

## IV.I.16 Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon

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### Project Scope

The goal of this project is to establish the scientific basis for designing the building blocks of carbon-based adsorbents that enable synergistic metal-carbon interactions, leading to enhanced hydrogen uptake at near-ambient temperatures. Our preliminary results suggest that addition of transition metal catalysts to nanoporous carbons with controlled nanoscale structure and porosity results in enhanced  $H_2$  adsorption. This appears to result from as yet poorly understood atomic-scale interactions between molecular  $H_2$ , metal particles, and carbon with proper nanostructures. Theoretical calculations demonstrate that uptake may be significantly increased if sufficient control of the structure can be attained. To optimize the design of such nanostructure, it is essential to develop atomistic models that realistically describe isotropic nanoporous carbons and to gain fundamental understanding, at the atomic and molecular level, of hydrogen interactions within metal-doped carbons. The project is focused on three specific aims: (1) modeling and characterization of medium-range order in partially amorphous – partially graphitic structures of nanoporous carbons; (2) understanding the mechanism of molecular activation of  $H_2$  by metal particles; and (3) elucidation of the energetics and dynamics of hydrogen species confined in the molecular space of pure- and metal-doped nanoporous carbons.

### Understanding and Modeling the Local Structure of Nanoporous Carbons and their Role on Hydrogen Storage

The lack of a fundamental understanding of structure-chemistry relationships has hindered a breakthrough in hydrogen storage capability in nanoporous carbon materials. Our focus in this task is on developing realistic and comprehensive models

of the structure of nanoporous carbons that allow us to understand the role of the local atomic structure, compositional changes, and degree of order on the mechanisms of hydrogen adsorption. This is a real challenge due to the lack of a clear atomic picture of the nanopores present in these important materials, and the degree to which preparation methods and metal additions may change the structure.

As an initial effort to model adsorption, and to identify local structures that assist in adsorption, we theoretically investigated the effect of interlayer spacing between graphite layers on the hydrogen uptake [1]. The weak binding of  $H_2$  on individual graphene sheets cannot support significant storage at ambient temperature. On the other hand, the interlayer spacing in crystalline graphite (0.335 nm) is too narrow to accommodate  $H_2$  molecules (0.406 nm). While some absorption would be possible if the interlayer spacing were allowed to expand [2,3], the layers are not free to expand significantly, and this limits the total absorption. Our ab-initio calculations indicated that it might be possible to store  $H_2$  molecules between graphene layers if the difficulty associated with the high energy barrier for uptake of  $H_2$  at the initial absorption stage could be overcome. Once the “initial”  $H_2$  molecules are absorbed, further lattice expansion is induced, which enables further  $H_2$  absorption. An optimal expansion near 60% was found, as shown in Figure 1. Graphite structures with pre-expanded interlayer spacing could be obtained by intercalation of metal atoms or other spacer molecules, or by cross-linked hydrocarbons with the appropriate geometries. In addition, slit-

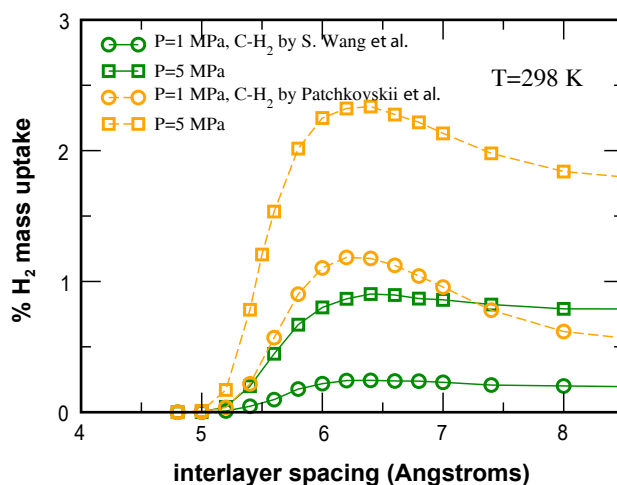


FIGURE 1. Grand Canonical Monte Carlo results (GCMC) for hydrogen uptake in expanded graphite as a function of interlayer spacing [1].

shaped pores in nanoporous carbons [4] having widths in the range of  $\sim 0.6$  nm (i.e. about 60% expansion of graphite interlayer) would also exhibit significant uptake at equilibrium. Our calculations also show that the stacking sequence makes important changes in the binding energy: changing from the normal A-B stacking in graphite to an A-A stacking lowers the energy significantly, roughly by  $\sim k_B T$  per molecule at ambient conditions, making the interaction stronger. This suggests that changes in local structure (such as stacking sequence and relative position of atoms) can have a dramatic change in adsorption.

On-going work is utilizing tight-binding molecular dynamics (TBMD) to examine possible amorphous structures, and comparing these with both high-resolution microscopy and careful diffraction studies being performed at ORNL. TBMD studies of amorphous carbon have already been demonstrated to produce results consistent with diffraction results. However, the atomic structure appears different from the partially graphitic structure observed in the high resolution microscopy obtained at ORNL. This demonstrates one of the fundamental complexities of the materials to be addressed in the current work: a simple categorization of “low density” or “three-fold” coordination fails to capture the range of experimental structures. Ultimately, the goal is to examine the adsorption of hydrogen in nanoporous carbon, using structures derived from molecular dynamics (MD) simulation (validated through diffraction experiments) in combination with Grand Canonical Monte Carlo (GCMC) simulations. We will examine not only the total adsorption capacity, but also the optimal sites for adsorption, and the structure distribution of adsorption enthalpies in the amorphous carbon. This will be done as a function of pressure and temperature, and also as a function of the structure of the amorphous carbon: different densities, graphitic order, and chemically bonded hydrogen may change the adsorption capacity significantly.

### Quantitative Structural Characterization of Porous, Disordered Carbons

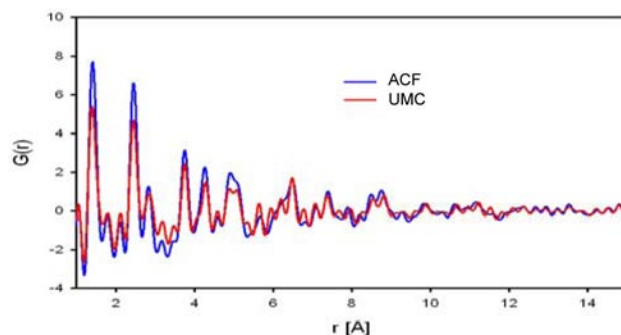
Nanoporous carbons are obtained through a complex sequence of elimination, cross-linking and condensation reactions during the carbonization stage, followed by selective etching and porosity development during activation. Therefore, nanoporous carbons should not be considered simply as geometrically modified graphite. Atomic level disorder that happens to be brought about by the process of making porous carbon can fundamentally change the arrangement of structural elements (graphenes, carbon bridges) and by controlling this process we can create/design new materials. Thus, very careful studies are required to

achieve meaningful characterization of such a complex structure.

The atomic pair-density function (PDF) describes the distribution of the distances between atoms in a material, and it is obtained by Fourier-transforming the structure function  $S(Q)$ , which is acquired from the synchrotron X-ray or neutron diffraction measurement ( $Q$  is a scattering vector). We have investigated the local atomic structure, using PDF analysis, of two carbon materials: activated carbon fibers (ACF) produced from a dense gas extracted pitch [5], and ultramicroporous carbon (UMC) obtained through chemical activation of a wood-derived precursor using KOH.

Experimental X-ray diffraction data were collected using the high energy beamline 6-ID-D, at the Advanced Photon Source, Argonne National Laboratory. The reduced PDF obtained by Fourier transformation of the structure function  $S(Q)$  is shown in Figure 2. The data shows that the first few peaks are common for both samples indicating similarity in the local structure. However, significant differences are observed in the range 5-7 Å. This may be related to pores sizes or interlayer defects; both could be significant for the ability to store hydrogen. Comparison with the ideal graphite structure reveals that stacking of layers in ACF and UMC carbons resembles the rhombohedral variation of the structure (R-3m), and not the commonly observed hexagonal (P63/mmc) structure. For further structural characterization, we plan two experiments to improve the accuracy and quality of data:

- X-ray scattering using focused beam. Packing efficiency of carbons is small and significant scattering comes from air. Focused beam will improve ratio of carbon/air scattering and therefore the signal to noise ratio in diffracted intensity.
- Neutron scattering at a pulsed neutron source (Los Alamos): Neutron scattering length does not depend on the scattering vector (like X-ray scattering factor) therefore more elastic scattering is present at the high  $Q$  range. This makes normalization



**FIGURE 2.** Pair distribution function for activated carbon fibers (ACF) and ultramicroporous carbon (UMC).

and Fourier transformation more reliable. Also the NPDF spectrometer at Los Alamos allows for measurement at 8-10 K, thereby reducing the contribution from thermal vibrations and improving resolution of the PDF analysis.

### Understanding the Role of Metals in the Storage Capacity of Nanostructured Carbons

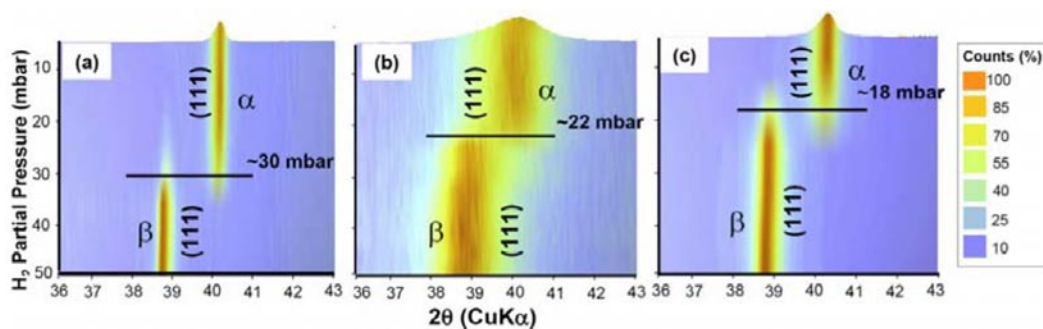
Understanding the synergistic interaction between metals and carbon is a key factor for successful development of metal-doped carbon materials for hydrogen storage applications at near ambient temperatures. At ORNL, the effort is directed at investigation of activated carbon fibers (ACF) modified with nanoparticles of a noble metal (Pd) dispersed in its nanostructured matrix. The Pd-ACF materials are synthesized and activated in collaboration with Clemson University[6]. Characterization by aberration-corrected, high resolution STEM showed that Pd is present both as small particles (~5 nm) and as isolated atoms or atom clusters [7]. The Pd-modified activated carbon fiber (Pd-ACF) showed 25-35% higher hydrogen adsorption capacity (at 25°C and 2 MPa) than pure activated carbon fiber (ACF), even after subtracting the contribution from formation of Pd hydride.

In order to understand the origin of enhanced hydrogen capacity of Pd-ACF, we investigated, separately, the effect of carbon on the H<sub>2</sub>-Pd interaction, and the effect of palladium on the H<sub>2</sub>-carbon interaction. The H<sub>2</sub>-Pd interaction was monitored using in situ high-pressure XRD and adsorption studies. The results showed that two factors contribute to destabilization of the hydrogen-rich β-PdH<sub>0.67</sub> hydride: an increase in number of Pd-carbon contacts, and cleaning residual oxygen from the carbon surface. This is illustrated in Figure 3 which shows the effect of H<sub>2</sub> on phase equilibrium between β and α Pd hydrides [8]. On the other hand, using inelastic neutron scattering to monitor the H<sub>2</sub>-carbon interaction showed that new C-H bonds were slowly formed at room temperature

when carbon was exposed to hydrogen in presence of Pd. This demonstrates that atomic H was formed on the surface of Pd-ACF in presence of hydrogen [9]. In combination, these two results revealed that oxygen-free nanostructured carbons have the capacity to ‘pump-out’ hydrogen from β-PdH<sub>x</sub>, and that the ‘pumped-out’ hydrogen occupies energetically favorable sites on carbon. In other words, these studies have isolated two elementary steps in the chain of events that compose the hydrogen spillover mechanism: (1) dissociation of molecular H<sub>2</sub> and (2) chemisorption to chemically unsaturated positions (dangling bonds) on the carbon surface. Based on the scale of the various effects, it appears that the contribution of spillover is secondary to physisorption, at least for Pd-ACF at near-ambient temperatures.

Recently we have also evaluated the H<sub>2</sub> adsorption properties at room temperature of an ultramicroporous carbon (UMC) obtained by activation of a wood-derived precursor using KOH. Analysis by PDF (Figure 2) revealed that this material has a distorted stacking sequence, while chemical analysis showed presence of alkali metals (Na, K) remnant after chemical activation. Adsorption measurements at room temperature showed an outstanding H<sub>2</sub> capacity and unusually large adsorption energy. We are currently investigating whether the presence of alkali metals, and the carbon structure resulting from KOH activation, contribute synergistically to polarization-induced enhanced physisorption of hydrogen. At the same time, we are investigating the hypothesis that Pd could be used as a source for hydrogen spillover in order to substantially accelerate the rate of adsorption.

Both ACF and UMC are derived from natural sources, petroleum pitch and wood, respectively. All carbon materials from natural sources inherently have uncontrolled composition and structure, along with trace impurities that might influence the hydrogen uptake. In order to eliminate such possibilities, we are now using a synthetic polymer, polyfurfuryl alcohol (PFA), as the source of carbon. Initial tests have shown that



**FIGURE 3.** Room temperature XRD patterns of Pd-ACF (a), commercial Pd-carbon catalyst (b), and Pd-black (c) as a function of  $P_{H_2}$ . The peaks correspond to (111) diffraction of  $\alpha$  and  $\beta$ -PdH<sub>x</sub> phases. Note that, with the decrease in the degree of Pd-C contacts, the equilibrium transition pressure decreases (marked with a black line). [8]

it is possible to synthesize nanostructured carbon with reproducible properties by controlling the conditions during polymerization, carbonization, and physical activation. Room-temperature adsorption of hydrogen on activated PFA-derived carbon (PFAC) showed that the hydrogen uptake capacity nearly equals that of ACF. The next step is doping this carbon with metals in order to understand and control the mechanisms that influence the hydrogen uptake properties of metal-modified nanostructured carbon materials.

## List of Publications and Extended Abstracts

### Journal Publications

1. Rachel S Aga, Chong Long Fu, Maja Krcmar, James R. Morris “The effect of graphite interlayer spacing on hydrogen absorption” *Phys Rev B* **76** (2007) 165404.
2. Xianxian Wu, Nidia C. Gallego, Cristian I. Contescu, Halil Tekinalp, Vinay V. Bhat, Frederick S. Baker, Mark C. Thies “The effect of processing conditions on microstructure of Pd-containing activated carbon fibers” *Carbon* **46** (2008) 54-61.
3. Cristian I. Contescu, Craig Brown, Yun Liu, Vinay V. Bhat, Nidia C. Gallego “Detection of hydrogen spillover in palladium-modified activated carbon fibers during hydrogen adsorption” *J. Phys. Chem. C* **113** (2009) 5886-5890.
4. Klaus van Benthem, Stephen J Pennycook “Electron microscopy at very high resolution” in “*Dekker Encyclopedia of Nanoscience and Nanotechnology*”, CRC Press, 2009, vol. 2, p. 1217.
5. Xianxian Wu, Nidia C. Gallego “Carbon-based nanostructures: Hydrogen storage” in “*Dekker Encyclopedia of Nanoscience and Nanotechnology*”, CRC Press, 2009, vol. 1, p. 535.
6. Vinay V. Bhat, Cristian I. Contescu, Nidia C. Gallego “The role of destabilization of palladium hydride on the hydrogen uptake of Pd-containing activated carbons” *Nanotechnology* **20** (2009) 204011 (Special Issue on Nanoscale Phenomena in Hydrogen Storage).

### Extended Abstracts

1. H.L. Tekinalp, E. Cervo, M.C. Thies, C.I. Contescu, N.C. Gallego, D.D. Edie; “The effect of pitch composition on the adsorption behavior of Pd-doped ACF”, Proc. *CARBON 2007 International Conference*, July 15–20, 2007, Seattle, WA.
2. K. van Benthem, C.I. Contescu, N.C. Gallego, S.J. Pennycook: “Microstructural characterization of activated carbon fibers using aberration corrected scanning transmission electron microscopy”, Proc. *CARBON 2007 International Conference*, July 15–20, 2007, Seattle, WA.

3. K. van Benthem, G.S. Painter, P.F. Becher, C.I. Contescu, N.C. Gallego, S.J. Pennycook; “High Resolution Microscopy with Single Atom Sensitivity using Aberration-corrected STEM”, Proc. *Microscopy and Microanalysis 2007 Conf.*, August 5–9, 2007, Ft. Lauderdale, FL.
4. C. I. Contescu, N. C. Gallego, X. Wu, H. Tekinalp, D. D. Edie, F. S. Baker: “Mechanism of enhanced hydrogen adsorption on palladium-doped nanoporous carbon fibers”, Proceedings of *CARBON 2007 International Conference*, July 15–20, 2007, Seattle, WA.
5. Nidia C. Gallego, Cristian I. Contescu, Vinay V. Bhat, Klaus van Benthem, Halil Tekinalp, Dan D. Edie: “Palladium-doped nanoporous carbon fibers for hydrogen storage”, in *Carbon 2008* (Proc. Intl. Carbon Conf., Nagano, Japan, July 13–18, 2008) paper P0672.
6. Vinay V. Bhat, Nidia C. Gallego, Cristian I. Contescu, Edward A. Payzant, Adam J. Rondinone, Hailil H. Tekinalp, Dan D. Edie: “In situ high-pressure XRD study on hydrogen uptake behavior of Pd-Carbon systems” in *Materials and Technologies for Hydrogen Storage*, Ed. G.A. Nazri, C. Ping, A. Rougier, and A. Hosseinmardi (Mat. Res. Soc. Symp. Proc. Vol. 1042E, Warrendale, PA, 2008) paper 1042-S07-03.
7. Cristian I. Contescu, Vinay V. Bhat, Nidia C. Gallego: “Hydrogen spillover: Its ‘diffusion’ from catalysis to hydrogen storage community”, in *Prepr. Pap. –Am. Chem. Soc., Div. Fuel Chem.* **2009**, 54 (1), 382-383.

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6. Wu X, Gallego NC, Contescu CI, Tekinalp H, Bhat VV, Baker FS, Thies MC, Edie DD: The effect of processing conditions on microstructure of Pd-containing activated carbon fibers, *Carbon* **45** (2008) 54-61.
7. van Benthem K, Pennycook SJ: Electron microscopy at very high resolution: in “*Dekker Encyclopedia of Nanoscience and Nanotechnology*”, CRC Press, 2009, vol. 2, p. 1217.

8. Bhat VV, Contescu CI, Gallego NC: The role of destabilization of palladium hydride on the hydrogen uptake of Pd-containing activated carbon, *Nanotechnology*, Special issue on Nanoscale Phenomena in Hydrogen Storage (April 2009).
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#### Postdocs:

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- Rachel Aga, Alloying Behavior and Design Group, ORNL (2005-2008), Partial support.

#### Technicians:

- Ashli Clark: Carbon Materials Technology Group, ORNL, Partial support.

#### Others:

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- Klaus van Benthem, Assistant Professor Department for Chemical Engineering and Materials Science, University of California, Davis, CA (subcontract – partial support)