IV.C.1i Nanoengineering the Forces of Attraction in a Metal-Carbon Array for H_2 Uptake at Room Temperature

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Objectives

- The primary objective is to design and produce nanoengineered carbon-metal media which is capable of achieving: 1) 65 g/L; 2) 7.5 wt% storage of hydrogen at near-ambient temperatures; 3) superior thermal management; 4) high energy efficiency; 5) 5 kg fill in 3.3 minutes; 6) 2,000 fill cycles; 7) low cost media less than $67 per kg H_2 stored; 8) 3 to 100 bar delivery; 9) near-ambient temperatures; and 10) avoid large temperature swings to obtain complete H_2 delivery.
- Develop a graphene slit-pore scaffold using very low cost ingredients to be within DOE cost targets.

Technical Barriers

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

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

Technical Targets

A. Develop nanoengineered graphene scaffolds (see Table 1) with metal atom functionalization for multilayer dynamical adsorption into the slit pore; B. The graphene-metal scaffold is readily made from low-cost graphite, sulfuric acid with common metal atom intercalants, and scalable fiber spinning to meet DOE cost targets; C. & E. The physisorption process has no energy barrier, thereby minimizing energy consumption, and no kinetic barrier for fast fill; J. Graphene has high thermal conductivity; hence use fibrous media to benefit from this; P. The uptake into the engineered nanopore is understood by a thermodynamic model.

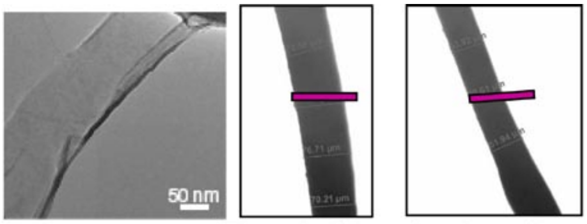
TABLE 1. Nanoengineeered Graphene Scaffolds

Storage Parameter	Units	2010 System Target	FY 2008 Nanoengineered Graphene (media only)	FY 2009 Nanoengineered Graphene
Specific Energy	kWh/kg (wt% H_2)	2.0 (6 wt%)	Calculated 2.5 kWh/kg 7.5 wt% excess capacity delivered	0.8 kWh/kg 1.4 wt% G 2.4 wt% CNT
Volumetric	kWh/L g/L	1.5 45	Calculated 2.2 kWh/L 65 g/L excess capacity delivered	Density = 1.3 18.2 g/L G 30 g/L CNT
Desorption Temp.	°K	2 bar min	Calculated $\geq$253	>77
Plateau Pressure	bar	2 bar min	100 bar fill/3 bar out	Measured at 2 bar

G – grapheme; CNT – carbon nanotube

Accomplishments

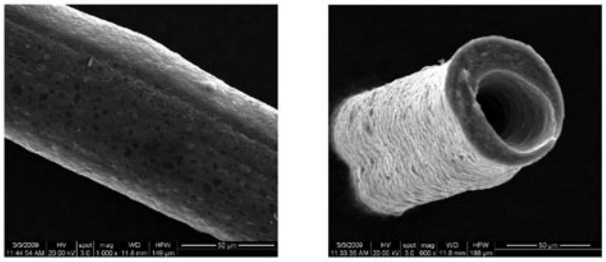
1. We produced graphene nanoribbons and used a scalable industrial-type spinning process, creating an entirely new type of fibrous nanoengineered slit pore H_2 storage media (Figure 1).
2. We created an engineered nanospace graphene slit pore scaffold and demonstrated enhanced H_2 storage properties similar to those for CNTs (Figure 2). This demonstrates our ability to transfer our extensive experience with CNT chemistry to nanoscale graphene chemistry.
3. We developed the concept of dynamic multilayer adsorption (Figure 3) with electrostatic enhancement for H_2 uptake near room temperature, with calculated excess adsorption of 65 g/L and 7.5 wt% (media only). Key steps: a) measured the enhanced H_2 uptake effect at 77 K for a graphene slit pore; and b) successful production of a charged donor-acceptor complex of sodium on CNTs (Figure 3, bottom).



graphene nanoribbon, TEM

Expanded fiber Crosslinked = 78 µm Optical micro.

Graphene fiber Control = 53 µm scale bar is 100 µm (crosslinker omitted)



graphene fiber, SEM 78 µm diameter

optional hollow core as H_2 conduit, SEM

FIGURE 1. Graphene Nanoribbon Fibers. An individual graphene nanoribbon is seen by transmission electron microscopy (TEM). These have been made into fibers by scalable spinning techniques also used for CNT, observed by scanning electron microscopy (SEM). The fiber responds to oleum expansion and crosslinking, just as for CNT. After swelling in oleum (fuming sulfuric acid), the methylene di-aniline compound binds to adjacent graphene surfaces and provides a chemically bonded molecular spacer holding the graphene sheets apart to form a slit pore. If no crosslinker is added, then the nanopores collapse and the fiber shrinks when the oleum is extracted (observed by optical microscopy).

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Introduction

We have made a major shift in our goals from spun fibers of carbon nanotubes to fibrous graphene scaffolds, using a material which was not even in the nanotechnologist's toolbox at the onset of this project [1]. As one of the leaders in nanoscale graphene chemistry, this appeared to be an opportunity for us to move to an ideal material to make a nanoengineered slit pore adsorption media, using very low-cost precursor materials. Creating alternating charged layers using metal atoms on graphene electrostatically attract H_2 bringing high density hydrogen storage up to room temperature (RT).

Approach

All the methods necessary to create low-cost metal-intercalated graphene scaffolds for hydrogen storage will leverage our extensive expertise developed for CNT scaffolds.

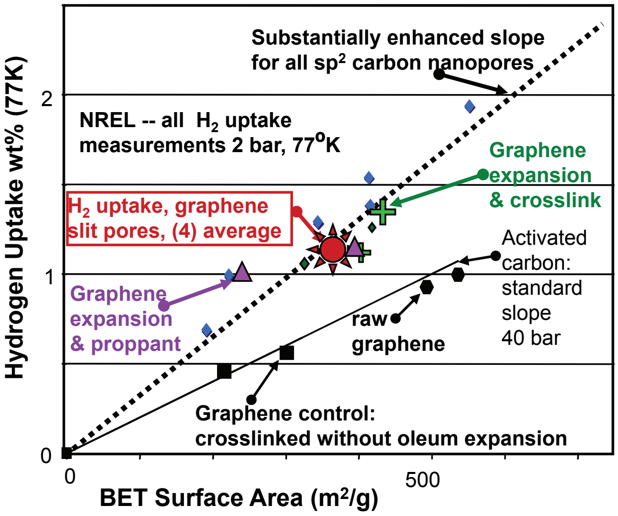

FIGURE 2. Enhanced Uptake H_2 also Observed in Graphene. Two oleum expanded graphene samples, one with diphenyl crosslinker (cross) and one with t-butyl aniline spacer (triangle), pre-baked at 500 and 700 C. Sunburst symbol = average of all four graphene measurements; this lies nearly on the same slope as the many measurements on nanoengineered CNT fibers (small diamonds) [Publication: 1.85x steeper slope vs. "Chahine's rule" for activated carbon, using only 2 bar H_2 uptake pressure—Leonard-Tour 2009]. Squares are graphene treated with diphenyl crosslinker, but without oleum expansion of the slit pores, and hexagon symbols are raw graphene starting material as controls. Unexpanded graphene samples fit the standard Chahine rule slope of 2 wt% per 1,000 m^2/g Brunauer-Emmett-Teller surface area [3] typical of activated carbons; lacking the expanded nanopores, this shows an absence of the enhancement effect. (All measurements by the National Renewable Energy Laboratory [NREL].) Similar enhanced H_2 uptake on sp^2 carbon surfaces: observed [4], theory [5].

1) Develop sources of graphene and graphene nanoribbons [publ. Kosynkin-Tour 2009] as a new low-cost slit-pore media (Figure 1).
2) Prop open graphene sheets to make engineered nanospaces.
3) Develop spinning methods for graphene to make fibrous media (Figure 1).
4) Verify ~2x enhancement in hydrogen uptake compared to typical activated carbons (Figure 2).
5) Develop alkali metal functionalization and diagnostics to show charge transfer.
6) Develop concept of alternating charge slit pore for enhanced uptake of H_2 near RT.

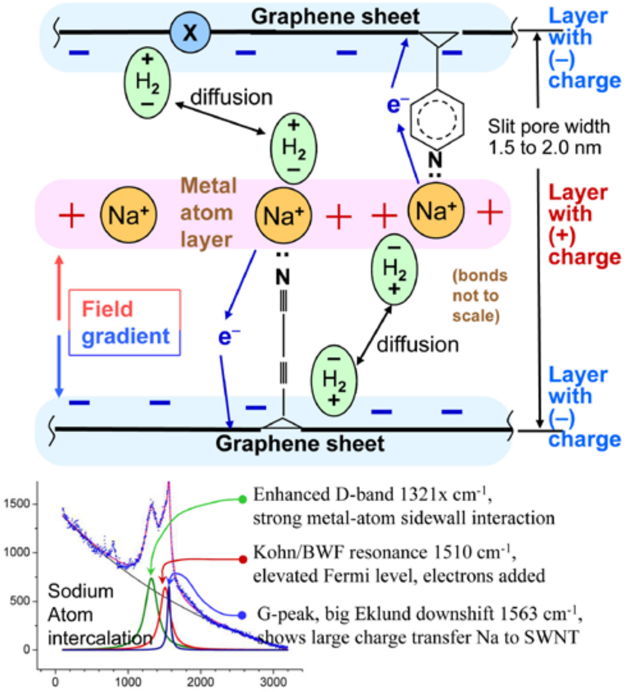

FIGURE 3. Dynamic Multilayer Adsorption (DMA) with Electrostatic Enhancement for H_2 Uptake at RT. This illustrates the concept of nanoengineered alternating charged slit pore with (+) sodium (or potassium) and (–) graphene layers that establishes the attractive electrostatic potential via dipole induced dipole forces on H_2. This donor-acceptor complex (DAC) provides the additional free energy to activate thermodynamic compression at RT, which considerably enhances the attractive potential compared to that of previous work [5]. The "X" substitutional atom (e.g., boron) in the graphene lattice is chosen to enhance the charge separation. This design makes entropy our friend, which prevents site specific binding of the H_2 to the metal atoms. The dynamic H_2 uptake (rather than static attachment to specific sites) considerably reduces enthalpy needed for uptake and consequent heat management problems, increases efficiency, and considerably reduces the range of temperatures necessary for desorption. For free energy $-\Delta F = 13$ kJ/mol, the (fugacity corrected for non-ideal gas behavior) equilibrium constant is 35, so that an external fill pressure of 100 bar corresponds to an internal "pressure" of 3.5 kbar, and the calculated electrostatic energy from the charge separation is sufficient [2] achieve the needed potential energy. Unlike static multilayer adsorption, the dynamic motion here causes all hydrogens to experience the same free energy of adsorption. At the bottom is a Raman spectrum of a sodium DAC. A large number of separated atoms donate electron charge to the CNT pi cloud (similar results obtained for potassium). The excitation wavelength is 785 nm. The appearance of the third resonance Raman feature at 1,510 cm^{-1} Kohn anomaly [6] can only occur if the electron donation is so large as to raise the Fermi level into the conduction band, and also provide a large downshift the G-peak [7] which also correlates with electron donation.

Results

Single sheet graphene was developed as a new material for nanospace engineering for enhanced H_2 uptake; graphene nanoribbons [publ. Kosynkin-Tour 2009] and spinning fibers from them (Figure 1).

Cost analysis: Approximate cost of raw materials in bulk: graphite \$550/tonne, sulfuric acid \$100/tonne, sodium \$500/tonne, ammonia - \$200/tonne (solvent for sodium) etc. for a raw materials cost of ~\$1.40/kg and \$1/kg to \$3/kg for spinning the fiber; therefore projected materials cost should be close to the DOE system target of \$67/kg H_2 stored using the calculated 7.5 wt% uptake.

From CNT to Graphene: Several proppants that worked well for carbon nanotubes as sidewall functional groups, including aryl sulfonates and t-butyl aniline, have now been developed for use with graphene [publ. Lomeda-Tour-2008]. Likewise, methyl di-aniline has proved suitable as a crosslinker to hold open the graphene slit pore. Pyridine functionalization has been demonstrated that will provide a "parking spot" for alkali metals so they are immobilized to prevent aggregation and loss of functionality.

H_2 uptake tests on graphene slit pores shows a similar enhancement in hydrogen uptake compared to typical activated carbons observed for CNT (Figure 2) [publ. Leonard-Tour 2009].

Metal atom intercalation with sodium exhibits a Raman spectrum commensurate with a strong DAC (Figure 3, bottom). DAC is needed to establish alternating charge layers for enhanced electrostatic attraction of the hydrogen into the nanopore.

Designed nanoengineered metal-graphene layered structure with slit pores. A free energy difference of only $-\Delta F = 13$ kJ/mol between the inside/outside the pore (Figure 3, also see [2]) will produce an equilibrium constant of $K = 35$ (corrected for fugacity) that will compress the hydrogen into the graphene pore. This is calculated to achieve the H_2 uptake amounts at near-ambient temperatures indicated above.

Conclusions and Future Directions

- The H_2 compression uptake mechanism is now understood to be a property of nanoporous sp^2 carbon as shown for both CNT and graphene nanoporous material.
- Expertise in CNT chemistry is successfully applied to graphene to make nanoporous scaffolds.
- An alternating charge layered structure can provide enhanced binding in the slit pore that will lead to high H_2 uptake at near ambient temperatures.
- We plan to transfer the enhanced hydrogen uptake concept of the CNT scaffold to the metal-graphene scaffold so that similar high density H_2 uptake occurs, but near RT.
- We will add metal atom intercalation to parking spots on grapheme.
- Our goal is to demonstrate 45 g/L hydrogen storage at near-ambient temperatures by constructing a metal/graphene structure similar to that of Figure 3 and determining H_2 uptake with pressures of 30 to 100 bar.

Presentations

1. Keynote Speaker Presentation by James Tour; Nanotechnology: The Passive, Hybrid and Active Sides" SERMACS Cope Scholar Symposium, Nashville, TN. (November 2008).

2. Keynote Speaker Presentation by James Tour; Wageningen Symposium on Organic Chemistry: Wageningen, The Netherlands. (April 2 and 4, 2008).

Publications

1. Ashley D. Leonard, James M. Tour, et al., "Nanoengineered Carbon Scaffolds for Hydrogen Storage", **Journal of the American Chemical Society, 131** (2), 723-728 (2009).

2. Dmitry V. Kosynkin, James M. Tour, et al., "Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons", **Nature 458,** 872 (2009).

3. Jay R. Lomeda, Condell D. Doyle, Dmitry V. Kosynkin, Wen-Fang Hwang, and James M. Tour; "Diazonium Functionalization of Surfactant-Wrapped Chemically Converted Graphene Sheets"; **Journal of the American Chemical Society, 130**, 16201 (2008).

References

1. Rickard Noorden, "Moving towards a graphene world", **Nature News,** Vol 442 page 228 (July 20, 2006).

2. Mina Yoon calculated 0.2 eV electrostatic attraction for each H_2 in the charge separated DAC = TTF/TCNQ, & calculated a similar electrostatic attraction for H_2 on charged C_{60}; Mina Yoon, et al., Presentation STP-26, DoE AMR2009; also submitted for publication.

3. Pierre Benard and R. Chahine, *Int. J. Hydrogen Energy* **26** (2001) 849–855.

4. K. Murata ... S. Iijima, et al., *J. Phys. Chem. B***, 106**, 11132-1 (2002); The authors termed the exceptionally high density as "supercritical H_2" uptake.

5. S. Patchkovskii, J.S. et al., *Proc. Nat. Acad. Sci,***102**;10439-10444 (2005).

6. Stefano Piscanec, et al., "Optical phonons in carbon nanotubes: Kohn anomalies, Peierls distortions, and dynamic effects" **Physical Review B 75**, 035427 (2007).

7. Bhabendra K. Pradhan, Peter C. Eklund, et al., "Experimental probes of the molecular hydrogen–carbon nanotube interaction" **Physica B** 323 (2002) 115–121.