ORNL/CP-99094

CONF-980561--

THE ADSORPTION OF WATER VAPOR ON CARBON FIBER COMPOSITE MOLECULAR SIEVE

RECEIVED
AUG 1 3 1998
OSTI

T. D. Burchell, R. R. Judkins and M. R. Rogers

INTRODUCTION

Carbon Fiber Composite Molecular Sieve (CFCMS) is a porous adsorbent carbon material manufactured from isotropic pitch derived carbon fibers and a phenolic resin binder via a slurry molding process. The material is produced in the form of a monolith and can be activated in steam, CO_2 or O_2, during which it develops high BET surface areas and micropore volumes. The material has a continuous carbon skeletal structure and is, therefore, electrically conductive. The passage of an electric current at low voltage allows for direct resistive heating of the carbon and thus provides an efficient method of desorbing adsorbed gasses. This method of separating gasses has been named electrical swing adsorption (ESA) and is analogous to thermal or pressure swing adsorption [1-3].

Recently, we have examined the potential of CFCMS/ESA for the adsorption and separation of water vapor. Frequently, water vapor must be removed from a gas stream before separation and processing can occur. To assess the potential of CFCMS for water adsorption a series of CFCMS samples were manufactured and activated to relatively high burn-off. Half of each sample was treated at 200°C in flowing oxygen to increase the number of chemisorbed surface functional groups. The amount of water adsorbed has previously been shown to be controlled by the availability of surface functional groups (such as carboxylic acid) which act as active sites for the adsorption of water. Here we report our preliminary study of the moisture adsorption behavior of treated and untreated CFCMS samples.

EXPERIMENTAL

The manufacturing process for our carbon fiber composite molecular sieve (CFCMS) materials has been reported elsewhere [1,4]. Activation was performed in a three-zone Lindburgh furnace fitted with an 20-cm diameter Inconel retort. The CFCMS samples were dried in vacuum at 300°C, heated to 850°C under CO_2 for periods of several hours until the required burn-off (weight loss) was attained. Micropore structure characterization was performed using a Quantichrome Autosorb-1 apparatus.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-96OR22464. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

The activated samples were treated in flowing O_2 at 200°C to increase the concentration of surface chemical functional groups and thus render the surface more hydrophilic. Evaluations of moisture uptake were performed gravimetrically on a Mettler microbalance. Before testing, each sample was dried by heating to 100°C in a vacuum followed by cooling to ambient temperature in flowing dry He. The sample was maintained at 21°C, and a stream of moisture saturated He (at a temperature of 18°C) was passed over the sample.

The electrical characteristics of a large billet of CFCMS were determined in the Electrical Swing Adsorption (ESA) sub-system of our newly constructed Gas Flow Loop (Fig. 1).

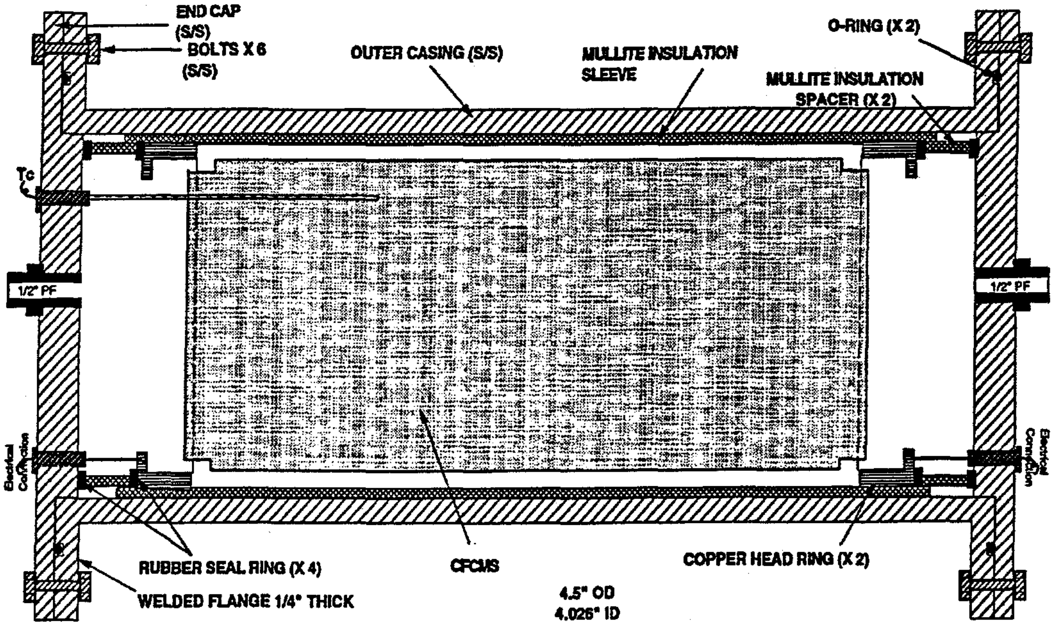

Figure1. Schematic illustration of the Gas Flow Loop Adsorption Cell.

RESULTS AND DISCUSSION

The ability of large CFCMS billets (9.5 cm diameter x 25 cm length) to be heated to temperatures exceeding 100°C has been demonstrated. Figure 2 shows the voltage-current relationship for the CFCMS sample in our ESA cell.

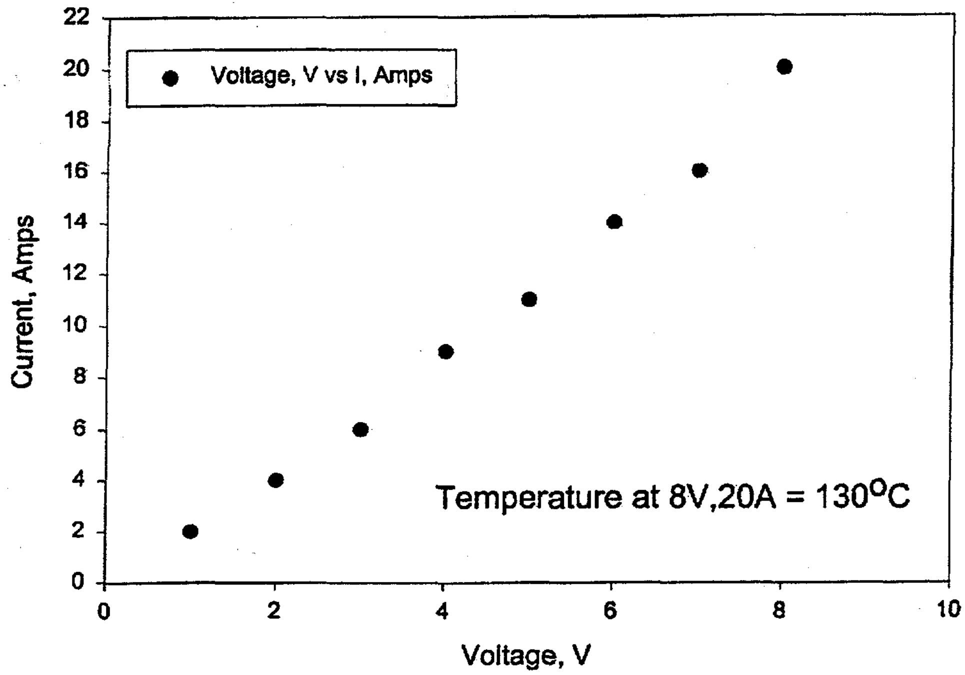

Fig 2. Current - voltage characteristics for a large CFCMS sample (95mm dia. x 250 mm len.)

The CFCMS attained a temperature in the ESA cell of 130°C when the applied voltage was 8V and the current was 20A.

A microbalance study was initiated to assess the ability of CFCMS to adsorb water from gas streams. Carbon materials are normally hydrophobic. However, it has long been known that water adsorption will occur if functional groups are added to the micropore surfaces. Consequently, a series of CFCMS samples was activated to develop large micropore volumes, and then soaked at 200°C for 2 hours in flowing oxygen. Details of the samples microporosity are given in Table 1 below.

Each of the four CFCMS specimens reported in Table 1 was sampled in two places and the microporosity characterized. Subsequent to characterization, the CFCMS specimen was cut into two, and one half of each specimen was exposed to flowing oxygen at 200°C for 2 hours. Samples from the treated and untreated CFCMS specimens were then placed in a microbalance and exposed to He saturated with water vapor at 18°C to determine their adsorption capacity. Water vapor adsorption measurements have been completed for all of the samples, in the oxygen treated and untreated conditions. The mass gains due to water vapor adsorption are reported in Table 2.

Table 1. Micropore characterization data for CFCMS samples

Sample Number	Burn-off (%)	BET Surface Area (m^2/g)	DR Micropore Volume (cm^3/g)	DR Micropore Width (nm)
SMS 1-1	**50.3**	**1886**	**0.68**	**2.2**
SMS 1-2	**50.3**	**2247**	**0.81**	**2.2**
SMS 2-1	**56.8**	**2144**	**0.75**	**2.3**
SMS 2-2	**56.8**	**2289**	**0.81**	**2.4**
SMS 3-1	**30.2**	**1271**	**0.48**	**1.9**
SMS 3-2	**30.2**	**1364**	**0.52**	**1.9**
SMS 4-1	**0**	**99**	**0.031**	**1.8**
SMS 4-2	**0**	**74**	**0.026**	**1.8**

Several significant observations can be made from the data in Table 2. Moisture uptakes in excess of 40 wt. % were observed for the activated and treated sample with the greatest micropore volume (SMS-2). For the activated samples, the amount of water adsorbed on the O_2 treated carbon is an order of magnitude greater than that adsorbed on the untreated carbon, demonstrating the role of surface functional groups in the water adsorption process. In the case of the unactivated sample, which exhibited very low surface area and micropore volume (Table 1), the amount of water adsorbed was still greater in the O_2 treated case than in the untreated case. In all cases the amount of water adsorbed tended to increase with each cycle. This was especially noticeable in the untreated case. The reasons for this are unclear at the present time, but may be due to irreversible pore expansion during adsorption, or the creation of additional adsorptive sites (surface functional groups) in the micropores. A correlation exists between the amount of water adsorbed and the micropore volume. For example, samples 1 and 2 exhibited the largest micropore volumes and the greatest moisture uptakes. The uptake of moisture onto the CFCMS is however relatively slow, taking several hours to reach saturation.

The combination of our ESA technique with a hydrophilic adsorbent, such as that reported above, allows for an electrically regenerable dehumidification system. Such a system would be particularly useful in natural gas processing, in gas separation where a dry gas stream is important, and in moisture removal and recovery (air conditioning). Regeneration of the CFCMS adsorbent would simply be achieved by passing a low voltage electric current through the material, thus raising its temperature above 100°C and causing the desorption of the water vapor. In a practical system a purge gas may be used to flush the moisture from the

Table 2. Moisture uptake data for CFCMS in the activated and Oxygen treated conditions

Adsorption Cycle Number	Mass Gain due to Moisture Adsorption (%)							
	Sample SMS-1		Sample SMS-2		Sample SMS-3		Sample SMS-4	
	Activated	Activated & O_2 Treated	Activated	Activated & O_2 Treated	Activated	Activated & O_2 Treated	Activated	Activated & O_2 Treated
1	0.75	21	2.0	41	0.5	24	2.6	6.6
2	0.90	31	1.5	45	1.5	27	5.7	6.6
3	2.10	34	1.5	45	6.5	31	5.5	6.9
Mean	1.25	29	1.7	42	3.0	27	4.6	6.7

adsorption chamber.

CONCLUSIONS

The treatment of CFCMS in flowing O_2 at 200°C successfully renders the CFCMS hydrophillic. The sample with the largest BET surface area and micropore volume (SMS-2) adsorbed greater than 40 wt. % moisture after O_2 treatment. The adsorption of water vapor was observed to be relatively slow. Further work is needed to optimize the activation and oxygen treatment conditions in order to maximize the adsorption of water vapor. The electrical heating of large billets of CFCMS has been demonstrated. Temperatures sufficient to cause the desorption of moisture from the CFCMS were readily attained at low applied voltages.

ACKNOWLEDGMENTS

This work was supported by the Advanced Research and Technology Development Program of the Office of Fossil Energy, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

REFERENCES

1. Burchell, T.D., Judkins, R.R., Rogers, M.R. and Williams, A.M. *CARBON,* **35** No. 9 (1997), pp. 1279-1294.
2. Burchell, T.D. and Judkins, R.R. *Energy Convers. Mgmt.* **37** Nos 6-8 (1996), pp.947-954.
3. Burchell, T.D. and Judkins, R.R. *Energy Convers. Mgmt.* **38** Suppl., (1997), pp.S99-S104.
4. Wei, G.C. and Robbins, JM. *Ceramic Bulletin,* **64** No. 5 (1985), pp. 691-699.