NATURAL GAS STORAGE MONOLITHS
BASED ON CARBON FIBERS

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Introduction

Adsorbed Natural Gas (ANG) is an attractive energy storage mode for gas powered light and medium duty vehicles. As part of an ongoing USDOE program directed toward NG powered trucks and fleet vehicles, ORNL has developed novel adsorbent carbon media [1]. ORNL's natural gas storage monoliths, based on isotropic pitch derived carbon fibers, have been developed and shown to store > 150 V/V of methane at ambient temperature and a pressure of 3.5 MPa (500 psi). A new series of monoliths in which the fiber length has been varied to improve the density have been prepared. Methane storage capacity data for these monoliths are reported and discussed in the context of monolith formulation, macro structure and micropore structure.

Experimental

Gas storage monoliths 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, Occidental Chemical Corp., N. Tonanwanda, NY 14120, USA). A schematic diagram of the fabrication route is in Figure 1. The monoliths were hot-pressed to densities in the range 0.8-1.1 g/cm^3, and carbonized prior to activation in a CO_2 atmosphere to the desired burn-off. Post activation analysis of the monoliths included micropore characterization via N_2 adsorption at 77K, and bulk density determination by mensuration. The standard monolith 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 (Figure 2) for testing in the gravimetric apparatus. The test samples were stacked in the test cell to completely fill the 50 cm^3 test cylinder cavity. The storage samples were vacuum outgassed at 473K 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. Methane uptake was measured at room temperature and 500 psi on 50-cm^3 volume samples using the apparatus pictured in Figure 3.
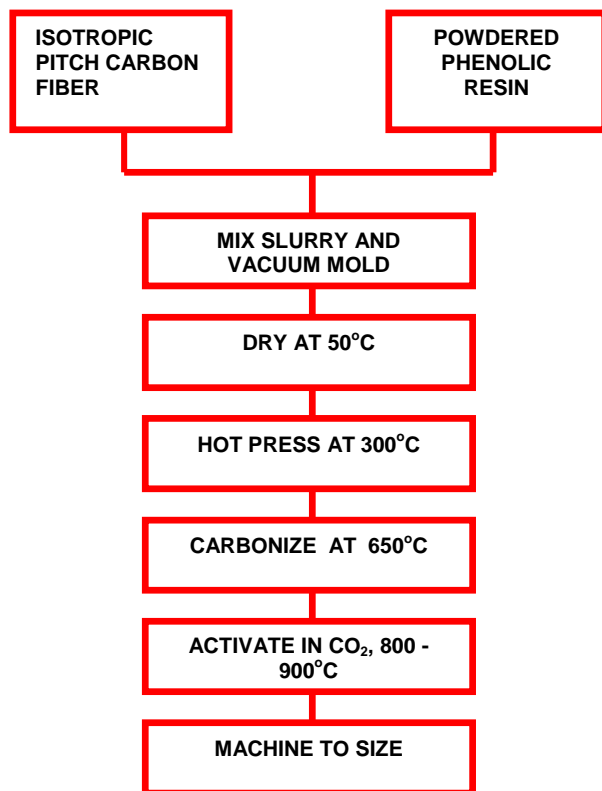

Figure 1. Monolith synthesis route

Figure 2. Gas storage monolith and test specimens

Figure 3. Methane adsorption test apparatus

characterization data determined from the N_2 @ 77K adsorption isotherms.

Table 1. Activation & micrpore characterization data for high density storage monoliths

Sample Number	Burn Off (%)	BET Surface Area (m^2/g)	DR Micropore Volume (cm^3/g)	DR Micropore Width (nm)
SMS-36	55.0	2557	0.88	2.6
SMS-37	48.1	2056	0.73	2.4
SMS-38	50.8	2113	0.73	2.5
SMS-39	58.8	1937	0.69	2.4
SMS-40	55.1	1876	0.67	2.4
SMS-41	46.9	1732	0.60	2.4
SMS-42	60.0	2056	0.71	2.5
SMS-43	50.6	2087	0.73	2.4
SMS-44	45.9	1775	0.63	2.4
SMS-45	47.2	1995	0.70	2.5

Methane storage capacity data (@for 500 psi) are reported in Fig 5. Moreover, some of the samples were tested at 900 psi, and the elevated pressure data are additionally reported in Fig. 5.
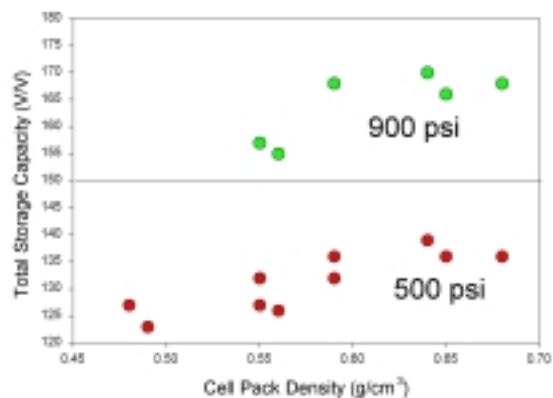
Results & Discussion

The as-carbonized density of our monoliths is reported in Figure 4. The density increased from less than 0.88 g/cm^3 at 0% jet-milled fiber to almost 1.1 g/cm^3 at 70% jet milled fiber.
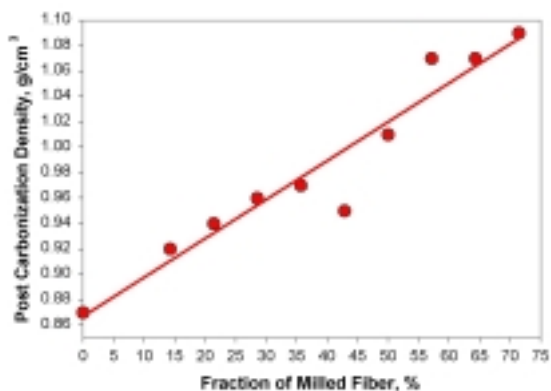
Figure. 4. The variation of as-carbonized monolith density with fraction of jet-milled fiber

The monoliths were activated to a target burn-off of 50%. Table 1 reports the burn-off attained and the micropore

Figure. 5. The total storage capacity for high density monoliths as a function of cell pack density (monolith density) at two test pressures

The storage capacity achieved for this series of monoliths at 500 psi varied from ~120 V/V to ~140 V/V. At a pressure of 900 psi the capacity varied from 166 to 170 V/V. At both pressures there is a clear trend for increasing capacity with increasing pack density. Many of the monoliths in this series were activated to burn-off > 50%. Although the activity of the carbon monoliths increases with burn-off (Fig. 6), inspection of storage data for all of the monoliths we have prepared (> 40), suggests that a

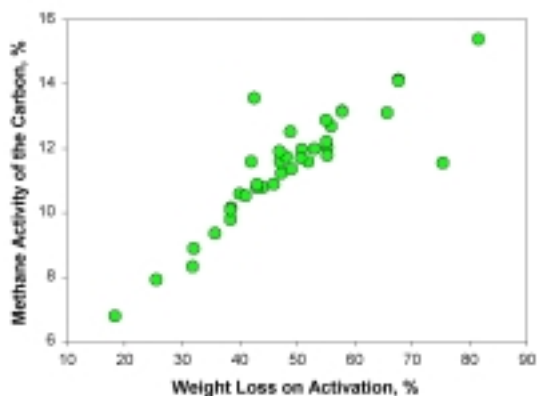slightly lower burn-off, ~ 40%, would closer to optimal (Fig. 7).

Figure 6. The methane weight activity of carbon in the storage monoliths as a function of weight loss
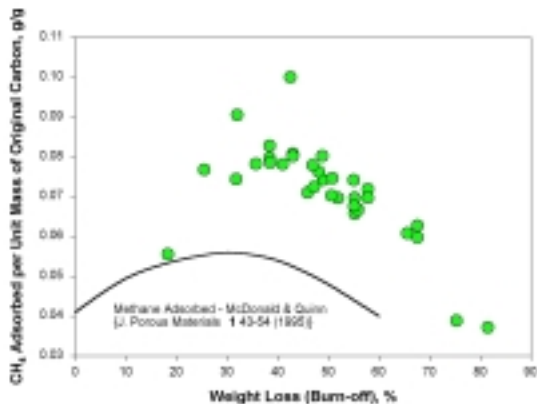

Figure 7. The gravimetric methane capacity of storage monoliths as a function of burn-off (solid line is data from MacDonald and Quinn [2])

The maximum in the data in Fig. 7 at ~ 40% burn-off is attributed to pore broadening with increased activation (Fig. 8) resulting in a reduced gas density in the micropores (Fig. 9).

The data reported here indicated that improved storage capacity maybe attained by careful control of the manufacturing and activation process. It is important to achieve the optimum degree of micropore development, yielding a high volume of small micropores close to the ideal size of 1.12 nm [3]. Excessive activation (burn-off) results in higher micropore volumes, but the mean pore size becomes too large (causing a reduced gas density in the micropores). Moreover, excessive burn-off additionally results in a reduction in the pack density, and hence the storage capacity.
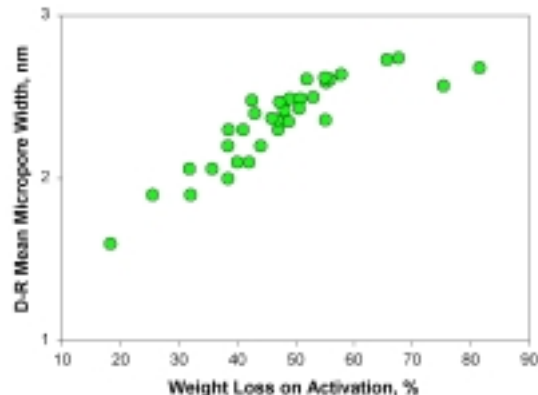

Figure 8. The variation of micropore width with burn-off for gas storage monoliths
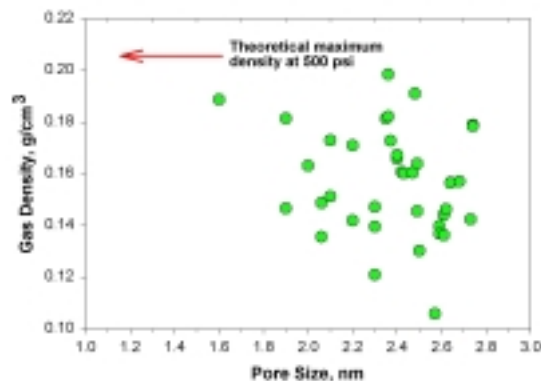

Figure 9. The variation of gas density in the micropores with micropore width for gas storage monoliths

Conclusions

A series of high-density gas storage monoliths have been fabricated and the methane storage capacity determined. A total storage capacity of ~ 140 V/V at 500 psi was attained. We have previously demonstrated capacities > 150 V/V. At a storage pressure of 900 psi the storage capacity increased to ~ 170 V/V. Further improvements in storage capacity will come from additional development and careful control of the synthesis process to attain the optimum combination of micropore volume, micropore size and monolith density.

References

1. Tim Burchell and Mike Rogers, SAE Paper 2000-01-2205, Pub. Society of Automotive Engineers, Inc. (2000).
2. J. A. F. MacDonald and D. F. Quinn, *J. Porous Mats*., 1, 43-54 (1995).
3. Z. Tan and K. E. Gubbins, *J. Phys. Chem*., 94, 6061, (1992).

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