

POROUS CARBON FIBER COMPOSITES FOR NATURAL GAS STORAGE

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Introduction

The U.S. Department of Energy (DOE) has funded research aimed at the development of suitable materials for the storage of natural gas in the physically adsorbed state. Adsorbed natural gas (ANG) is conventionally stored in porous carbon materials at a gas pressure of 3.5 MPa (500 psi). This lower storage pressure reduces the cost of the storage vessel and represents a lesser safety hazard than the higher pressures used for CNG [1,2]. The DOE storage target for ANG has been set at 150 V/V, i.e., 150 STP (0.1 MPa, 298 K) liters of gas stored per liter of pressure vessel internal volume.

A novel adsorbent carbon composite based on carbon fibers has been developed at the Oak Ridge National Laboratory (ORNL) and offers a solution to the limitations of conventional activated carbons for ANG applications [3,4]. Because of its composite structure the material is abrasion resistant. Moreover, the continuous carbon skeleton allows for the liberation of practically all of the adsorbed gas via low-voltage electrical stimulation. Similarly, the continuous carbon skeleton of our composites offers enhanced thermal conductivity over packed beds of carbon [5]. This translates to smaller temperature gradients during tank charging and discharging. The development of storage composites has been ongoing at ORNL for the past few years and we have attained storage capacities in excess of the DOE target of 150 V/V [6].

The physical adsorption of gasses occurs preferentially in micropores with widths

< 2 nm [7]. Consequently, high micropore volumes are desirable if large storage capacities are to be obtained in a given adsorbent. Here we show that the storage capacity of our composites is directly related to the micropore volume. Moreover, direct evidence obtained through a high resolution transmission electron microscopy (HRTEM) examination is reported for the presence of micropores within the structure. A promising method of acquiring pore size and distribution data is small angle neutron scattering (SANS). A beam of neutrons is directed at a shallow incident angle onto a sample. The beam is scattered by porosity within the samples. The extent of scattering is dependant upon the amount and size of the inherent porosity. Moreover, by filling the pores with a contrast-matched gas, the whereabouts of the adsorbent sites in the pore structure may be determined [8]. Here we report direct SANS evidence for the adsorption of deuterated methane (CD_4) in the micropores on our carbon fiber based composites.

Experimental

Gas storage composites were fabricated from isotropic pitch-derived carbon fibers (Carboflex fibers, Anshan East Asia Carbon Company, Anshan, China) and a powdered phenolic resin (Durez grade 7716, Durez Corporation, 5000 Packard Road, Niagara Falls, NY 14304, USA). A schematic diagram of the fabrication route is in Figure 1. The composites were hot-pressed to densities in the range 0.7-0.92 g/cm³, and carbonized prior to activation in a CO_2

atmosphere to the desired burn-off. Post-activation analysis of the composites included micropore characterization and bulk density determination. The conventional method of determining the micropore volume and size distribution of an activated carbon, i.e., through the interpretation of an adsorption isotherm, typically that of nitrogen measured at 77 K, using one of several methods [7,9,10], was employed. Methane adsorption isotherms were determined over the pressure range 0-2 MPa using a high-pressure gravimetric analysis system and small (~100 mg) samples of the gas storage composites.

samples using a purpose built test stand [3]. The standard composite size (as manufactured) was ~ 115-mm (4.5-inches) diameter and 38-mm (1.5-inches) thick. From this part a series of smaller samples [~ 23-mm (0.9-inch) diameter] were machined for testing in the gravimetric apparatus. The test samples were stacked in the test cell to completely fill the 50-cm³ test cylinder cavity. The storage samples were vacuum outgassed at 473 K in the test cylinder, cooled to ambient temperature, and then slowly filled (near isothermal) to 3.5 MPa (500 psi) pressure. The storage capacity and carbon activity was then calculated from the cylinder's mass gain on charging.

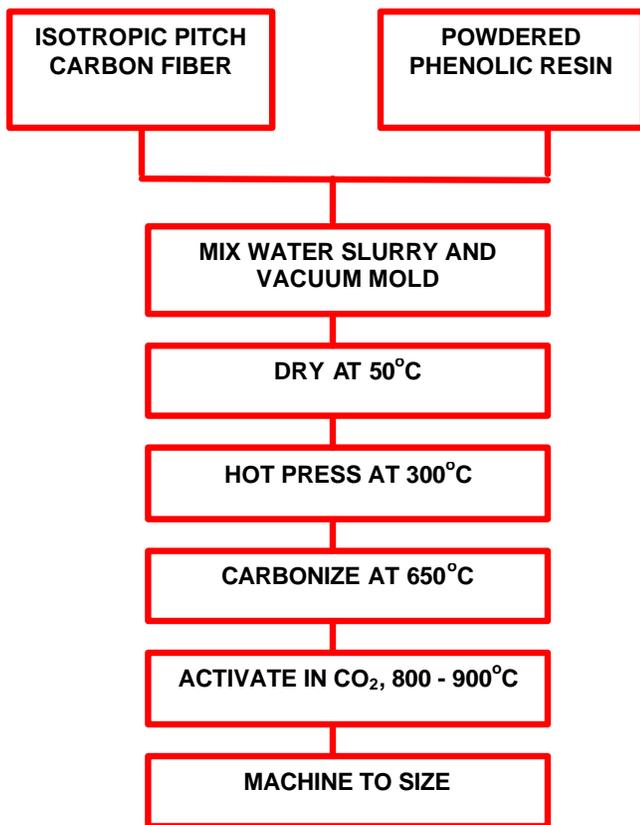


Figure 1. The synthesis route for porous carbon fiber based composites

Methane uptake was measured gravimetrically at room temperature and 3.5 MPa (500 psi) on 50-cm³ volume

The microstructure of the adsorbent carbon composites was investigated using a Hitachi S4700 Field Emission SEM at a working distance of 5 mm. The accelerating voltage was 5 kV and the emission current was 15µA. HRTEM analysis was conducted using a Hitachi HF-2000 Field Emission HRTEM at 200 kV. The carbon monoliths were ground to fine pieces and supported on a “holey” carbon-coated copper grid prior to TEM investigation.

In-situ small-angle neutron scattering was carried out on the small-angle diffractometer (SAD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. SANS data were collected in deuterated methane gas (CD₄) at pressures of 3.5 MPa (500 psi), 6.2 MPa (900 psi), and 20.7 MPa (3000 psi) on a sample from adsorbent composite SMS-44.

Results and Discussion

The structure of our carbon fiber based adsorbent composite is illustrated in Figure 2. The individual carbon fibers are bonded at their contact point to form a rigid, yet open, structure. The composite structure

makes the material more rugged than conventional granular activated carbons. During the thermal activation process, carbon is gasified from the surface through oxidation reactions and porosity within the carbon fibers and carbon binder becomes accessible to the fiber surface. With continued activation (burn-off) additional porosity becomes accessible and existing porosity is further enlarged.

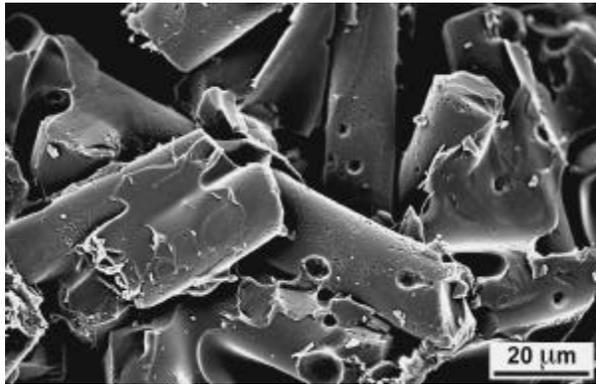


Figure 2. Porous carbon fiber composite structure revealing surface pitting (SMS-44)

Figure 2 shows the fiber surface in an activated composite. Numerous surface oxidation pits may be observed which allow access for the adsorbate gas to porosity within the core of the fiber. Adsorption is understood to occur preferentially within narrow micropores (< 2 nm) and mesopores (2-50 nm). Pores with nanometric dimensions, such as micropores, can only be imaged in a high-resolution transmission electron microscope. The micropore structure of an activated carbon fiber is shown at extremely high magnification in Figure 3. Distortion and folding of the turbostratic graphene sheets in the carbon fiber structure creates nano-dimensioned pores such as those indicated at (A) in Figure 3.

Information relating to the micropore structure may also be obtained by interpreting the adsorption isotherm. The

conventional technique (N_2 at a temperature of 77 K) has been applied here to analyze the adsorbent composites, and the Dubinin-Radushkevich (DR) [7,9,10] micropore volume and mean micropore width were determined. To date more than 45 gas storage composites have been synthesized and characterized. The micropore volume data are plotted in Figure 4 as a function of the weight loss on activation.

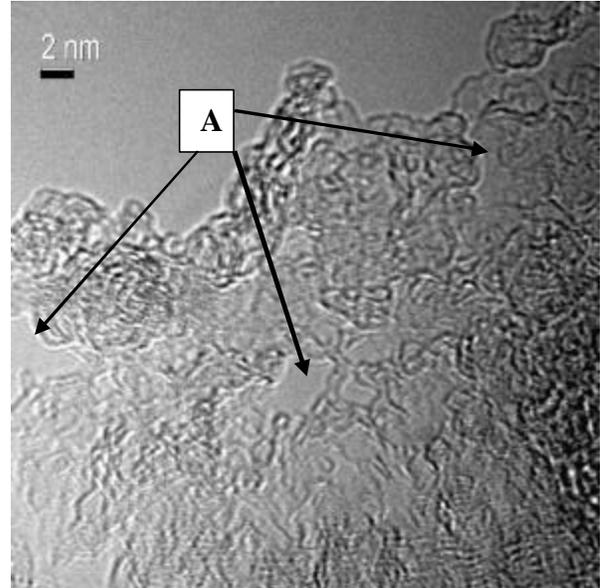


Figure 3. TEM image of an activated carbon fiber showing nano-sized micropores (SMS-44)

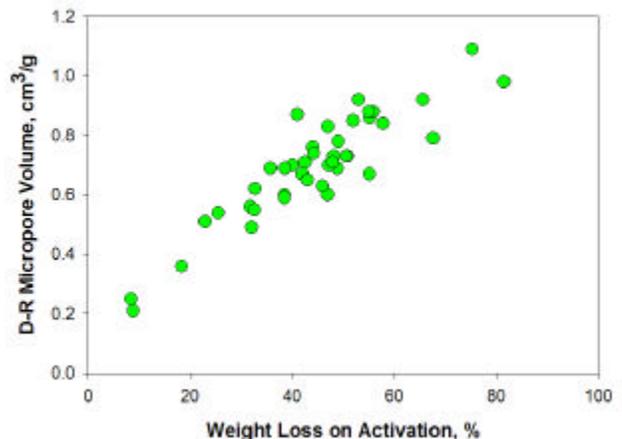


Figure 4. D-R micropore volume as a function of weight loss on activation for adsorbent composites showing the increase of micropore volume with increased activation (burn-off)

The micropore volume increases with increasing weight loss. The development of micropore volume with burn-off is also accompanied by a concomitant increase in the mean micropore width from ~ 1.5 nm to > 2 nm. This is problematic since it has been reported that the adsorption of methane is strongest in pores of < 1.5 -nm width [11].

Representative methane storage data for our adsorbent carbon fiber composites are given in Table 1. The % burn-off represents the weight loss on activation, or the degree of activation. The cell pack density is the mass of carbon packed into the test cell divided by the cell volume. For the samples tested here, this is equivalent to the composite materials bulk density. The methane activity is a calculated parameter that represents the fraction of the methane in the test cell that is adsorbed into the carbon's micropores (represented as a percentage of the carbon's mass). The storage capacity

represents the total volume of gas stored at 3.5 MPa, and includes the gas physically adsorbed in the micropores as well as the gas compressed in the larger pores. Each sample designation represents a different composite formulation or activation level.

A typical methane isotherm from our high-pressure microbalance is shown in Figure 5 for sample SMS-23. This sample had a relatively low burn-off (Table 1) and hence the weight gain from adsorption when pressurized to 20 bars is only $\sim 9\%$ (Figure 5). The methane uptake increases rapidly at low pressures, but approaches a linear rate of increase at higher pressures. Thus, the enhancement due to physical adsorption is most beneficial at lower pressures. Indeed, the increases in storage capacity above pressures of about 6-7 MPa is solely attributable to the compression of the methane in the larger pores rather than the physical adsorption of methane in the micropores.

Table 1. Methane storage data for adsorbent carbon fiber composites

Sample	Burn-off (%)	Cell Pack Density (g/cm ³)	Methane Activity (%)	Storage Capacity (V/V)
SMS-11	43	0.53	10.9	114
SMS-12	41	0.60	10.5	121
SMS-15	57	0.57	11.8	128
SMS-16	75	0.48	11.6	111
SMS-17	52	0.56	11.6	124
SMS-18	49	0.53	11.4	118
SMS-19	56	0.65	12.7	149
SMS-22	58	0.63	13.2	152
SMS-23	32	0.70	8.3	112
SMS-30	82	0.39	15.4	120
SMS-32	68	0.42	14.1	118
SMS-38	51	0.55	12.0	127
SMS-43	51	0.64	11.7	139
SMS-44	46	0.68	10.9	136
SMS-45	47	0.65	11.2	136

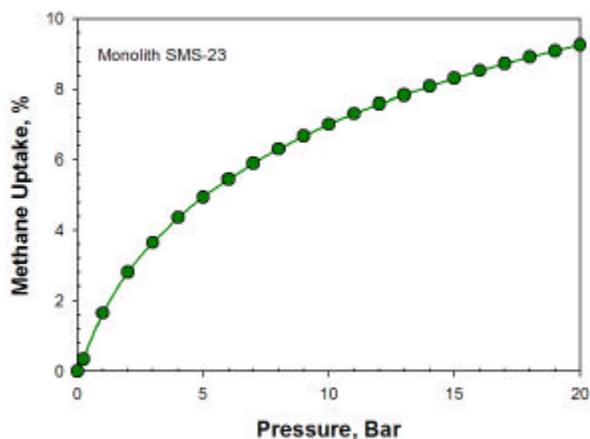


Figure 5. Methane adsorption isotherm (ambient temperature) measured on a sample of ORNL composite SMS-23.

Activation of the composites results in the development of microporosity. Increasing the degree of burn-off increases the micropore volume and the mean micropore size (Figure 4). Although increased micropore volume is beneficial, since the gas is adsorbed into the micropores, there is a limit to this benefit. At very large burn-offs the density of the composite is low, and the mean micropore size becomes large and far from the optimum value of 1.12 nm [11]. Consequently, excessive burn-off is not productive. This point is illustrated by the data for samples SMS-23 and SMS-30 (Table 1). In the former, the density is large but the methane activity is rather low and the resultant capacity was only 112 V/V. In the latter case, the activity was much greater (15.4 cf. 8.3%), but the density is extremely low (0.39 cf. 0.7 g/cm³), and the resultant capacity is not greatly improved. The optimum storage composite is, therefore, one that exhibits high methane activity (which is a function of micropore size and total micropore volume) and high density. Storage capacity and weight activity are plotted as a function of burn-off in Figures 6 and 7. The optimum burn-off appears to be in the range 50-60% (corresponding to a methane activity of ~ 13-15%) but at a cell

pack density (composite bulk density) of > 0.6 g/cm³.

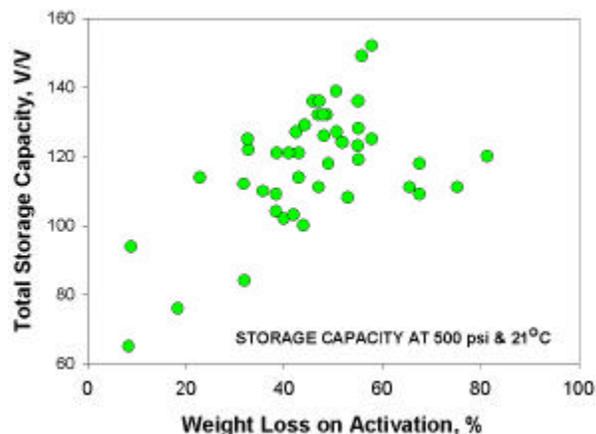


Figure 6. The total methane gas storage capacity of ORNL adsorbent composites at a pressure of 3.5 MPa and 21°C

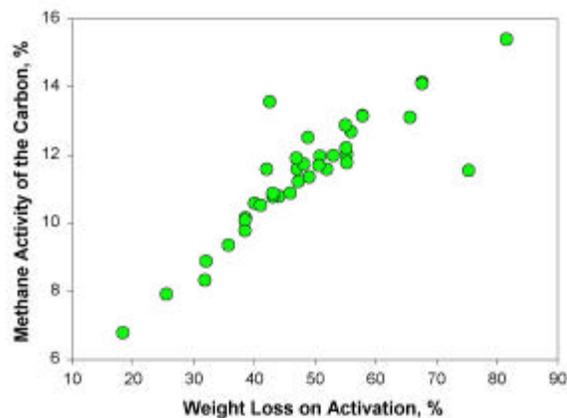


Figure 7. The variation of methane activity of the carbon with weight loss of activation for ORNL adsorbent composites at a pressure of 3.5 MPa and 21°C

In Figure 3 we showed HRTEM evidence for the existence of micropores (width < 2 nm). The adsorption data reported here correlates with weight loss on activation and consequently, with increasing micropore volume. Moreover, the significance of pore size has been demonstrated. However, we have no direct evidence that the micropores are responsible for the enhanced adsorption of methane at moderate pressures

(0-6 MPa). To obtain direct evidence of the role of micropores we have applied *in-situ* SANS.

The results of our *in-situ* SANS experiments are shown in Figure 8. Scattering data are reported for ambient gas pressure and at three elevated pressures: 3.5 MPa (500 psi), 6.2 MPa (900 psi), and 20.7 MPa (3000 psi), on a sample from gas storage composite SMS-44. The measured momentum transfer ($Q=4p \sin(q/2)/\lambda$) is from 0.008 to 1.8 \AA^{-1} , representing a pore size, d , ranging from 78.6 to 0.087 nm ($d=2\pi/Q$). The data quality in Figure 8 decreases at a Q -range of 0.5 \AA^{-1} and higher, which is at the high- Q limit of the available SANS instrument. However, the data in the Q range 0.008-0.5 \AA^{-1} is considered acceptable. In all cases the scattering intensity decreases with increasing Q . However, the 3.5 and 6.2 MPa curves deviate from the ambient

curve in the Q range 0.1-0.5 \AA^{-1} , corresponding to a pore size range from 1.3 to 6 nm, where the scattering intensity is decreased compared to the ambient curve. The decrease occurs over this pore size range because the CD_4 preferentially fills the smallest pores at low pressure. At 20.7 MPa, the decrease of scattering intensity starts at a lower Q value ($<0.05 \text{\AA}^{-1}$ equivalent to pores larger than 13 nm), which suggests that larger pores (mesopores) are being filled with CD_4 .

Our SANS data demonstrate that at moderate storage pressures the methane gas is preferentially adsorbed in pores with nanometric dimensions, where $Q > 0.3$ (corresponding to a pore size of 2 nm or less).

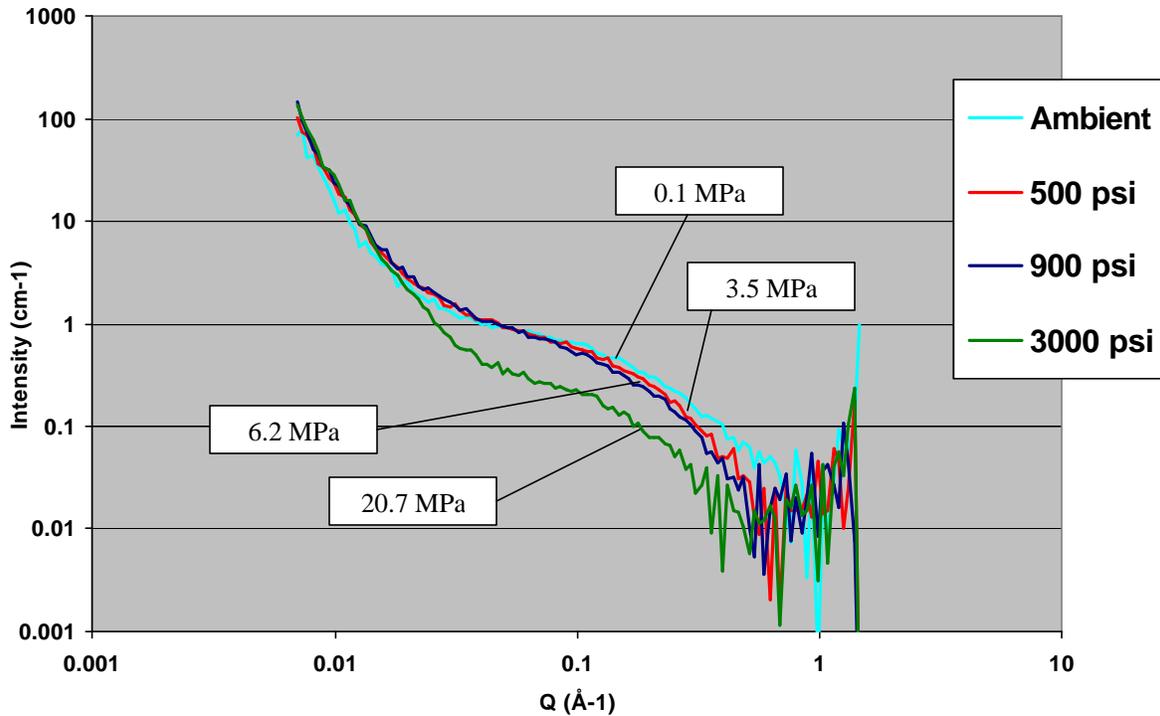


Figure 8. High-pressure SANS of carbon composite (SMS44) in CD_4

Conclusions

Adsorbent carbon fiber composites were developed that can store methane in the physically adsorbed state at capacities of 150 V/V at 3.5 MPa (500 psi) pressure. The composite structure offers distinct advantages over conventional powdered and granular adsorbents, including improved ruggedness, superior thermal conductivity, and electrical stimulated desorption and regeneration. HRTEM examination of the fibers in our composites revealed the presence of micropores (< 2-nm width). A large number of gas storage composites were synthesized and tested and the DOE storage capacity target of 150 V/V was satisfactorily met. Attainment of this storage capacity required a composite that combined a relatively high bulk density (> 0.6 g/cm³) with a high methane activity, i.e., a large micropore volume. The importance of microporosity to the storage of methane at low pressures was inferred from the gas storage capacity data and the N₂ adsorption at 77 K micropore characterization data. However, direct evidence of the key role of microporosity in the adsorption of methane was obtained from *in-situ* SANS. The scattering data clearly revealed that methane gas occupied the nano-sized pores at moderate pressures and occupies larger pores at much higher pressures.

Acknowledgements

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