



N₂ plasma treatment on activated carbon fibers for toxic gas removal: Mechanism study by electrochemical investigation



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HIGHLIGHTS

- SO₂ adsorption properties of activated carbon fibers (ACFs) were studied based on N₂ plasma treatment.
- The nitrogen functional groups, especially quaternary nitrogen groups were successfully introduced on the ACFs surface.
- Quaternary nitrogen groups were employing a semi-ionic introduction with SO₂ molecules.
- Pyridine N-oxide (N-X) functional group exhibited acidic properties and had a neutralizing effect on the ACFs' surface.

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ABSTRACT

The mechanisms of the SO₂ adsorption properties of activated carbon fibers (ACFs) after plasma treatment were studied. The surfaces of the ACFs were modified by a plasma treatment using N₂ gas to enhance the SO₂ adsorption of the fibers based on the effects of introduced nitrogen functional groups, especially quaternary nitrogen groups. Through the comparative analysis of X-ray photoelectron spectroscopy (XPS), especially the N1s component and SO₂ adsorption data, quaternary nitrogen groups were determined to be effectively introduced onto the surface of the ACFs. SO₂ molecules have lone pair electrons and attach themselves to the ACFs' pores as the concentration of quaternary nitrogen increases. However, the pyridine N-oxide (N-X) functional group exhibited acidic properties and had a neutralizing effect on the ACF surfaces, reducing the strength of electrostatic interactions with the SO₂ molecules. These types of mechanisms are proved by various physicochemical and electrical characterizations, especially the SO₂ sensing capability of plasma-treated ACFs. The reversible sensing indicates that N₂ plasma treatment changed the electrical properties of the carbon sample, leading to an intriguing sensing mechanism.

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1. Introduction

In addition to its inherent toxicity, SO₂ is one of the main precursors for acid rain generation, which is one of the most serious global environmental concerns. Thus, a number of processes have been studied to remove or adsorb SO₂ gases [1]. In gas phase adsorption processes, activated carbons are widely used in a variety of areas. Notably, SO₂ adsorption from coal and oil combustion exhaust using activated carbon has been widely

studied [1–4]. Additionally, active carbon fibers (ACFs) have been used for toxic gas removal because of their positive adsorption properties based on specific surface area, micropores, safety, reproducibility, and processing ability [5]. Many research studies have been performed using chemical impregnation methods resulting in strong adsorption properties of ACFs; most commonly, a variety of metal/oxides have been used in ACF doping. SO₂ removal can occur through both physical and chemical adsorption.

In physical adsorption, the adsorption capacity of ACFs is largely linked to their pore volume, surface area and pore size distribution (PSD) [6,7]. The adsorption of polar molecules, such as SO₂ and NO, can also be strengthened by specific interactions with the chemical groups present on the carbon surface [8–10]. In typical industrial conditions, SO₂ adsorption efficiencies depend mostly on the

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chemical properties of the carbon surface rather than general textural parameters [11,12]. Additionally, a homogeneous micropore size distribution (MPSD) with a mean pore diameter of approximately 7 Å can substantially enhance the SO₂ adsorption capacity [13,14]. Therefore, controlling their physical and chemical properties and determining the best combination of physical and chemical properties are both important for creating ACFs with high adsorption properties.

SO₂ adsorption research is focused primarily on the development of materials with basic nitrogen groups [15,16]. SO₂ adsorption is influenced by the chemical characteristics of the materials' functionalities. Research studies have examined the chemical effects on SO₂ retention induced by enhanced concentrations of pyridine and quaternary nitrogen on ACFs; an evident correlation between the SO₂ capacity and the surface basicity was noted [17]. Typically, treated ACFs display a high stability of the aromatic nitrogen groups, enabling a number of sorption cycles without any significant decrease in the SO₂ adsorption capacity [18].

Most methods for nitrogen treatment of porous carbon can be divided into two groups. The first treats activated carbon using ammonia, ammonia–air or ammonia–steam mixtures at high temperatures [19,20]. The second involves the compressed-phase pyrolysis of nitrogen-containing precursors [21,22] or the thermal decomposition of a nitrogen carrier with a carbon precursor by the activation of the carbons. In addition to preparing the activated carbons with controlled microporosity and surface basicity, the nitrogen precursor must also be optimized in terms of the weight ratio of carbon [23].

In this work, ACFs free of mineral ashes and ranging in nitrogen content were treated under various nitrogen plasma conditions. Plasma treatment is considered to be a promising technique for several reasons. It is simple to operate and can easily be controlled. Additionally, it is solvent free and induces fast reactions. Furthermore, it is easy to create oxidative, reductive, or inactive reaction atmospheres by changing the feed gas. Finally, it can produce chemically active sites on material surfaces to change their chemical functions without significantly changing their properties [24–26]. Here, changes in the micro-textural properties were prepared via pyrolysis of Lyocell fibers, followed by steam activation. We then focused on evaluating the chemical and textural properties of prepared carbons for their potential use in SO₂ adsorption applications.

2. Experimental

2.1. Materials

In this study, Lyocell fibers (Kolon Industries Co., Republic of Korea) were used. The fibers had a length of 20 cm and an approximate weight of 10 g. For the chemical treatment, flame-retardant di-ammonium-hydrogen phosphate (DAHP, Sigma-Aldrich Co.) was chosen because it is considered to be the most efficient reagent for yield enhancement [27]. To develop a porous structure after carbonization, potassium hydroxide (KOH, bead, 98%, Samchun Co.) was used as a chemical activation agent.

2.2. Chemical treatment of Lyocell fibers

DAHP was used for chemical treatment of the Lyocell fibers to enhance the carbonization yield. First, 10 g of raw Lyocell fibers was immersed in 100 mL of a DAHP solution for 30 min at 60 °C. Excess solution was removed by centrifugation and drying overnight at 70 °C under vacuum. The optimal chemical treatment conditions (5 wt% of DAHP solution exhibited the best yield

enhancement of the Lyocell fibers) were determined from our previous results [28].

2.3. Preparation of activated carbon fibers

Before carbonizing the Lyocell fibers, they were stabilized at 300 °C for 30 min in air. The stabilized Lyocell fibers were then heat-treated in a nitrogen atmosphere at 1000 °C under the following conditions: a heating rate of 10 °C/min, a holding time of 1 h and a nitrogen feed rate of 100 mL/h. After heat treatment, the samples are hereafter referred to as carbon fibers (CFs).

In addition, a 6 M KOH solution was prepared as the chemical activation agent based on our previous work [29]. The CFs were placed in an alumina boat within a reactor. A KOH solution was added at a ratio of 15 mL/g and activated at 750 °C for 3 h in a nitrogen atmosphere. The heating rate was 5 °C/min, and the nitrogen feed rate was 100 mL/min. After the reaction, the samples were washed with distilled water several times to remove residual potassium and dried for 24 h in a 120 °C oven [30]. These activated samples were denoted as activated carbon fibers (ACFs).

2.4. N₂ plasma treatment of activated carbon fibers

A custom-designed radio frequency inductively coupled plasma (RF-ICP) reactor was used for the N₂ treatment of ACFs. The main components of the system consist of the planar coil, 50 kHz RF generator, the stainless steel chamber, and the gas flow controller [31]. The great advantage of using a planar coil is that it can produce high density and uniform plasma over a large area of the samples. In the typical coating procedure, the reactor was evacuated to a pressure of 1.0×10^{-3} Torr using a rotary vane pump. Next, the chamber was filled with the desired pressure of N₂ gas. The samples were exposed to the plasma at various N₂ flowrates ranging from 20 to 80 cc/min over a fixed treatment time of 10 min and an RF power of 120 W. The untreated ACFs were denoted 'Raw'. The plasma-treated ACF samples are hereafter referred to as PT_20, PT_40, PT_60 and PT_80, depending on the N₂ gas flowrates, which were 20, 40, 60 and 80 cc/min, respectively.

2.5. Physicochemical characterization

The ACF samples were heated in vacuum condition at 150 °C for 8 h to remove the water and some of the impurities that were adsorbed in samples before analysis, which is the same preparation method used in the Brunauer–Emmett–Teller (BET) analysis, because we assume that the same conditions should be reached before performing the analysis.

The pore structures of the samples were confirmed by N₂ adsorption at –196 °C using an ASAP2020 (Micromeritics, USA). The specific surface areas of the samples were obtained by the BET equations. The pore size distributions (PSDs) of the samples were determined using the Horvath–Kawazoe (HK) and Barrett–Joyner–Halenda (BJH) methods.

Elemental analysis of the plasma-treated samples was performed using X-ray photoelectron spectroscopy (XPS) with a MultiLab 2000 spectrometer (Thermo Electron Corporation, England). Monochromatized Al K α (1485.6 eV) radiation was used as the X-ray source, with a constant analyzer pass energy of 14.9 keV, a 4.6 A filament current and a 20 mA emission current.

Fig. 1 shows the fixed bed reactor in which the SO₂ adsorption experiments were performed. In these experiments, 0.1 g of ACF was placed in a vertical stainless steel reactor (internal diameter: 5 mm). The thermocouple was located 1 mm above the ACF sample to measure the internal bed temperature. The total flow was kept constant at 1500 cc/min, whereas the SO₂ concentration was approximately 40 ppm, and the analyzer continuously monitored

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