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Room Temperature Hydrogen Storage in Nano-Confined Liquids

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Project ID # ST102

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Overview

Timeline

- Project start date: 1 April 2012 (*est*)
- Project end date: 31 March 2015
- Percent complete: 0%

Technical Barriers

- A. System weight and volume
- C. Efficiency
- E. Charging and discharge rates

Budget

- Total project funding
  - DOE share: $1.2M
  - Contractor share: $0.3M
- Funding received in FY11: $0 (*new project*)
- Funding for FY12: $0.25M (*planned*)

Partners

- No partners

Project Goals and Objectives

Goal

Develop hydrogen storage materials with (*material basis*) hydrogen densities of ≥ 6 wt% and 50 g/l at room temperature and <350 bar that are compatible with the vehicle engineering and delivery infrastructure for compressed gas storage

Overall Objective

Use measurements and simulations to characterize, understand, and optimize the (*enhanced*) hydrogen storage capacity of liquids confined within the pore volume of nanoporous scaffolds

For March 2011 – March 2012

N/A (*new project*)

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Background/Motivation

- **Always interested in whether dissolution in liquids could be used to store hydrogen (***because it seems simple: molecular, relatively fast, near RT, low ΔH***)**
  - **A simple answer for bulk liquids is – No, solubility is much too low:**
    eg*, S(H_2/hexane, RT, ~100 bar***) = 8 mole% = 0.18 wt%**
    S(*H_2/hexane, RT, ~700 bar***) = 0.97 wt%**
  - **Need (***at least***) a 10x increase in solubility**

- **Solubility of H_2 may be viewed as the "molecular" limit of adsorbents:**
  activated carbon (*σ = 100's to 1000's m^2/g***)** $\rightarrow$
  single graphene layer thick carbon (*σ = 2600 to ~3500 m^2/g***)** $\rightarrow$
  MOFs (*σ = >4000 m^2/g***)** $\rightarrow$
  individual molecules (*σ > 10,000 m^2/g??***)**

- **Focus on maximizing the number of H_2 binding sites**
  (*don't worry about adsorption energy, make up for it with pressure and lots of sites***)**

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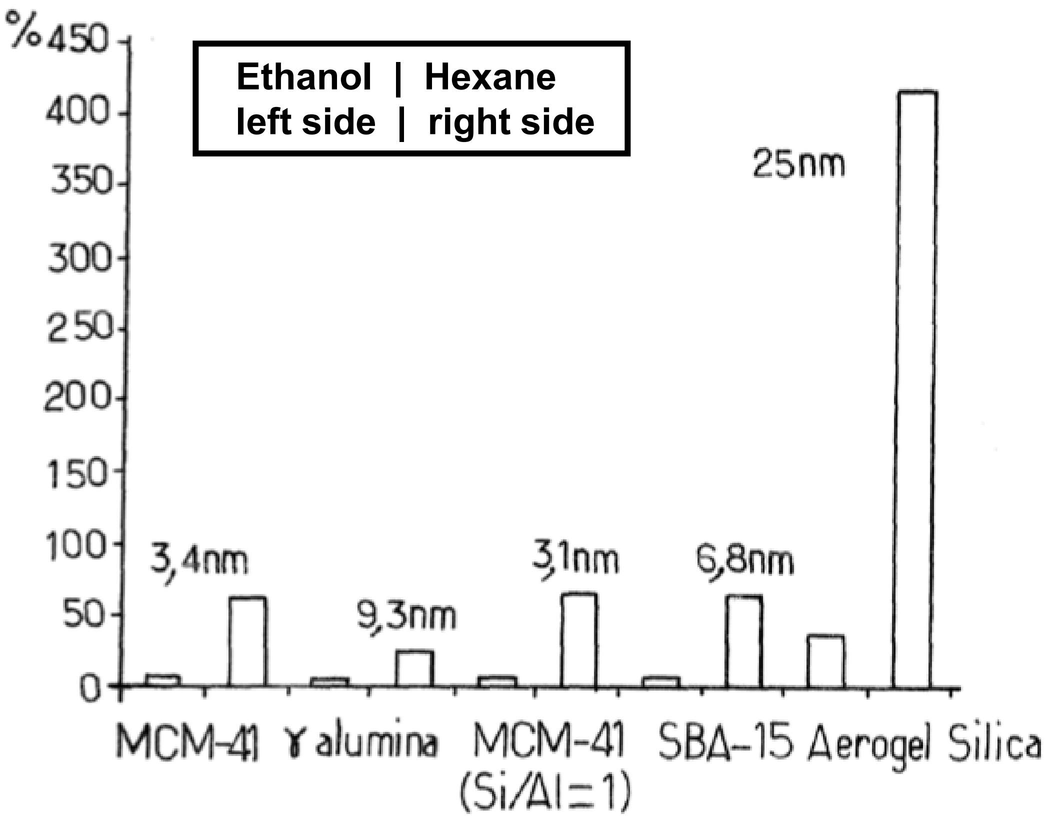
Enhanced Solubility in Nano-Confined Liquids

- **Marc Pera-Titus and coworkers (***Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS – Université de Claude Bernard Lyon, Villeurbanne Cedex, France***) have studied the solubilities of gasses in solvent liquids that are nano-confined, within porous scaffolds**

- **They report solubilities that are enhanced relative to the bulk, for example:**
  - **H_2 in CCl_4 (***confined in nanoporous Al_2O_3***) – a 4.4 x enhancement**
  - **C_2H_6 in CCl_4 (***confined in nanoporous Al_2O_3***) – a 2.3 x enhancement**
  - **CH_4 in CCl_4 (***confined in nanoporous SiO_2***) – a 2.1 x enhancement**
  - **H_2 in H_2O (***confined in nanoporous Al_2O_3***) – a 6.3 x enhancement**
  - **H_2 in hexane (***confined in nanoporous Al_2O_3***) – a 13.8 x enhancement**
  - **H_2 in hexane (***confined in MCM-41***) – a 16 x enhancement**
  - **H_2 in hexane (***confined in silica gel with 8.7 nm pores***) – a 50 x enhancement**

Enhanced Solubilities

Hydrogen solubilities (*From US 2010/0089238 A1*)



Definition of solubility
(*expressed as percent*)

$\ell_g = C_L(\mathrm{mol/L})/C_g(\mathrm{mol/L}) \cdot 100\%$

C_L = liquid phase mole density

C_g = gas phase mole density

ℓ_g = 100% is equal in-gas and in-liquid densities (*Note: >100% solubility is required for improvement over compressed gas storage*)

- **Solubility > 50% for several scaffolds**
- **Extremely high solubility (*>400%*) reported for H_2/hexane/silica gel**

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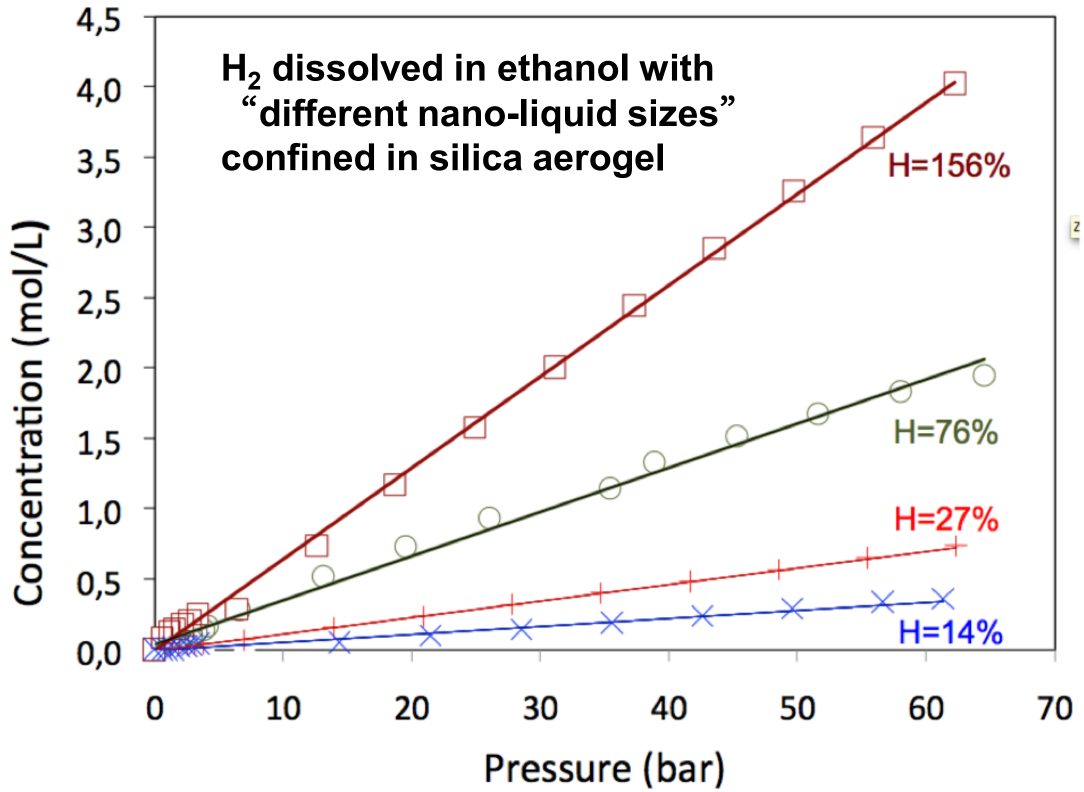
Enhanced Solubility: Higher Pressures

Hydrogen dissolved in nano-confined ethanol

Enhanced hydrogen solubility in nanosized ethanol and n-hexane confined in a silica aerogel matrix, *Unpublished conference abstract* 2010



- Data extends maximum pressure from 4 to 60 bar, >10 x increase
- Highest capacity data (*4 mol/L*) shows 156% solubility, linear up to 60 bar

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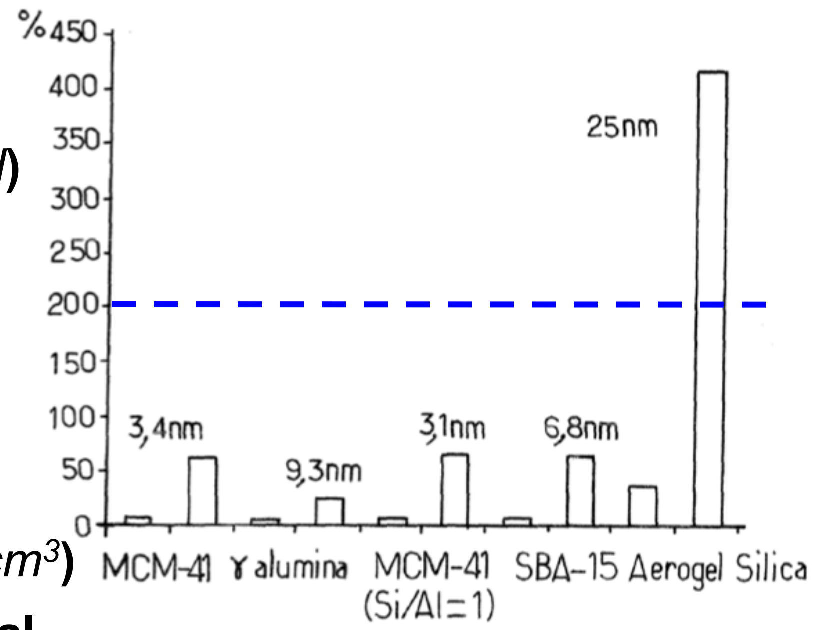
Technological Prospects

What gravimetric and volumetric storage densities could be obtained?

1) **Assume a solubility = C_L/C_g of 200% for H_2 in, *eg*, nano-confined hexane** (*high, but within demonstrated range*)

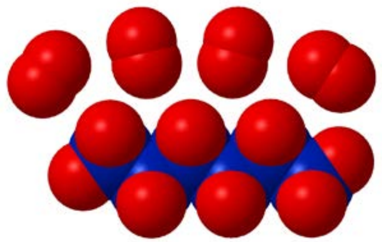


2) **Assume 200% can be achieved at 350 bar** (*big assumption, but 156% at 60 bar reported*)

- **$C_g(H_2@350\ bar)$ = ~14.5 mol/L**
- **Therefore, C_L = 29 mol/L**

3) **Assume 4.0 cm^3/g pore volume scaffold** (*very high but possible, demonstrated*)

- **4.0 cm^3 gives 2.64 g-hexane** ($\rho = 0.66\ g/cm^3$)
- **1 g-scaffold + 2.64 g-hexane = 3.64 g-total**
- **29 mol/L in 0.004 L gives 0.23 g-H_2**
- **0.23 g-H_2/3.64 g gives ~6 wt% H_2** (~3.5 H_2/C_6H_{14})
- **0.23 g-H_2 in (*est*) 0.0045 L gives 50 g-H_2/L**



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Issues/Opportunities

1) Achieving solvent/scaffold with sufficient H_2 solubility (*eg, 200%*)

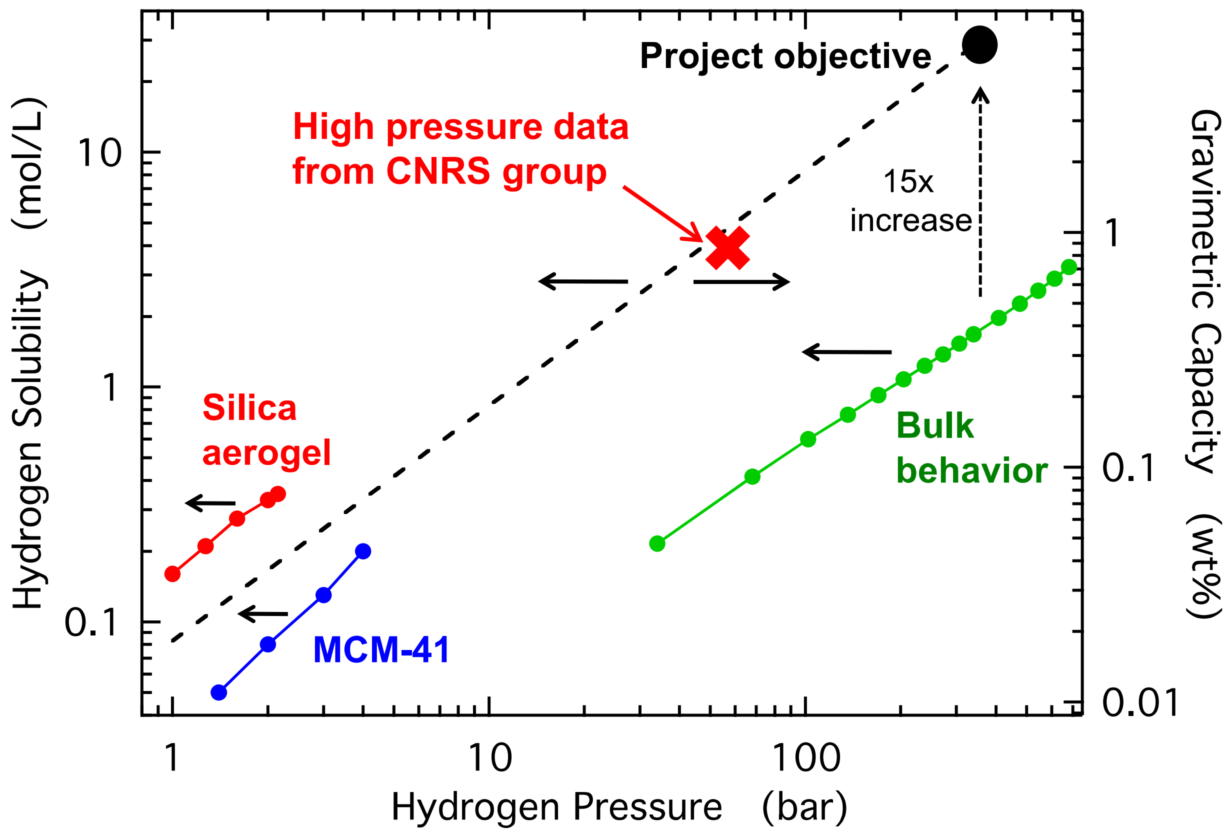
- **only a small number of scaffolds tested (***mainly porous silica's and alumina's***)**
- **there is a large range of possible scaffold materials to try, *eg*:**
  - **carbon's (***activated, aerogel, mesoporous, templated***)**
  - **MOF's**
  - **porous polymers**
- **other than the relationship with pore size, what determines the solubility is unknown (***ie, why does hexane in 8.7 nm silica aerogel give 400%***), *eg*:**
  - **solvent size/pore size systematics**
  - **solvent functional groups**
  - **pore surface chemistry**

2) Recovered hydrogen will be contaminated by solvent vapor

- **engineering solutions (***eg, selective membrane/filter, condense and recycle***)**
- **material solutions:**
  - **use higher molecular weight solvents**
  - **use ionic liquids with alkyl side chains**
  - **polymerize or oligomerize solvent**
  - **tether solvent to scaffold**

This Project

Hydrogen storage in nano-confined solvent/porous scaffold composites



Details:

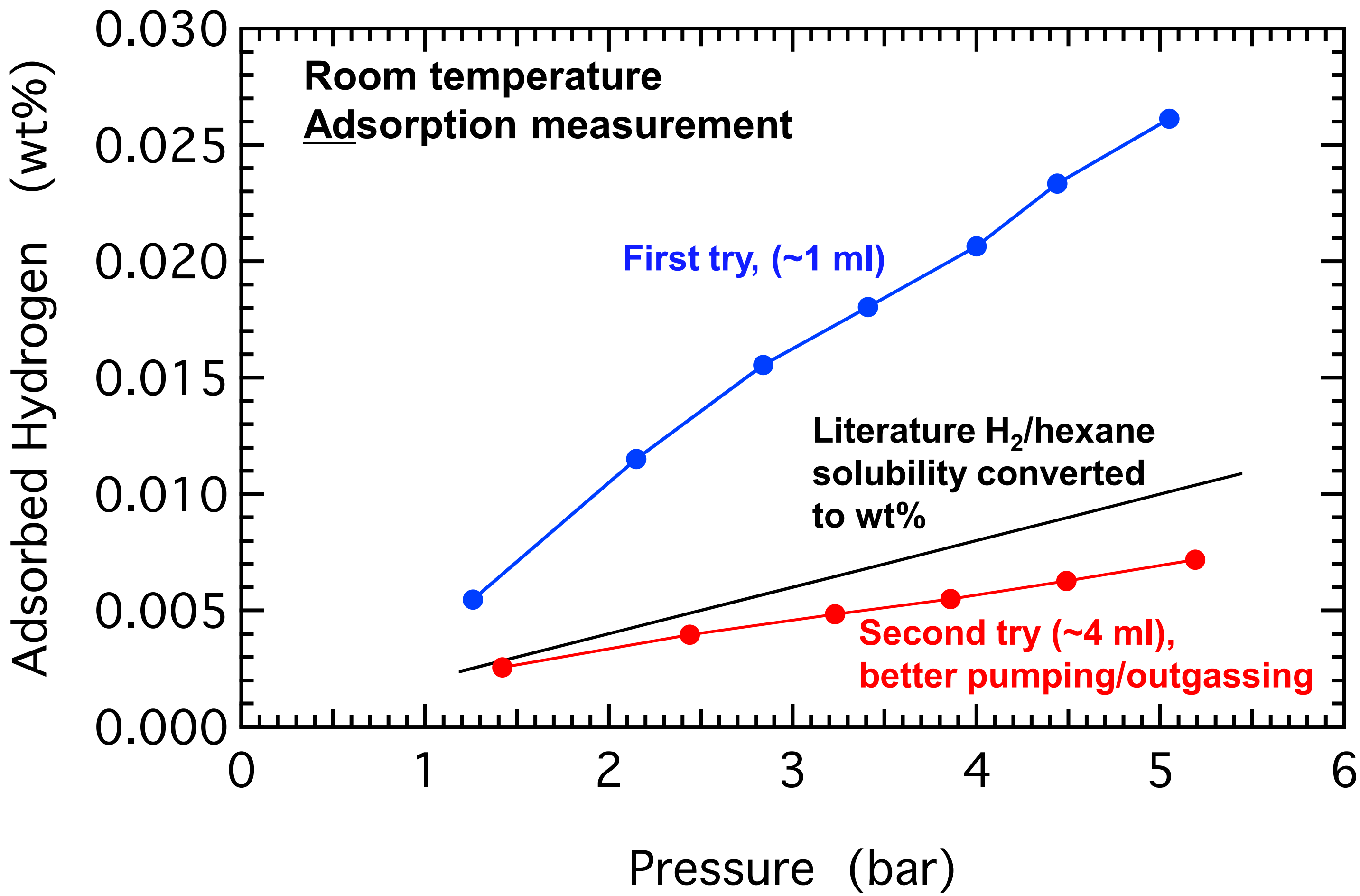
- **data for hexane**
- **except single high pressure data point, which is for ethanol**
- **gravimetric capacity axis assumes 200% solubility in hexane and 4 cm³/g pore volume scaffold**

- **Validate and understand enhanced solubility effect**
- **Implement/advance effect to achieve storage targets**

Accomplishments –

Preliminary work: Solubility Measurements

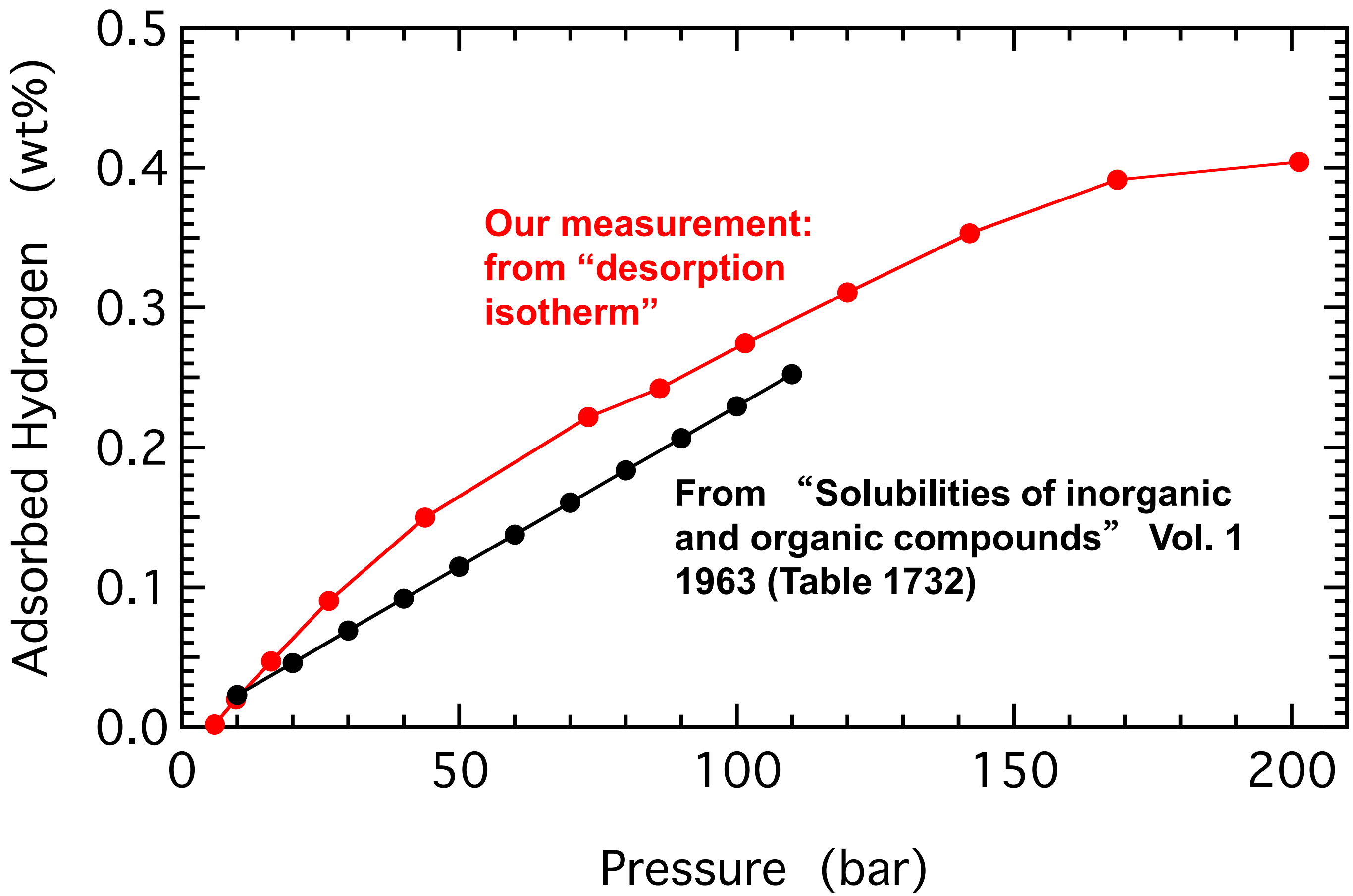
Using volumetric apparatus to measure H_2 solubility in bulk hexane at <~5 bar



- **2nd measurement within 30% of literature value (*need to show consistency*)**
- **Next, adopt technique for nano-confined liquids**

Preliminary Work: High Pressure Measurements

Try to measure H_2 solubility in bulk hexane as a "desorption isotherm"



- **Data shows distinct curvature (*OK for first try, but need better*)**
- **Loss of solvent due to vapor pressure may be issue**

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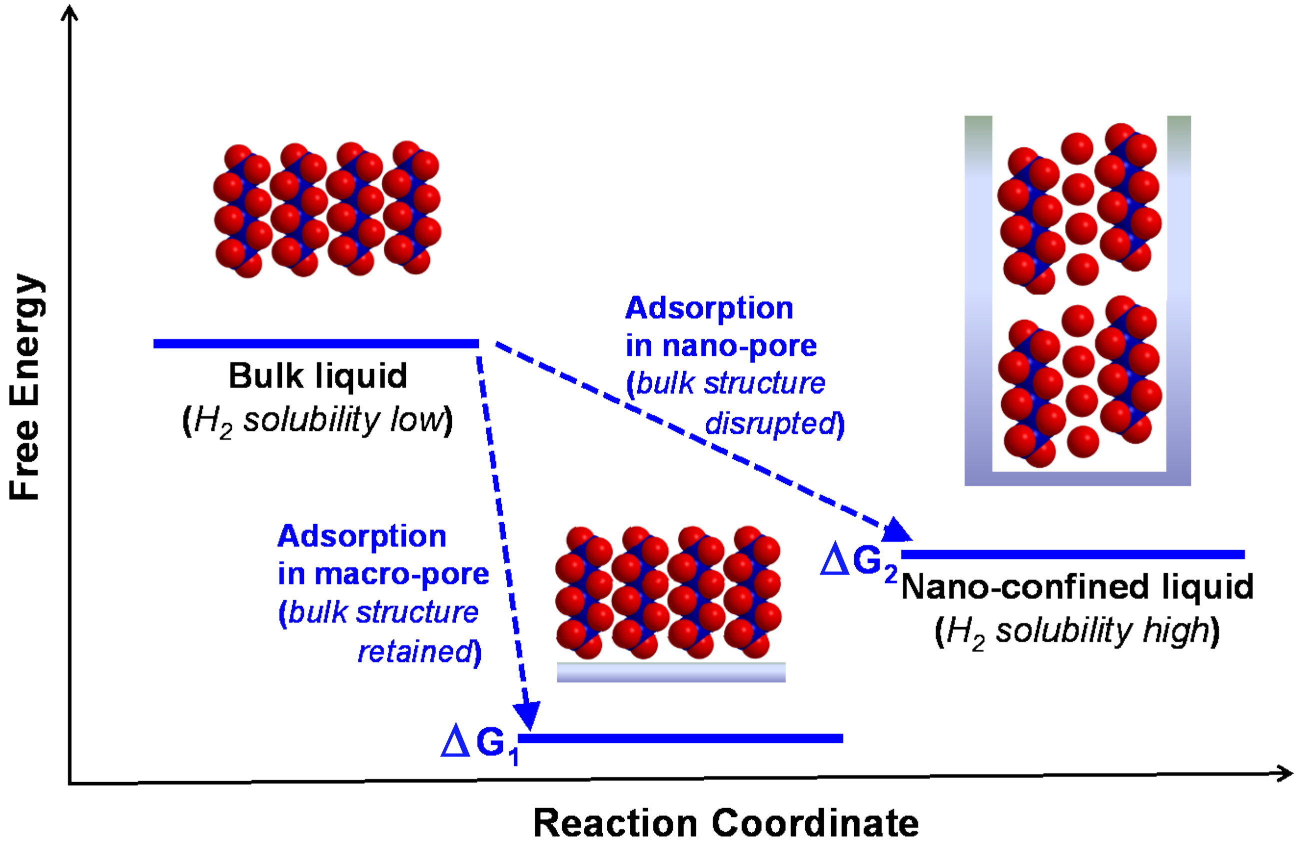
Mechanism for Enhanced Solubility: Our Thoughts



- **Simulation effort will try to test and understand this mechanism**

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Tasks/Milestones/Go/No-Go: Phase 1

Task 1: Perform hydrogen sorption measurements at high pressure

1.1 Adapt volumetric adsorption apparatus for handling volatile liquids

1.2 Measure hydrogen storage in solvents confined in nanoporous scaffolds

Task 2: Optimize scaffold/liquid composition to optimize capacity

2.1 Investigate effect of nanoporous scaffold composition

2.2 Investigate effect of scaffold architecture

2.3 Investigate effect of scaffold surface chemistry

2.4 Investigate the effect of solvent

Task 3: Theory and mechanism

3.1 Molecular simulations to describe candidate hydrogen sorption models.

3.2 Determine thermodynamic parameters

3.3 Validate theoretical simulation results with experiments

Task 4: Reduced liquid vapor pressure

4.1 Investigate oligomerization/polymerization

Task 5: Project management

Milestones:

- Month 6: accurately measure H_2 solubility
- Month 12: measure storage in nano-confined liquid up to 100 bar
- Month 18 **(Go/No-Go)**: demonstrate possibility to achieve 1 wt% storage

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Tasks/Milestones: Phase 2

Task 6: Extend hydrogen sorption measurements to higher pressure

6.1 Upgrade system for measurements up to 350 bar

Task 7: Optimize scaffold/liquid composition to optimize capacity

7.1 Investigate downselected scaffold compositions for >1 wt%

7.2 Investigate downselected scaffold architecture for >1 wt%

7.3 Investigate downselected scaffold surface chemistry for >1 wt%

7.4 Investigate downselected solvents for >1 wt%

Task 8: Theory and mechanism

8.1 Use simulation to guide optimization

8.2 Perform kinetic measurements to determine exchange rates

Task 9: Reduced liquid vapor pressure

9.1 Optimize oligomerization/polymerization and determine H_2 composition

Task 10: Project management

Milestones:

- Month 24: demonstrate mechanism to achieve 2 wt% (<200 bar, >1 g sample)
- Month 36: demonstrate mechanism to achieve 6 wt% (<350 bar, >5 g sample)

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Summary

- **Recent reports claim enhancements of ~2x up to 50x for the solubility of gasses, including hydrogen, in liquid solvents that are nano-confined within scaffolds having pore sizes <~10 nm**

- **For the best cases, reported absolute solubilities for hydrogen exceed 100% (***up to 400% has been claimed***), which gives an increased volumetric density in the dissolved phase relative to the pure compressed gas phase**

- **Estimates indicate that with a solubility of 200% at 350 bar and a scaffold with a pore volume of 4.0 cm^3/g, material-based hydrogen storage densities at room temperature of 6 wt% and 50 g/L are possible**

- **This phenomena has not been thoroughly explored (***only a limited number of solvents and scaffolds have been characterized***) or understood**

- **This approach has the potential to significantly improve the capacity of compressed hydrogen systems with minimal changes to vehicle engineering and delivery infrastructure, thus facilitating technology transition**