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## Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon

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### Program Scope

This program received initial funding from the Office of Basic Energy Science in August 2005. The research program was built upon initial results from a Laboratory-Directed Research and Development (LDRD) grant at Oak Ridge National Laboratory (ORNL).

The project is directed towards the development of a broad science foundation to identify and understand the atomistic mechanisms of metal-assisted hydrogen storage in nanostructured carbons. It capitalizes on strengths in synthesis and behavior of nanostructured carbons, sub-angstrom resolution electron microscopy, neutron scattering, and theoretical modeling. ORNL, in partnership with Clemson University, is investigating the mechanisms of metal-assisted hydrogen storage in nanostructured carbon in terms of catalytic activation of molecular H<sub>2</sub>, surface diffusion of H atoms, and subsequent incorporation on carbon structural defects through either chemical bonding or intercalation. The work plan is organized on three interactive levels: (1) First principles computations for simulation of hydrogen interactions with graphite-like structures and prediction of optimal material properties; (2) Synthesis of metal-doped activated carbon fibers and identification of the microstructures of the fibers and catalyst; and (3) In-depth examination of the nanostructures of the carbon substrate and metal catalyst particles, and correlation of these structures with the hydrogen storage characteristics of the fibers. This project addresses the long-term program targets of BES in the area of design, modeling, fabrication, and characterization, at the nanoscale level and with atomic precision, of novel materials for energy-related applications. The research will provide a sound understanding of the fundamental factors that influence hydrogen sorption on carbon materials and how they can be manipulated to attain the on-board storage targets for the FreedomCAR Program.

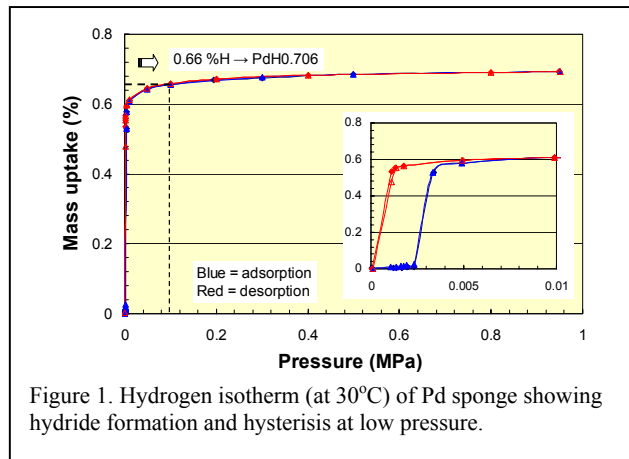
### Recent Progress

#### (a) *Initial synthesis activities and building of inventory of Pd-doped activated carbon fibers.*

A series of Pd-containing activated carbon fibers (ACF) were prepared at Clemson University by melt-spinning an isotropic pitch precursor mixed with a Pd salt (Pd content in pitch precursor: 1 wt%). Additionally, a series of ACF without metal doping were prepared under equivalent processing conditions. After melt-spinning, all samples were stabilized and carbonized in a nitrogen atmosphere. After heat treatment, samples were activated in CO<sub>2</sub> to develop the micropore structure and large surface area. The level of activation (or percent burn-off) was varied systematically from 0% to 80%. Characterization of these samples (surface area, pore size and distribution, electron microscopy, X-ray analysis, etc) is under way.

Work has also started on fractionation of isotropic pitch by solvent extraction with high density supercritical gas. This work will lead to separation of pitch into components of various molecular

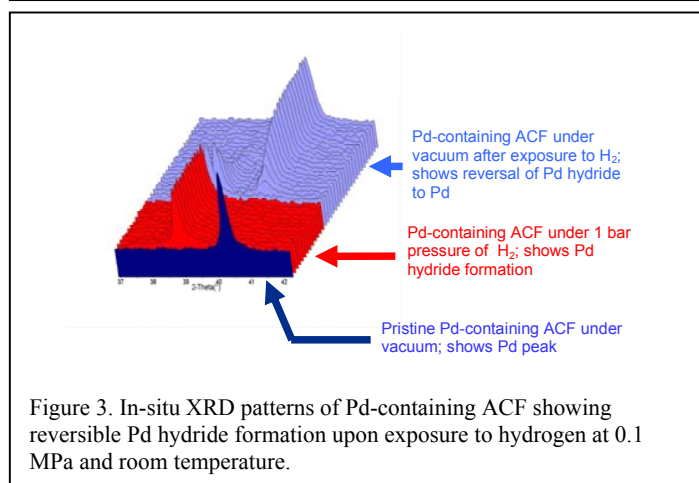
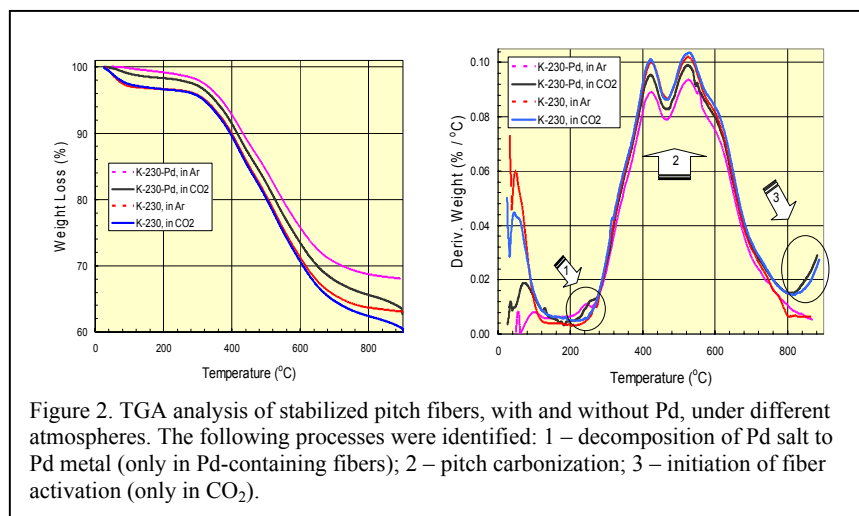
weights, which will be used for the production of ACF. The effect of several of these components on metal particle dispersion within the ACF will be studied.



(b) *High pressure adsorption*

Hydrogen sorption measurements are made using an Intelligent Gravimetric Analyzer (IGA) from Hiden Analytical, coupled with an on-line mass spectrometer. The system accounts for buoyancy effects and temperatures variations. To verify the accuracy of our measurements, a calibration run using a Pd sponge was performed. Figure 1 shows the hydrogen isotherm at 30°C for the Pd sponge. It is seen that at 0.1 MPa, the hydrogen uptake of 0.66% corresponds to the formation of Pd hydride (PdH<sub>0.706</sub>). The inset in Figure 1 shows the low-pressure hysteresis typical of this phase.

(c) *Structural changes in Pd-doped carbon fibers during carbonization and exposure to hydrogen*



A distinctive feature of the systems investigated in this project is that the carbon structure develops around pre-existing metal particles (Pd), unlike traditional carbon-supported catalysts in which the metal component is dispersed upon a pre-existing carbon support. This process causes specific ordering of the carbon atoms around Pd nanoparticles.

A major task of this project is to develop a basic understanding of the chemical

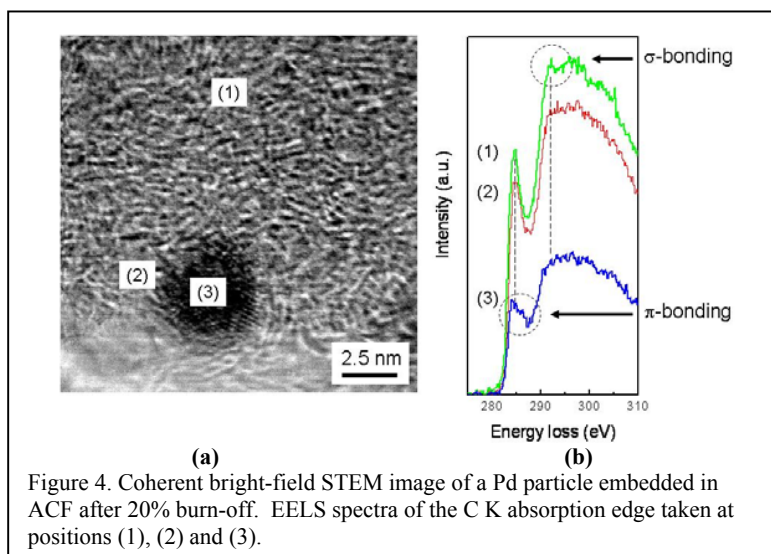
interactions occurring between pitch components and metal precursors in the early stages of fiber formation, and to tailor the metal-doped carbon structures through the carbonization and activation stages. Accordingly, a detailed understanding of particle growth (or sintering) during thermal treatments is needed. To this end, a combination of thermo-gravimetric analysis (TGA), electron microscopy and X-ray diffraction (XRD) was used to determine the temperatures at which: (1) the Pd salt

decomposes to Pd metal, (2) pitch carbonization is accomplished, and (3) activation (burn-off) starts (Figure 2).

In-situ XRD analysis of Pd-doped ACF showed that after exposure to hydrogen at 0.1 MPa and room temperature, Pd is quickly transformed into Pd hydride. This transformation is completely reversible if vacuum is applied to the system. Figure 3 shows the XRD patterns for these series of events.

(d) *Characterization of carbon nanostructures in Pd-containing ACF using aberration-corrected STEM (poster presentation by K. van Benthem, X. Wu, S. J. Pennycook, C. I. Contescu, and N. C. Gallego)*

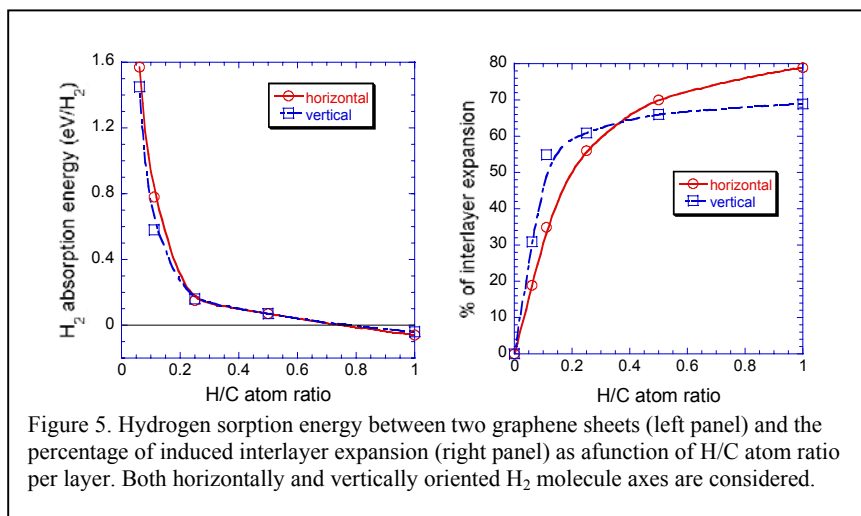
Aberration-corrected scanning transmission electron microscopy (STEM) is being used to characterize the atomic and electronic structure of activated and non-activated carbon fibers in the vicinity of embedded Pd particles. STEM analysis coupled with electron energy-loss spectroscopy (EELS) measurements will allow for the determination of the local electronic structures and bonding character at about 0.1 nm spatial resolution. The C K absorption edge is used to quantitatively determine  $sp^2/sp^3$  hybridization ratios of the local carbon nanostructure.



Preliminary results show that development of carbon structure during carbonization is influenced by presence of Pd particles. Figure 4a shows the coherent bright-field STEM image of a Pd particle embedded in ACF after 20% burn-off. EELS spectra of the C K absorption edge (Figure 4b) were taken at three different positions. It is observed that in the vicinity of the Pd particle (positions 1 and 2) the C K-edge reveals a more dominant  $\sigma^*$ -type bonding behavior, while underneath the Pd particle (position 3), the C K-edge spectra show slightly modified  $\pi^*$  states.

(e) *Theoretical investigation of the energetics of hydrogen interaction with graphene layers: the effect of interlayer spacing on hydrogen storage (Poster presentation by Rachel Aga. Maja Krčmar, J.R. Morris and C-L. Fu)*

Carbon layers are stacked too close to each other in graphite for  $H_2$  molecules to fit between graphene sheets. Theoretical models show that it would be difficult to dissociate  $H_2$  between rigid graphene layers because of the high activation energy required, but relaxation of carbon atoms from their rigid positions is energetically feasible upon interaction with hydrogen. First-principle calculations show that high concentrations of  $H_2$  molecules can be stabilized energetically in an intercalated state between graphene layers. Figure 5a shows the dependence of  $H_2$  sorption energy on graphite interlayer spacing upon intercalation of molecular  $H_2$  between two adjacent graphene sheets. Although, in the dilute limit, the existence of intercalated  $H_2$  molecules is energetically unfavorable, at high concentrations a large number of  $H_2$  molecules can be stabilized in the graphite lattice through a dramatic expansion of the lattice (Figure 5b).



additional lattice expansion is induced and further hydrogen sorption is facilitated.

### Future Plans

- In-situ X-ray diffraction studies at high pressures (up to 10 bars) will be performed. The results will reveal the type of structural changes occurring in the metal and carbon phases of the activated carbon fiber under exposure to hydrogen at high pressures.
- In-situ X-ray diffraction studies at high temperatures will be performed. The results will show the phase transformations occurring during the heat treating processes required for the production of activated carbon fibers.
- Characterization of hydrogen storage capacity by measurements of hydrogen uptake at pressures of up to 20 bar on selected Pd-doped ACF will continue.
- 3-D imaging will be used to study the structure of carbon-supported Pd particles and metal-carbon interface; as well as the 3-D sp<sup>2</sup>/sp<sup>3</sup> ratios in carbon structures surrounding embedded Pd particles.
- Grand canonical Monte Carlo simulation will be performed to study the adsorption/desorption of hydrogen in graphene sheets

### Publications and Presentations

1. N.C. Gallego. "Materials and Solutions for Hydrogen Storage". Invited talk at the *AutoPolymers 2005 Workshop*, Charleston, SC, October 28-31, 2005.
2. N.C. Gallego, F. S. Baker, C.I. Contescu, X. Wu, C.L. Fu, D.D. Edie, and T. Burchell, "Metal-Assisted Hydrogen Storage in Nanostructured Carbons", invited keynote presentation at Symposium on "Advanced Materials for Energy Conversion", The Minerals, Metals, and Materials Society (TMS) Annual Meeting and Exhibition, San Antonio, TX, March 12-16, 2006.
3. N.C. Gallego, X. Wu, C.I. Contescu, F.S. Baker, H. Tekinalp, D.D. Edie. "Effect of Pd on the hydrogen adsorption capacity of activated carbon fibers". Materials Research Society – Spring Meeting. San Francisco, CA, April 17-21, 2006.
4. N.C. Gallego, F.S. Baker, C.I. Contescu, X. Wu, S.A. Speakman, H. Tekinalp, and D.D. Edie, "Effect of Pd on the Hydrogen Adsorption Capacity of Activated Carbon Fibers", Carbon 2006, International Carbon Conference, Aberdeen, U.K., July 16-21, 2006.