

LOW PRESSURE STORAGE OF NATURAL GAS FOR VEHICULAR APPLICATIONS

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ABSTRACT

Natural gas is an attractive fuel for vehicles because it is a relatively clean-burning fuel compared with gasoline. Moreover, methane can be stored in the physically adsorbed state [at a pressure of 3.5 MPa (500 psi)] at energy densities comparable to methane compressed at 24.8 MPa (3600 psi). Here we report the development of natural gas storage monoliths [1]. The monolith manufacture and activation methods are reported along with pore structure characterization data. The storage capacities of these monoliths are measured gravimetrically at a pressure of 3.5 MPa (500 psi) and ambient temperature, and storage capacities of >150 V/V have been demonstrated and are reported.

INTRODUCTION

Methane (the major constituent of natural gas) has a higher H/C ratio than any other fuel, and consequently a higher Research Octane No. than other fuels (130 compared to 87 for unleaded gasoline). Unfortunately, methane cannot be stored at a density as high as other fuels, and thus has an energy density approximately one-third that of gasoline (11 MJ/L for compressed natural gas at 24.8 MPa (3600 psi) compared with 32 MJ/L for gasoline). Thus a compressed natural gas (CNG) fuel tank would need to be approximately three times larger than a gasoline tank to allow a vehicle the same driving range. The use of CNG has its disadvantages. The CNG storage tanks must be pressure vessels and are thus constrained in their geometry (they are typically cylindrical), and are also rather heavy (≈ 1 kg/L for steel tanks). Moreover, attainment of >20.7 MPa (3000 psi) pressure requires costly multi-stage compression.

For these reasons the US Department of Energy has pursued a research program 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, allows the use of single stage compressors, and represents a lesser safety hazard than the higher pressures used for CNG. The DOE storage target for ANG has been set at 150 V/V, i.e., 150 STP (101.325 KPa, 298K) liters of gas stored per liter of pressure vessel internal volume.

A novel adsorbent carbon monolith 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. Because of its monolithic nature 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 monoliths offers enhanced thermal conductivity over packed beds of carbon. This translates to smaller temperature gradients during tank charging and discharging. The development of storage monoliths has been ongoing at ORNL for the past three years, and we recently attained storage capacities in excess of the DOE target of 150 V/V. With continued process development and materials optimization it is anticipated that storage capacities of >180 V/V (delivered) can be attained - giving approximately one-fourth the driving range of an equivalent volume gasoline tank.

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. Tonawanda, NY 14120, USA). A schematic diagram of the fabrication route is in Figure 1. The monoliths were hot-pressed to densities in the range 0.7-0.92 g/cm³, and carbonized prior to activation in a CO₂ atmosphere to the desired burn-off. Post activation analysis of the monoliths included micropore characterization via N₂ adsorption at 77K, and bulk density determination by mensuration. Methane uptake was measured at room temperature and 500 psi on 50-cm³ volume samples using the apparatus pictured in Figure 2.

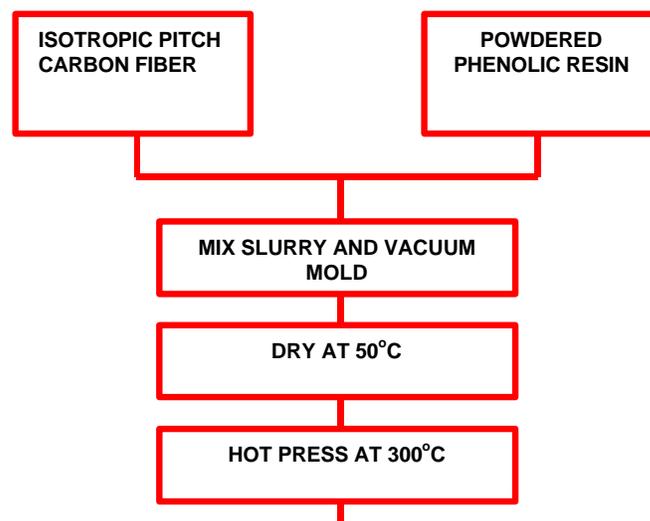


Figure 3. Gas storage monolith and test specimens



Figure 1. Monolith synthesis route



Figure 2. Methane adsorption test apparatus

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 3) 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 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.

RESULTS AND DISCUSSION

The results of our recent micropore characterization and gas storage studies are reported in Tables 1 and 2. A storage capacity of 150 V/V at 3.5 MPa (500 psi) and 294K has been attained, which is comparable to the best commercially available gas storage carbons [2]. The storage capacity is temperature sensitive. For example, the storage capacity of sample SMS-22 was 150 V/V at 294K, but increases to 159 V/V at 285K (Fig. 4).

Activation of the monoliths (burn-off) results in the development of microporosity, as indicated by the BET and micropore volume data in Table 1. Increasing the degree of burn-off increases the micropore volume and the mean micropore size (Figs. 5 and 6). Although increased micropore volume is beneficial, since the gas is adsorbed into the micropores, it is so only to a point. At very large burn-off the density of the monolith is small, and the mean micropore size becomes large and far from the optimum value of 1.12 nm [3]. Consequently, excessive burn-off is not productive.

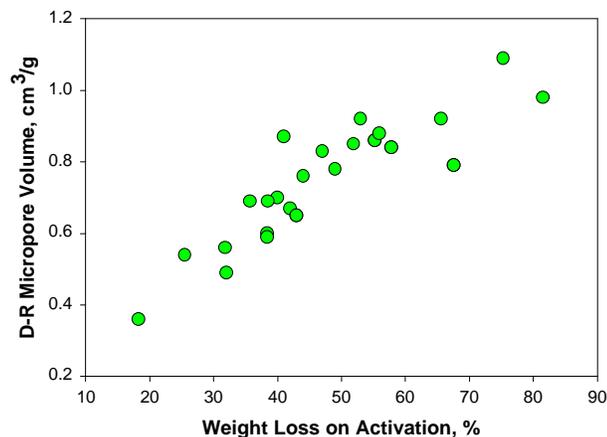


Table 1. Micropore characterization data for our methane storage monoliths

Sample	Burn-off (%)	BET Area (m ² /g)	DR Micropore Volume (cm ³ /g)	DR Micropore Width (nm)
SMS-15	55.2	2524	0.86	2.59
SMS-16	75.3	3173	1.09	2.57
SMS-17	51.9	2454	0.85	2.61
SMS-18	49.0	2237	0.78	2.49
SMS-19	55.9	2552	0.88	2.61
SMS-22	57.8	2451	0.84	2.64
SMS-23	31.8	1494	0.56	2.06
SMS-30	81.5	2860	0.98	2.68

Table 2. Methane gas adsorption and storage data for our storage monoliths

Sample	Cell Pack Density (g/cm ³)	Methane Activity (%)	Storage Capacity (V/V)
SMS-15	0.57	11.8	128
SMS-16	0.48	11.6	111
SMS-17	0.56	11.6	124
SMS-18	0.53	11.4	118
SMS-19	0.65	12.7	149
SMS-22	0.63	13.2	150
SMS-23	0.70	8.3	112
SMS-30	0.39	15.4	120

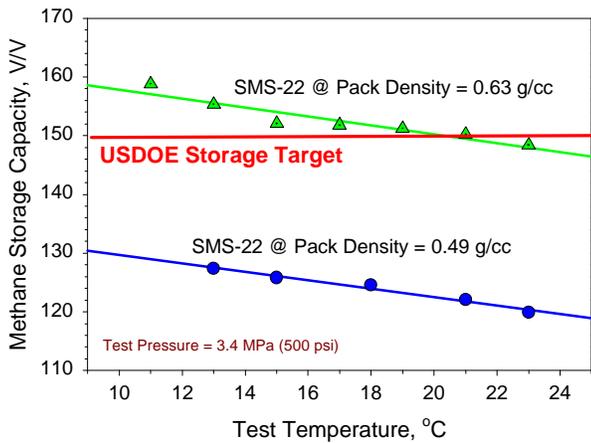
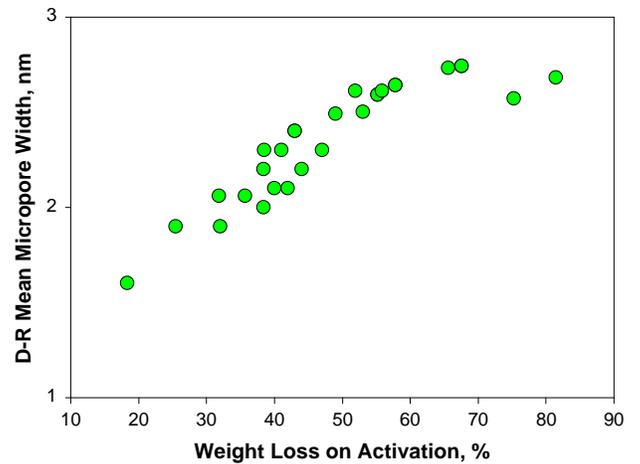


Figure 4. The variation of methane storage capacity with ambient temperature

Figure 6. The variation of mean micropore size with monolith burn-off

This point is illustrated by the data for samples SMS-23 and SMS-30 (Tables 1 and 2). 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 monolith is, therefore, one which exhibits high methane activity (which is a function of micropore size and total micropore volume) and high density. Such a monolith might be expected to store as much as 180 V/V of methane at 3.5 MPa (500 psi) - the revised DOE target storage capacity.

The attainment of a methane storage capacity of 180 V/V is particularly significant, since at that level comparable energy



densities to compressed natural gas at 24.8 MPa (3600 psi) are achieved. Our anticipated progress toward demonstrating a storage capacity of 180 V/V is shown in Figure 7 below.

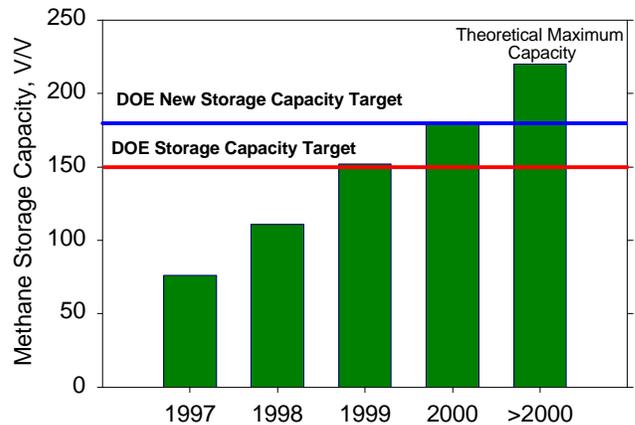


Figure 5. The variation of micropore volume with monolith burn-off

Figure 7. Methane storage capacities of ORNL's novel monoliths

A unique feature of our monoliths is worthy of discussion. The material exhibits a continuous carbon skeleton (Figure 8) and thus exhibits superior thermal conductivity and is electrically conductive. This latter phenomenon enables all of the adsorbed gas to be delivered by electrically stimulating desorption of the gas.



Figure 8. The microstructure of ORNL's novel gas storage monolith

Typically, 10-20% of the gas adsorbed into the monolith is retained when the gas pressure is reduced to one atmosphere. This is illustrated in Figure 9, where the uptake of methane is shown for a repetitive charge/discharge cycle. In the first cycle the cylinder is charged from vacuum to 3.5 MPa (500 psi) under near isothermal conditions. When the gas is released and the pressure drops to atmospheric pressure some fraction of the adsorbed gas is retained in the carbon. As the data in Figure 9 indicates, the amount of gas retained does not appear to increase as the adsorbent is cycled. However, the amount of delivered gas is less than the total amount stored. The use of electrical stimulation to desorb the adsorbed gas (4) allows all of the adsorbed gas to be delivered, thus increasing the range of a vehicle fuelled from an adsorbed natural gas tank.

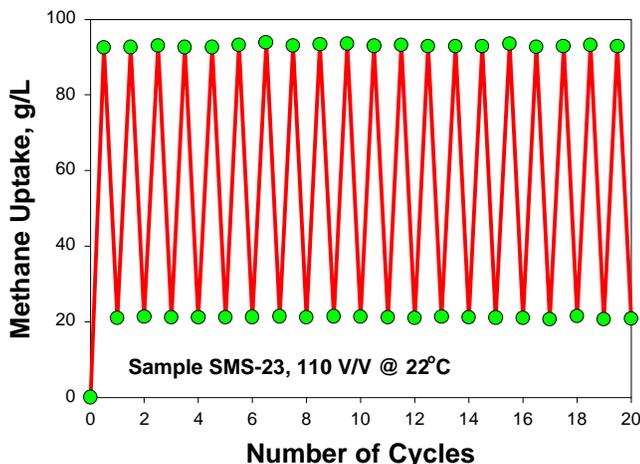
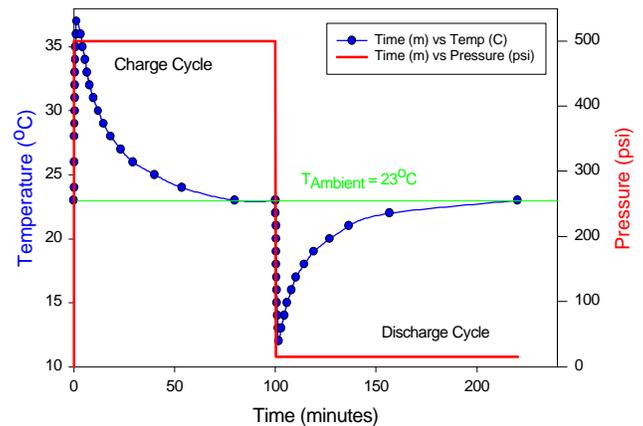


Figure 9. Methane uptake of an ORNL storage monolith over several cycles of charge and discharge

Enhanced thermal conductivity is also advantageous during rapid methane charge and discharge situations. Since the adsorption of methane onto activated carbon is an exothermic process, the adsorbent heats during adsorption. Similarly, desorption of methane is an endothermic process and, therefore, the adsorbent temperature drops as the gas is desorbed. The extent of these temperature changes is illustrated in Figure 10 for a fast charge/discharge of our standard 50-cm³ monolith filled test cylinder. These temperature changes have design implications and, therefore, minimizing the temperature changes is particularly important. The amount of gas adsorbed decreases as the temperature increases. Therefore, on filling, the capacity of the tank is diminished by the rise in adsorbent temperature and it is necessary to overpressurize the tank to achieve the desired storage capacity. When the adsorbent cools the gas pressure drops to the working pressure. Moreover, when the tank is discharged, the adsorbent temperature drops and the adsorbed gas is not released. Consequently, the gas pressure in the tank falls and the gas flow to the engine may be interrupted. Enhanced thermal conductivity will tend to reduce the significance of the two phenomena. Moreover, the ability to electrically stimulate desorption of the adsorbed gas [4] offers the possibility of completely eliminating the gas pressure/supply



problem associated with fast discharge.

Figure 10. Variation of our methane test cylinder (50 cm³ volume) temperature during a fast fill/discharge cycle

CONCLUSIONS

A novel gas storage monolith based on carbon fibers has been developed that can store and deliver >150 V/V of methane. The monolith is rugged and durable. Moreover, the monolith offers enhanced thermal conductivity over conventional adsorbent carbons, which will reduce the deleterious effects of temperature gradient that develop during tank charge and discharge. The monoliths are electrically conductive, allowing the liberation of all of the adsorbed gas and maximizing the amount of gas delivered to the engine. It is anticipated that the revised methane storage capacity of 180 V/V will be attained in the near future.

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