

**Materials Science and Technology Division**

**ACTIVATED CARBON COMPOSITES FOR AIR SEPARATION**

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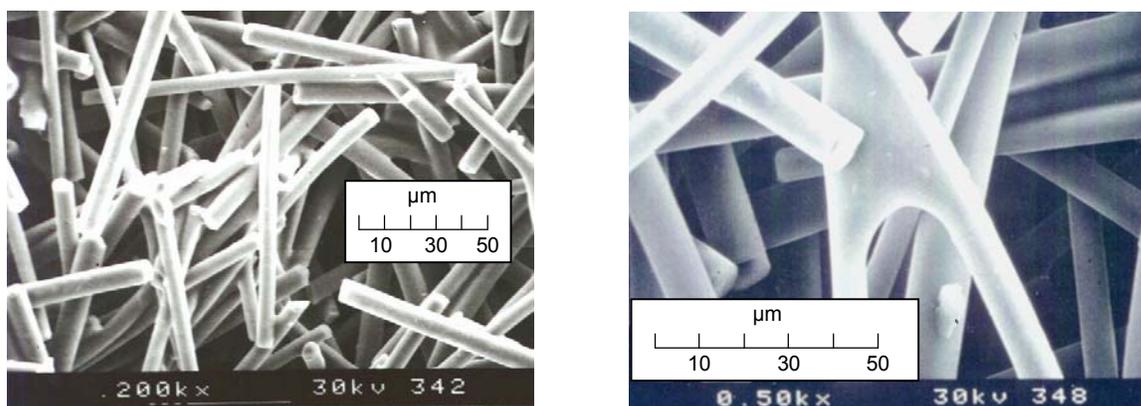
## ABSTRACT

With increased emphasis being placed on the development of fuel cells, coal-derived synthesis gas is a potential major source of hydrogen. Oxygen-blown coal gasification is the most effective and efficient approach to achieving the goal of producing hydrogen from coal, but a cost-effective means of enriching O<sub>2</sub> concentration in air is required. A key objective of this project is to assess the utility of a system that exploits a porous carbon material and electrical swing adsorption (ESA) to produce an O<sub>2</sub>-enriched air stream suitable for coal gasification. Technical performance indicators include development of an adsorbent with pronounced molecular sieving properties to obtain effective separation of O<sub>2</sub> and N<sub>2</sub> from air via a fast-cycling process, and with the desired characteristics to exploit the ESA techniques to obtain a seamless production of an O<sub>2</sub>-enriched air stream.

To better tailor the porosity of the carbon composite material to enhance molecular sieving properties, emphasis was placed on deriving a fundamental understanding of how precursor properties and activation conditions can be manipulated to obtain the desired pore size characteristics in the composite material. As a complement to O<sub>2</sub> and N<sub>2</sub> adsorption measurements, CO<sub>2</sub> was introduced as a more sensitive probe molecule for the characterization of molecular sieving effects. To further enhance the potential of activated carbon composite materials for air separation, work was implemented on incorporating a novel twist into the system; namely the addition of a magnetic field. On theoretical grounds, it has been postulated that magnetic fields should influence gas adsorption which is accompanied by a transition between the paramagnetic and diamagnetic states of the adsorbate, as possible for the O<sub>2</sub> molecule. Indeed, Judkins and Burchell have been granted a United States patent on the separation of gases via magnetically-enhanced adsorption. The preliminary findings in this respect are discussed. Future directions for the project include in-house production of carbon fibers from more suitable precursor materials, evaluation of composite adsorbents comprising carbon and zeolite, and production of lower pressure drop honeycomb monoliths.

## 1. INTRODUCTION

A novel adsorbent material, carbon fiber composite molecular sieve (CFCMS), has been developed by the Oak Ridge National Laboratory (ORNL).<sup>[1-3]</sup> Upon thermal activation, usually in CO<sub>2</sub> or steam, the carbon fiber-based material develops a large micropore volume (0.5-1.0 cm<sup>3</sup>/g) and high BET surface area (1000-2200 m<sup>2</sup>/g). As shown in the scanning electron microscopy (SEM) image in Figure 1, the structure of CFCMS comprises carbon fibers (about 10 μm in diameter) bonded at their contact points to provide a continuous carbon skeleton that is electrically conductive. The structure is open and permeable, which allows fluids to readily flow through the material with minimal pressure drop. The unique combination of the open structure, microporosity, and electrical continuity allows the material to be used in a regenerative, electrical swing adsorption (ESA) system.<sup>[4-6]</sup>



**Fig. 1. SEM images showing the structure of CFCMS material.**

In essence, ESA is an electrical analog of pressure swing adsorption (PSA), whereby desorption of the adsorbate is facilitated by the passage of an electric current through the adsorbent to obtain resistive heating.<sup>[5,6]</sup> In this context, CFCMS represents an enabling technology for an ESA process in which efficient desorption could be achieved in the absence of pressure swings. The bottom line is that significant energy savings could be realized because the adsorption beds do not, in principle, require repressurization after each desorption step.

Preliminary work demonstrated that CFCMS material has the potential for separating O<sub>2</sub> and N<sub>2</sub> in air.<sup>[7]</sup> However, the findings also indicated that a more efficient separation could be obtained if the micropore size distribution of the activated carbon fiber component could be better tailored for this purpose. Therefore, to provide the foundation for developing a suitable CFCMS material, a series of isotropic pitch-based activated carbon fiber monoliths was prepared in which the degree of activation of the fiber was varied in the range of 5-30% (carbon burn-off). The pore size distributions of these products were characterized, and correlated with the kinetics of adsorption of O<sub>2</sub> and N<sub>2</sub>, respectively, on the activated carbon fibers. The results revealed that O<sub>2</sub> was more rapidly adsorbed on the carbon fiber than N<sub>2</sub>, and with higher equilibrium uptakes, provided the fiber contained a high proportion of very narrow micropores. Thus, it was concluded that CFCMS activated under certain conditions is able to separate O<sub>2</sub> and N<sub>2</sub> from air based on kinetic effects, i.e. the difference in diffusion rates of the two molecules in the narrow micropore network of the activated carbon fibers.

To further enhance the potential of CFCMS material for O<sub>2</sub> – N<sub>2</sub> separation, a magnetic field was added to the adsorption system. Based on theoretical grounds, magnetic fields should affect phase change equilibria (such as adsorption and desorption) if the phase changes are accompanied by a significant variation of magnetic properties. The literature on magnetic field effects on adsorption and desorption (MAD) is scarce. For several microporous materials a correlation was reported between MAD effects and certain properties of the adsorbate-adsorbent system, such as molecular magnetic properties, nature and

concentration of adsorption sites, and porosity of solids. For example, nitrous oxide (NO) is paramagnetic in the gas phase, but (NO)<sub>2</sub> dimers condensed on solids are diamagnetic, and because of that the capillary condensation on microporous solids is greatly enhanced by magnetic fields.<sup>[8]</sup> Gaseous oxygen is paramagnetic, but oxygen dimers (O<sub>2</sub>)<sub>2</sub> adsorbed in micropores of zeolites at temperatures lower than 100 K are diamagnetic.<sup>[9]</sup> Generally speaking, magnetic energies are insignificant in comparison with thermal energy. Therefore, while one would expect MAD effects in ferromagnetic systems (such as H<sub>2</sub> on LaCo<sub>5</sub>H<sub>x</sub> hydrides),<sup>[10]</sup> it is less likely that such effects would be detected in paramagnetic systems, much less for a diamagnetic system such as water.<sup>[11]</sup> However, magnetic fields effects on adsorption have been demonstrated even for water<sup>[12]</sup> and some organic molecules.<sup>[13]</sup> This may be an indication that the magnetic properties of such molecules change upon interaction with the adsorbent, but it also highlights the fact that more experimental studies on magnetic field effects on gas adsorption are needed in order to shed light on this poorly understood phenomenon.<sup>[11]</sup>

In microporous materials such as activated carbon, MAD effects depend strongly on the nature of solids and gases, temperature, and the intensity of magnetic fields. An appropriate combination of these factors could lead to a separation process based on selective adsorption from a mixture of gases. In this context it has been reported that separation of O<sub>2</sub> and N<sub>2</sub> in high magnetic fields is in principle plausible in a steady magnetic field through adsorption of paramagnetic O<sub>2</sub> molecules into micropores of porous ferromagnetic solids.<sup>[11]</sup> A series of tests have been carried out in order to check this assumption.

## 2. DISCUSSION OF CURRENT ACTIVITIES

### 2.1 AIR SEPARATION BY MOLECULAR SIEVING EFFECTS

#### 2.1.1 Materials Preparation and Characterization

Samples (about 140 mg) of isotropic pitch-based carbon fibers (Anshan East Asia Carbon Co.) were activated to the desired level of carbon burn-off, as measured by weight loss, at a temperature of 835°C in an atmosphere of pure CO<sub>2</sub> (at ambient pressure) using a Hiden Analytical gravimetric analyzer (IGA-1). The surface area and pore size distribution of representative samples of activated carbon fibers were characterized by N<sub>2</sub> adsorption at 77 K and CO<sub>2</sub> adsorption at 273 K using a Quantachrome Autosorb-1 instrument. The apparent surface areas were derived from the N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms using the BET method.<sup>[14,15]</sup> Pore size distributions were calculated using the density functional (DFT) approach,<sup>[16,17]</sup> and micropore volumes were estimated using Dubinin-Astakhov (DA) equation,<sup>[15]</sup> applied to adsorption data. The results are shown in Table 1.

**Table 1. Surface area and micropore volume data for activated carbon fiber products**

Burn-off level (%)	5	10	15	20	30
N <sub>2</sub> BET area (m <sup>2</sup> /g)	15	415	<i>790</i>	730	960
CO <sub>2</sub> BET area (m <sup>2</sup> /g)	550	635	795	955	1170
Micropore volume (< 2 nm, DFT)	0.00	0.16	<i>0.32</i>	0.29	0.38
Micropore volume (< 2 nm, DA)	0.00	0.19	<i>0.33</i>	0.34	0.44

Except for the values shown with italic characters, the N<sub>2</sub> and CO<sub>2</sub> adsorption data show the expected trend in the development of surface area and micropore volume with the progress of activation

(as measured by the burn-off level). However, at the lowest burn-off level of 5% a very pronounced molecular sieving effect between N<sub>2</sub> and CO<sub>2</sub> was observed. The micropores of the sample with 5% burn-off were so narrow that the N<sub>2</sub> molecules could not penetrate the ultra fine structure, resulting in an apparently very low BET surface area (15 m<sup>2</sup>/g) and no measurable pore volume. In contrast, the flat CO<sub>2</sub> molecules were able to enter the fine pores at 273 K, revealing a significant surface area (550 m<sup>2</sup>/g) and details of the smallest micropores.<sup>[18]</sup>

### 2.1.2 Dynamic O<sub>2</sub> and N<sub>2</sub> Adsorption Studies

The rates O<sub>2</sub> and N<sub>2</sub> adsorption, respectively, on the activated carbon fibers were measured at 294 K. Each gas was dosed to the sample at two linear rates of pressure increase of 0.015 and 0.025 MPa/minute, respectively, over the pressure range of 0.001-0.1 MPa. The rates of O<sub>2</sub> and N<sub>2</sub> adsorption are summarized in Figure 2. More experimental details and an analysis of results were presented elsewhere.<sup>[19]</sup>

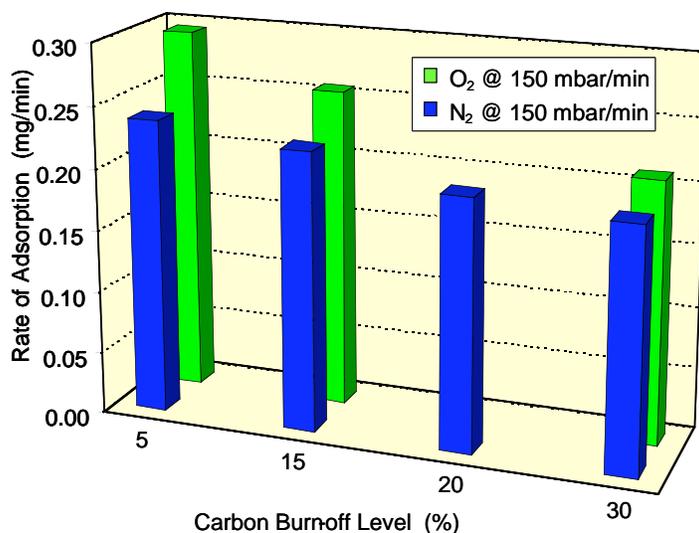


Fig. 2. Rates of O<sub>2</sub> and N<sub>2</sub> adsorption at 294 K as a function of carbon burn-off level.

The rate of O<sub>2</sub> adsorption was markedly higher than that of N<sub>2</sub>, notably on the carbon fibers of the lowest burn-off of 5% which exhibited a 25% higher rate of O<sub>2</sub> adsorption (on a mass basis). The rate of adsorption of both O<sub>2</sub> and N<sub>2</sub> fell with progressive increase in the degree of activation of the carbon fibers. The amount of N<sub>2</sub> adsorbed at equilibrium at 0.1 MPa increased at the highest burn-off level of 30%, indicative of the larger pore volume in this material. A sharp discontinuity was observed in the rate of N<sub>2</sub> adsorption, at a pressure of about 0.045 MPa, and only on the 5 and 15% burn-off carbon fiber products. This effect, which could be associated with a very pronounced molecular sieving effect of these materials, is significant for the separation of O<sub>2</sub> and N<sub>2</sub> relying on differences in the diffusion rates of these molecules in narrow pore networks. The closer the pore width is to the molecular dimensions of the gasses, the more significant the kinetic effects will be. A lower carbon burn-off level appeared to be advantageous in this respect; higher levels (> 15%) increased micropore width to the point where molecular sieving effects were eliminated, which is counter-productive for air separation.

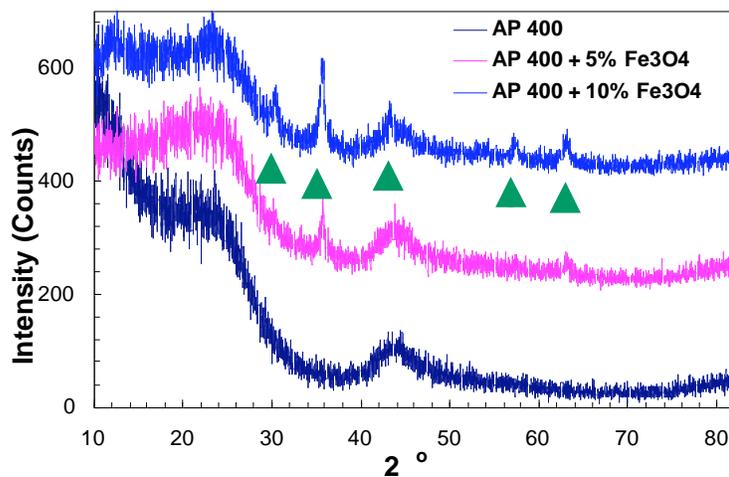
In addition to activation parameters, the adsorptive characteristics of activated carbon fibers are dependent on the nature of the precursor. In this context, lignin is a precursor known to produce highly microporous activated carbon products. In a very preliminary work, an activated carbon fiber was produced from a kraft hardwood, melt-spun lignin fiber. Characterization of adsorption properties

indicated that its microporous structure is more developed compared to the pitch-based fibers at comparable burn-off.

## 2.2 INFLUENCE OF MAGNETIC FIELDS ON OXYGEN ADSORPTION

### 2.2.1 Materials Preparation and Characterization

For the study of magnetic fields effects on O<sub>2</sub> adsorption, commercially available activated carbon fibers made from an isotropic pitch precursor (AP-400 fibers furnished by Anshan East-Asia Carbon Co.) were used. In order to mimic a ferromagnetic microporous adsorbent, the fibers were modified by depositing nanosized magnetite (Fe<sub>3</sub>O<sub>4</sub>) onto activated carbon fibers, using a cold precipitation method.<sup>[20]</sup> In contrast with the ceramic method for synthesis of magnetite, which involves high temperature processes and results in a highly sintered product, the cold synthesis method (< 120°C) preserves the nanosized colloidal particles of magnetite. Several runs were made to obtain different loadings of magnetite in the activated carbon fibers. The presence of the magnetite phase in the activated carbon fibers was confirmed through X-ray diffraction (XRD) measurements (Figure 3). For the highest loading of 10 wt % Fe<sub>3</sub>O<sub>4</sub>, the BET surface area of the activated carbon fibers was reduced from 1530 to 1170 m<sup>2</sup>/g, and the average pore size increased from 1.4 nm to 1.7 nm due to obliteration of the smallest pores. The magnetite particles were well dispersed on the activated carbon fibers, with an average particle size of 16 nm, calculated from broadening of XRD lines.

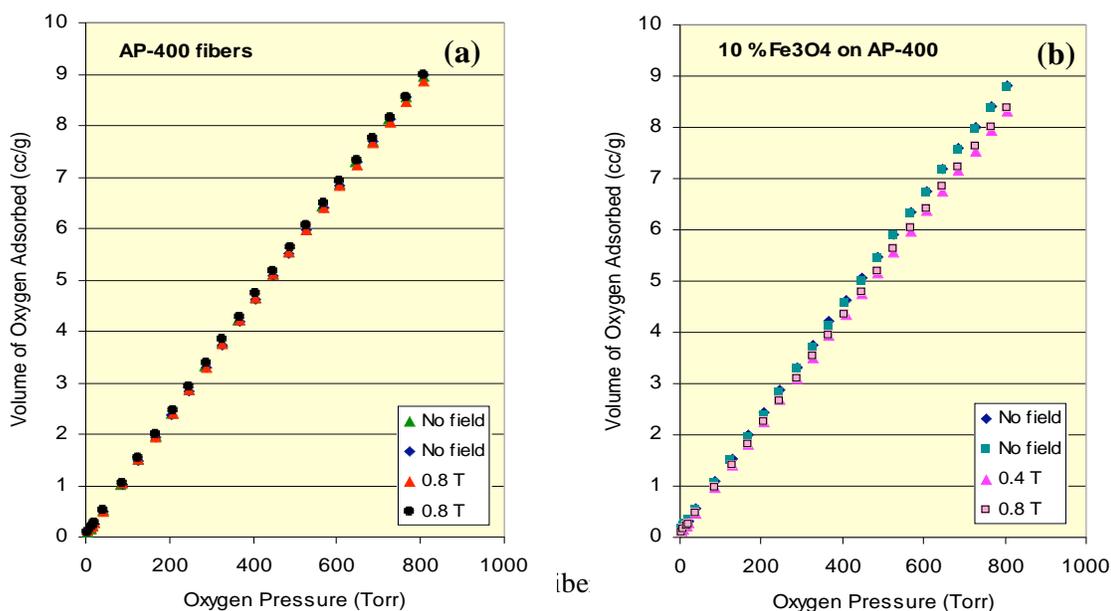


**Fig. 3. X-ray diffraction patterns of pure AP-400 fibers and fibers with magnetite loading.**  
The arrows indicate the position of X-ray diffraction peaks attributed to magnetite (Fe<sub>3</sub>O<sub>4</sub>).

Magnetic susceptibility at room temperature of carbon fiber materials with and without magnetite loading was measured using a MSB auto magnetic susceptibility balance (Sherwood Scientific, U.K.). Although pure carbon is diamagnetic ( $\chi = -2 \times 10^{-5}$  for diamond,  $\chi = -2 \times 10^{-5}$  for graphite), the activated carbon fibers AP-400 were slightly paramagnetic ( $\chi = +1.8 \times 10^{-6}$ ). The paramagnetism of activated carbons is caused by the existence of impaired electrons and dangling bonds at carbon atoms exposed at the extended surface of these materials.<sup>[21]</sup> On the other hand, in contrast with the notorious ferromagnetic character of magnetite, susceptibility measurements for magnetite loaded carbon fibers indicated a paramagnetic character ( $\chi = +1.2 \times 10^{-4}$  for 5 wt % Fe<sub>3</sub>O<sub>4</sub> and  $\chi = +3.6 \times 10^{-4}$  for 10 wt % Fe<sub>3</sub>O<sub>4</sub>). The phenomenon by which magnetic materials exhibit a behavior similar to paramagnetism even at temperatures below the Neel or the Curie temperatures is known as superparamagnetism. This effect is observed in very fine particles, each behaving as an individual magnetic domain, for which the energy

required to align the direction of magnetic moments is comparable to thermal energy.<sup>[22]</sup> The superparamagnetism of Fe<sub>3</sub>O<sub>4</sub> supported on AP-400 carbon fibers, corroborated with the information from XRD analysis, indicates that each Fe<sub>3</sub>O<sub>4</sub> nanoparticle (average size of 16 nm) is an individual magnetic domain.

Oxygen adsorption measurements on the activated carbon fibers, with and without magnetite, were made at room temperature over the pressure range of 5-800 Torr (0.66-105 KPa), using a volumetric adsorption instrument (Autosorb-1, Quantachrome Instruments). The sample (~ 200 mg) was outgassed in high vacuum at 300°C overnight immediately before the adsorption measurements. For the adsorption measurements in the presence of a magnetic field, a pair of rare earth permanent magnets (NdFeB 36, Edmunds Industrial Optics) was placed around the glass tube containing the sample and in the immediate vicinity of the sample. The separation between the magnets was in the range of 1.0-1.2 cm. The intensity of the magnetic field was enhanced by adding a second pair of permanent magnets. The magnetic field intensities measured in the immediate vicinity of the sample were 0.45 and 0.82 Tesla (T) for one and two pairs of magnets, respectively. The setup is extremely accurate for gas volumetric measurements, as shown by the perfect overlap of data point in a series of repeated baseline tests with pure carbon materials in absence of magnetic fields.



**Fig. 4. O<sub>2</sub> adsorption on activated carbon fibers in presence of a magnetic field (at room temperature)**

The results revealed that magnetic fields of intensity of up to 0.8 Tesla (T) had almost no effect on O<sub>2</sub> adsorption on pure carbon fibers (Figure 4 a). However, when magnetite was incorporated into the carbon fiber to amplify the magnetic field, the amount of O<sub>2</sub> adsorbed in presence of magnetic fields (up to 0.8 T) were slightly lower than the amounts measured at equal pressures but without applied magnetic field. With 10 wt % magnetite, the amount of O<sub>2</sub> adsorbed at near atmospheric pressure (800 Torr) decreased from 8.8 to 8.3 cc/g (STP basis) when the magnetic field was applied; i.e., a decrease of about 6%. This was an unexpected result, whereby a magnetodesorption, not magnetoadsorption effect was observed. Nevertheless, the existence of a magnetodesorption effect at room temperature for O<sub>2</sub> on magnetite supported on activated carbon has not been previously reported in the literature.

A brief explanation of this effect is provided below on the thermodynamic grounds developed by Ozeki and Sato.<sup>[11]</sup> When the equilibrium pressure of a gas-solid adsorption system changes by  $\Delta p$  on application of a magnetic field  $H$  at constant temperature  $T$ , the total variation of the free energy of the

system,  $\Delta G$ , has a pressure component,  $\Delta G_p = RT [\ln (p+\Delta p) - \ln p]$ , and a magnetization component,  $\Delta G_m = \Delta MH$ , where  $\Delta M$  is the magnetization change of the system per mol of gas adsorbed. The equilibrium condition is  $\Delta G = \Delta G_p + \Delta G_m = 0$ , which gives  $\Delta p/p = -\Delta MH/RT$  (assuming  $p \gg \Delta p$ ). This relationship demonstrates that, whenever the magnetization of the adsorption system changes during adsorption, the equilibrium pressure in the system should change; for example, a negative  $\Delta M$  can cause an increase in equilibrium pressure, i.e., magnetodesorption (as observed with  $O_2$  on  $Fe_3O_4$  supported on activated carbon).<sup>[11]</sup>

In the system investigated here, oxygen is adsorbed on carbon at room temperature in absence of external magnetic fields (Figure 4, a). The state of  $O_2$  molecules confined in the narrow micropores of activated carbon is not entirely clear. Depending on oxygen pressure, pore size, and temperature,  $O_2$  molecules may form random clusters containing spin-interacting molecules, with the result that the paramagnetism of isolated  $O_2$  molecules is replaced by the random magnetism of these clusters.<sup>[23]</sup> On zeolites, oxygen forms diamagnetic clusters.<sup>[9]</sup> On activated carbon fibers, chemisorbed oxygen is stabilized in a non-magnetic state through spin interactions with dangling bonds of graphene layers.<sup>[24]</sup> Because adsorption and clustering of  $O_2$  molecules confined in narrow micropores leads always to a *decrease* in magnetization of the system (compared to the state of a non-adsorbing system), i.e.,  $\Delta M < 0$ , a magnetodesorption effect should be measured ( $\Delta p > 0$ ), as predicted above on thermodynamic grounds. The effect is however too weak to be observed (at room temperature and with the magnetic fields available in this study) on a weakly paramagnetic adsorbent, such as the pristine AP-400 fiber (Figure 4, a). However, if the adsorbent has a paramagnetic susceptibility larger by two orders of magnitude (as is the case with 10 wt %  $Fe_3O_4$  on AP-400 fiber), the influence of external magnetic fields in carbon micropores is amplified, and the magnetodesorption effect becomes measurable even at room temperature and in relatively weak magnetic fields (Figure 4, b).

The observation of magnetodesorption of  $O_2$  from a microporous carbon fiber loaded with a superparamagnetic  $Fe_3O_4$  phase, made in this study, confirms predictions in the literature according to which magnetic separation of  $O_2$  and  $N_2$  in steady magnetic fields is plausible.<sup>[11]</sup> To exploit the magnetodesorption effect and to achieve air separation it might be useful to optimize the system for adsorption at equilibrium of  $N_2$  (not  $O_2$ ) by the activated carbon fibers in a steady magnetic field. It might also be useful to modify the adsorbent by incorporation of zeolites (where oxygen is adsorbed in a diamagnetic state),<sup>[9]</sup> to use much higher intensity magnetic fields, and possibly to design a “magnetic swing adsorption” system with the adsorbent in a column configuration.

### 3. CONCLUSIONS

The findings reported here confirm that CFCMS materials have the potential for separating  $O_2$  and  $N_2$  from air on the basis of the different diffusion rates of the two molecules in the composite.  $O_2$  is more rapidly adsorbed on the activated carbon fiber than  $N_2$ , and with higher uptake under equilibrium conditions, providing the fiber contained a high proportion of very narrow micropores. This depends on identifying and demonstrating alternative techniques of activation, and using new carbon precursors (such as lignin) that are known to produce extensive networks of uniformly narrow micropores. The oxygen adsorption measurement performed in the presence of a magnetic field demonstrated an effect of the field when the adsorbent was magnetite supported on activated carbon fibers. These data require additional measurements, using much higher intensity magnetic fields, to verify the preliminary results and determine whether magnetic fields can be exploited for separation of  $O_2$  and  $N_2$  from air.

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