

CARBON MATERIALS FOR HYDROGEN STORAGE

Nidia C. Gallego, Timothy D. Burchell, Ashli M. Clark
Carbon Materials Technology Group
Metals and Ceramics Division
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6087

Corresponding author e-mail address: gallegonc@ornl.gov

Introduction

In 2003 President Bush launched the Hydrogen Fuel Initiative to ensure US energy security and environmental viability [1]. The use of hydrogen will diversify energy sources, and reduce pollution and greenhouse gas emissions. Hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell power technologies in transportation, stationary and portable applications. The current available technologies for on-board hydrogen storage include: (i) physical storage via compression or liquefaction, (ii) chemical storage in irreversible hydrogen carriers (e. g., methanol, ammonia), (iii) reversible metal hydrides and (iv) gas-on-solid adsorption [2]. However, none of these approaches satisfies all of the efficiency, size, weight, cost and safety requirements for transportation or utility use. The main drawbacks for physical storage include the need of high pressure and/or low temperature (21 K for liquefaction) as well as the high cost. Chemical storage generally needs a conversion process which makes the system more complicated. Storage by metallic hydrides has the advantage of low pressure, but the storage system is heavy and additional heating is needed for hydrogen release. The last possibility, hydrogen adsorption in porous solids such as activated carbons, has been studied since the 1960s[3]. Recent research has focused on finding the ideal adsorbent that, used at room temperature, allows the storage of desirable amounts of H₂. This has generated renewed interest in the use of carbon materials for hydrogen storage. Hydrogen storage in a carbon-based material offers significant advantages associated with its low mass density. Early experimental data for hydrogen storage in carbon nano-materials was initially promising, indicating high hydrogen storage capacities exceeding DOE targets. However, the more recent experimental data obtained with different methods and on various carbon nanostructures are contradictory with large variance in the amount of hydrogen stored [4].

This project seeks to explore the role of nanostructure in hydrogen storage on carbons through a comprehensive study of several forms of carbon, from the very amorphous activated carbons to the ordered forms such as graphite and nanostructured carbons. Advanced structural characterization and measurement of hydrogen isotherms are underway. The data presented here represents preliminary results of the undergoing study.

Experimental

A test matrix of ~20 different carbon samples, including commercial activated carbons, adsorbent carbon fibers and fiber composites, graphite nanofibers, carbon nanowebs and single walled carbon nanotubes was assembled. Characterization via N₂ adsorption at 77K was conducted on the majority of the samples; for this a Quantachrome Autosorb-1 system was used. Selected samples were examined for their ability to adsorb H₂ at pressures up to 20 bar, at both room and cryogenic temperatures. Measurements were conducted using a gravimetric technique utilizing a Hiden Technologies, Intelligent Gravimetry Analyzer (IGA) system. To date we have measured H₂ adsorption isotherms at ambient temperature (0-20 bar) on ~10 different carbons. Isotherms at 77K (0-20 bar) have also been determined on 5 of the more promising samples.

Results and Discussion

Selected samples were examined for their ability to adsorb H₂ at pressures up to 20 bar (290 psi). Table 1 list the measured BET surface area of the samples.

Table 1 Bulk density and specific surface area of selected carbon materials.

| Sample | Bulk density [g/cc] | BET Surface area [m ² /g] |
|----------------------------|---------------------|--------------------------------------|
| Anshan Fibers | n/a | 1500 |
| Fiber monolith SMM-19 | 0.21 | 2000 |
| Wood-based carbon | 0.25-0.30 | 2200 |
| As-produced nanotubes (NT) | n/a | 419 |
| Purified nanotubes (NT) | n/a | 1667 |

a. H₂ Adsorption at Room Temperature: Fig. 1 compares hydrogen uptakes for (i) commercially available pitch-based carbon fibers (Anshan fibers), steam activated with a BET surface area of ~ 1500 m²/g; (ii) ORNL fiber monoliths (isotropic pitch based fibers and activated with CO₂) with a BET surface area of ~2000 m²/g; and (iii) a wood-based activated carbon with at BET surface area of ~2200 m²/g. From this figure it is observed that the H₂ uptakes are very low at room temperature for all carbon samples.

Figure 2 compares the room-temperature adsorption behavior of carbon nanotube samples. The as-produced sample contains nanotubes, catalyst and 'soot', or amorphous carbon, from the manufacturing process (laser ablation). The second sample has undergone extensive purification and is essentially pure nanotubes. The shape of the isotherms in the two cases are dissimilar. The isotherm for the as-produced nanotubes exhibit a classical Type I isotherm shape indicating a microporous

material. The isotherm for the purified sample exhibit a much less pronounced curvature (more like a Type II isotherm for a non porous solid).

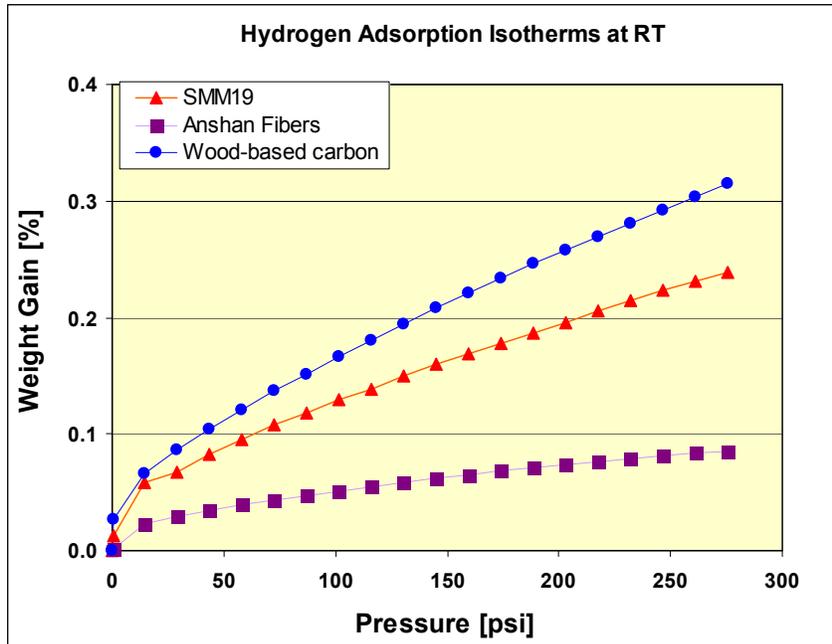


Figure 1. Room-temperature hydrogen isotherms for a variety of carbon materials.

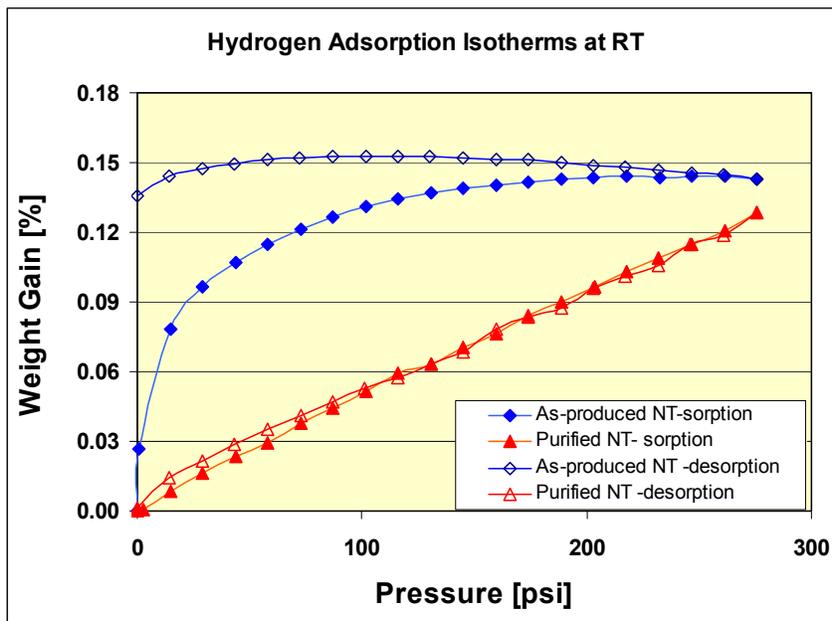


Figure 2. Room temperature hydrogen isotherms for as-produced and purified nanotubes.

In the case of the as-produced nanotubes, it is probable that adsorption is occurring in the disordered carbon (soot) that is incorporated into the sample, hence the Type I isotherm. The purified sample only contains nanotubes and the hydrogen may be adsorbing only on the external surfaces and not penetrating the internal space or interbundle voids at the pressures used in this work. Additionally, the hysteresis exhibited by the as-produced sample may indicate some absorption due to the catalyst. This effect, as expected, is not observed in the purified sample, which does not contain any catalyst.

For the samples tested in this project, there is a fairly linear relationship between BET surface area and H₂ uptake at 20 bar, as seen in Figure 3. However, this relationship does not apply to the as-produced nanotube sample. As mentioned earlier, this sample is composed of not only nanotubes but it also contains catalyst and soot (amorphous carbon). The higher H₂ uptake in the as-produced sample, despite their lower BET surface area, may be explained by the effect of the catalysts present in this sample.

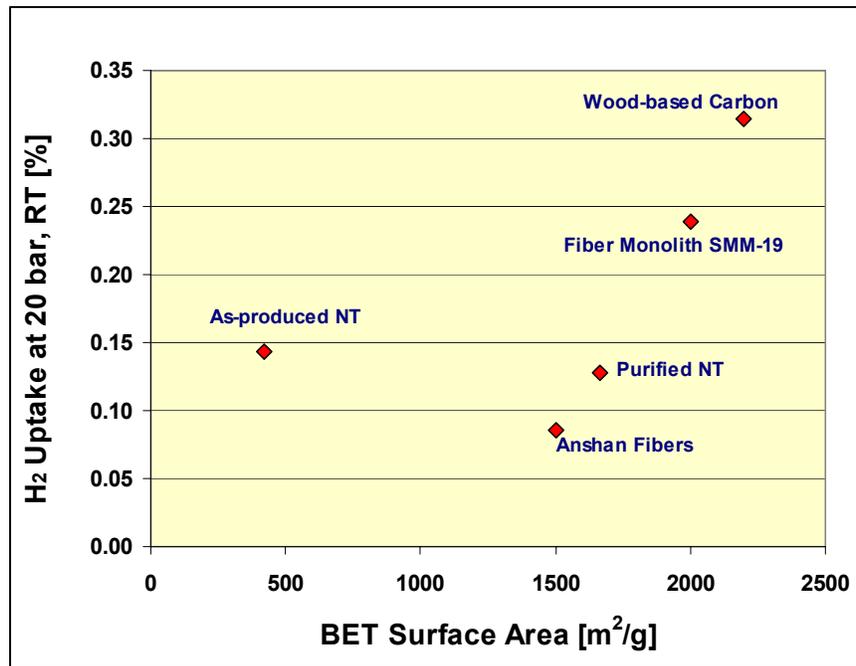


Figure 3. Correlation between BET surface area and H₂ uptake at RT and 290 psi (20 bar).

b. H₂ Adsorption at Cryogenic Temperature: Figure 4 compares the hydrogen uptake at room temperature and 77K for the wood-based material of large surface area. As observed in this figure, the uptake at 77K was considerably higher (~5.5 wt.%) than that at room temperature (~0.32 wt. %).

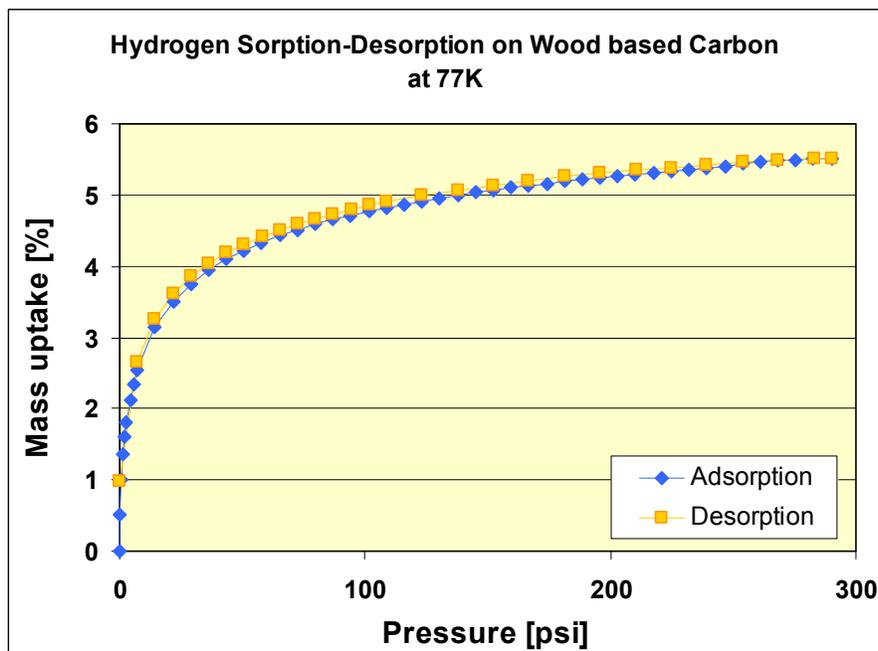


Figure 4. Hydrogen isotherm at LN₂ temperature for a high-surface area wood-based carbon

Conclusions

The H₂ adsorption behavior of a broad selection of nanoporous carbons was determined over the pressure range 0-20 bar and at ambient and liquid N₂ (77K) temperature. None of the samples tested to date have shown significant ambient temperature H₂ uptakes (typically <0.2 wt% uptake). The greatest uptake at ambient temperature was ~0.3 wt % (wood-based activated carbon). However, the same sample exhibited a H₂ uptake of ~ 5.5 wt % at 77K and 20 bar.

To date we have found no evidence of significant hydrogen adsorption on carbons at ambient temperature. However, modeling suggests that metal catalyst particles play a crucial role in facilitating adsorption. Consequently, future work will focus on the experimental determination of the role of the metal catalyst in the interaction of H₂ on carbons. The influence of catalyst morphology on the interaction between C and H will be examined. Comparisons of pure and impure nanotubes and activated carbons and fibers with and without dispersed metal catalyst will provide insight into the role of the catalyst.

Acknowledgments

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