

IV.C.1f Hydrogen Storage Media through Nanostructured Polymeric Materials

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Project Start Date: July 1, 2007
Project End Date: June 30, 2012

It supports DOE's initiative in developing adsorption-based storage technology with high uptake capacity, reversibility, and stability. The successful outcome of the project will produce a new storage material that meets the recently revised DOE 2015 targets:

- Gravimetric density: 1.8 kWh/kg
- Volumetric density: 1.3 kWh/L
- Cost: \$2/kWh net

Accomplishments

- Three classes of polymers with over 50 different structures were synthesized and characterized. Polymers with specific surface area (SSA) as high as $\sim 1,900$ m²/g and tunable pore size from 0.6 to 0.9 nm were prepared.
- Excess H₂ uptake of 5.1 wt% at 77 K (40 bar) was achieved, a nearly 150% improvement over Fiscal Year 2008 results.
- H₂-polymer interactions were investigated through a) theoretical and experimental studies on the heat of adsorption; and b) high pressure ¹H nuclear magnetic resonance (NMR) measurement on the state of hydrogen in the micropores.



Objectives

- To design, synthesize, and evaluate nanostructured polymeric materials (NPM) as new hydrogen storage adsorbents for transportation applications.
- To support materials development with in-depth understanding of hydrogen-NPM interaction through modeling/simulation and advanced characterization.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability

Technical Targets

The focus of this project is to prepare NPMs as new hydrogen adsorbents with improved storage capacity and heat of adsorption through rational design, guided by computational modeling and advanced characterization.

Introduction

The capacity of on-board hydrogen storage is critical to hydrogen-powered fuel cell vehicles. For practical applications, the storage system must meet the gravimetric and volumetric densities as well as the cost target set by DOE. These requirements pose significant challenges to storage material development. We plan to address these challenges by exploring a new class of hydrogen adsorbent, nanostructured polymeric materials. Compared with other adsorbents, polymers have excellent thermal stability and tolerance to gas contaminants such as moisture. Polymers also have low skeleton density and high intrinsic porosity via covalent bonds, capable of maintaining SSA during high pressure pelletizing for better volumetric density. Furthermore, they can be produced at a commercial scale with the existing industrial infrastructure. Significant progress has been made in polymer gas adsorbent research [1-2]. Our approach focuses on improving hydrogen uptake capacity and the heat of adsorption by enhancing SSA, porosity, and framework-adsorbate interaction through rational design and synthesis at the molecular level.

Approach

Our design principles aim at improving the following attributes of the polymers: (a) high SSA to provide sufficient interface with H_2 ; (b) narrow pore diameter to enhance van der Waals interactions in the confined space; and (c) “metallic” features, either through π -conjugation or metal doping, to promote electronic orbital interactions with hydrogen. During FY 2009, we carried out parallel studies of three different categories of polymers. We continued our investigation on SSA enhancement and porosity regulation using simple aromatic monomers with contorted cores and hyper-crosslinking chemistry. We explored several nanoporous polymers with monomers containing heterocyclic functional groups for better conductivity or polarizability. We initiated study of the transition metals containing porous polymers either through post-doping or direct synthesis. The surface property, hydrogen uptake capacity, and isosteric heat of adsorption were measured through N_2 -Brunauer-Emmett-Teller (BET) and Sievert isotherm methods. In addition, theoretical modeling using ab initio and density functional theory (DFT) calculations were conducted to compare with the experimental results for better understanding of the hydrogen-polymer interaction. Through collaboration with our Hydrogen Sorption Center of Excellence (HSCoE) partners Professors Y. Wu and A. Kleinhammes of The University of North Carolina, the hydrogen-polymer interactions were investigated using high pressure 1H -NMR.

Results

We continued to explore new polymers with a variety of monomers and synthesis techniques as our main focus in FY 2009. We successfully prepared over 50 polymers using different monomers and synthesis schemes, followed by spectroscopic and surface characterizations. Shown in Figure 1 are 3-dimensional (3-D) drawings of several representative polymers. The hydrogen storage capacities were measured at both liquid nitrogen and ambient temperatures using a Sievert-type isotherm apparatus. The results for selected polymers are listed in Table 1. While SSA's of these polymers vary from ~ 900 m^2/g to nearly $1,900$ m^2/g , one common feature among them is the narrow pore size distribution, with most of the surface area from micropores with diameters between 6 to 9 Å. This is clearly demonstrated by Figure 2 in which the incremental surface area of a representative polymer is plotted as a function of pore size, calculated using a non-localized DFT method with the data obtained from N_2 -BET measurement. The most significant peak centers at 8 Å. This property represents a major difference from some other high SSA amorphous materials where the mesopores and macropores make up a significant fraction of the total surface area. The micropores in

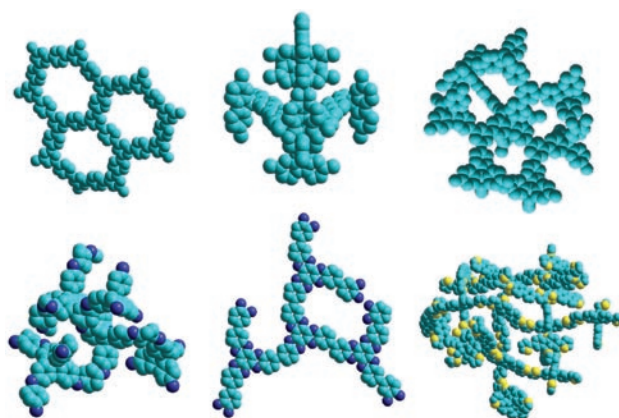


FIGURE 1. 3-D Structures of Selected Polymers Prepared by Argonne and University of Chicago Team

TABLE 1. Hydrogen Adsorption Capacities for Selected Polymers

Sample	Gr. Uptake (77 K, 40 bar) ^a	Gr. Uptake (RT, 70 bar)	BET SSA (m^2/g)	Polymer type ^b
ANL-C1	4.0%	0.21%	1,233	C
ANL-C2	4.4%	0.35%	1,593	C
ANL-C5	5.1%	0.52%	1,863	C
UC-C10	2.8%	0.18%	1,043	C
UC-X4	3.2%	0.45%	971	X
UC-M12	3.6%	0.40%	1,060	M

^a Gravimetric uptake unit is (kg H_2 /kg adsorbent + H_{2ads})

^b C = polymers contains only aromatics, X = polymers with non-C element substitutions, M = polymers incorporated with transition metals
RT - room temperature

our polymers are generated by crosslinking of contorted monomers with the intrinsic hindrance at the molecular dimension, which is believed more efficient for hydrogen adsorption. At the macro-dimension level, the van der Waals interaction between different polymer strands or planes will minimize the voids through close packing. Figure 3 shows a DFT calculation of the 3-D structure of the micropore formed through the cross-linking of spirobifluorene. The pore size in the resulting structure is very similar to that measured experimentally. The computation model also individually places H_2 molecules inside of the pore with their position fully optimized, followed by the calculation of the binding energy for comparison with the experiment.

Isosteric heat of adsorption, ΔH_{ads} , is an important property for hydrogen adsorbents. To maintain sufficient anchoring of H_2 at ambient temperature without consuming excessive energy for extraction, the preferred ΔH_{ads} is from 15 kJ/mol to 20 kJ/mol. We investigated the heat of adsorption of several representative polymers designed for altering ΔH_{ads} by functional group, porosity, H_2 uptake level, etc. Shown in Figure 4 is the heat of

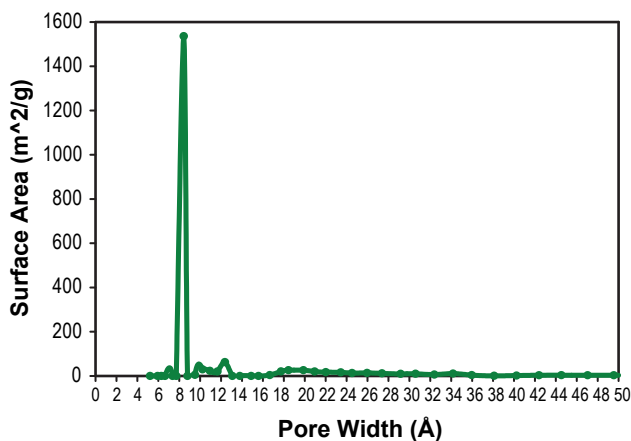


FIGURE 2. An Example of Incremental Surface Area as the Function of Pore Size for a Representative Polymer

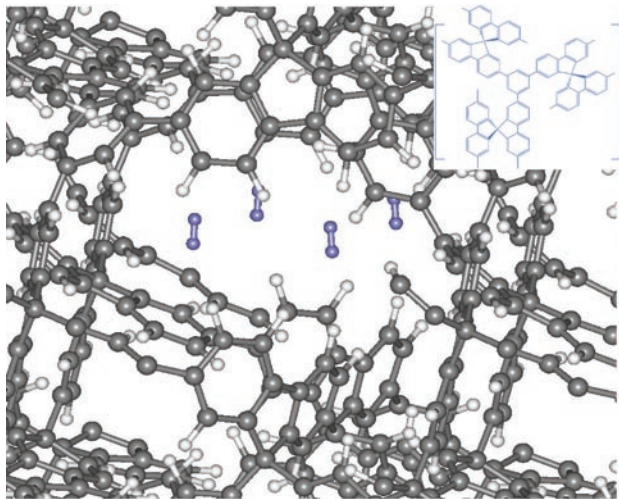


FIGURE 3. Optimized pore structure containing H_2 for a representative polymer through DFT calculation. The inset represents a unit cell of the polymer.

adsorption as the function of hydrogen loading for a representative polymer containing a non-C functional group. The value of ΔH_{ads} was obtained from the adsorption isotherm data measured at the temperatures of 77 K, 87 K, 197 K, 273 K, and 297 K. At low hydrogen coverage with less than 5 H_2 /polymer unit, the ΔH_{ads} has the values of 6 kJ/mol to 7 kJ/mol. The absolute value, however, decreases quickly with increasing hydrogen loading. Although detailed theoretical modeling and characterization are needed for more accurate interpretation, we postulate such change is the result of spreading hydrogen from tighter binding sites closer to the framework wall to less confined space at the center of the cavity. The preliminary pair-distribution function calculation also supports such a hypothesis.

The porous polymers we prepared are generally amorphous without well-defined crystal structures.

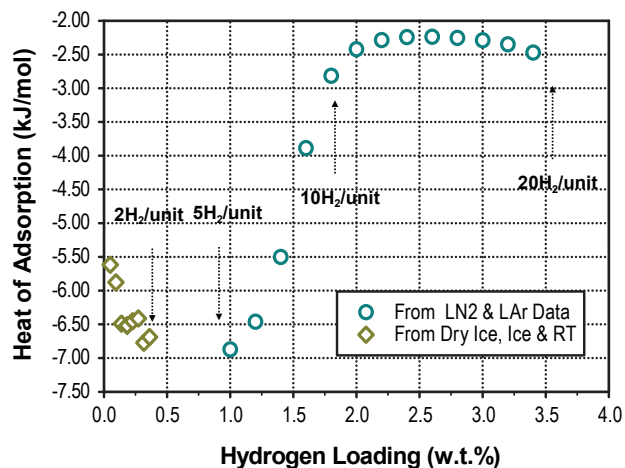


FIGURE 4. Measured Isothermic Heat of Adsorption at Different H_2 Loading for a Representative Polymer

Since the micropores are constructed by covalent bonds of light elements, it is possible to pelletize the polymer powder to a higher material density without affecting the overall surface area, thereby substantially increasing the volumetric capacity. We tested a number of our polymers by compressing them under the pressure up to 50,000 lb/in². We found that such approach can lead to a 3 to 5 time increase of adsorbent packing density without significantly reducing SSA. For example, the polymer with 5% hydrogen gravimetric uptake capacity has a loose-powder packing density of ~0.2 kg/L. Increasing the packing density by a factor of 4, we could achieve an excess volumetric capacity of 0.04 kg H_2 /L adsorbent. At present, we still have a number of engineering issues in pelletizing polymers. We plan to continue to explore this pelletizing approach as a method of improving volumetric capacity.

Conclusions and Future Directions

In summary, we prepared over 50 porous polymers from three structural categories in FY 2009. We investigated their surface properties and hydrogen storage capacities in addition to their isothermic heats of adsorption. We also explored the volumetric density enhancement via pelletization based on compressibility of the polymers. Parallel to material development, we carried out computational modeling and advanced characterization for better understanding of the polymer-hydrogen interaction. Our effort for future study will be focused on the following areas:

- Improve H_2 -adsorbent interaction (uptake capacity and ΔH_{ads}) through pore size control and rational design.
- Explore new synthesis methods for metal-containing polymers and to investigate structure-heat of adsorption correlations.

- Refine modeling on H₂-adsorbent interactions, provide guidance to the polymer design.
- Investigate the kinetics and transient properties of hydrogen adsorption over polymers.
- Collaborate with HSCoE on structural and mechanistic studies via advanced characterization (NMR, neutron scattering, etc.).

FY 2009 Publications/Presentations

1. “Hydrogen storage through nanostructured polymeric materials” Di-Jia Liu, Shengwen Yuan, Brian Dorney, Scott Kirklin, Suhas Niyogi, Shengqian Ma, Ricky Regalbuto, Peter Zapol, Jiangbin Xia, Zhuo Wang & Luping Yu, Presentation ST-27, DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA, May 21, 2009.
2. “Nanoporous Polymers Containing Stereo-contorted Cores for Hydrogen Storage”, S. Yuan, S. Kirklin, B. Dorney, D.-J. Liu, and L. Yu, *Macromolecules* **2009**, 42(5), 1554-1559.
3. “Functional polymers for energy harvesting and hydrogen storage” L. Yu, (Invited) Presentation at US Chinese Chemical Society meeting, September, 2008.
4. “Facile Synthesis of Nanoporous Polymers and Fine Tuning of their Pore Structures”, S. Yuan; B. Dorney; S. Kirklin; L. Yu; D-J Liu, *to be submitted*.

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2. McKeown, N.B.; Ghanem, B.; Msayib, K.J.; Budd, P.M.; Tattershall, C.E.; Mahmood, K.; Tan, S.; Book, D.; Langmi, H.; Walton, A. *Angew. Chem. Int. Ed.* **2006**, 45, 1804-1807.