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

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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 on hydrogen adsorption over NPMs through modeling/simulation and advanced characterization.

Technical Barriers

This project addresses the following technical barriers from the 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 design and synthesize NPMs as new hydrogen storage adsorbents for transportation applications. It aims at improving hydrogen-polymer interaction and storage capacity through rational design and improved understanding on the adsorbent structure. 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 hydrogen storage material that meets DOE 2015 targets:

- Gravimetric density: 3kWh/kg
- Volumetric density: 2.7kWh/L
- Cost: $2/kWh

Accomplishments

- Three series of new polymers were successfully synthesized with experimental Brunauer-Emmett-Teller (BET) surface area of >1,000 m^2/g and average pore diameter of 6 Å.
- Gravimetric hydrogen adsorption capacities of 0.4 wt% and 3 wt% were observed at ambient and liquid nitrogen temperatures, respectively.

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Introduction

On-board hydrogen storage technology is critical to H_2-powered fuel cell vehicles in future transportation applications. To be practical, the storage system must have a gravimetric capacity of at least 0.06 kg H_2/kg and a volumetric capacity of 0.045 kg H_2/L at ambient temperature. Furthermore, the adsorbent should be able to be produced at commercial scale to bring the cost down. All these pose significant technical challenges to the hydrogen storage materials.

We plan to address these challenges by developing a new class of physisorption-based hydrogen adsorbent, NPMs. Polymers usually have excellent thermal stability within typical adsorbent operating temperature and tolerance to moisture and other contaminants. Furthermore, they can be produced at commercial scale with the current industrial infrastructure. The uses of porous polymers as hydrogen adsorbent have been reported by several groups [1-3]. Our approach focuses on improving hydrogen uptake capacity and the heat of adsorption by enhancing surface area and porosity and increasing framework-adsorbate interaction through rational monomer design and optimal polymerization conditions.

Approach

Our approach is to modify the polymer properties through synthetic chemistry methods. Our polymer design principles for the hydrogen adsorbent include (a) a high surface area to provide sufficient interface

with H_2; (b) a narrow pore diameter distribution to anchor H_2 in the confined space through enhanced van der Waals interactions; (c) a conductive or "metallic" feature, either through an extended π-electron system or by metal doping, to promote hydrogen electron transfer and spillover effect; and (d) a semi-rigid framework capable of trapping higher levels of H_2 through conformational change at ambient temperature and elevated pressure. We plan to achieve the desired adsorbent properties through close collaboration between polymer design and synthesis, characterization, and theoretical modeling. The polymer synthesis will focus on exploring new types of porous polymers with three-dimensional (3-D) frameworks using a molecular engineering approach. We will design and synthesize a variety of monomers with the stereo-contorted core for the preparation of polymer with high surface area and intrinsic porosity. We will incorporate different heterocyclic functional groups into the polymer conductive backbone and introduce atomically-dispersed transition metals to fine-tune the dispersive interaction with H_2. The polymer characterization covers a broad range of studies, including molecular structure, physical properties, and hydrogen uptake. In addition, we will carry out advanced synchrotron X-ray methods such as the pair-distribution-function (PDF) approach to investigate hydrogen-polymer interactions under simulated storage pressure and temperature. The theoretical modeling will aim at improving the molecular level understanding of the interactive force between hydrogen and polymeric functional group. Simulation tools from high level *ab initio* calculation to the classical molecular dynamics will be applied to provide the guidance for the polymer design, synthesis and optimization.

Results

From the project inception, we have focused on exploring a variety of new polymers with different functional groups and morphologies. We successfully prepared three groups of porous polymers. The first group includes the polymers containing a spiral core connected by phenyl and di-phenyl groups. The aromatics are linked by spirobifluorene and tetraphenylmethane to create porosity and high specific surface areas (SSA >1,000 m^2/g). The second group includes the polymers with electronically conductive backbones. Specifically, thiophene and bithiophene groups were integrated with the conjugated aromatics. Shown in Figure 1(a) is the molecular drawing of cross-linked tetrathiophene-9,9'-spirobi[9H-fluorene] and Figure 1(b) is its simulated 3-D structure. Again, the high SSA and porosity was achieved through the spiral core cross-linkers. The third group includes the polymers incorporated with polyimide groups to improve the thermal stability and to enhance the dipole/induced-
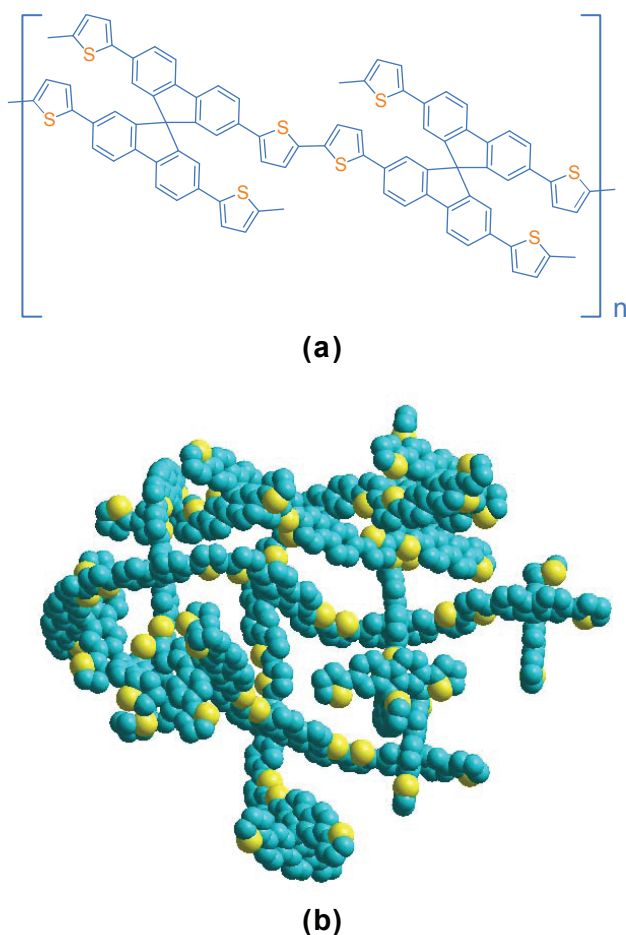

(a)

(b)

FIGURE 1. (a) Molecular Structure and (b) 3-D Structure of Cross-Linked Tetrathiophene-9,9'-spirobi[9H-fluorene]

dipole interactions with functional groups such as C=N and C=O. The results for this group of polymers are mixed and further improvement is necessary.

Parallel to polymer synthesis, we conducted an extensive investigation on the surface properties using nitrogen BET method. We found that first and second groups of polymers have similar SSA, ranging from 500 m^2/g to >1,000 m^2/g, depending on the molecular structure and the synthesis conditions. We also calculated the surface area and pore volume distributions using different physical models. Plotted in Figure 2 is an example of the incremental surface distribution versus pore width calculated by density function theory (DFT) for the cross-linked tetrathiophene-9,9'-spirobi[9H-fluorene]. The distribution is a relatively representative case among all the polymers investigated. Generally, the polymers prepared via cross-linking with spiral core appear to have similar pore distribution with the majority of micropores populated at width less than 10 Å. The average pore diameter for most of the polymers centers around 6 Å.
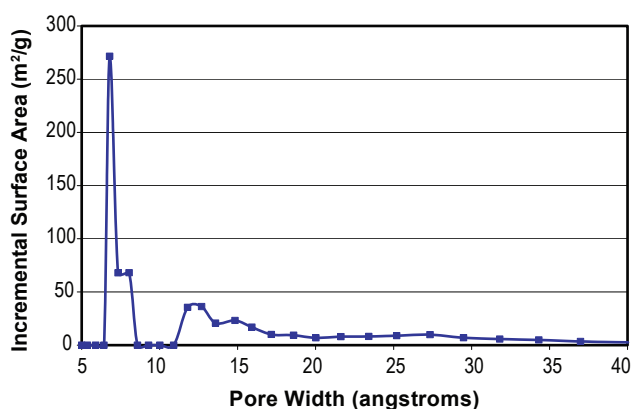
FIGURE 2. An example of incremental surface area distribution derived from DFT analysis for the cross-linked tetrathiophene-9,9′-spirobi[9H-fluorene].
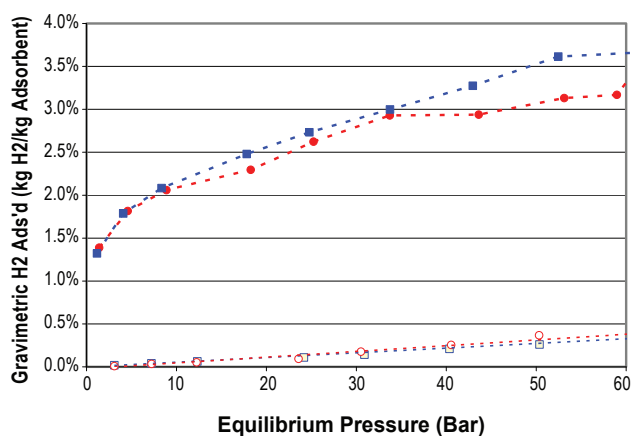

FIGURE 3. Gravimetric hydrogen adsorption uptake for cross-linked 9,9′-spirobifluorene (square) and tetrathiophene-9,9′-spirobi[9H-fluorene] (circle) at both ambient (hollow symbols) and liquid nitrogen (solid symbols) temperatures.

Hydrogen adsorption isotherm measurements were carried out for all the polymer samples using a Sievert-type apparatus at both liquid nitrogen and ambient temperatures. Shown in Figure 3 are the gravimetric hydrogen uptakes of two representative polymers as the function of the equilibrium pressure. At 77 K, the adsorption exhibits Langmuir type isotherm with the capacity essentially being proportional to the surface area. At ambient temperature, a near-linear dependence on pressure was observed and the overall capacities are found in the range of ~0.4-0.5 wt% at 60 bars. The pressure dependences and capacities of these two samples are typical for all the polymers we have investigated so far.

Conclusions and Future Directions

In summary, we accomplished the following major tasks in the first year since the project inception:

- Completed the initial design and synthesis of eleven polymers from three structural groups.
- Completed the surface property characterizations for all the samples using the BET method.
- Complete the hydrogen storage measurement for all the polymers at both ambient temperature and 77 K. Identified the future direction for improvement.

Apparently, the hydrogen storage capacities from our preliminary polymer systems require significant improvement in order to reach the DOE targets. Our effort for the next year will be focused on the following key tasks:

- Continuing to optimize the synthesis conditions of the current polymer systems to further enhance the surface property and storage capacity.
- Continuing to improve the storage capacity measurement and to obtain a better understanding of the adsorption behavior at high pressure (up to 100 bars).
- Continuing to explore alternative polymer design and synthesis by introducing new functional groups, elemental substitution, and metal doping.
- Initiating a preliminary X-ray PDF experiment to probe polymer structure and its interaction with hydrogen under elevated pressure.
- Continuing computational modeling of hydrogen-polymer interaction and the conformation change at elevated pressure.

Special Recognitions & Awards/Patents Issued

1. "Porous polymeric materials for hydrogen storage", Luping Yu, Di-Jia Liu, Shengwen Yuan and Junbing Yang, U.S. Patent Application, Filed June, 2008.

FY 2008 Publications/Presentations

1. "Hydrogen storage through nanostructured polymeric materials" Di-Jia Liu, Scott Kirklin, Brian Dorney, Suhas Niyogi, Junbing Yang, Peter Chupas, Peter Zapol, Shengwen Yuan & Luping Yu, Presentation FC #21, DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA, June 11, 2008.

2. "Nanoporous Polymers Containing Stereo-contorted Cores for Hydrogen Storage", Shengwen Yuan, Di-Jia Liu & Luping Yu, Manuscript under preparation.

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