Nanostructured Polymeric Materials for Hydrogen Storage

Chemical Sciences and Engineering Division

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DOE Award #: CPS Project 18670 and Agreement No. 16316-ANL

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Executive Summary

Nanostructured Polymeric Materials for Hydrogen Storage

On-board hydrogen storage technologies are critical in future transportation applications, such as H₂-powered fuel cell vehicles, in the new hydrogen-based economy. To be practical, the performance targets set by Department of Energy for 2017 include a system gravimetric capacity of at least 0.055 kg H₂/kg_{system} and a system volumetric capacity of 0.040 kg H₂/L at ambient temperature on the system basis. These targets represent extremely high technical challenges for the storage material development.

The objective of this project is to develop a new class of hydrogen storage adsorbent, nanostructured porous organic polymers (POPs), through collaboration between Argonne National Laboratory and The University of Chicago. POPs have excellent thermal stability and tolerance to gas contaminants such as moisture. They also have low skeleton density and high intrinsic porosity via covalent bonds, capable of maintaining specific surface area (SSA) during high pressure pelletizing for better volumetric density. Furthermore, they can be produced at a commercial scale with the existing industrial infrastructure. The team's approach focused on improving hydrogen uptake capacity and the heat of adsorption by enhancing SSA, porosity control, and framework-adsorbate interactions through rational design and synthesis at the molecular level. The design principles aim at improving the following attributes of the polymers: (a) high SSA to provide sufficient interface with H₂; (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.

Since the project inception in the summer of 2007, the team has successfully prepared over 100 POP materials in three different categories of POPs including aromatic, hetero-aromatic and transition metal (TM) doped systems, and investigated the surface structural and chemical impacts to the adsorption enthalpy. To improve the capacities and heat of adsorption for ambient temperature storage, the team studied specific surface area (SSA) enhancement and porosity regulation using simple aromatic monomers with contorted cores and hyper-crosslinking chemistry; explored a series of nanoporous polymers with monomers containing heterocyclic functional groups for better conductivity or polarizability; prepared and studied the hydrogen interaction with transition metal (TM) containing porous polymers either through post-doping or direct synthesis. The team has produced polymers with SSA as high as ~3,143 m²/g and tunable pore size from 0.6 to 0.9 nm. The excess H₂ uptake of 5.5 wt% at 77 K (40 bar) was also achieved. In addition to polymer design and synthesis, the team also conducted various characterization studies on POPs' surface property, hydrogen uptake capacity, isosteric heat of adsorption and hydrogen-POP interaction. The team also conducted *ab initio* and density functional theory (DFT) calculations to compare with the experimental results for a better understanding of the hydrogen-polymer interaction on the surface or inside of a confined space. In addition, the team was also a member of DOE's Hydrogen Sorption Center of Excellence (HSCoE) and supported the Center through independent and collaborative research.

Although the project did not produce an adsorbent suitable for on-board H₂ storage application, a substantial amount of new science and technology information, particularly in the areas of pore-size control and the metal-promoted binding energy enhancement, was generated which sets a solid foundation for the next-phase of development. A number of publications and patents were produced. The new POP materials also found other potential application in the areas of catalysis, electrocatalysis and natural gas storage for transportation applications.

Introduction/Background

1.1 Technical Concept/Objectives

On-board hydrogen storage technology represents a critical component for transportation applications in the future H₂-based economy. To meet DOE's 2017 targets, the storage system must have a minimum gravimetric capacity of 0.055 kg H₂/kg and a volumetric capacity of 0.04 kg H₂/L at a cost that is competitive of incumbent technologies. *No current technology meets these goals.*

The DOE Fuel Cell Technologies Office has sponsored the research on several classes of hydrogen storage materials including metal hydrides, chemical hydrides, and sorption-based materials. Among them, the sorption-based materials have some unique advantages. Hydrogen adsorption on the open surface originates from van der Waals attraction with a low free energy of ~3.8 kJ/mol. This weak interaction enables H₂ molecules to physisorb on the adsorbent surface with high mobility, yet allows them to release easily with minimum energy when needed. Metal and chemical hydrides, on the other hand, require significant energies to extract H₂ by breaking the chemical bonds. The sorption-based materials are also, in general, lightweight, inexpensive and do not require on-board processing when compared with some hydrides. The low H₂ adsorption enthalpy by the physisorption, on the other hand, makes it difficult to retain molecular hydrogen in the adsorbent under the ambient condition. The average kinetic energy of H₂ at ambient temperature is comparable to that of physisorption, which limits the storage capacity of open-structured adsorbents, such as activated carbons, even if they have relatively high specific surface areas. An ideal sorption-based material should have H₂ adsorption energy in the range of 15~20 kJ/mol for storage at ambient temperature.¹

Various next-generation hydrogen sorption materials were developed in the last few years. Most notable among them are metal-organic frameworks (MOFs) and porous organic polymers (POPs).²⁻²⁰ Improvements in hydrogen adsorption capacity and enthalpy have been made. Substantial enhancements in specific surface area, pore size distribution and surface-hydrogen interaction have been observed with the new MOFs and POPs although the DOE's storage targets are yet to be met.

The objective of our project was to develop a novel, nanostructured porous organic polymer (POP) system as a H₂ adsorbent that meets DOE's targets for the transportation application. Our research was accomplished through a collaborative work between Argonne National Laboratory and The University of Chicago. Our project addressed four technology barriers for the on-board hydrogen storage system. They were a) system weight and volume, b) system cost, c) efficiency and d) durability/operability, respectively. Our design principles of POP based adsorbent included the following properties: (i) a high surface area to provide sufficient interface between H₂ and the adsorbent; (ii) a narrow pore diameter distribution, preferably ranging from 0.5 to 1.0 nm, to anchor H₂ in the confined space through enhanced van der Waals interaction; (iii) a conductive or "metallic" feature either built intrinsically through an extended π -electron conjugation or by metal doping to promote hydrogen electron transfer and (iv) a semi-rigid framework capable of undergoing a conformational change at ambient temperatures and elevated pressures to trap a higher level of H₂.

Based on these design criteria, our team focused on the development of three categories of POPs throughout the project. They were a) POPs synthesized with aromatic monomers with contorted cores; b) POPs prepared with heteroatom substituted monomers, and c) POPs prepared with the monomers containing transition metal exchange site. The utilization of aromatic monomers with contorted cores targeted mainly surface area enhancement and pore size control since there are many applicable synthetic routes and the selections of monomers. As we will demonstrate in the following section, we have indeed achieved high

surface area and tunable pore size for this class of POPs. The POPs with heteroaromatic function groups were prepared with the monomer in which one or more carbons are substituted by B, N, S, etc. The design concept behind this class of POPs is to improve hydrogen-POP interaction through dipole-induced dipole interaction. Introducing non-C element into aromatic group generally breaks down the symmetry and creates a permanent dipole moment in the function group. Such group, once incorporated into the POP, could in principle polarize the molecular hydrogen for a stronger binding energy. In the case of boron, study has demonstrated that the electron-deficiency it created in an aromatic plane could lead a higher heat of adsorption.²¹ The transition metal doped POPs were prepared by cross-linking monomers containing metal exchange site. The atomically dispersed metals, typically in the ionic form, can be added into the POPs through metal-ligand coordination. Under certain situations, relatively high binding energy can be achieved through π - d orbital interaction between hydrogen and transition metal, also known as a Kubas interaction.

The technical approaches of the project included three key tasks: *polymer design and synthesis, surface property and storage capacity characterizations*, and to a lesser degree, *computational modeling and simulation*. Details on each task will be discussed for each individual class of POPs.

1.2 Accomplishments against Milestones

A number of milestones were established in each fiscal year through the duration of the project. The milestones listed below represent a selected group of milestones and brief summary on their status through the project:

- Complete the experimental optimization of TBHTP system for hydrogen storage. **09/2007**

Tribenzohexazatriphenylene (TBHTP) was the first POP system we developed at Argonne before the project inception. The POP was prepared through condensation reaction between hexaketocyclohexane and diaminobenzidine. We found a relatively high surface area (~400 m²/g) and excess hydrogen storage capacity compared with other porous polymers at the time. First task of this project was to further optimize the surface property and storage capacity through optimization of the reaction condition. This task was completed as scheduled although the surface property could not be significantly enhanced after 20 batches of additional sample preparation. We moved to new and better polymers and synthesis approaches after the completion of this milestone.

- Complete the synthesis of one or more porous polymers reported in the open literature as benchmark materials for the current study. **05/2008**

We completed this milestone by successfully duplicated a porous polymer system reported by A. Cooper using Friedel-Crafts crosslinking reaction of acyl halide or benzylic halide.¹¹ We also characterized the surface area and hydrogen storage capacity and found that they were consistent with the reported value in the literature. In addition, we also synthesized or acquired several other high surface area adsorbents such as MOF-5, AX21, carbon molecular sieve, etc. and investigated their hydrogen storage uptakes. The results we obtained were generally consistent with the literature reports and followed the so call "Chahine rule" (~1% excess hydrogen uptake for every 500 m²/g surface area).

- Complete the design, synthesis and characterization of aromatic POPs and measure their hydrogen storage capacities and heats of adsorption. **02/2009**

We completed this milestone by developing over sixty aromatic POPs using a wide variety of monomers and crosslinking chemistries. A significant number of these POPs had very high

surface areas (up to 3143 m²/g BET) and narrow pore size distribution (from 0.5 to 0.9 nm). We also developed a new synthesis strategy that could fine-tune POP's pore size between 0.7 to 0.9 nm. Hydrogen storage excess capacities up to 5.5 wt.% (gravimetric) or 0.024 kg_{H2}/Liter were achieved at 40 bar pressure under LN2 temperature.

- Complete computational modeling of the interactions between hydrogen and model polymer systems, **08/2009**

Hydrogen adsorption energy and site distribution on model POPs with or without transition metal sites were simulated using quantum mechanical calculation at MP2/DFT level. The result indicated that adsorption on the metal site tends to be dissociative with binding energy significantly higher than the desired value. The binding energy does not always improve with introduction of non-C element in the monomer.

- Complete the design, synthesis, structural property and excess hydrogen storage capacity characterizations of POPs incorporated with non-C main group elements, **07/2010**

We completed this milestone by developing over thirty heteroaromatic POPs using monomers containing non-C element such as N, S, O, B, etc. We conducted extensive surface property characterization and found that many POPs from this group have relatively high surface area and narrow pore size distribution. We also completed the hydrogen storage isotherm study for a selected group of heteroaromatic POPs and derived the adsorption enthalpies. We found that introduction of non-C element could add or reduce the heat of adsorption although the impact was limited.

- Complete adsorption kinetics and charging time investigation for selected POPs **05/2011**

We completed adsorption charging time study for a selected POP in attempt to understand the adsorption kinetics over the porous polymer. We found that the time to reach the adsorption saturation is inversely proportional to the adsorbent bed temperature. The process was generally robust for physisorption process.

- Complete the design, synthesis, structural property and excess hydrogen storage capacity characterizations for transition-metal doped POP systems. **08/2011**

We completed this milestone by developing over ten different POPs containing atomically dispersed, coordinatively-unsaturated transition metals including Ni, Co, Fe, etc. with the record surface areas (up to 2303 m²/g) and narrow pore size distributions achieved. We also completed the hydrogen storage isotherm study for the transition metal doped POPs and derived the adsorption enthalpies. The improvement of the hydrogen adsorption enthalpy was clearly observed with the values typically in the range of 8 to 10 kJ/mol, compared to 6 to 7 kJ/mol for carbon or aromatic POP materials. Such increase suggested that the metals do promote the non-dissociative interaction with hydrogen although the magnitude was less than what one would expect from a Kubas-type of interaction.²² Furthermore, these values still need to be enhanced by at least 50% in order to meet the proposed targets.¹

Project Activities

2.1 Scientific Hypothesis

The two critical challenges for sorption based hydrogen storage technology are the low adsorption enthalpy and insufficient adsorbent capacity, respectively. To meet these challenges, multiple approaches have to be applied to improve the material properties. The adsorption enthalpy is generally associated with the hydrogen-adsorbent surface interaction. For sorption based material, such interaction is dominated by non-dissociative, van der Waals (vdW) type of binding. vdW interaction is very sensitive to the adsorbent-adsorbate distance, therefore, a confined adsorbent void space slightly larger than kinetic diameter of hydrogen is desirable. The POP materials according to our approach should have narrow pore size distribution with diameter less than one nanometer. Even with such narrow pore distribution, the heat of adsorption from simply vdW interaction on non-polarizing surface is still limited to about 4 to 7 kJ/mol, which is comparable to the kinetic energy of molecular hydrogen at ambient temperature and significantly less than the 20 kJ/mol required for an ideal adsorbent. Other approaches with potential to further improve the hydrogen-adsorbent interaction hence the potential well for anchoring hydrogen need to be evaluated, as is shown by Figure 1. For example, by introducing permanent dipole to the adsorbent surface one could in principle enhance the hydrogen adsorption energy through dipole-induced dipole interaction. Coordination-unsaturated transition metals also have empty d-orbital which could share the electron from hydrogen therefore increases the binding energy. In addition to the adsorption enthalpy, the capacity represents another key storage parameter. For sorption based storage material, the excess adsorption capacity is generally directly proportional to the specific surface area accessible by the adsorbate. Therefore, a key POP property for hydrogen storage is the high surface area. A general observation of hydrogen storage over high surface adsorbent has found that, 500 m²/g surface area is required for every one percent of weight capacity at 77 K. Therefore, the minimal POP surface area has to be significantly higher than 2800 m²/g in order to reach 5.5 wt.% goal at the system level.

Figure 1. Potential diagram of H₂ adsorption on the POP through vdW and enhanced vdW interactions.

2.2 POP Synthesis & Characterization

To meet these technology challenges, our POP design was targeted at improving the following material properties: high specific surface area, narrow pore size distribution, built-in surface dipole, and unsaturated transition metal doping, respectively. Through the project, We have focused on the development of three categories of POPs They were a) POPs synthesized with aromatic monomers with contorted cores; b) POPs prepared with heteroatom substituted monomers, and c) POPs prepared with the monomers containing transition metal exchange site. Various synthetic schemes were used for POP synthesis including dioxane formation, Sonogashira-Hagihara cross-coupling, Friedel-Crafts reaction, oxidative coupling, trimerization of ethynyl groups, amide or imide formation and homocoupling of aromatic bromides, etc. Detailed discussion on several examples will be given in the following section on each of the three classes of POPs developed by our team.

Characterization study consists of three core components: polymer structural investigation, POP surface property and hydrogen adsorption capacity/enthalpy measurements. Hydrogen storage was investigated using a modified Siebert isotherm. We generally measured the equilibrium excess uptake at different H_2 pressures up to 80 bars. For each sample, the POP's skeleton space was first calibrated with ultrahigh purity of helium. GASPak software was used to calculate the hydrogen and helium at different pressures and temperatures. Typically, four storage temperatures was used for each POP adsorbent, including liquid nitrogen (77K), liquid argon (87K), dry ice/acetone mixture (195K) and ambient temperature (298K). For hydrogen uptake at liquid nitrogen or liquid argon temperature, a hydrogen adsorption baseline was first established by an isotherm measurement on the empty vessel where the POP skeleton space was replaced by stainless rod or beads. Such baseline would be later used to subtract the value measured over the actual POP adsorbent. The isotherm measurements at different temperatures were also used to extrapolate the adsorption enthalpy (ΔH_{ads}) based on the van't Hoff equation. Polymer structural characterization was an essential part of the POP synthesis. It was carried out simultaneously with the synthetic work using various standard laboratory techniques, such as FTIR, solid-state NMR, elemental analysis, temperature-programmable desorption, etc. The polymer surface properties such as porosity and surface area were determined by the nitrogen adsorption isotherm using BET method. The pore size distribution expressed by the incremental surface area as the function of the pore width was usually calculated from N_2 -isotherm data using non-localized density function theory (DFT). A particularly important observation was that most of the POPs we investigate had relatively narrow pore size distribution with a majority of pores having the width ranging from 0.6 to 0.9 nm.

2.3 Aromatic POPs

Among many different aromatic POPs we prepared through this project, two groups of examples are included in this report. The first group of POPs was produced by crosslinking aromatic monomers with contorted cores. Generally, the polymer contains long chain organic moieties. Under vdW force, the individual strand inside the polymer attaches closely to each

i) $CHCl_3$, Fe powder (6%mol); ii) Br_2 (neat, 4.3eq) was added at $0^\circ C$, then warm to RT 3-5h; iii) $i-Pr_2NH$, (Trimethylsilyl)acetylene (4.8eq), $PdCl_2(PPh_3)$ (8%mol), CuI (4%mol), PPh_3 (16%mol), reflux for 12h; iv) CH_2Cl_2 , $NaOH$ (10eq) in CH_3OH , RT, 6h; v) Dioxane (dry), $Co_2(CO)_8$ (0.24 eq for **PS4AC1**, 2/3 eq for **PS4AC2**), $110^\circ C$, 1h.

Scheme 1. Synthesis of PS4AC1 and PS4AC2 using spirobifluorene as contorted core.

other in forming bundles, leaving no voids in between hence no surface area and porosity. To design POPs, we introduced the crosslinking chemistry of monomers with contorted cores such as spirobifluorene or tetraphenylmethane. The spirobifluorene and tetraphenylmethane cores were synthesized according to modified literature procedures.^{23,24} These hydrocarbons were further converted into tetrabromo compounds. The palladium mediated Sonagashira and Stille coupling reactions were used to introduce the acetylenyl and thiophenyl units, respectively. The monomers containing terminal acetylene groups were subject to trimerization catalyzed by cobalt carbonyl complex, which led to cross-linked polymers PS4AC1, PS4AC2, and PT4AC. Shown by Scheme 1 and Scheme 2 are two representative reactions in forming POPs with spirobifluorene or tetraphenylmethane core.

Scheme 2. Synthesis of PT4AC using tetraphenylmethane as contorted core

The resulting polymers are all heavily cross-linked and insoluble in any solvent, which limited our means to perform structural characterization. However, FTIR spectrometers offer assistance in deciphering the structural information. The degree of trimerization of the terminal acetylene groups was determined by comparing the FTIR spectra of the polymers and respective monomers. Relative peak intensity of the C-H stretching from C≡C-H (around 3300 cm⁻¹) and C-H bending from Ar-H (around 820 cm⁻¹) of the monomers and polymers were calculated using the absorbance ratio $R = A(3300\text{ cm}^{-1})/A(820\text{ cm}^{-1})$ where A is the absorbance peak height at the specified frequency. The values obtained are: $R_{\text{MS4AC}}=1.33$, $R_{\text{PS4AC1}}=0.25$, $R_{\text{PS4AC2}}=0$, $R_{\text{MT4AC}}=0.63$, $R_{\text{PT4AC}}=0.25$, (**MS4AC**, and **MT4AC** are the two monomers corresponding to the synthesis of polymers **PS4AC1**, and **PT4AC**, respectively.) Since the bending vibration intensity of C-H from Ar-H will not be affected much by the polymerization, the decrease in the value of this ratio indicated the degree of the cross-linking. The polymerization shown by IR spectra, however, is not complete except for **PS4AC2**. This result is consistent with our controlled reaction condition. The trimerization reaction proceeds very quickly and the polymers precipitated out within minutes before the cobalt catalyst can diffuse into the reaction mixture. These factors led to low cross-linking density and low porosity in polymer **PS4AC1** and **PT4AC**. When the catalyst ratio of Co over the triple bonds was increased to 1/3 while keeping other conditions unchanged, polymer **PS4AC2** was obtained with almost completed conversion of the terminal acetylene units. Consequently, an enhanced surface area was achieved through nitrogen adsorption isotherm measurement at 77 K. The surface property, together with the excess hydrogen gravimetric uptake at both liquid nitrogen and ambient temperatures, are given in Table 1.

Table 1. Surface properties and excess H₂ uptake capacities of PS4AC1, PT4AC and PS4AC2

	BET Surface Area (m ² /g)	Langmuir Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)	Excess H ₂ Gravimetric uptake @77K (kg _{H2} /kg adsorbent+H2ads)	Excess H ₂ Gravimetric uptake @298K (kg _{H2} /kg adsorbent+H2ads)	Excess H ₂ Volumetric uptake @77K (kg _{H2} /Liter adsorbent)	Excess H ₂ Volumetric uptake @298K (kg _{H2} /Liter adsorbent)
PS4AC1	769	1122	0.427	0.249	2.8%	0.44%	0.016	0.0026
PT4AC	762	1114	0.425	0.226	2.2%	0.50%	0.013	0.0030
PS4AC2	1043	1412	0.477	0.251	3.7%	0.43%	0.021	0.0025

The excess hydrogen adsorption capacities of polymers were measured by a Sievert type isotherm apparatus. For all the POP materials, the excess gravimetric hydrogen uptakes were measured at both liquid nitrogen and ambient temperatures. A type II isotherm at 77 K and near linear uptake at room temperature as the function of adsorption pressure was observed, a characteristic for all the polymers of this study. Complete overlap between adsorption and desorption curves was found, suggesting no hysteresis between the two processes. We also investigated adsorption/desorption in multiple cycles and found the isotherm plots essentially repeat with each other within the measurement error. Listed in Table 1 are the average excess hydrogen adsorption capacities of all the polymers measured at both temperatures. The excess adsorption capacity was generally proportional to the BET surface area at 77K, following so called “Chahine rule”²² despite the differences in the polymer molecular structures. This is relatively easy understood since, at 77K, the kinetic energy of hydrogen molecule succumb to the heat of adsorption at the polymer surface and H₂ will adsorb and populate any available surface.

The second group of examples is the aromatic POP with tunable pore size distribution below 1 nm in dimension. In this case, four aromatic monomers, **M1** through **M4**, with different number and position of ethynyl group substitution in the aromatic ring were used to prepare **POP1** through **POP4** using trimerization reaction, shown by Scheme 3.

Scheme 3. (a) four aromatic monomers with different ethynyl group substitution; (b) an example of trimerization reaction.

Using dicobalt octacarbonyl as a catalyst, the terminal ethynyl groups of the respective monomers were trimerized, and four polymers were readily obtained in quantitative yield. A

representative polymerization to prepare polymer **POP-1** from **M1** is outlined in Scheme 3. A similar reaction was used for preparation of **POP-2**, **POP-3**, and **POP-4** from **M2**, **M3**, and **M4**, respectively.¹⁵ While **M1** was purchased commercially, monomers **M2**, **M3** and **M4** were synthesized by coupling the aromatic bromides and trimethylsilylacetylene under Sonogashira reaction conditions, followed by deprotection of the trimethylsilyl (TMS) groups. These monomers were designed in such a way that they could potentially form porous structures with different pore diameters and cross-linking density.

The structural properties of these polymers were characterized by Fourier transform infrared spectroscopy. The characteristic vibration band of alkynyl carbon-hydrogen at 3300 cm^{-1} is completely diminished for **POP-1** and **POP-2**, indicating the completion of the trimerization reaction; whereas this band was weakly observable for polymers **POP-3** and **POP-4** due to the residual ethynyl groups, suggesting that even higher surface area maybe achievable should the trimerization be completed. The thermal gravimetric analysis (TGA) in air showed high thermal stability for polymers **POP-1**, **POP-2**, and **POP-3** with no sign of decomposition up to 360 °C. Polymer **POP-4** was also stable up to ~ 330 °C after an initial weight loss of about 10 % due to the removal of residual moisture or air upon heating.

Surface properties of these polymers were characterized with nitrogen adsorption analysis at 77.3 K using a Micromeritics ASAP 2010 system. Nitrogen adsorption isotherms are shown in Figure 2. The inset of Figure 2 is the expanded plots at the low pressure region where nitrogen uptake is most sensitive to micropores (logarithmic pressure scale was used). The differences in nitrogen adsorption isotherms among these polymer samples were distinct. The inflection points of nitrogen uptake followed the sequence of **POP-2** < **POP-1** < **POP-4** < **POP-3**, suggesting their micropore diameters following the same order. The nitrogen adsorption isotherms shown by Figure 2 were also used to calculate the differential pore volume distributions as a function of pore width using non-localized density functional theory (NLDFT). Micropores are dominant for all four polymers. More importantly, there was clearly distinction in pore size distribution among these POPs with diameters ranging from 0.7 to 0.9 nm.

Figure 2. Nitrogen adsorption isotherms measured at 77.3K for polymers POP-1 (square), POP-2 (diamond), POP-3 (hexagon), and POP-4

Excess hydrogen adsorption capacities of these four polymers were measured with a Sievert isotherm apparatus. Hydrogen adsorption/desorption isotherms were measured under four different temperatures for each polymer. Shown in Figure 3 (a) is a complete set of four isotherms for polymer **POP-3** with hydrogen uptakes up to 3 wt.% obtained at 77 K and 60 bar. Figure 3 (b) shows the heats of adsorption derived from the hydrogen adsorption isotherms at 195 K and 298 K, from which the initial adsorption energy can be calculated more accurately. **POP-4** and **POP-3** exhibited relatively higher initial heat of adsorption, ΔH_{ads} , around 9 kJ/mol, whereas **POP-1** and **POP-2** showed values of ΔH_{ads} near 7.5 kJ/mol. This observation offers little correlation between ΔH_{ads} and PDs obtained from N_2 adsorption isotherms. Instead, we found an interesting correlation between ΔH_{ads} and N_p where N_p represents the average number of phenyl groups connected to a benzene after trimerization. The N_p values for **POP-2** and **POP-1** of 2.3 and 2.5 are considerably lower than those for **POP-3** and **POP-4**, of 3 and 3.5,

respectively. Quantum chemical calculations at MP2/6-311++G(2d,2p)//MP2/6-31+G* level for H₂ adsorption on **M1**, **M3** and **M4** monomers simulating different arrangements of neighbouring phenyl groups in the polymers resulted in binding energies of 5.1 kJ/mol, 5.5 kJ/mol and 6.0 kJ/mol, respectively. Other phenyl groups adjacent to the H₂ could also contribute to the van der Waals interaction, particularly at low H₂ coverage. It is substantiated by calculations of the binding energies of H₂ to two monomers, which come out to be 10.6 kJ/mol, 12.6 kJ/mol and 12.9 kJ/mol for **M1**, **M3** and **M4**, respectively. Larger N_p leads to higher ΔH_{ads} as the order of **POP-4** > **POP-3** > **POP-1** ≥ **POP-2** we observed in Fig. 4 at low hydrogen coverage. Heat of adsorptions at higher coverage were also extrapolated from isotherms at 77 K and 87 K, the values of ΔH_{ads} at around 1.5 wt. % hydrogen loading were in the range of 4.5-6.5 kJ/mol, and did not correlate with PD or N_p . This is somewhat expected since hydrogen adsorption is less sensitive to the surface structure at 77 K or 87 K as hydrogen loading increases.

Figure 3. (a) Hydrogen adsorption (solid symbols) / desorption (open symbols) isotherms for polymer POP-3 under 77 K (squares), 87 K (circles), 195 K (triangles), and room temperature (diamonds); (b) Heat of adsorption at low coverage for POP-1 (red square), POP-2 (yellow diamond), POP-3 (magenta hexagon), and POP-4 (cyan triangle).

Figure 4. (a) Hydrogen adsorption isotherms of ANL prepared PAF-1 measured at different temperatures; (b) heat of adsorption of H₂ over PAF-1 at different loadings.

In the process of our development of the aromatic POP, a report in the literature demonstrated a very high surface area POP (PAF-1) prepared by Yamamoto homo-coupling of

tetrakis(4-bromophenyl)methane.²⁰ Since such approach was in line with our originally planned strategy, we also synthesized the POP using the similar chemistry. The POP we prepared had the surface area of 3143 m²/g and the excess hydrogen adsorption of 5.5 wt.%. This value represents the highest gravimetric capacity among our porous polymers. Shown in Figure 4a are the hydrogen adsorption isotherms over this POP at three different temperatures. We should point out, however, that the hydrogen adsorption enthalpy (6.5 kJ/mol) over PAF-1 was among the lowest in all the POPs we have investigated, as is shown by Figure 4b.

2.4 Heteroaromatic POPs

Scheme 4. Synthesis of polymer PmCB-2

Heteroaromatic POPs refer to a group of polymers in which the monomers contain non-C main-group elements. The elements could be oxygen, nitrogen, sulfur, oxygen and boron. The purpose of introducing such element-substitution is to improve the interaction of POP with hydrogen, either through dipole-induced dipole interaction or electronic orbital interaction. We have developed a number of such POPs through the project.¹⁶ Included in this report is an example of B-substituted POP.

Boron-doped carbon has been considered as a promising hydrogen storage medium through possible interaction between H₂ and electronically deficient carbon.^{21,25} Carborane is highly electron deficient with excellent thermal stability. We developed a series of synthetic approaches in preparing porous polycarborane through ethynyl trimerization and Friedel Crafts alkylation reactions. Relatively high specific surface areas and narrow pore dimension distributions were found for these POPs. We also observed a good correlation between the hydrogen heat of adsorption and boron/carbon ratios among the new carborane containing POPs.

We have prepared three different carborane containing POPs. One of the examples, **PmCB-2**, will be briefly discussed. To prepare the POP, a carborane monomers with two ethynyl groups was first synthesized. The monomer was subsequently cross-linked through via ethynyl trimerization reaction through Scheme 4.

In addition to **PmCB-2**, another two carborane containing POPs, **PmCB-3** and **PmCB-4**, were prepared through Friedel Crafts reaction.

Table 2. Surface properties and hydrogen adsorption properties of **PmCB-2**, **PmCB3**, and **PmCB-4**

	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g) ^a	Micropore Volume (cm ³ /g)	Dominant Pore Diameter (nm)	H ₂ Gravimetric uptake @ 77K (kg _{H2} /kg adsorbent+H ₂ ads)	H ₂ Volumetric uptake @ 77K (kg _{H2} /Liter adsorbent)	Boron/Carbon ratio	Initial heat of adsorption (kJ/mol)
PmCB-2	422	0.14	0.04	0.68	0.013	0.014	10/18	10.2
PmCB-3	864	0.57	0.30	0.76	0.021	0.014	10/16	9.0
PmCB-4	1037	1.12	0.33	0.77	0.027	0.016	10/30	8.2

The surface properties of B-containing POPs were characterized by the nitrogen adsorption isotherm measurement at 77 K using a Micromeritics ASAP 2010 system. Both **PmCB-2** and **PmCB-3** exhibit type IB adsorption isotherms with hysteresis on their desorption branches, which was likely due to the pore opening/closing. The isotherm of **PmCB-4** had a type II characteristic and exhibits no hysteresis on its desorption branch. Listed in Table 2 are several key structural properties derived from the isotherm data, including BET and Langmuir surface areas, micropore volume, total pore volume, and dominant pore diameter based on non-local density functional theory (NLDFT) calculation.

The excess hydrogen adsorption capacities of these polymers were measured by the aforementioned Sievert type isotherm apparatus. The adsorption isotherms were taken at three different temperatures of 77 K, 195 K and 298 K. Excess hydrogen adsorption capacity up to 28.4 mg/g was obtained by polymer **PmCB-4** under liquid nitrogen temperature. The maximum excess hydrogen uptake for **PmCB-2** and **PmCB-3** at 77 K was 13.7 mg/g and 21.0 mg/g, respectively. The excess uptake capacity was generally proportional to their respective BET surface areas. We also calculated the isosteric heat of adsorption, ΔH_{ads} , toward hydrogen from the isotherms measured at 195 K and 298 K. Figure 5 showed the values of ΔH_{ads} as the function of excess hydrogen uptake capacities. The extrapolated heats of adsorption at near zero coverage for **PmCB-2**, **PmCB-3**, and **PmCB-4** are ~10.2 kJ/mol, ~9.0 kJ/mol, and ~8.2 kJ/mol, respectively. These ΔH_{ads} values correlate positively with the concentration of carborane in the porous polymer network: the higher carborane content the higher initial isosteric heat of adsorption at near zero hydrogen coverage. This could presumably be attributed to the strong electrophilicity of the highly electronically deficient carborane units. Boron-doped graphite in a boron puckered configuration was suggested to possess high heat of adsorption (up

Figure 5. Isosteric heats of adsorption for **PmCB-2**, **PmCB-3**, **PmCB-4**.

to 20 kJ/mol) toward hydrogen due to the p-type property of the boron dopants. Carborane, however, only shows moderate enhancement on the heat of adsorption although it contains higher boron content. It is possible that the aromatic nature of the carboranes delocalizes the charge distribution therefore leads to weaker interaction with dihydrogen. The details of such interaction, however, require comprehensive molecular modeling. One should also note that even though the initial ΔH_{ads} values of **PmCB-2** was the highest among all three polymers, it decreased more rapidly than that of the other two as the hydrogen coverage increased. This was probably due to fewer accessible carboranes in **PmCB-2**, considering its lower surface area of only 422 m²/g. The exposed carboranes as high electrophilic sites were quickly saturated as more hydrogen molecules were adsorbed.

2.5 Metal doped POPs

Metal doped POPs refer to a group of polymers in which the monomers contain the coordination site that can ligate with the transition metals. The ligation sites generally contain nitrogen or oxygen in the form of pyridine, pyrrole, catechol, etc. The transition metals usually include iron, cobalt, nickel, etc. Again, the purpose of introducing atomically dispersed transition metals aims at improving the interaction between POP and hydrogen, possibly through the electronic orbital interaction such as those found in so called “Kubas reaction”. We have developed a number of such POPs through the project containing atomically dispersed Fe, Ni or Co coordinated by the organic ligands cross-linked into the POPs’ framework. The specific surface area of an iron-doped polyporphyrin, P(FeTTPP) reached to 2303 m²/g, the highest value on the metal-doped polymers reported in the literature to our knowledge. The excess hydrogen adsorption of 4.8 w.t.% was achieved over this polymer. In this report we included several examples metalloporphyrin POPs to demonstrate different synthetic methods and their impacts to the properties of metal-doped POPs.

Metalloporphyrins belong to a class of metal complexes related to naturally abundant porphyrins. They have facilitated some of nature’s most important chemical processes including photosynthesis, oxygen transport and catalytic oxidations. With the square-planar coordination site, a large number of metal ions could be readily incorporated into the porphyrin center, which could serve as the building block of polymers with the coordinationally unsaturated metal center. Porous network polymers based on porphyrin and phthalocyanine have been previously synthesized via dioxane formation reactions with BET surface areas below 1000 m²/g.^{26,27} Through this project, we have developed Fe, Co and Ni containing polyporphyrins with highest BET surface area among the literature.¹² Here we discuss our effort in preparing several Ni containing highly porous porphyrinic polymers using Sonagashira–Hagihara coupling, alkyne-alkyne homocoupling and alkyne trimerization reactions. These polymers exhibited narrow pore size distributions and high BET surface areas up to 1700 m²/g. We conducted isotherm measurements of H₂, CH₄ and CO₂ adsorption over these polyporphyrins at several temperatures. We found that they demonstrated excellent excess hydrogen uptakes with capacity larger than 3.5 mass % excess at 77 K and 50 bar achieved. These nickel-chelated porphyrin polymers also produced promising potentials for methane storage and carbon dioxide capture with relatively high adsorption enthalpies and storage capacities. For example, up to 12.3 wt% of adsorbed CH₄ at 35 bar and 12.8 wt% of adsorbed CO₂ at 1.08 bar were achieved, respectively.

The polyporphyrin polymers were synthesized according to Scheme 5. The 5,10,15,20-Tetrakis-(4-(ethynyl-phenyl)porphyrin **1** was synthesized according to the literature procedure.²⁸ The monomer 5,10,15,20-Tetrakis-(4-(ethynyl-phenyl)porphyrinNi(II) **2** was synthesized by heating compound **1** with metal acetate in DMF. The resulting porphyrin monomer was

polymerized through three types of polymerization reactions, namely Sonagashira–Hagihara coupling with tetraiodophenylmethane, alkyne trimerization and alkyne-alkyne homocoupling reactions.

Scheme 5. Multi-routes of preparation of polyporphyrin polymers

Table 3. Surface properties and excess gas adsorption capacities for POP Ni-Por-1 to Ni-Por-4.

Sample	BET SSA (m ² /g)	H ₂ Max Gr. Uptake Excess (77K) (kg H ₂ /kg adsorbent+H ₂ ads)	H ₂ Max Vol. Uptake Excess (77K) (kg H ₂ /L adsorbent)	μ-Pore /Total Pore (cm ³ g ⁻¹ /cm ³ g ⁻¹)	Hydrogen ΔH _{ads} (kJ / mol)	CH ₄ Uptake (273K, 1.08 bar) (mmol/g adsorbent)	CO ₂ Uptake (273K, 1.08 bar) (mmol/g adsorbent)
Ni-Por-1	1711	0.035	0.023	0.69/0.90	8.0	0.98	3.13
Ni-Por-2	1393	0.028	0.023	0.54/0.96	8.2	0.85	2.66
Ni-Por-3	894	0.019	0.017	0.38/0.59	8.8	0.80	2.55
Ni-Por-4	778	0.017	0.016	0.38/0.62	7.8	0.68	2.26

Surface area and pore size distribution were characterized with a Micromeritics ASAP 2020 accelerated surface area and porosity analyzer using nitrogen as probing gas at 77 K. All polymers exhibited the type I adsorption isotherm, which was the characteristics of a microporous POP material. The calculation using the non-local density function theory (NLDFT)

based on isotherm data showed that a majority of the pore volume of these polymers was contributed by the micropores with pore sizes distribution narrowly centered at about 0.6-1.0 nm, a desirable dimension for gas adsorption. Table 3 summarizes the surface properties and selected excess gas adsorption capacities of the polymers.

Hydrogen adsorption isotherms were measured with a Sievert type apparatus. Figure 6a shows the excess H₂ adsorption capacities of Ni-Por-1 measured under various equilibrium pressures at three different temperatures. The maximum excess H₂ uptake capacity for polymer Ni-Por-1 reached 3.5 mass% excess at 77 K and 40 bar, which followed so-called “Chahine’s rule”, similar to its rigid counterparts, such as activated carbon and MOFs.

The isosteric heat of adsorption at low coverage region was derived from the isotherms measured at 195 and 298 K. We chose these two temperatures because the corresponding isotherms were well-separated, thus the heat of adsorption for hydrogen could be more accurately deduced, in contrast to the approach that uses isotherms at 77 and 87 K. In addition, hydrogen adsorption was more selective toward the stronger binding site at higher temperature. The heats of adsorption as the function of hydrogen loading for Ni-Por-1 is shown in Figure 6b, where the initial adsorption enthalpy, ΔH_{ads} could be extrapolated to be about 8 kJ/mol, indicating an incremental improvement over the commonly reported heat of adsorption for pure carbon-hydrogen porous polymers.

Figure 6. a) The excess H₂ uptake isotherms for Ni-Por-1 at liquid nitrogen bath (LN, T = 77 K), dry ice/acetone bath (DIA, T = 195 K), and room temperature (RT, T = 298 K). b) H₂ heat of adsorption as function of hydrogen uptake for Ni-Por-1.

We also measured methane and CO₂ adsorption over these nickel-doped porphyrin POPs using the Micromeritics ASAP 2020 system. Adsorption isotherms of methane and carbon dioxide were measured at both ice/water bath and 25 °C water bath at a gas pressure up to 1.08 bar. CH₄ uptake at ice/water bath reached 15.7 mg_{CH4}/g_{ads}, while CO₂ uptake at the same temperature reached 138 mg_{CO2}/g_{ads}. The heats of adsorption for both CH₄ and CO₂ generally followed the same trend: $\Delta H_{Ni-Por-1} < \Delta H_{Ni-Por-2} < \Delta H_{Ni-Por-3} \leq \Delta H_{Ni-Por-4}$. The initial heat of adsorption was estimated to be up to 23 kJ/mol for CH₄ and 29 kJ/mol for CO₂, respectively. Gas adsorption selectivity of CO₂ over N₂ was calculated using the similar approach by Rosi *et al.*²⁹ based on single gas sorption isotherms, the selectivity follows the sequence of Ni-Por-1 < Ni-Por-2 < Ni-Por-4 < Ni-Por-3, with values of 14.4, 15.4, 17.4, and 19.1, respectively; while the

selectivity of CO₂ over CH₄ is 3.6, 3.7, 4.15, and 4.22 respectively for Ni-Por-1, Ni-Por-2, Ni-Por-3, and Ni-Por-4. Such gas selectivity sequences are consistent with the heat of adsorption data. When using room temperature isotherms for calculation, the value of gas selectivity for these two types of gases remained about the same as that obtained from ice/water bath isotherms. The pronounced selectivity for CO₂ over N₂ makes this type of transition metal doped POPs good candidates for CO₂ capture and separation from the flue gas stream, where CO₂ and N₂ accounts for around 12 mol% and 64 mol% of the total gas content, respectively. Methane adsorption at the pressure up to 45 bar was also measured with the high-pressure Sievert isotherm apparatus. At ice/water bath, the excess CH₄ storage capacity of over 168 mg/g, or 153 V/V was achieved for Ni-Por-1 at 45 bar. The CH₄ uptake capacities at 35 bar for the other three polymers were also measured. In general, the methane storage capacities of these POPs are comparable to that of a microporous zeolite 5A and some MOFs. The results listed in Table 3 indicate that the excess gas adsorption capacities of H₂, CH₄ and CO₂ are essentially proportional to the POPs' specific surface areas in all three cases. The results on isosteric heat of adsorption, however, are interesting particularly in the case of methane and carbon dioxide where higher adsorption enthalpies were found in Ni-Por-3 and -4. Since the micropore size distributions are nearly the same for all four POPs, we expect that their contributions to the van der Waals interaction in the confined space are similar. The difference, therefore, could arise from the chemical environment. Four synthesis routes shown in Scheme 5 indicate that Ni-Por-3 and -4 do not involve a secondary monomer during the polymerization. The distances between the adjacent porphyrins in these polymers are shorter, leading to a higher surface concentration of the metal center. We speculate that higher metal center density may lead to a stronger interaction between the POP and CH₄ or CO₂ through electronic orbital coupling although more targeted experiment or theoretical calculation is needed to quantify this conjecture. The impact of metal center in Ni-Por to H₂ heat of adsorption at 77 K does not follow this trend although their average values are higher on average over those non-metal doped POPs.

2.6 Modeling/Simulation

During the initial phase of the project, our team devoted a small effort in modeling/simulation of the hydrogen/POP interaction in a few selected systems. Both *ab initio* and density function theory (DFT) tools were applied to calculate POP structures and the H₂-POP interactions. The calculated results were applied to guide the POP design or to interpret the experimental observations. For example, Figure 7a shows a DFT simulation of the 3-D structure of the micropore formed through the cross-linking of spirobifluorene. The initial structure was created by modeling of spirobifluorene cross-linking reaction in a 3-D periodic

Figure 7. (a) Calculated porous structure of the cross-linked spirobifluorene containing dihydrogen (blue) with their distributions optimized by DFT; (b) Partial radial distribution functions for H₂ molecules at different loading concentrations

box. The atomic positions of atoms were then fully optimized using DFT method at the GGA level in the VASP code. The pore size in the resulting structure was very similar to that experimentally measured (ca. 7 Å). Hydrogen molecules were placed at the concentrations of 0.2, 2.2 and 4.4 wt.% in the structure and their positions were optimized in each case. The resulting binding energies per hydrogen molecule were 6.77, 6.53 and 5.29 kcal/mol. The trend in the decrease of the binding energy with increase in hydrogen concentration corresponded well to that observed experimentally although the absolute values were off by nearly a factor of four. To explain this trend, the partial radial distribution functions for hydrogen were also investigated. The onset of distance distribution between a hydrogen atom in an adsorbed molecule and other atoms showed a noticeable decrease with increasing concentration, as is shown by Figure 7b. This indicated that the repulsive interactions among adsorbed molecules are partially responsible for the decrease in the binding energy.

In an attempt to improve adsorption enthalpy, we also studied hydrogen interaction with the atomically dispersed transition metals inside the POPs. For example, we performed the first-principles calculations of hydrogen adsorption energies on Co-dimethylbipyridine in Co-doped polybipyridine-spirobifluorene (PBPY) POP. We utilized two different levels of theory (hybrid functional B3LYP with a double-zeta and triple-zeta basis set for single point) for geometry optimizations at the DFT level. Both low-spin and high-spin solutions were explored. We found that H₂ strongly bound to the Co atom, both dissociatively and non-dissociatively. For nondissociative adsorption, the energy was calculated to be 76 kJ/mol, whereas for dissociative adsorption the energy increased to 105 kJ/mol. There was a relatively high barrier of 68 kJ/mol for dissociative adsorption. Upon addition of second hydrogen molecule, we found several different bonded configurations, with both H₂ molecules dissociated, one of them dissociated or both H₂ nondissociated. The total binding energy of two H₂ molecules became 32 kJ/mol, 92 kJ/mol, and 124 kJ/mol for the three cases, respectively. This indicated that nondissociative binding was preferred for two hydrogen molecules. The third hydrogen molecule does not bind in all three cases. We also performed the experimental measurement of the hydrogen adsorption enthalpy over Co-doped PBPY. We found that, although the presence of cobalt definitely improved the heat of adsorption, the absolute value was significantly less than the calculated ones.¹⁷

2.7 Collaborations

Collaboration plays a significant role in this project. The team by itself requires close interaction between Argonne National Laboratory (prime) and The University of Chicago (subcontractor). Our team was also a member of DOE Hydrogen Sorption Center of Excellence (HSCoE) under the research clusters of “Engineered Nanospace” (RC1) and “Substituted Materials” (RC2). The team had made significant contribution to the center’s activities and achievement, and shared 2010 “DOE Hydrogen Program Team Award” with other center members. Meanwhile, the team was also benefited substantially through the interaction with other members in the center and was able to

Figure 8. Peak broadening as the function of pressure for hydrogen adsorbed in the micropore of POP prepared by ANL-UC team

keep abreast with the state-of-the-art development in the sorption material for hydrogen storage application.

One specific example was high pressure ^1H NMR study through the collaboration with the team from University of North Carolina (Professor Yue Wu lead). Porous polymer samples were provided to UNC team. The physisorption of hydrogen over the polymer surface was measured at 100 K with pressure up to 100 bars. Figure 8 shows the ^1H NMR peak broadening as the function of hydrogen pressure. The relative broad peak in comparison with other systems indicated that the micropore environment in the POP is somewhat heterogeneous.

Other collaborations include sample sharing in a cross-laboratory hydrogen uptake test with NREL and computational result sharing with the members from ORNL and RPI. During early phase of the project, Argonne/UofChicago team has sent representative samples to NREL team for cross-laboratory measurement validation. The purpose of such study is to valid measurement accuracy of Argonne's Sievert isotherm setup. For example, NREL team repeated one of ANL's sample which was measured earlier with the excess hydrogen adsorption capacity of 3.7 w.t%. NREL's measurement showed a 3.4% instead. Although the discrepancy was within 10%, ANL team recalibrated its measurement using the most conservative method according to the document of DOE's best practices. All the data reported since were based on the most conservative measurement.

2.8 Summary

In summary, the Argonne/U of Chicago team has developed over 100 POP materials since beginning of the project. These POP are decorated by monomers with different functionalities including aromatic, hetero-aromatic and transition metal (TM) doped ligands. The impact of these functional monomers to the hydrogen adsorption energy was systematically investigation. In addition, the effects of the specific surface area (SSA) and porosity regulation to the excess hydrogen storage capacity and the adsorption enthalpy were also studied. The team has produced polymers with SSA as high as $\sim 3143 \text{ m}^2/\text{g}$ and tunable pore size from 0.6 to 0.9 nm. The excess H_2 uptake of 5.5 wt% at 77 K (40 bar) was also achieved. The team also conducted various characterization studies on the correlation between POPs' surface property, hydrogen uptake capacity, isosteric heat of adsorption and hydrogen-POP interaction and carried out *ab initio* and density functional theory (DFT) calculations to compare with the experimental results. The structural properties and excess hydrogen uptake capacities of several selected POPs developed by the team are listed in Table 4. In addition, the team also collaborated closely with other members of DOE HSCoE and supported Center's activities throughout the program.

The results produced by the team clearly demonstrated that POP is now becoming a great platform as hydrogen adsorbent due to its high surface area and narrow pore (vs. carbon) and excellent chemical stability (vs. MOF). Although unmodified aromatic POPs will unlikely reach desired H_2 adsorption enthalpy for room temperature application even with increased surface area or adjustable porosity, further development through the surface modification by incorporating metal or other elements could promote higher H_2 binding energy to possibly achieve the near-ambient temperature storage application. New surface modification techniques, departing from the conventional synthetic approaches, have the potential to produce high binding energy sites predicted by theory. POPs with tailored surface property and chemical composition can also serve as precursor of fabricating new adsorbent after additional chemical/physical processing. Furthermore, several POPs developed through this program are now being evaluated as the new adsorbents for other gases such as methane and carbon

dioxide storage and separation. In addition, they are also being investigated as new support materials for heterogeneous catalysis.

Table 4. The structural properties and excess H₂ uptake capacities of selected POPs by ANL/UC team

Sample	BET SSA (m ² /g)	Gr. Uptake Excess (77K, 40 bars) (kg _{H2} /kg adsorbent+H2ads)	Vol. Uptake Excess (77K, 40 bars) (kg _{H2} /L adsorbent)	Gr. Uptake Excess (RT, 70 bars) (kg _{H2} /kg adsorbent+H2ads)	Vol. Uptake Excess (RT, 70 bars) (kg H ₂ /L adsorbent)	ΔH_{ads} (kJmol ⁻¹)	Type of POP*
ANL-C1	1233	0.040	0.010	0.0021	0.0005	...	A
ANL-C2	1593	0.044	0.009	0.0035	0.0007	...	A
ANL-C5	1863	0.051	0.011	0.0052	0.0012	...	A
UC-C10	1043	0.028	0.010	0.0018	0.0006	...	A
ANL-POP1	1031	0.028	...	0.0022	...	8.5	A
ANL-POP2	1013	0.027	...	0.0022	...	8	A
ANL-POP3	1246	0.031	...	0.0020	...	9	A
ANL-POP4	1033	0.024	...	0.0015	...	9.5	A
PAF-1	3143	0.055	0.020	0.0053	0.0018	6.5	A
PTTPP	1522	0.050	...	0.0040	...	7.5	A
UC-X4	971	0.032	0.0085	0.0045	0.0012	...	H
PTA-3	870	0.029	0.021	0.0024	0.0017	6.6	H
PmCB-2	422	0.013	0.014	0.0016	0.0017	10.2	H
PmCB-3	864	0.021	0.014	0.0018	0.0012	9.0	H
PmCB-4	1037	0.027	0.016	0.0030	0.0015	8.2	H
UC-M12	1060	0.036	0.0051	0.0040	0.0006	...	M
P(FeTTPP)	2303	0.048	0.024	0.0043	0.0027	8.0	M
Ni/Por-1	1711	0.035	0.023	0.0038	0.0022	8.0	M
Fe-Co/Por	1571	0.034	0.022	0.0041	0.0026	7.4	M
Ni/HQ-1	596	0.017	0.015	0.0019	0.0017	8.0	M
Co/HQ-1	580	0.017	0.016	0.0019	0.0017	9.9	M

*Type of POP, A = aromatic, H = heteroaromatic, M = metal doped

Publications/Patents/Presentations/Recognitions

Listed in the following sections represent the patents, publications, presentations and recognitions directly and indirectly generated from this project.

3.1 Publications & Patents

Publications

1. "Nanoporous Porphyrin Polymers for Gas Storage and Separation", Zhuo Wang, Shengwen Yuan, Alex Mason, Briana Reprogle, Di-Jia Liu, and Luping Yu, accepted by *Macromolecules* **2012**, doi.org/10.1021/ma301426e
2. "Improving Hydrogen Adsorption Enthalpy through Coordinatively Unsaturated Cobalt in Porous Polymer", S. Yuan, D. White, A. Mason, B. Reprogle, M. Ferrandon, L. Yu, and D-J Liu, *Macromolecular Rapid Communication*. **2012**, 33, 407–413, DOI = 10.1002/marc.201100797
3. "Exploring applications of nanomaterials for fuel cell & hydrogen storage", Di-Jia Liu, Shengwen Yuan, Gabriel Goenaga, Junbing Yang, Desiree White and Alex Mason, *Prep. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **2011**, 56 (1), 393
4. "New Approaches to Non-PGM Catalysts through Rational Design", Di-Jia Liu, Gabriel Goenaga, Shengqian Ma, Shengwen Yuan, Jianglan Shui, *ECS Transactions* **2011**, 30, 97-104
5. "Porous Organic Polymers Containing Carborane for Hydrogen Storage", Shengwen Yuan, Desiree White, Alex Mason, and Di-Jia Liu, *Int. J. of Energy Research*. Published online July 15, **2011**. DOI: 10.1002/er.1886.
6. "New Approaches to Non-PGM Electrocatalysts Using Porous Framework Materials", Gabriel Goenaga, Shengqian Ma, Shengwen Yuan, and Di-Jia Liu, *ECS Transactions* **2010**, 33 (1), 579-586
7. "Microporous Polyphenylenes with Tunable Pore Size for Hydrogen Storage", Shengwen Yuan, Brian Dorney, Desiree White, Scott Kirklin, Peter Zapol, Luping Yu and Di-Jia Liu, *Chem. Comm.* **2010**, 46, 4547 - 4549
8. "Nanoporous Polyporphyrin as Adsorbent for Hydrogen Storage", Jiangbin Xia, Shengwen Yuan, Zhuo Wang, Scott Kirklin, Brian Dorney, Di-Jia Liu and Luping Yu, *Macromolecules*. **2010**, 43, 3325–3330 DOI: 10.1021/ma100026f
9. "Microporous Polymers Containing Stereo-contorted Cores", Shengwen Yuan, Scott Kirklin, Brian Dorney, Di-Jia Liu and Luping Yu, *Macromolecules* **2009**, 42(5), 1554-1559

Patents & Applications

1. "Porous polymeric materials for hydrogen storage", Luping Yu, Di-Jia Liu, Shengwen Yuan, Junbing Yang US Patent **8076382**
2. "Porous polymeric materials for hydrogen storage", Luping Yu, Di-Jia Liu, Shengwen Yuan, US Patent Application **US 2012/0065289 A1**
3. "Non-Platinum Group Metal Electrocatalysts Using Porous Polymers and Method of Preparation", Di-Jia Liu and Shengwen Yuan, US Patent Application filed June 2011

3.2 Presentations

1. "Hydrogen Storage through Nanostructured Polymeric Materials", D.-J. Liu (invited), DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA, June 11, 2008
2. "Hydrogen storage through nanostructured polymeric materials", D.-J. Liu (invited), DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA, May 21, 2009
3. "Hydrogen storage through nanostructured polymeric materials", D.-J. Liu (invited), DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA, May 21, 2009
4. "Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)", D.-J. Liu (invited), DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C. , June 7-11, 2010
5. "Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)", D.-J. Liu (invited), DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C. , May 9-13, 2011
6. "Functional polymers for energy harvesting and hydrogen storage" L. Yu, (Invited) Presentation at Northern Illinois University, April 15, 2008
7. "Functional polymers for energy harvesting and hydrogen storage" L. Yu, (Invited) Presentation at US Chinese Chemical Society meeting, September, 2008.
8. "Functional polymers for energy harvesting and hydrogen storage" L. Yu, (Invited) Presentation at 32nd Annual Symposium of the Macromolecular Science and Engineering Center, University of Michigan, October 22, 2008.
9. "Hydrogen storage material research at Argonne National Laboratory", D.-J. Liu, (Invited) Presented at GM R&D Center, January 16, 2009
10. "Hydrogen storage media through nanostructured polymeric materials" S. Kirklin, B. Dorney, S. Yuan, L. Yu & D-J Liu, Poster Presentation at American Physical Society Spring Meeting, March 16-20, 2009.
11. "Nanostructured Polymers as Sorption Based Hydrogen Storage Materials", Di-Jia Liu, Task-22 IEA HIA Expert Meeting, Jeju Island, Korea, April 19, 2009
12. "Nanoporous Polymers for Hydrogen Storage", S. Yuan, L. Yu, & D-J Liu, Presented at Chicago Catalysis Club Spring Symposium, Naperville, IL, May 18 2009
13. "Characterization of Nanoporous Polymer Materials for Gas Storage Applications" B. Dorney, S. Kirklin, S. Yuan, D-J Liu, Presentation at 31st Annual Michigan Catalysis Society Spring Symposium
14. "Advanced Materials & Characterizations for Energy Storage & Fuel Cell Applications", D.-J. Liu, (Invited) Presented at Department of Chemistry, Northern Illinois University, Sept 28, 2009
15. "Next Generation Materials and Characterization Techniques for Energy Efficiency and Renewal Energy Applications" D.-J. Liu, (Invited) Presented at Department of Chemistry, University of Illinois, Nov 5, 2009
16. "Advanced Materials for Energy Storage and Conversion" D.-J. Liu, (Invited) Presented at Department of Chemistry, Hunter College, NY, Jan 27, 2010
17. "Porous Organic Polymers (POPs) and their Hydrogen Uptake Properties", S. Yuan, J. Xia, S. Kirklin, B. Dorney, D. White, L. Yu, & D-J Liu, Presented at American Chemical Society National Meeting, San Francisco, CA , March 21-25, 2010.
18. "Porous Organic Polymers (POPs) for Hydrogen Storage", S. Yuan, B. Dorney, S. Kirklin, D. White, J. Xia, Z. Wang, L. Yu, and D.-J. Liu, (Poster Prize) Presented at 1st International Conference on Materials for Energy, Karlsruhe, Germany, July 4-8, 2010.

19. “Exploring applications of nanomaterials for fuel cell & hydrogen storage”, Di-Jia Liu (invited) Presentation at American Chemical Society National Meeting, Anaheim, CA, March 26-31, 2011.

3.3 Awards & Recognitions

1. Research on tunable porous polymer pore size study was selected as one of Argonne's highlight to DOE, Office of Science in November, **2010**
2. Received **2010 “DOE Hydrogen Program Team Award”** as a member of Hydrogen Sorption Center of Excellence from Office of Fuel Cell Technologies Program
3. Argonne/UofC porous polymer based hydrogen storage material was cited as one of the technical accomplishment highlights by FreedomCAR and Fuel Partnership, **2010**
4. Won the **Poster Prize** for presentation on porous polymer at 1st International Conference on Materials for Energy, Karlsruhe, Germany, July **2010**.

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