IV.C.8 HyMARC Seedling: Developing a Novel Hydrogen Sponge with Ideal Binding Energy and High Surface Area for Practical Hydrogen Storage

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Overall Objectives

- Within 18 months of the project starting, develop at least one B-polymer network structures with a surface area of at least 3,000 m$^2$/g with average hydrogen binding energy ($\Delta H$) of at least 15 kJ/mol and hydrogen adsorption capacity in the range of 5 wt% excess on a material basis.
- Ultimately design, synthesis, and evaluation of a new class of B-containing polymer networks that can simultaneously exhibit a $\Delta H$ of 15–25 kJ/mol, a specific surface area (SSA) >4,000 m$^2$/g, and a material density >650 g/L on a material basis.
- Ultimate goals also include achieving the 2025 DOE targets, with a gravimetric capacity of 1.8 kWh/kg (5.5 wt% H$_2$) and volumetric capacity of 1.3 kWh/L (40g H$_2$/L) at ambient temperature and mild pressure on a system basis.
- Molecular simulation and advanced structural characterization to support scientific understanding and polymer materials development.
- Collaboration with HyMARC core team for H$_2$ adsorption isotherm measurements and understanding the structure-property relationship.

Fiscal Year (FY) 2017 Objectives

- Developing chemical routes for the preparation of two proposed nanoporous $\pi$-electron conjugated B-containing polymer networks.
- Structural characterization of the resulting B-polymer networks by the combination of Fourier transform infrared spectroscopy (FTIR), $^1$H, $^{11}$B, and $^{13}$C nuclear magnetic resonance (NMR) spectroscopic techniques.
- Applying volumetric gas adsorption techniques, with CO$_2$, N$_2$, and H$_2$ gases under various temperatures and pressures, to understand the nanoporous textures, specific surface areas, and H$_2$ adsorption profiles of the synthesized polymers.
- Collaboration with HyMARC core team for H$_2$ adsorption isotherm measurements.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(E) Charging/Discharging Rates
(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Design and synthesis of hydrogen storage materials that meet the following DOE onboard 2020 automotive usable hydrogen storage targets.

- 1.5 kWh/kg system (4.5 wt% H$_2$)
- 1.0 kWh/L system (0.030 kg H$_2$/L)
- Cost of $10/kWh ($333/kg H$_2$ stored)
- Operating at ambient temperatures (-40°C to 60°C)
- Onboard efficiency of 90% and minimum hydrogen delivery pressure of 5 bar
- Total refuel time of 5 minutes

FY 2017 Accomplishments

- Synthesis and characterization of two proposed nanoporous $\pi$-electron conjugated B-containing polymer networks, with a combination of spectroscopic techniques to determine the molecular structure and volumetric gas adsorption technique to understand
their nanoporous textures, specific surface area, and H₂ adsorption profiles.

- Discovery of a π-electron conjugated B-moieties in a B-containing polymer network with enhanced H₂ binding energy (exact value to be validated in FY 2018).
- Collaboration with HyMARC core team for H₂ adsorption isotherm measurements.

INTRODUCTION

A practical hydrogen storage technology is essential in realizing the H₂ economy, especially for onboard applications. Current H₂ storage methods, including compressed gas, cryogenic liquid, metal hydrides, chemical hydrides, and adsorbents, all show significant deficiencies and limitations. Among them, adsorbents would be ideal materials for practical applications if the adsorbent could show a sufficient gravimetric capacity (>5 wt%) at moderate operational temperatures (−20°C to 40°C) and pressures (20–100 bar). The primary barrier is the H₂ binding energy on traditional high SSA adsorbents (i.e., metal-organic frameworks, carbons) is too weak (in the range of 4–7 kJ/mol). Thus, the physisorption of H₂ requires very low temperatures (liquid N₂ temperature).

APPROACH

The primary objective of this research project is to develop a specific polymer network with surfaces that can display H₂ binding energies in the range of 15–25 kJ/mol. In addition, the targeted polymers will also exhibit a nanoporous morphology with high surface areas greater than 4,000 m²/g and mass densities >0.65 g/cm³. In general, the adsorption capacity is proportional to the SSA accessible to H₂, ~1 wt% per 500 m²/g as predicted by the Chahine rule. We propose to develop a new class of H₂ adsorbing polymer networks (H₂ sponges) that can automatically form free volume with continuous nanoporous channels (~1 nm in diameter) to achieve the specific surface area and mass density targets. These thermoplastic-based materials can be produced in large-scale with robotic properties and have the potential to achieve the 2025 DOE targets, with a gravimetric capacity of 1.8 kWh/kg (5.5 wt% H₂) and volumetric capacity of 1.3 kWh/L/H₂ at ambient temperature and mild pressure.

In the first phase of this research project, we focus on the synthesis and characterization of two proposed B-containing polymer networks (A) and (B), with an objective to study the correlation between B-moiety and H₂ binding energy. After the discovery of a suitable B-moiety with the potential to meet the specific metrics and a go/no-go decision scheduled in December 2017, we will fine-tune the network morphology (polymer free volume) with the assistance of molecular simulation and a good understanding of structure-property relationships by collaborating with the HyMARC core team. The objective is to identify the most suitable H₂ sponge that meets all DOE metrics, including thermodynamic and kinetic properties. Since the proposed H₂ sponge is a polymer-based material with spontaneously formed open morphology, the adsorbent shall exhibit strong, reliable, and easy handling as many plastic materials do.

RESULTS

Synthesis and Molecular Structure Characterization

We have synthesized both B-polymer networks (A) and (B). The B-polymer network (A) was prepared by 2,6-divinyl-9,10-dimethoxyboraanthracene monomer that contains two pairs of active sites, including two B-OCH₃ groups and two styrenic groups, which can engage in two independent polycondensation reactions. Several B-polymer network (A) samples were prepared and showed the spontaneous formation of nanoporous morphology with pore sizes less than 1 nm. However, the specific surface area is quite small (~500 m²/g), which may be due to the structural inhomogeneity in the network (A). It is somewhat difficult to control the sequential polycondensation reactions in this reaction scheme. Thus, we have been focusing on B-polymer network (B) that can be formed by two consecutive reactions with good control in each step. As shown in Figure 1, the chemistry involves butylenyl styrene monomer (I) with two reaction steps. First is the metalloocene-mediated polymerization of butylenyl styrene (I) that contains two asymmetric olefinic units (styrene and α-olefin). We select a suitable homogeneous syndio-specific metalloocene catalyst that can selectively initiate styrene polymerization to form syndiotactic poly(butylenyl styrene) (II) with high polymer molecular weight, high syndiotacticity, and high yield. The stereo-selectivity results in an alternating arrangement of butylenylphenyl side chains, located along the polymer backbone. This stereo-arrangement is essential to create free volume and nanopores. The second reaction step involves facile hydroboration reaction of the pending olefinic groups with tri-valent BH₃ to form highly cross-linked boron-containing poly(butylenyl styrene) network (B-PBS) (III). During the slow titration of BH₃/tetrahydrofuran (THF) reagent into polymer solution, the hydroboration reaction was very effective at room temperature to form an insoluble B-PBS network (III) which automatically precipitated out from the solution. The resulting B-PBS network (III) was further heat-treated at 200–300°C to form the objective π-electron conjugated B-polymer network (B). The acidic B-moieties, connecting the conjugated side chains, serve as in situ p-type dopants to increase the surface energy around the nanoparticles (automatically created by free volume). It is interesting to note that this low temperature (<300°C)
thermal-induced dehydrogenation reaction was also observed in our previous study [1–7] in the preparation of boron-substituted carbon materials by using boron-containing precursors. As shown in the pictures, the transparent and colorless polymer film of B-PBS (III) gradually increases its color with heating. At 300°C for 1 h, the polymer becomes very dark, indicating long conjugated sequences that absorb all visible light.

Figure 2 (left) shows FTIR spectra of three thermal-treated B-PBS samples at 200°C, 230°C, and 270°C for 1 h, respectively. Upon heating, a new broad band with two absorption peaks at 1,017 cm\(^{-1}\) and 1,090 cm\(^{-1}\), corresponding to C=C-B vibrational modes, appear at 200°C and sharply increases intensity at 230°C. These peak intensities then level off at 270°C. Evidently, the FTIR results show the thermal transformation of organoborane moieties into the \(\pi\)-electrons conjugated B-polymer network (B), which shall be directly relative to their \(H_2\) binding energy. Figure 2 (right) shows a magic angle spinning \(^{11}\)B solid state NMR spectrum of B-PBS-230 network, formed after heating the corresponding B-PBS (III) at 230°C for 1 hr. Three chemical shift bands, peaked at 50 ppm, 25 ppm, and 17–10 ppm, imply multiple acidic boron moieties. Since the sample only contains B, C, and H elements, without exposure to air, the chemical shifts imply the boron moieties with various \(\pi\)-conjugated structures. The most acidic B species peaked at 50 ppm may only have two \(\pi\)-conjugated ligands as indicated by the structure in Figure 2 (right). The other high field chemical shifts (between 30 ppm and 10 ppm) may be associated with tri-valence \(\pi\)-conjugated ligands having different conjugation lengths. In other words, there are significant inhomogeneity of \(\pi\)-electron conjugated B-moieties in this B-polymer network (B) sample, which may exhibit several \(H_2\) binding energy sites on the surfaces. The most acidic B-moiety (peaked at 50 ppm) with about 50% content (based on the peak intensity) shall offer the highest \(H_2\) binding energy.
Pore Size Distribution and Hydrogen Adsorption Isotherm

All the resulting B-polymer network (A) and (B) samples were examined by volumetric gas adsorption technique, using CO$_2$, N$_2$, and H$_2$ gases under various temperatures and pressures, to understand their nanoporous textures and adsorption capacities. The mass density of samples were also determined by a pycnometer. Figure 3 shows pore size distribution curves of two representative B-polymer network (B) samples, including B-PBS-230 and B-PBS-300, respectively, with their surface areas and mass density information. The pore size distribution was determined from adsorption isotherms of N$_2$ (77 K) and CO$_2$ (273 K) measurements at low pressure (<1 bar) with BJH (Barrett, Joyner, and Halenda) and D–R (Dubinin-Radushkevich) calculation methods, respectively. It is interesting to note that the surface areas measured by CO$_2$ adsorption consistently show high values, but almost no N$_2$ adsorption in both samples. Since the CO$_2$ measurement is capable of covering the extremely small nanopores (size <12 Å), all B-polymer network samples with free volume only contain nanopores with relatively low nanopore volumes. In fact, all samples also show mass density at about 1 g/cm$^3$, which is only about 10–20% below many typical hydrocarbon polymers with dense morphologies.

In the B-PBS-230 sample, the pore sizes are in the range of 5–8 Å with a surface area of 1,150 m$^2$/g (so far, the highest SSA in this B-polymer network system). The pore size slightly increases to the range of 8–11 Å in B-PBS-300 sample, after increasing the heat-treatment temperature to 300°C. However, the surface area reduces somewhat to 800 m$^2$/g. We were somewhat surprised with the relatively small surface area for the material that has a molecule-level controlled free volume morphology. The possibility of underestimated the surface area does exist as some sub-nano size pores may be difficult to form the continuous open pore channels required for gas access under low pressure conditions, especially the accessibility to H$_2$ molecules.

We measured H$_2$ adsorption isotherms by volumetric measurement under various temperature and pressure conditions. Figure 4 shows the H$_2$ adsorption isotherms of B-PBS-230 at 298, 273, and 77 K, respectively. Under 70 bar H$_2$ pressure, the absorption capacity of B-PBS-230 sample reaches to 1 wt% and 0.7 wt% at 0°C and 25°C, respectively. The linear H$_2$ absorption isotherm profiles indicate the adsorption capacity well below the saturation level. Thus, we measured the isotherm at 77 K with the attempt to observe the saturation level. A typical Type I isotherm was observed with the saturation level at above 2 wt%, which is quite in consistent with the adsorbent with SSA about 1,150 m$^2$/g, based on the Chahine’s rule. Comparing with the known adsorbents with similar surface areas, this B-PBS-230 sample shows a significantly higher H$_2$ uptake at ambient temperature, implying a high H$_2$ binding energy. We are currently arranging the validation experiment with the National Renewable Energy Laboratory group to confirm the isotherm results and estimate the H$_2$ binding energy.
IV.C Hydrogen Storage / Advanced Materials

FIGURE 3. Pore size distribution (with specific surface area and mass density) of two B-PBS polymer networks after the heat-treatment at 230°C (bottom) and 300°C (top) for 1 h.

FIGURE 4. H₂ adsorption isotherm of B-PBS-230 at 77 K, 273 K, and 298 K.
CONCLUSIONS AND UPCOMING ACTIVITIES

This research project proposes the investigation of two B-polymer networks with the objective to simultaneously show three essential properties, including high $H_2$ binding energy 15–25 kJ/mol, high surface area $>4,000 \text{ m}^2/\text{g}$, and mass density $>0.65 \text{ g/cm}^3$. If successful, the new sorbent material should achieve the 2020 DOE hydrogen storage targets with a material gravimetric capacity of 4.5 wt% $H_2$ and volumetric capacity of 30 g $H_2$/L under mild condition. Among three key properties, the surface binding energy is the most challenging one. So far, there is no known adsorbent material that exhibits a $H_2$ binding energy in the range of 15–25 kJ/mol (most of them showing less than a half). Thus, in our research strategy, the initial priority is to tackle the specific surface functionality that can show the desirable $H_2$ binding energy. If successful, we will adopt the known network material design principles to prepare the B-polymer network with desirable nanoporous morphology that can offer high surface area and suitable mass density.

In the past three quarters of this Phase I period, we have developed the chemical routes to prepare two proposed B-polymer network structures (A) and (B). Several B-polymer network (B) samples were systematically synthesized by using boron-containing poly(butylene styrene) (B-PBS) precursor and the subsequent heat-treatment procedure to achieve the B-polymer network (B) with a $\pi$-electrons conjugated framework containing B-moieties. Some resulting B-polymer network (B) samples were carefully examined to understand their molecular structures, nanopores morphology based on automatically formed free volume, and $H_2$ adsorption isotherms under various temperatures and pressures to know their $H_2$ sorption capacities and profiles, as well as the structure-property relationship. The resulting $\pi$-electrons conjugated B-moieties in the B-polymer framework (B) show strong acidity, which may offer high $H_2$ binding energy. However, it requires further confirmation.

The other immediate research activity is to modify the reaction condition to prepare B-polymer network (B) with only a well-defined $\pi$-electrons conjugated B-moieity that shows the desirable $H_2$ adsorption profile. At the same time, we will expand the molecular structure design to increase the specific surface area. Following the known network design principles for high surface areas, we hope to prepare the next generation of B-polymer frameworks with a uniform nanoporous morphology (pore size about 1 nm), which shall offer both high surface area and high mass density. During the entire research period, we will continue the collaboration with Sandia core team and understand the structure-property relationship.

FY 2017 PUBLICATIONS/PRESENTATIONS


REFERENCES

6. Youmi Jeong and T.C. Mike Chung, Carbon 2011, 49, 140.