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HIGH-SURFACE-AREA BIOCARBONS FOR REVERSIBLE ON-BOARD STORAGE OF NATURAL GAS AND HYDROGEN

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ABSTRACT

An overview is given of the development of advanced nanoporous carbons as storage materials for natural gas (methane) and molecular hydrogen in on-board fuel tanks for next-generation clean automobiles. The carbons are produced in a multi-step process from corn cob, have surface areas of up to 3500 m²/g, porosities of up to 0.8, and reversibly store, by physisorption, record amounts of methane and hydrogen. Current best gravimetric and volumetric storage capacities are: 250 g CH₄/kg carbon and 130 g CH₄/liter carbon (199 V/V) at 35 bar and 293 K; and 80 g H₂/kg carbon and 47 g H₂/liter carbon at 47 bar and 77 K. This is the first time the DOE methane storage target of 180 V/V at 35 bar and ambient temperature has been reached and exceeded. The hydrogen values compare favorably with the 2010 DOE targets for hydrogen, excluding cryogenic components. A prototype adsorbed natural gas (ANG) tank, loaded with carbon monoliths produced accordingly and currently undergoing a road test in Kansas City, is described. A preliminary analysis of the surface and pore structure is given that may shed light on the mechanisms leading to the extraordinary storage capacities of these materials. The analysis includes pore-size distributions from nitrogen adsorption isotherms; spatial organization of pores across the entire solid from small-angle x-ray scattering (SAXS); pore entrances from scanning electron microscopy (SEM) and transmission electron microscopy (TEM); H₂ binding energies from temperature-programmed desorption (TPD); and analysis of surface defects from Raman spectra. For future materials, expected to have higher H₂ binding energies via appropriate surface functionalization, preliminary projections of H₂ storage capacities based on molecular dynamics simulations of adsorption of H₂ on graphite, are reported.

INTRODUCTION

According to the State Alternative Fuels Plan [1] of the California Air Resources Board and California Energy Commission, adopted October 31, 2007, in response to Assembly Bill 1007, the State of California will take action to increase its use of natural gas (NG, methane, CH₄) as motor fuel from currently 0.6% to 19% (aggressive scenario) of the state’s on-road

Both fuels meet the “No Net Material Increase in Emissions” standard [1,3]. For both fuels, the “holy-grail” on-board tank [4] is a lightweight, flat-panel (conformable) tank, under the floor or in other unused space of an automobile, that has a driving range of more than 300 miles, can be fueled in less than 3 minutes, and requires a minimum of auxiliary on/off-board equipment and infrastructure. However, most current natural-gas vehicles run on compressed natural gas (CNG), with on-board NG stored in bulky, heavy-walled cylinders at 250 bar (3600 psig). Likewise, hydrogen fuel cell vehicles under development store hydrogen in cylinders at 350-700 bar. Such high-pressure tanks are difficult to integrate within the space available in a passenger car and give the vehicle a limited fuel storage capacity, whence limited driving range. This makes on-board storage a major barrier to the use of NG and hydrogen for advanced transportation, in the transition to non-petroleum transportation fuels.

The key to remove this barrier is to store the fuel in a porous solid, as adsorbed natural gas (ANG) or adsorbed hydrogen, designed to hold the fuel at low pressure (e.g., 35 bar, 500 psig) with a storage density comparable to that in a high-pressure tank. The low pressure allows for thin tank walls and a conformable shape (Figure 1). In this paper we report significant progress toward this goal, based on novel nanoporous carbons developed by our team (Alliance for Collaborative Research in Alternative Fuel Technology—ALL-CRAFT [5]), both for CH$_4$ and H$_2$. Earlier work found nanoporous carbons crisscrossed by a nearly space-filling network of channels, ~1.5 nm wide [6], close to the optimal width of 1.1 nm for CH$_4$ storage [4].

For CH$_4$, the DOE in 2000 defined the volumetric storage target at 35 bar and room temperature as 180 V/V, that is, the adsorbent stores 180 its own volume of methane at 1 bar and 298 K [7]. This translates into 118 g CH$_4$/liter carbon. Characteristics of earlier ANG projects, prior to the ALL-CRAFT materials, are summarized in Table I.

For H$_2$, the 2010 DOE volumetric and gravimetric targets (system targets) are 45 g H$_2$/liter tank and 60 g H$_2$/kg tank (“6.0 mass%”) at 293 K.

**EXPERIMENTAL DETAILS**

Nanoporous carbons were made by pyrolysis of ground waste corncob using a proprietary multi-step procedure [8]. Samples were prepared in granular form. For the prototype tank (Fig-

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**Figure 1.** Left: Schematic of a multi-cell, conformable ANG tank, filled with carbon briquettes. Center and right: ALL-CRAFT prototype ANG tank and fuel delivery system, currently being road-tested.
Table I. Comparative characteristics of ANG projects up to 2006 [9]. Not included in the table is methane storage work done by Yaghi’s group on metal-organic frameworks [10]. The storage capacities reported in Figures 2-3 below correspond to the entry “Tank uptake V/V” in the table.

<table>
<thead>
<tr>
<th>PARAMETERS AND CONDITIONS</th>
<th>AGLARG (Atlanta Gas Light Adsorbent Research Group)</th>
<th>EU FPS LEVINGS program (coordination by FIAT)</th>
<th>OAK RIDGE NATION. LABORATORY (ORNL)</th>
<th>HONDA MOTORS</th>
<th>UNIVERSITY OF PETROLEUM CHINA (UPC)</th>
<th>Brazilian Gas Technology Center (CTGAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigation method</td>
<td>Chrysler B-van, Dodge Dakota Truck</td>
<td>FIAT Marea, On-board, field testing</td>
<td>Laboratory investigations</td>
<td>Tank development Adsorbent - laboratory tests</td>
<td>Car X1ALI 7131U On-board, field testing</td>
<td>Laboratory investigation on full-size prototype</td>
</tr>
<tr>
<td>Pressure, bar</td>
<td>35-40</td>
<td>35-40</td>
<td>35</td>
<td>50</td>
<td>125</td>
<td>35-40</td>
</tr>
<tr>
<td>Tank uptake V/V</td>
<td>150 In laboratory condition, 142 on-board</td>
<td>123</td>
<td>150</td>
<td>155</td>
<td>100-110</td>
<td>1/0-180</td>
</tr>
<tr>
<td>Tank delivery V/V (to engine)</td>
<td>135 (approx)</td>
<td>107</td>
<td>Not relevant</td>
<td>-</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Adsorbent presumed cost</td>
<td>Prohibitive</td>
<td>High, but about 10 times less than the AGLARG</td>
<td>Supposedly very high</td>
<td>Supposedly similar to AGLARG</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Vessel (tank) design features</td>
<td>Multicell of extruded aluminum</td>
<td>Multicell of steel tubes</td>
<td>Small laboratory vessel of volume 0.05 L.</td>
<td>Multicell</td>
<td>Unknown</td>
<td>Cylindrical form with volume 30 liters</td>
</tr>
</tbody>
</table>

The granular carbon was pressed into disk-shaped briquettes (monoliths), 3.5 inches in diameter and 0.5-1.0 inches thick, using a binder and heat treatment. We manufactured over 300 briquettes (~25 kg), loaded them in the prototype tank and fuel delivery system constructed by the Midwest Research Institute, and installed the system on a NG vehicle (Ford F-150 bifuel pickup truck) on loan from the Kansas City Office of Environmental Quality. The tank was showcased in Kansas City, 2/16/07 [11], and has been on the road in Kansas City ever since.

Methane uptakes were measured as excess adsorption, \( m_{\text{ads}} \) (total mass of methane in the pore space minus the mass of bulk methane that would be present in the absence of adsorption) on a custom-built gravimetric instrument (sample masses 1-5 g) and on a custom-built volumetric instrument for briquettes (Sievert apparatus). Excess adsorption was converted into total amount stored, \( m_{\text{st}} \) (mass of adsorbed and nonadsorbed methane in the pore space), using

\[
m_{\text{st}} = m_{\text{ads}} + \left( \rho_s - \rho_a \right) \rho_{\text{gas}} m_s
\]

where \( \rho_s, \rho_a, \rho_{\text{gas}}, \) and \( m_s \) are the apparent density of the sample (including pore space), skeletal density of the sample (without pore space), density of bulk gas, and mass of the sample, respectively. Hydrogen uptakes were measured as excess adsorption on the custom-built gravimetric...
instrument (University of Missouri), a Hiden IGA-001 instrument (Hiden Isochema Ltd.), and a Hy-Energy PCTPro2000 instrument (National Renewable Energy Laboratory), and converted into total amount stored using Eq. (1), just as in the methane case.

Surface areas and pore-size distributions were obtained from N2 adsorption at 77 K on an Autosorb-1-C instrument (Quantachrome), computed from density functional theory (DFT) analysis of the N2 isotherm (Quantachrome). Scanning electron microscopy (SEM) was performed on a Hitachi S-4700 FESEM instrument, with beam energy set to 5 kV and a small working distance (3-4 mm). Transmission electron microscopy (TEM) was performed on a JEOL 1200EX TEM instrument, with beam energy 100-120 kV. Small-angle x-ray scattering data was collected on Beamline 32-ID-B USAXS (Ultra-Small-Angle X-Ray Scattering) at the Advanced Photon Source, Argonne National Laboratory.

Temperature-programmed desorption (TPD) spectra for hydrogen and Raman spectra were measured at the National Renewable Energy Laboratory. In the TPD experiments, a sample was sequentially degassed in vacuum with steps up to 523 K, in order to ensure that no adsorption sites were blocked. After each degassing step, the sample was exposed to 500 torr H2 at room temperature, cooled to ~190 K, followed by evacuation of the chamber. H2 evolution was then monitored with a mass spectrometer as the sample was heated with a linear heating rate.

RESULTS AND DISCUSSION

Methane Storage

Figures 2 and 3 show methane storage isotherms (total amount stored) for a typical ALL-CRAFT carbon briquette, and volumetric vs. gravimetric storage isotherms of our best samples to date (S-33/k and Batch 5.32). The data shows that the carbon-filled tank stores 5-6 times more methane than a tank without carbon at 35 bar, despite the fact that the carbon skeleton occupies 20-30% of the tank volume. To store 118 g CH4/liter without adsorbent, the tank pressure would have to be 180 bar, much more than what a flat tank can bear. The target pressure of 35 bar (500 psig) of the ANG tank equals the pressure in typical NG pipelines and, therefore, elimi-
Figure 3. Left: Best volumetric storage capacity, 130 g CH$_4$/liter carbon (199 V/V) at 35 bar and 293 K, for Sample S-33/k. Right: Best gravimetric storage capacity, 247 g CH$_4$/kg carbon at 35 bar and 293 K, for Sample Batch 5.32. The reversal of maximum storage capacity, if one goes from volumetric to gravimetric capacity, Eqs. (2) and (1), is due to the difference in apparent density of the two samples: \( \rho_a = 0.58 \text{ g/cm}^3 \) for S-33/k and \( \rho_a = 0.38 \text{ g/cm}^3 \) for Batch 5.32. The respective porosities are 0.71 and 0.81.


nates costly compression of NG from 500 psig to 3600 psig (CNG tank).

Since excess adsorption measures the difference between the mass of methane adsorbed and the mass of an equal volume of nonadsorbed methane, it follows that excess adsorption depends only on the surface area and how strongly the surface adsorbs methane, but not on the pore volume of the sample. For the total amount stored, Eq. (1), the situation is different: the volumetric storage capacity, \( \frac{m_{st}}{m_s} \rho_a \), increases if the apparent density, \( \rho_a \), increases,

\[
\frac{m_{st}}{m_s} \rho_a = \left( \frac{m_{ads}^c}{m_s} - \frac{\rho_{gas}}{\rho_s} \right) \rho_a + \rho_{gas} \tag{2}
\]

all other parameters being equal. Inversely, the gravimetric storage capacity, \( \frac{m_{st}}{m_s} \), increases if the apparent density decreases, Eq. (1). Samples S-33/k and Batch 5.32 in Figure 3 conform perfectly with this structure-function relation: the DFT surface area is 2150 m$^2$/g for both samples; the skeletal density is 2.0 g/cm$^3$ for both samples; and excess adsorption is 193 g CH$_4$/kg carbon and 197 g CH$_4$/kg carbon, respectively. So the volumetric capacity of S-33/k is higher than that of Batch 5.32, and the gravimetric capacity is lower than that of Batch 5.32, because the apparent density of S-33/k is higher (Figure 5).

This observation indicates that the binding energy of CH$_4$ on the two samples is the same. The surface packing density, defined as excess adsorption divided by surface area [12], gives 0.0338-0.0345 CH$_4$ molecules per Å$^2$. Since excess adsorption is a lower bound to absolute adsorption (mass of adsorbed film), the reciprocal of the packing density gives an upper bound of 29-30 Å$^2$ for the surface area per CH$_4$ adsorption site on the two samples, at 35 bar and 293 K.

**Hydrogen Storage**

Sample S-33/k, which is our best-performing volumetric methane storage material (Figure 3), is simultaneously also our best hydrogen storage material (Figure 4 and Table II).
Figure 4. Gravimetric \( \text{H}_2 \) storage isotherm (total amount stored) on Sample S-33/k, a nanoporous carbon made from corncob. The excess adsorption isotherm was measured at Hiden Isochema, and converted into amount stored using Eq. (1) and the same structural data as in Figure 3.

Table II. Validation of \( \text{H}_2 \) storage results on S-33/k in three independent laboratories, and comparison with adsorbents in the literature (AX-21 is a commercial activated carbon; MOF-177 is a metal-organic framework). The values in the table are amount stored, and 79 g \( \text{H}_2 \)/kg adsorbent is reported as 7.9 mass%. The values reported for Hiden are extrapolated from Figure 4.

<table>
<thead>
<tr>
<th></th>
<th>77 K, 47 bar</th>
<th>293 K, 47 bar</th>
<th>293 K, 80 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-33/k, Hiden</td>
<td>7.9 mass%</td>
<td>1.2 mass%</td>
<td>1.9 mass%</td>
</tr>
<tr>
<td>S-33/k, U. Missouri</td>
<td>7.3-9.1 mass%</td>
<td>1.0-1.2 mass%</td>
<td>–</td>
</tr>
<tr>
<td>S-33/k, NREL</td>
<td>~8 mass%</td>
<td>1.4-1.6 mass%</td>
<td>2.1-2.4 mass%</td>
</tr>
<tr>
<td>AX-21 [13]</td>
<td>5.1 mass%</td>
<td>0.6 mass%</td>
<td>–</td>
</tr>
<tr>
<td>MOF-177 [14]</td>
<td>~10 mass%</td>
<td>~2.4 mass%</td>
<td>–</td>
</tr>
</tbody>
</table>

Surface and Pore-Space Characterization

Figures 5 and 6 collect structural data for the pore space of Sample S-33/k. The pore-size distribution shows that an extensive nanoporosity, bimodally peaked around 0.6 nm and 1.1 nm. The two peaks coincide with the optimum pore width of 0.6-0.7 nm and 1.1 nm predicted for maximum \( \text{H}_2 \) and \( \text{CH}_4 \) storage, respectively [4]. This may explain why S-33/k performs so well both for hydrogen and methane storage. The absence of any hysteresis in the \( \text{N}_2 \) adsorption and desorption isotherm, as well as transmission electron micrographs (not shown), confirm that S-33/k consist almost exclusively of pores less than 2 nm in width.

Figure 6 shows the SAXS data for S-33/k. SAXS is one of the few experimental methods that can “see” the spatial organization of pores across the entire solid, over 4 decades of length, 0.5-5000 nm. Structure at small length scales scatters at large wave vectors \( q \), and structure at large length scales scatters at small \( q \). Interestingly, the data at large wave vectors cannot be fitted by treating the pores in Figure 5a as independent scatterers. Instead, the “knee” in Figure 6 can be well fitted by the scattered intensity for cylindrical pores. The cylinder shape makes the pores correlated, and the best fit gives a pore width of 0.5 nm and a length of 1.4 nm [16].
Figure 5. (a) Left: Pore-size distribution of S-33/k from N₂ adsorption. Most pores are in the range 0.5-1.0 nm. The volume of pores with diameter < 2.0 nm (micropore volume) is 1.2 cm³/g. The DFT and BET surface area of the sample are 2150 m²/g and 2500 m²/g. Since the BET theory is not applicable to microporous systems [15], we quote BET areas just as figure of merit. (b) Right: Scanning electron micrograph of S-33/k, showing a rare large pore.

is in excellent agreement with the pore size data from N₂ adsorption (Figure 5a). At small $q$, the extended power law, $I \propto q^{-3.7}$, indicates the presence, at large length scales, of an external surface with fractal dimension ~2.3 [17], consistent with the mild roughness of the external surface visible in Figure 5b.

The extensive nanoporosity of S-33/k suggests that the surface has few graphitic domains. This is borne out by the Raman spectra of three different samples (Figure 7). The Raman spectrum of S-33/k is more consistent with an amorphous carbon structure than with a highly graphitic structure such as a carbon multi-wall nanotube (MWNT). The Raman spectrum of S-37 is more consistent with the spectrum that would be observed with a graphitic MWNT network [18]. It is possible that a surface richer in defects, which would result in a Raman spectrum

Figure 6. Small-angle x-ray scattering data of S-33/k. The red curve is the best fit of the knee at large scattered wave vectors, corresponding to cylindrical pores of width 0.5 nm and length 1.4 nm, consistent with the pore-size distribution in Figure 5a.
similar to amorphous carbon, as in S-33/k, may have a higher H2 adsorption capacity. However, the H2 desorption peaks in the TPD spectra are all centered at ~150 K (Figure 7), consistent with that the surface of S-33/k physisorbs H2 with a binding energy of ~4 kJ/mol, comparable to the binding energy on graphite. In pores of width 1.1 nm, this is not unreasonable, but in pores of width 0.6 nm, one would expect binding energies larger than 4 kJ/mol.

**Computational work**

Theoretical predictions of H2 storage capacities under two distinct scenarios—localized and mobile adsorption—were carried out using the Langmuir adsorption isotherm and molecular dynamics simulations. Using the highly parallelized NAMD2 code [19], the simulations were carried out in a computational cell of size of approximately 100 Å × 100 Å × 100 Å, bisected by 6 layers of graphite, in which H2 molecules interact via Lennard-Jones potentials with each other and with the carbon atoms in the graphite. A total of \( N = 1545, 3290, 4936, \) and 6581 H2 molecules were used at each temperature, the time step for the integrations was \( \Delta t = 1 \) fs, and 100,000-200,000 time steps were used for each simulation. The sum of the Lennard-Jones potentials between a H2 molecule and all carbon atoms gives an adsorption potential \( V(x, y, z) \) with a strongly \( z \)-dependent attractive part and a weakly \((x, y)\)-dependent corrugation part. Using the experimental binding energy of 5.0 kJ/mol for H2 on graphite [20], we obtained approximately 0.5 kJ/mol for the peak-to-peak amplitude of the corrugation potential.

Simulated adsorption isotherms (Figure 8) were computed for various pairs \((N, T)\), and equivalently for various pairs \((P, T)\). From extrapolation of the number of molecules in the first layer at very high pressure, the surface area per adsorption site, \( \alpha(T) \), was calculated. With appropriate values for the vibrational frequencies \( \nu_x, \nu_y, \nu_z \) of H2 in the adsorption potential, Eqs. (4) and (5), this gave the framework to calculate the Langmuir isotherm,

\[
\theta(p, T) = \frac{\chi(T)p}{1 + \chi(T)p}, \tag{3}
\]
Figure 8. Snapshots of computer simulations showing adsorbed layers of H$_2$ on graphite at 77 K (blue) and 293 K (red). In both cases, the density of H$_2$ is noticeably higher near the graphite surface. The 6 layers of graphite creating the adsorption potential $V(x, y, z)$ are shown in green.

for surface coverage $\theta$ (number of adsorbed H$_2$ molecules per adsorption site, $0 \leq \theta \leq 1$), as a function of gas pressure $p$ and temperature $T$. The expressions for the Langmuir constant $\chi(T)$ for localized and mobile adsorption are

$$\chi(T) = \frac{e^{E_B/(N_A kT)}}{\sinh(h \nu_x / (2kT)) \sinh(h \nu_y / (2kT)) \sinh(h \nu_z / (2kT)) \sqrt{(8\pi m)^3 (kT)^5}},$$  \hspace{1cm} (4)

$$\chi(T) = \frac{\alpha(T)e^{E_B/(N_A kT)}}{\sinh(h \nu_z / (2kT)) \sqrt{h^6/(8\pi m(kT)^3)},}$$  \hspace{1cm} (5)

respectively. In these expressions, $E_B > 0$ is the binding energy, defined as the depth of the minima of the potential energy $V(x, y, z)$, per mole of H$_2$; $m$ is the mass of the H$_2$ molecule; $N_A$ is Avogadro’s constant; $k$ is Boltzmann’s constant; and $h$ is Planck’s constant. The surface area per site, $\alpha(T)$, is temperature-dependent because adsorbed molecules are densely packed at low temperature, but occupy a larger area at higher temperature due to thermal motion in the $x, y$ direction. We note the elementary, but informative inequality $\alpha(T) < (\text{surface packing density})^{-1}$ from the discussion following Eq. (2).

Figure 9 shows excess adsorption isotherms calculated at 77 K and 293 K. The localized adsorption model at 77 K and the mobile adsorption model at 293 K, calculated with $E_B = 5.0$ kJ/mol, agree qualitatively well with experimental data over a broad of pressures. However, the Langmuir fit for 77 K falls below the experimental data at low pressures, consistent with the picture that sites with binding energies larger 5.0 kJ/mol, undoubtedly present in S-33/k, are occupied first and entail a higher coverage than with 5.0 kJ/mol. This agreement is remarkable in view of the experimental and theoretical input from widely different sources. Moreover, it allows us to discriminate experimentally between two vastly opposed situations of how molecules do or do not move along the surface, how such lateral dynamics (competition of vibrational and translational degrees of freedom) affects the H$_2$ storage capacity, and how control of such dynamics, e.g., by surface functionalization, may offer new venues to increase storage capacities by as much as a factor of two (ratio of mobile to localized adsorption at 77 K and ~40 bar in Figure 9).
CONCLUSIONS

A novel class of carbons, made from waste corn cob—a low-cost, renewable raw material, with superior storage capacities for natural gas (methane) and hydrogen has been presented. Volumetric and gravimetric methane capacities reported here, at room temperature, are 130% and 145%, respectively, of the best carbon in the literature we are aware of. The hydrogen capacities at cryogenic and room temperature are ~160% and 200%, respectively, of the best carbon we know of. Our cryogenic hydrogen capacity is about 80% of that of the best metal-organic framework. The natural-gas work is an integrated, lab-to-prototype RD&D effort. Remarkably, the best-performing material for natural gas is also a top performer for hydrogen storage. Evidence has been presented that this may be due to a bimodal pore-size distribution, with most pores having a width of less than 1.5 nm. Computational work has been presented that allows us to distinguish experimentally between localized and mobile hydrogen adsorption, that provides first evidence that the materials with high hydrogen storage capacity do carry a significant fraction of sites with high binding energies, and that offers design principles for surface-functionalized materials with improved hydrogen storage capacities.

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