

## IV.C.1f Nanoengineering the Forces of Attraction in a Metal-Carbon Array for H<sub>2</sub> Uptake at Room Temperature

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### Objectives

- Create nanoengineered fibrous storage media with uniform pore size and begin development of graphene-based media based on knowledge of carbon nanotube (CNT) chemistry
- Measure hydrogen uptake in partnership with the National Renewable Energy Laboratory (NREL).
- Verify and develop an understanding of enhanced H<sub>2</sub> uptake and the “nanopump” concept.
- Develop intercalation methods for lithium and other metals without aggregation.
- Design layered carbon-metal media with nanoengineered attractive forces capable of exceeding 80 g/L volumetric uptake of dihydrogen at -20°C, by controlling four forces: 1) van der Waals attraction, 2) dipole induced-dipole attraction, 3) charge induced-dipole attraction, and 4) Kubas-type interaction for transition metal atoms.
- Design for dynamic equilibrium: high density dihydrogen “visits” all sites; hence H<sub>2</sub> is not bound to any particular surface or any metal atom.

### Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) Cost
- (C) Efficiency
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Technical Targets

- A. The 3-dimensional nanoengineered scaffold exhibits 2x greater uptake per unit surface area than most carbon materials. The target is a metal intercalated rigid scaffold that will adsorb high density dihydrogen at room temperature (RT) to meet DOE goals for weight and volume.
- B. The alternating layer graphene-metal scaffold is readily made from graphite, sulfuric acid with common metal atom intercalants – all very low cost precursors to make a low cost storage media.
- C. This dihydrogen physisorption process has no energy barrier, minimizing energy consumption.
- J. Single wall nanotubes (SWNTs) best known uniaxial thermal conductor; graphene a superb conductor for thermal management.
- P. The engineered nanopore is understood by a thermodynamic model developed for high density H<sub>2</sub> uptake at both cryogenic temperature and ambient temperature, and results of measured uptake.

Storage Parameter	Units	2010 System Target	Nanoengineered fiber (FY 07)	Nanoengineered graphene (media only) FY 08
Specific Energy	kWh/kg (wt% H <sub>2</sub> )	2.0 (6 wt%)	0.67 2.0 wt%	Calculated 3.5 kWh/kg 10.9 wt%; 9.5 wt% excess
Volumetric	kWh/L g/L	1.5 45 g/L	Density = 1 0.67	Calculated 2.7 kWh/L 81 g/L; 71 g/L excess capacity
Desorption temperature	K	2 bar min	>77 K	Calculated ≥253 K
Plateau Pressure	bar	2 bar min	Measured 2 bar	100 bar fill/ desorb ≥2 bar

Fiscal Year 2008: Calculated gravimetric H<sub>2</sub> using K atom on a post and Ru in the crosslinker (H<sub>2</sub> delivered)

## Accomplishments

1. We used fluorination to compromise the  $sp^2$  character of the nanoengineered pore, reducing the enhanced  $H_2$  uptake from 2x down to only 1.1x, and thereby gaining understanding of the 2x enhancement mechanism of the “nanopump” to produce high density  $H_2$  uptake that is crucial for the design of nanospaces for high volumetric and gravimetric uptake.
2. We developed a slit-pore design with four nanoengineered forces of attraction using alternating layers of graphene and metal atoms to provide high efficiency thermodynamic compression of hydrogen such that a  $-\Delta F = 13$  kJ/mol is calculated to yield 81 g/L volumetric and 10.9 wt% gravimetric  $H_2$  capacity (delivered), and began nano-construction of the media with anchored metal atoms and a graphene crosslinked scaffold.
3. We are transitioning via our CNT expertise to use thermally conductive graphite which well under \$1/kg in bulk and build nanoengineered scaffolds using other very low cost major components of sulfuric acid, and e.g., calcium and iron, to also meet DOE cost targets for the media.



## Introduction

For energy efficiency, reduced volume, and ease of use, it is desirable that the storage media operate near RT. And the media should be made from low-cost materials.  $H_2$  packing density into the pores may be greatly enhanced by a strongly favorable equilibrium constant. In addition to the nanoengineered framework, we are also nanoengineering the forces of attraction so the hydrogen molecules will experience just the right potential when it enters the pore. This allows optimization of a “just right” free energy that reversibly packs hydrogen into the pore at ambient temperatures which will also have high efficiency and fast kinetics. A straightforward thermodynamic model shows that this “nanopump” approach will provide a considerably higher volumetric capacity compared most other approaches for storing dihydrogen. It has high energy efficiency, unlimited cycling, fast kinetics, and is constructed of very low cost materials with superb thermal conductivity. Due the design using weak-binding metals, accidental oxidation may be readily reversed in situ, mitigating long-term degradation.

## Approach

All of the work here is directed towards construction of the target media of an alternating graphene-metal nanoengineered scaffold, and

nanoengineering the forces of attraction that will strongly pull the dihydrogen into the pore. All sites intentionally have enthalpy too low to individually bind  $H_2$ . With four forces working collectively to attract the dihydrogen into the pore,  $H_2$  is held in the pore as a high density gas. This is the concept of the nanopump. This avoids the problem of site-specific binding to a metal and the risk of irreversible chemisorption binding to the metal, and the large entropy penalty of site-specific is most beneficial in inhibiting this. The averaging effect of diffusion also eliminates the problem of a wide range of binding energies that would require a very wide range of desorption temperatures. Many experiments are needed to bring about this entropy-friendly design. These include developing appropriate expansion and crosslinking methods, transferring this methodology from SWNT to graphene to make the slit-pores, constructing parking spots for the metal atoms, and determining that they are stable. We also developed the design that would provide favorable thermodynamics for high density  $H_2$  uptake. Many accomplishments work synergistically in making the metal-graphene scaffold. To enhance understanding of the nanopump concept, we intentionally disrupted the  $\pi$  cloud as a control.

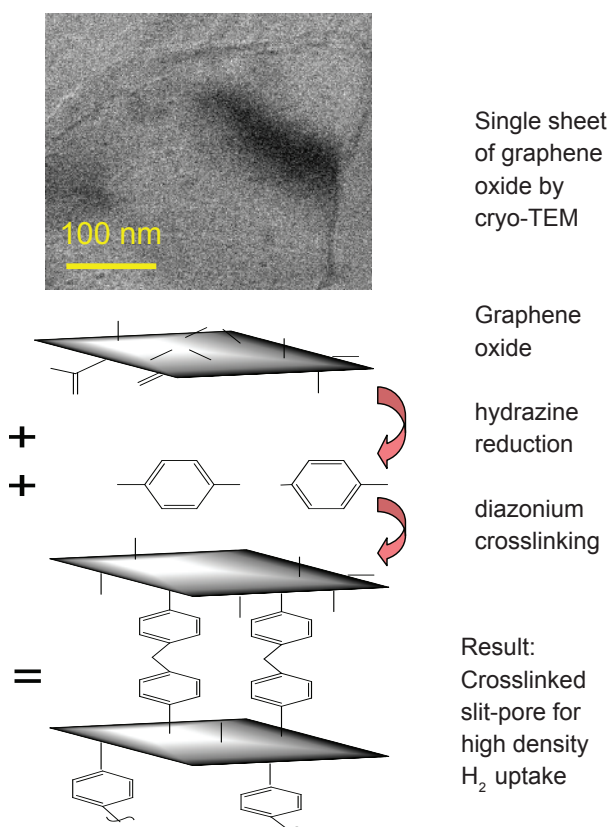
## Results

Experiments all have a common purpose: making the new scaffold design with four nanoengineered forces of attraction for RT uptake of high density  $H_2$  to equal or exceed 2015 volume and weight goals (media).

**Single sheet graphene** is now being developed as a new material for nanospace engineering, and functionalization transfers our SWNT expertise into the field of single sheet graphene functionalization chemistry. We have shown that graphene can also be crosslinked to make rigid nano slit pores (Figure 1). This also opens the door to low cost media; the main ingredient, graphite is well under \$1/kg, which is solubilized with sulfuric acid + oxidizer and intercalated with metals, e.g., calcium, iron, all very low cost.

**Metal intercalation** has yielded preliminary results which show that metals may be intercalated into the separated graphene sheets as has been previously done with CNTs. This is a necessary first step towards making the layered metal scaffold.

**Fluorination disrupts the enhanced uptake** which is the control experiment yielded the understanding that in addition to the nanoporous structure of the fiber, the  $\pi$  cloud of  $sp^2$  carbon is necessary for the high density 2x enhancement in packing of the pore; this enhancement was reduced to 1.1x (see Figure 2). Fluorination also provides a non-acidic expansion method that has yielded a large pore spacing of 1.3 nm, getting very close to our design target of 1.5 nm for the metal-layered scaffold for  $H_2$  uptake at RT.

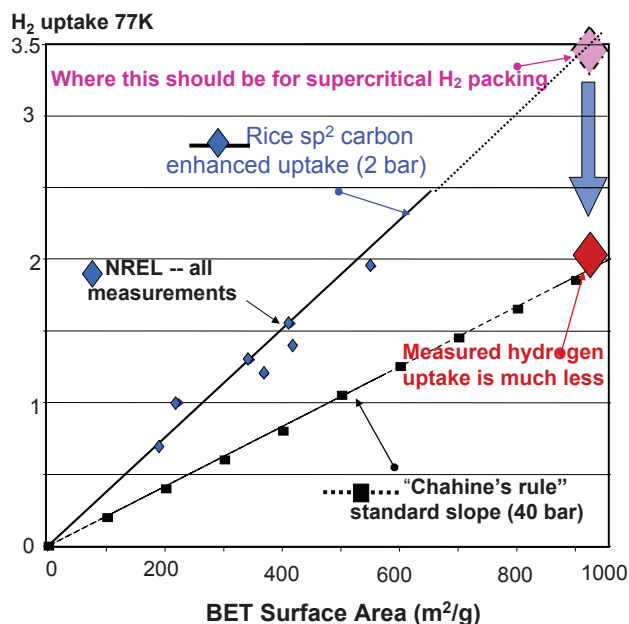


**FIGURE 1. Constructing the Graphene Slit Pore** – Graphite is converted to water soluble graphene oxide as individual sheets (transmission electron microscopy). It is reduced with hydrazine in a surfactant to prevent aggregation. These sheets are crosslinked using a bifunctional diazonium salt. These species become crosslinkers between the graphene sheets to make a rigid layered nanoporous structure. This new type of engineered nanospace makes slit pores with width determined by the length of the crosslinking molecule. (TEM - transmission electron microscopy)

**A monitor for metal atom migration** has been developed. Neutral metal atoms deposited by e-beam evaporation onto the ends of a CNT array migrated and clustered in the presence of hydrogen at 200°C, compared to -100°C. Understanding and controlling metal migration is essential for RT  $H_2$  uptake.

**A parking spot for Li metal atoms** demonstrated that they have been attached to a pyridine post to provide a secure spot elevated above the surface. The Raman G-band shift shows that charge transfer still takes place between the metal atom and the  $\pi$  cloud, with up to 0.05 electron/carbon. Calcium doping of expanded and crosslinked fibers has also been tested, with successful charge transfer, an essential step for a metal-enhanced nanoengineered forces to nanopump the  $H_2$  into the pore.

**Designed nanoengineered metal-graphene layered structure** with tailored pore size and nanoengineered forces that create a  $-\Delta F = 13$  kJ/mol and equilibrium

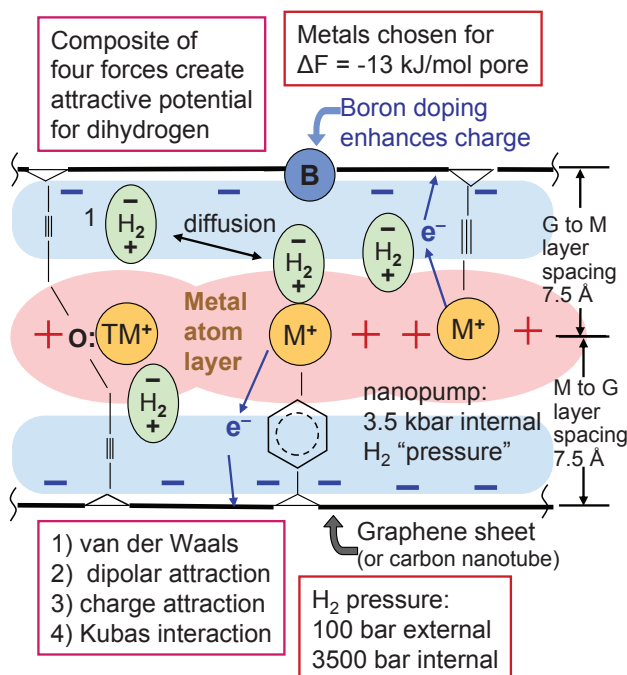


**FIGURE 2. Supercritical Uptake Inhibited** – Many measurements made for us by NREL of  $H_2$  in expanded CNT fibers shows the approximately 2x enhanced uptake at 77 K and only 2 bar and similar supercritical behavior observed by the Iijima group [2]. However, the fluorination disrupts the  $\pi$  cloud conjugation, and the enhancement is lost, as the data point falls down almost to the standard Chahine slope, ca 40 bar [3]. This provides experimental verification that is the  $\pi$  cloud responsible for the "nanopump" concept theoretically predicted by [4], [1].

constant of  $K = 35$  (corrected for fugacity) to obtain 81 g/L volumetric and 10.9 wt% gravimetric capacity for  $H_2$  (delivered) ~RT (see Figure 3.)

## Conclusions and Future Directions

- Uptake mechanism is understood: nanopump concept is verified with control at 77 K.
- Expertise in SWNT chemistry is shown to be transferable to graphene.
- Charge transfer to  $sp^2$  is verified when metal is attached to a parking spot.
- Diffusion of metal atoms can be monitored and understood.
- Calculations show that nanoengineered forces can lead to very high  $H_2$  uptake at RT.
- Transfer the enhanced hydrogen uptake concept of the CNT scaffold to the metal-graphene scaffold near RT, i.e., make the "nanopump" for dihydrogen work at RT like it did at 77 K.
- Begin  $H_2$  uptake tests on nanoengineered and layered metal-carbon pores, add temperature programmed desorption in situ ability.
- Determine conditions for  $H_2$  induced transition metal mobility.



**FIGURE 3. Alternating Charge Slit Pore Nanopump for  $\text{H}_2$  Uptake at RT** – This illustrates the concept of the alternating layers of positive metal atoms and negatively charged graphene to adjustable forces of attraction that can be tailored to provide the optimum free energy to activate thermodynamic compression at ambient temperature which pulls the  $\text{H}_2$  into the pore according to the nanopump concept [4] [1]. The cooperative forces of attraction operating on  $\text{H}_2$  (listed in the figure) are: 1) Van der Waals attraction to  $\pi$  cloud of  $\text{sp}^2$  carbon surface, 2) dipole induced-dipole attraction between (+) metal atom layer and (-) graphene layer, 3) charge induced-dipole attraction near charged metal atoms, and 4) a Kubas-type interaction for transition metal atoms [5]. Boron doping of the graphene sheet enhances the charge separation. The hydrogen is expected to freely diffuse throughout the pore, indicated by the several polarized  $\text{H}_2$  molecules in the figure. Then they will experience a composite free energy due to the overall attractive potential for the pore. With a geometry of 0.75 nm spacing between the alternating layers and the metal atoms on a 0.96 grid spacing (four graphene hexagons), a free energy  $-\Delta F = 13 \text{ kJ/mol}$ , the (fugacity corrected) equilibrium constant is 35, so that an external fill pressure of 100 bar corresponds to an internal "pressure" of 3.5 kbar.  $K$  increases exponentially, hence it doubles for  $-\Delta F$  increase of only 1.5 kJ/mol, for a reduced supply pressure and/or even higher  $\text{H}_2$  density in the pore.

- Current model shows that H only occupies about 40% of the "hard sphere" volume, for 81 g/L; can this be boosted to 60% density, for 120 g/L predicted by [1].
- Verify uptake mechanism as supercritical gas using engineered fourfold attractive forces.

### FY 2008 Presentations

1. C. Kittrell, A.D. Leonard, S. Chakraborty, H. Fan, E. Billups, R.H. Hauge, H.K. Schmidt, M. Pasquali, J.M. Tour; "H<sub>2</sub> Storage in nanoengineered scaffolds of carbon nanotubes"; International Symposium on the Hydrogen Economy, Richmond Virginia, Puru Jena chair, Nov. 12-15, 2007.

### FY 2008 Publications

1. Stephenson, J.J.; Hudson, J.L.; Leonard, A.D.; Price, B.P.; Tour, J.M. "Repetitive Functionalization of Water-Soluble Single-Walled Carbon Nanotubes" *Chem. Mater.* 2007, 19, 3491-3498.

### References

1. A. Kuc, L. Zhechkov, S. Patchkovskii, G. Seifert, and T. Heine, **7**, 1, (2007).
2. K. Murata ... S. Iijima, et al., **106**, 11132-1 (2002).
3. Pierre Benard and R. Chahine, **26** (2001) 849–855.
4. S. Patchkovskii, J.S. et al., **102**; 10439-10444 (2005).
5. Gregory J. Kubas, **635** (2001) 37–68.