Title: **Development of Doped Nano-Porous Carbons for Hydrogen Storage**

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OBJECTIVE

The objective of the project is to understand the active adsorption sites in carbon materials that have been activated with nanocatalysts, and use this knowledge to enhance synergistic effects that create new adsorption sites and activate the carbon nanomaterials for adsorption in the DOE target temperature and pressure range. To understand, identify, and optimize specific adsorption sites, *in situ* high-pressure analytical techniques will be used to fully characterize these sites at the pressures of interest.

ACCOMPLISHMENTS TO DATE

Materials Synthesis. We have explored the synthesis of new metal-intercalated graphite nanofibers (M/GNF), and investigated activation processes to create microporosity in graphite nanofibers. We have synthesized and characterized catalyzed carbon materials prepared via ball milling and incipient wetness. We also investigated porosity change of KOH-modified activated carbon. We have synthesized new metal doped carbon materials, Palladium doped carbide derived carbon. To investigate the effect of –O groups, we have functionalized the surface of activated carbon with –OH and =O groups by oxidation of activated carbon with hydrogen peroxide.

Characterization. We have adapted multi-wavelength Raman spectroscopy to analyze unusual high-frequency peaks, and developed high-pressure *in situ* Raman. We have obtained high-pressure *in situ* Raman data and corresponding high-pressure adsorption data for platinum-doped single-walled carbon nanotubes (1% Pt/SWCNT). We have found corroborating evidence that hydrogen treatment at 200 ^{o}C shifts the radial breathing modes 1% Pt/SWCNT. We have obtained high-pressure *in situ* Raman data for single-walled carbon nanotubes after heating at different temperatures and in different atmospheres to study the temperature and surrounding environment effect on the Raman spectra of carbon nanomaterials.

Hydrogen Storage Measurements. We have built, installed, calibrated, and tested a differential Sievert's apparatus to quantify hydrogen storage. We have conducted parallel hydrogen uptake and Raman measurements on multi-walled carbon nanotubes and the preliminary results suggest subtle changes in the relative intensities of the Raman features; the mass uptake data suggests hydrogen uptake is a function of temperature and not pressure for these materials. We investigated the carbon bridge effect in hydrogen uptake. KOH-modified activated carbon were tested and found to be a good hydrogen receptor in a hydrogen spillover experiment when the pH value of the material is larger than 7. We have also studied hydrogen spillover phenomenon and discovered that hydrogen spillover can take place at very low pressure. We have obtained hydrogen storage measurements for oxidized carbon materials at room temperature and pressures up to 20 bar using gravimetric measurements.

FUTURE WORK

The ultimate goal is to extend these measurements to 100 bar to delineate surface sites by factors such as their hybridization state, potential to (reversibly) rehybridize upon application of pressure, attached chemical functional groups, local bonding environment, and the nature of their binding to hydrogen, combined with adsorption measurements will lead to site specific structure composition relationships and optimization of material design based on this site specific knowledge. In the upcoming year, we plan to:

- Measure hydrogen adsorption of synthesized materials (exfoliated graphite, metal doped CDC, etc.) up to 100 bar
- Characterize of the attached chemical functional groups by XPS, Raman, FTIR, etc.
- Investigate the role of chemical functional groups in hydrogen spillover process.
- Publish results regarding low-pressure hydrogen spillover and effect of carbon oxidation on hydrogen spillover.

LIST OF PAPER PUBLISHED

Fonseca, D.A.; Gutierrez, H.R.; **Lueking, A.D.** "Morphology and porosity enhancement on graphite nanofibers through chemical etching," *Microporous and Mesoporous Materials,* XXX.

Badding, J.; Lueking, A.D. "Reversible high pressure sp^2–sp^3 transformations in carbon," *Phase Transitions,* 80 (10-12), 1033-1038.

Jain, P.; **Fonseca, D.A.** Schaible, E.; **Lueking, A.D.** "Hydrogen Uptake of Platinum Doped Graphite Nanofibers and Stochastic Analysis of Hydrogen Spillover," *J. Phys. Chem. C* **111,** 1788-1800, (2007).

CONFERENCE PRESENTATIONS

Sakti, A.; Clifford, C.E.B.; **Lueking, A.D.** "Hydrogen Production from and Subsequent Trapping in Ball Milled Anthracite Coal" *Pittsburgh Coal Conference,* September 27, 2006.
(Selected for Award: Honorable Mention, Technical Poster)

Li, Q.; Lueking, A.D. "Carbon oxidation to enhance hydrogen storage by hydrogen spillover," *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 53 (2), 2008.

Sakti, A.; Clifford, C.E.B.; **Lueking, A.D.** "Structural Evolution of Anthracite Coals During Reactive Ball Milling," *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 53 (1), 2008.

Fonseca, D.A.; Lueking, A.D. "Influence of Thermal Treatment on the Structure of Exfoliated Graphite Nanofibers" *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 51 (2), 2006.

STUDENTS SUPPORTED UNDER THIS GRANT

Qixiu Li, 1/1/2007- present
Michael Schimmel, 1/1/-2006-8/1/2006; Apurba Sakti, 8/1/2006-12/31/2006
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