared sample. The gas sensing device was prepared with two Pt electrodes and a SiO₂ plate. The plates were cut into 0.5 × 0.5 cm² square pieces to measure the electrical resistivity. This measurement was carried out in a stainless steel chamber with a volume of 1000 cm³. The prepared gas sensor sample was placed in a sealed vacuum chamber at a pressure of 1 × 10⁻⁶ mbar. Initially, air was injected into the chamber to stabilize the electrical resistance. A mixture gas was prepared, and the change in the electrical resistance was measured at 22°C ± 1°C as the mixture gas containing 50 ppm of CO in dry air was injected into the chamber at a fixed rate of 500 sccm. The chamber was covered by a circulated water tube to maintain a regular temperature [9].

In the chemical activation of carbon precursors with phosphoric acid, p-containing carbonaceous structures, such as acid phosphates and polyphosphates, are formed in the samples carbonized in the presence of H₃PO₄. Upon pyrolysis, this favors crosslink reactions and aromatization at lower temperatures; it also inhibits tar formation, which reduces volatile loss and therefore results in an increase in the carbon yield. Additionally, it has also been shown that H₃PO₄ produces activation through the formation of phosphate and polyphosphate bridges that connect the crosslink polymer fragments, avoiding contraction of the material due to temperature. Removal of the activating agent during the washing step will lead to a matrix in an expanded state with an accessible pore structure.

The pore structure of carbon fiber was developed by chemical activation. A summary of textural properties is presented in Table 1. Specific surface area and pore volume were increased after chemical activation. The BET specific surface area of ACF-HP4 increased approximately 50-fold from 11 to 525 m²/g, compared with the non-activated sample CF. The pore volume also increased through activation. For example, the ACF-HP4 sample exhibited a total pore volume of 0.398 cc/g.

**Fig. 1.** Pore distribution for volume.**Fig. 2.** Pore distribution for surface area.

Since the micropores of porous carbon materials play an important role in gas adsorption [10,11], the micropore fraction of prepared samples was calculated using the DFT (density functional theory) equation. The obtained micropore fractions of the pore volume and surface area are presented in Table 1. With the exception of the ACF-HP4 sample, all activated samples show micropore fractions of approximately 40%. To study this in more detail, the pore size distribution was calculated.

Figs. 1 and 2 show the pore size distributions of phosphoric acid activated CFs. The DFT can determine the successive pore size distribution curve from micropore and mesopore to mac-

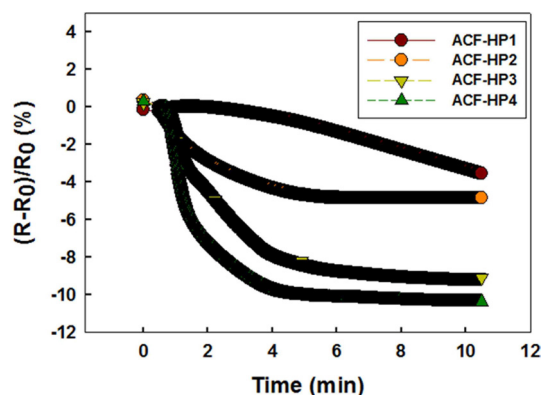


Fig. 3. CO gas sensing by prepared porous carbon fibers.

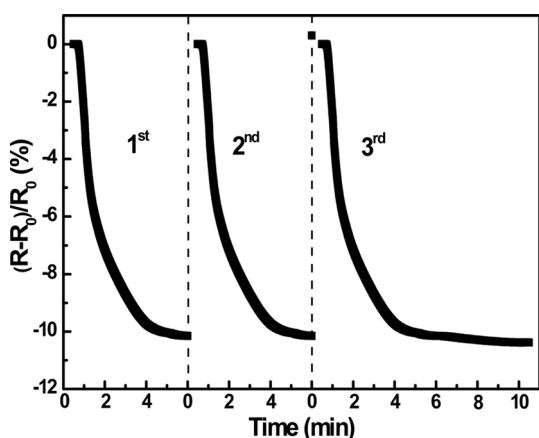


Fig. 4. Recovery of CO gas sensing properties of the ACF-HP4 sample.

ropore scale. DFT assumes each pore acts independently. Each pore size present in the system then contributes to the total adsorption isotherm in proportion to the fraction of the total area of the sample that it represents [5]. The pore diameters mainly range from 1 to 4 nm. The pores in the mesopore diameter range (from 2 to 50 nm) are small-sized mesopores. The shifting peak position of ACF-HP4 (indicated by the red arrow in Fig. 1) is due to merging of the micropores during the chemical reaction. Thus, the micropore fraction of ACF-HP4 decreased even though the total pore volume and specific surface area increased. The effects of the pore size, pore volume, and specific surface area for a high performance gas sensor were investigated, and the results are shown in Fig. 3.

The resistive response is plotted versus the time of exposure to the CO gas in Fig. 3. The CF sample showed less than a 1% resistive response with a non-reproducible result due to the inactive CO gas adsorption sites and because it is a non-porous material. Therefore, the gas sensing behavior was investigated in activated CFs. The development of a porous structure enhanced the CO gas sensing ability by more than 10%, as shown for the ACF-HP4. This result implies that the porous structure generated by chemical activation effectively improved the gas adsorption sites. It is noted that the gap in the resistance change is too small when comparing ACF-HP4 and other materials based on the high pore volume of the specific surface area of

ACF-HP4. This is explained by the relatively small micropore fraction of ACF-HP4. Generally, the gas adsorption occurs more effectively in the micropores. This is the origin of the high gas sensing performance of ACF-HP3. Fig. 4 presents the data for the reproducibility of gas sensing by representative samples of ACF-HP4. A perfect reproducibility was observed, which is attributed to the excellent gas desorption properties of ACF during the recovery process consisting of a low degassing pressure and a high temperature. Such excellent desorption is one of the general advantages of porous carbon materials.

The electrical resistance depended on the relationship between adsorbed molecules and pores in activated carbons. The electrical change was then effectively transferred by the electrically conductive network. The reduced electrical resistance is mostly attributed to the effects of electron localized CO molecules compared with the electron non-localized air gas. Before inducing CO target gas to the gas sensing material, air gas was introduced as a stabilization step. In light of the stable electron configuration reported by another group [12], the introduction of air gas may decrease the electrical resistance in activated carbon, showing an insulator effect. However, the introduction of easily electron polarized molecules, such as CO, reduced the electrical resistance compared with air gas. This appears to cause electron hopping effects in the pores [13]. Therefore, it can be concluded that activated carbons, especially those with a seriously degraded graphite structure, can lose their semiconductor characteristics and then solely serve for efficient target gas adsorption. It can also be concluded that the electrical change on the surface was transferred effectively by the conduction band (CB) of the electrical conduction network. It is further concluded that the micropores play an important role for CO gas adsorption and detection, even though the pore volume and specific surface area are still critical factors.

This paper reports a high performance CO gas sensor electrode prepared by electrospinning and chemical activation. A pore structure for CO gas adsorption was developed, reaching a specific surface area of 525 m²/g and a pore volume of 0.398 cc/g. Even when the pore volume and specific surface area were increased through the use of a different, more commonly used chemical agent, the micropore fraction decreased after some time, due to the micro pore merging effect. The CO gas sensing results also show the critical role of the micropores. The ACF-HP4 sample showed CO gas sensing performance that was almost identical to that of ACF-HP3, even with higher pore volume and specific surface area. To conclude, a high performance CO gas sensor was fabricated by pore size control technology using a phosphoric acid chemical activation process.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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References

- [1] Sun Z, Yu Y, Pang S, Du D. Manganese-modified activated carbon fiber (Mn-ACF): novel efficient adsorbent for Arsenic. *Appl Surf Sci*, **284**, 100 (2013). <http://dx.doi.org/10.1016/j.apsusc.2013.07.031>.
- [2] Zheng J, Zhao Q, Ye Z. Preparation and characterization of activated carbon fiber (ACF) from cotton woven waste. *Appl Surf Sci*, **299**, 86 (2014). <http://dx.doi.org/10.1016/j.apsusc.2014.01.190>.
- [3] Bai BC, Kim EA, Lee CW, Lee YS, Im JS. Effects of surface chemical properties of activated carbon fibers modified by liquid oxidation for CO₂ adsorption. *Appl Surf Sci*, **353**, 158 (2015). <http://dx.doi.org/10.1016/j.apsusc.2015.06.046>.
- [4] Mirzaei A, Park S, Sun GJ, Kheel H, Lee C. CO gas sensing properties of In₄Sn₃O₁₂ and TeO₂ composite nanoparticle sensors. *J Hazard Mater*, **305**, 130 (2016). <http://dx.doi.org/10.1016/j.jhazmat.2015.11.044>.
- [5] Goto T, Itoh T, Akamatsu T, Izu N, Shin W. CO sensing properties of Au/SnO₂-Co₃O₄ catalysts on a micro thermoelectric gas sensor. *Sens Actuators B: Chem*, **223**, 774 (2016). <http://dx.doi.org/10.1016/j.snb.2015.09.146>.
- [6] Cuong ND, Khieu DQ, Hoa, TT, Quang DT, Viet PH, Lam TD, Hoa ND, Hieu NV. Facile synthesis of α-Fe₂O₃ nanoparticles for high-performance CO gas sensor. *Mater Res Bull*, **68**, 302 (2015). <http://dx.doi.org/10.1016/j.materresbull.2015.03.069>.
- [7] Vetter S, Haffer S, Wagner T, Tiemann M. Nanostructured Co₃O₄ as a CO gas sensor: temperature-dependent behavior. *Sens Actuators B: Chem*, **206**, 133 (2015). <http://dx.doi.org/10.1016/j.snb.2014.09.025>.
- [8] Kang SC, Im JS, Lee SH, Bae TS, Lee YS. High-sensitivity gas sensor using electrically conductive and porosity-developed carbon nanofiber. *Colloids Surf A: Physicochem Eng Asp*, **384**, 297 (2011). <http://dx.doi.org/10.1016/j.colsurfa.2011.04.001>.
- [9] Im JS, Kang SC, Bai BC, Bae TS, In SJ, Jeong E, Lee SH, Lee YS. Thermal fluorination effects on carbon nanotubes for preparation of a high-performance gas sensor. *Carbon*, **49**, 2235 (2011). <http://dx.doi.org/10.1016/j.carbon.2011.01.054>.
- [10] Sazama P, Wichterlova B, Dedecek J, Tvaruzkova Z, Musilova Z, Palumbo L, Sklenak S, Gonsiorova O. FTIR and ²⁷Al MAS NMR analysis of the effect of framework Al- and Si-defects in micro- and micro-mesoporous H-ZSM-5 on conversion of methanol to hydrocarbons. *Microporous Mesoporous Mater*, **143**, 87 (2011). <http://dx.doi.org/10.1016/j.micromeso.2011.02.013>.
- [11] Do DD, Tan SLJ, Zeng Y, Fan C, Nguyen VT, Horikawa T, Nicholson D. The interplay between molecular layering and clustering in adsorption of gases on graphitized thermal carbon black: spill-over phenomenon and the important role of strong sites. *J Colloid Interface Sci*, **446**, 98 (2015). <http://dx.doi.org/10.1016/j.jcis.2015.01.028>.
- [12] Kobayashi N, Enoki T, Ishii C, Kaneko K, Endo M. Gas adsorption effects on structural and electrical properties of activated carbon fibers. *J Chem Phys*, **109**, 1983 (1998). <http://dx.doi.org/10.1063/1.476774>.
- [13] Chiu HS, Lin PI, Wu HC, Hsieh WH, Chen CD, Chen YT. Electron hopping conduction in highly disordered carbon coils. *Carbon*, **47**, 1761 (2009). <http://dx.doi.org/10.1016/j.carbon.2009.03.002>.