IV.C.2 Room Temperature Hydrogen Storage in Nano-Confined Liquids

John J. Vajo
HRL Laboratories, LLC
3011 Malibu Canyon Road
Malibu, CA 90265
Phone: (310) 317-5745
Email: jjvajo@hrl.com

DOE Managers
Katie Randolph
Phone: (720) 356-1759
Email: Katie.Randolph@go.doe.gov
Grace Ordaz
Phone: (202) 586-8350
Email: Grace.Ordaz@ee.doe.gov

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Overall Objectives

- Characterize the enhanced solubility of hydrogen in nano-confined liquids
- Optimize the confining scaffold and solvent liquid for room temperature hydrogen storage
- Understand the effect of nano-confinement on solvent properties and the mechanism of solubility enhancement

Fiscal Year (FY) 2013 Objectives

- Extend solubility measurements from bulk liquids to nano-confined liquid/scaffold composites
- Validate the reported enhanced solubility for hydrogen in nano-confined hexane/mobile crystalline material (MCM)-41 composite
- Develop molecular dynamics simulations for nanoscale scaffold pore and bulk solvent liquids

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3.5) of the Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(C) Efficiency

(E) Charging/Discharging Rates

Technical Targets

This project is conducting initial studies of enhanced hydrogen solubility in nano-confined liquid solvents. Results from these studies will be applied to developing nano-confined liquid/nanoporous scaffold composite hydrogen storage materials that meet the following DOE targets:

- Specific energy: 6 wt% hydrogen (material basis)
- Energy density: 50 g/L hydrogen (material basis)

FY 2013 Accomplishments

- Developed technique for measuring hydrogen solubility in bulk and nano-confined liquids using helium purging with freeze/pump/thaw cycles for degasing and ultrasonic agitation to achieve equilibration.
- Developed methods for preparing nano-confined solvent/scaffold composites with specific and homogeneous compositions.
- Measured hydrogen solubility in nano-confined hexane/mesoporous silica (MCM-41) composite. No solubility enhancement was observed, contrary to published results.
- Developed molecular dynamics simulations of a nanoscale silica pore and bulk liquid hexane that give accurate Si-O bond lengths and hexane densities and heat capacities.

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INTRODUCTION

The prospect of storing hydrogen by dissolving molecular H_2 in a liquid solvent is compelling because dissolution is a chemically simple, readily reversible, room temperature process that occurs with low enthalpy. Despite these attractive attributes, the solubility of hydrogen in bulk liquid solvents is much too low to be technologically useful. For example, hexane, which has a relatively high hydrogen solubility, dissolves <0.2 wt% H_2 at 100 bar and <1 wt% at 700 bar. These solubilities are at least 10x too low for storage applications.

However, the solubilities of gases in liquids have been reported to be greatly enhanced when the liquid is confined within the pores of nanoporous scaffolds [1]. For example, a 16x enhancement was reported for H_2 dissolved in hexane that was confined within nanoporous silica with 3.4 nm pores while a 50x enhancement was claimed for a silica gel with 8.7 nm pores.

These enhanced solubilities are sufficiently high for practical applications. Specifically, we estimate that if an enhancement for hexane of 25x was achieved at 350 bar, then using a scaffold with a pore volume of 4 cm^3/g could enable material basis storage densities of 6 wt% and 50 g/L at room temperature. An enhancement of 25x is high but within the reported range. Attaining this enhancement at 350 bar is an extrapolation that must be tested because previous measurements have been conducted only up to 60 bar. A scaffold with a pore volume of 4 cm^3/g is very high but such pore volumes have been demonstrated.

Because of the similarity and compatibility with compress gas storage, hydrogen storage in nano-confined liquids could significantly improve compressed gas systems with minimal changes to compressed gas vehicle designs and delivery infrastructure, thus facilitating technology transition. Operation at room temperature also addresses current limitations of high capacity metal hydride materials, which require elevated temperatures, and adsorbents, which require cryogenic cooling.

APPROACH

Our approach is to study composites consisting of a liquid solvent for molecular hydrogen that is infiltrated into and confined within a nanoporous scaffold. We will investigate a variety of liquid solvents and scaffold materials. The solvents will include linear, branched, and cyclic molecules while the nanoporous scaffolds will include aluminosilicates, e.g., silica gels and zeolites, and carbon, e.g., activated carbon and carbon aerogel. Volumetric hydrogen storage measurements will be used to determine hydrogen storage capacities and explore the effects of pairing different scaffold-pore and solvent-molecule sizes, shapes, and chemistries. In addition, computational simulations will be performed to understand the mechanism of solubility enhancement by evaluating the effects of nano-confinement on liquid structure, e.g., excess molar volume, pair correlation distributions, and local ordering. Storage capacity measurements together with the simulations will be used to optimize performance and assess the possibility for hydrogen storage via enhanced solubility to meet the DOE goals.

RESULTS

To enable accurate comparison of the solubility of hydrogen in bulk and nano-confined liquids, work began by developing volumetric techniques that could be used for both types of liquids. Solubility measurements of gases in liquids, including hydrogen, have been made for more than 100 years by a variety of techniques including volumetric methods. While these techniques have been optimized for bulk liquid samples, most would not also work well for samples where the liquid is confined within the pore volume of a nanoporous scaffold. For example, bulk liquids are often mechanically stirred to achieve equilibrium solubility and evaporated under vacuum to remove dissolved gases. In contrast, nano-confined liquid/scaffold composites are often dry powders or granules, which cannot be effectively stirred, even when the scaffold pores are completely or nearly completely filled with liquid. In addition, loss of an undetermined amount of the confined liquid through evaporation during degasing is unacceptable if the composite composition is to be controlled and homogeneous. To address these issues for both bulk and nano-confined liquids, we used ultrasonic agitation and helium purging. We modified our sample fixtures to include a thin extension tube, which enabled the sample vessel to vibrate slightly and couple to the ultrasonic energy from a standard ultrasonic bath. Vibration from the bath promoted hydrogen dissolution without bulk stirring. Samples were also prepared under helium with solvent liquid that was thoroughly purged with helium to remove condensable gases such as nitrogen, oxygen, argon, carbon dioxide, and water. After loading, any dissolved helium was removed by using at least three liquid nitrogen freeze/pump/thaw cycles. This procedure yielded degased samples while preventing any loss of volatile solvent.

Figure 1 shows an example solubility measurement. Hydrogen is expanded from a reservoir into contact with a sample of bulk liquid hexane at ~1.7 hr. Over the next 0.5 hr hydrogen dissolution occurs very slowly as indicated by the slow decrease in pressure. At ~2.2 hr an ultrasonic cleaner, in which the sample vessel was immersed, was turned on for 5 min. During this interval a rapid decrease in the pressure occurred resulting from dissolution of hydrogen. At ~2.9 hr the treatment was repeated but, this time, no noticeable change occurred indicating that the dissolution of hydrogen

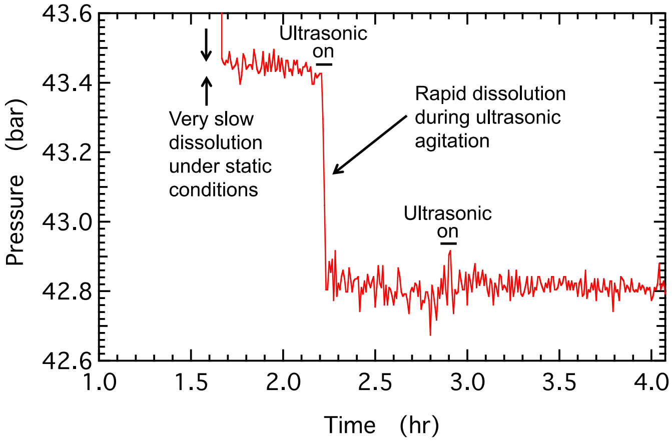

FIGURE 1. Hydrogen solubility measurement using ultrasonic agitation. The system pressure versus time is shown after exposing a bulk sample of hexane to hydrogen at ~43 bar. Under static conditions, from 1.7 hr to 2.2 hr, hydrogen uptake (dissolution) is very slow. During 5 min with ultrasonic agitation, indicated by the line segment under the "Ultrasonic on" label, rapid dissolution occurs. A second ultrasonic treatment at 2.9 hr shows no effect indicating that dissolution had reached equilibrium.

in the hexane was already at equilibrium. From the difference between the moles of hydrogen initially in the reservoir and the final moles of hydrogen in the gas phase, determined by calibrating the system volumes and measuring the initial and final pressures, the moles of dissolved hydrogen and, thereby, the hydrogen solubility was determined. This technique is applicable to both bulk and nano-confined liquid materials.

Using this procedure, the solubility of hydrogen in bulk hexane was measured as a function of pressure using two HRL Sieverts apparatus. The results are shown in Figure 2 and compared with published state-of-the-art results [2]. The error bars for the HRL data originate from uncertainty in accounting for the vapor pressure of the hexane. The positive error direction gives the solubility assuming that the hexane vapor pressure was equal to its equilibrium value, while the negative direction assumes zero vapor pressure. Thus far, we have been unable to convincingly determine the actual hexane pressure during the hydrogen solubility measurements. The solubilities from both apparatus agree with each other and with published values to within ~15%.

After establishing measurements on bulk liquids, nano-confined liquid/porous scaffold composites were carefully prepared. Scaffolds were first thoroughly dried by heating at ~250°C under dynamic vacuum for ~10 hr. The scaffolds were then backfilled with helium and infiltrated with helium-purged solvent under a helium atmosphere. Scaffold filling was expressed as vol%, i.e., the fraction of the scaffold pore volume that was filled with solvent. This filling was determined by weight using the accepted bulk liquid density and the scaffold pore volume, determined separately by nitrogen adsorption. To ensure that the solvent was homogeneously distributed throughout the scaffold, liquid/scaffold composites were place in a sealed volumes and heated to ~85°C for several days. Homogenized composites were connected to a Sieverts apparatus and degased using freeze/pump/thaw cycles with liquid nitrogen.

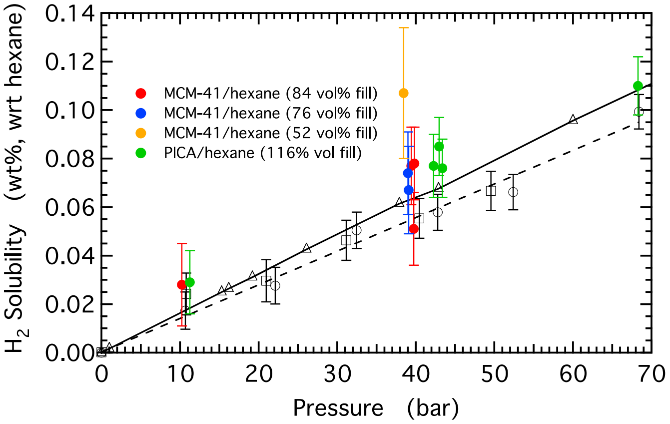

FIGURE 2. Hydrogen solubility in bulk and nano-confined hexane. Open symbols show hydrogen solubility in bulk hexane from reference 2 (open triangles) and two HRL Sieverts apparatus (open circles and squares). The Henry's law constants, proportional to the slope of the linear fits, are equal for the HRL data (dashed line) and ~15% lower than the published data (solid line). The error bars for the HRL data reflect the uncertainty introduced by the vapor pressure of hexane as described in the text. Several nano-confined hexane composites are shown, as indicated (filled circles) with varying volume fillings for hexane/MCM-41 and for hexane/PICA activated carbon.

Hydrogen solubilities for nano-confined hexane/scaffold composites are shown in Figure 2. The solubility is expressed as wt% hydrogen with respect to the mass of hexane to facilitate comparison to bulk hexane. The first composite studied was hexane/mesoporous silica (MCM-41). This composite was chosen because a 16x hydrogen solubility enhancement was reported for this system [1]. In addition, MCM-41 mesoporous silica is commercially available and has a well characterized and controlled structure consisting of hexagonally close-packed 1-dimensional pores with 3.4 nm diameter hexagonal cross sections [3]. Composites with volume fillings of 52%, 76%, and 84% showed no enhancement in hydrogen solubility within the uncertainty given by the hexane vapor pressure. In addition, a hexane/PICA activated carbon composite was tested as a function of pressure. PICA activated carbon is a microporous carbon with <2 nm slit-shaped pores. Again, no enhancement was observed.

The lack of enhancement for the hexane/MCM-41 composite is in contrast to published results, which claim a 16x enhancement. A comparison is shown in Table 1. Hydrogen capacities for the empty MCM-41 scaffold and bulk hexane are roughly similar, within ~2x. However, the capacities for the hexane/MCM-41 composites and the enhancement factors relative to both the bulk hexane and the empty scaffold differ considerably. While a 15.9x enhancement is reported with respect to bulk hexane, our measurement gives 1x. With respect to the empty scaffold a 3x increase was claimed whereas our measurements show a decrease, ~0.5x. The origin of this discrepancy is not clear. However, preparation of the composite in the published results was reported to include evacuation at room temperature. This procedure seems questionable considering the volatility of hexane.

An effort was made to resolve these discrepancies with the published results by contacting the Le Centre National de la Recherche Scientifique (CNRS) group. Through email exchanges, the difficulty of these measurements was stressed and alternative solvents and scaffolds were suggested. However, no specific, actionable advice regarding the hexane/MCM-41 composite was received. At this point we plan move beyond this system and screen a variety of solvent/scaffold composites to experimentally verify an enhanced solubility effect.

In parallel with the experiments described above, computational verification of an enhanced solubility effect was studied using molecular dynamics simulations. To begin, simulations of an empty scaffold and a bulk solvent were conducted separately. These simulations will eventually be

TABLE 1. Comparison of Hydrogen Capacities for Hexane/MCM-41 Composite

Hydrogen Capacity	Bulk n-Hexane (mmol/cm^3)	Empty MCM-41 (mmol/cm^3)	Composite Hexane/MCM-41 (mmol/cm^3)	Capacity ratio wrt bulk hexane	Capacity ratio wrt empty MCM-41
CNRS Chem Phys Lett 2010 JACS 2012	0.17	0.87	2.7 (60 vol%)	15.9 x large enhancement	3.1 x large enhancement
HRL	0.185	0.4 ± 0.1	0.19 (52 vol%) 0.18 (76 vol%) 0.18 (84 vol%)	1.03 x 0.97 x 0.97 x no enhancement	0.48 x 0.45 x 0.45 x lower

CNRS - Le Centre National de la Recherche Scientifique; wrt - with respect to

combined, and the solvent will be simulated confined within the scaffold with an ultimate plan to also include dissolved H_2. All simulations were performed using the large-scale atomic/molecular, massively parallel, molecular dynamics simulator, developed by Sandia National Laboratories, with chemistry at Harvard macromolecular mechanics force fields. These force fields are Lennard-Jones potentials with variable cutoff distances and widths.

Simulation of the scaffold began with bulk silica followed by simulations of a nanoscale silica pore. The initial and final configurations of a ~2-nm diameter silica nanopore are shown in Figure 3. The final Si-O bond length is 0.1626 +-0.0027 nm, which agrees well with experimental values of 0.1600 nm to 0.1615 nm. After running the simulation for 2,000 ps, more disorder is seen near the pore, reflecting relaxation to minimize the pore energy. This simulation of a silica scaffold is now ready for inclusion of a liquid solvent, such as hexane.

Simulation of bulk liquid hexane is shown in Figure 4. Over the course of the simulation at 300 K, the density rises as the periodic volume contracts from an intentionally chosen dilute initial state. The final simulated density of 0.662 g/cm^3 agrees well with the experimental density of 0.659 g/cm^3. The heat capacity was also determined by performing simulations and monitoring the enthalpy at several temperatures, from 250°C to 300°C. The heat capacity was found to be extremely sensitive to the Lennard-Jones potential cutoff distance and cutoff length. When optimized, a heat capacity of 216 J/mol-K was obtained, ~9% larger than the experimental value of 198 J/mol-K. This simulated hexane will next be used in a confined configuration formed with perfectly reflective smooth walls in two dimensions while retaining a periodic boundary in one direction.

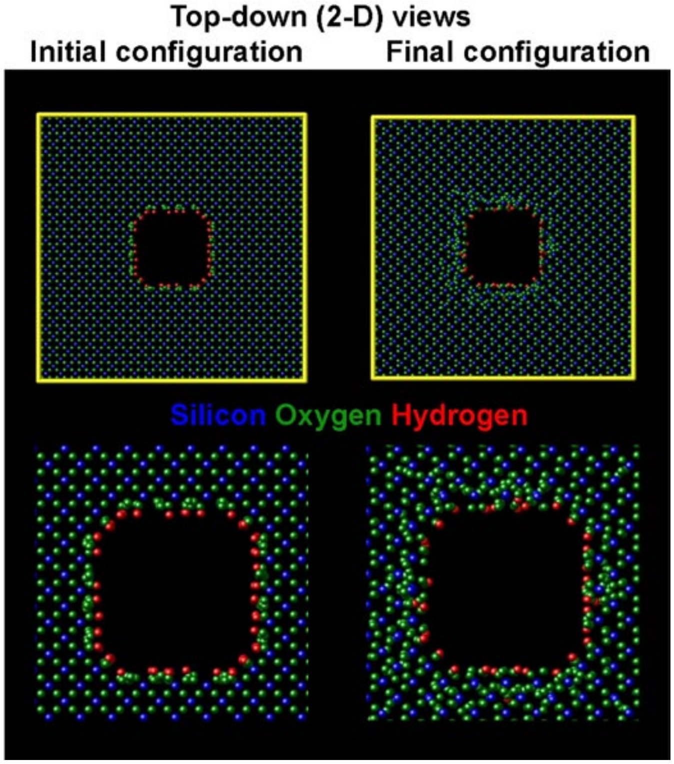

FIGURE 3. Molecular dynamics simulation of silica nanopore. Top-down 2-dimensional views are shown of the initial configuration (left) and final configuration (right); (top) full view and (bottom) close-up of pore. The overall volume with periodic boundary conditions is ~6.5 x 6.5 x 6.5 nm^3 containing ~16,000 atoms with an ~2-nm diameter pore. The surface of the pore contains Si-O-Si and Si-OH surface terminations. The simulation temperature is 300 K.

SUMMARY

Techniques have been developed for accurate measurements of hydrogen solubility in both bulk and nano-confined liquids. An attempt to verify the enhanced solubility reported for hydrogen in the nano-confined liquid/porous scaffold composite, hexane/MCM-41, was unsuccessful. Work is continuing to test for enhanced solubility in a variety of liquid/scaffold composites. Molecular dynamics simulations have also been developed for a silica nanopore and bulk liquid hexane. These simulations will next be combined to look for changes in the structure of nano-confined hexane.

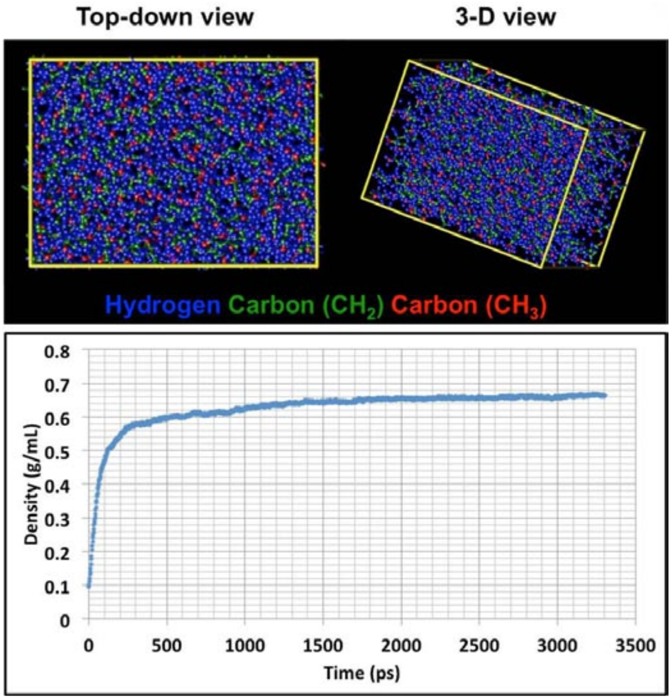

FIGURE 4. Molecular dynamics simulation of bulk liquid hexane. (top) Top-down and 3-dimensional views. (bottom) Hexane density during simulation. 250 hexane molecules were simulated at 300 K. The final volume was 4.5 x 3.25 x 3.7 nm^3 with periodic boundary conditions.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Room temperature hydrogen storage in nano-confined liquids, Presentation to the Hydrogen Storage Tech Team, Southfield, MI, September 20, 2012.

2. Room temperature hydrogen storage in nano-confined liquids, Presentation at the Hydrogen Storage PI Meeting, Washington, DC, November 27, 2012.

3. Room temperature hydrogen storage in nano-confined liquids, Presentation at the 2013 DOE Fuel Cell Technologies Program Annual Merit review, Crystal City, Virginia, May 2013.

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1. V. Rakotovao, R. Ammar, S. Miachon, M. Pera-Titus, “Influence of the mesoconfining solid on gas oversolubility in nanoliquids”, *Chem. Phys. Lett.*, **485**, 299-303 (2010).

2. E. Brunner, “Solubility of Hydrogen in 10 Organic Solvents at 298.15, 323.15, and 373.15 K”, *J. Chem. Eng. Data*, **30**, 269-273 (1985).

3. http://www.zeolite.utm.my/images/mcm41.gif.