



Global Climate & Energy Project  
**STANFORD UNIVERSITY**

## C-H Bonds in Carbon Nanotubes as an Energy Carrier

### Investigators

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### Objective

The goal of this project is to develop a new energy storage device based on carbon-hydrogen bonds. The stored energy will be extracted electrochemically, eliminating the need to form molecular hydrogen during the conversion process. The research will reveal the structure and kinetics of hydrogen bonded to carbon nanotubes in an electrochemical environment.

### Background

There have been many proposed visions of a hydrogen-based energy system. Most of them share a common set of assumptions:

- 1) Molecular hydrogen ( $H_2$ ) is produced via electrolysis or hydrocarbon reforming
- 2) Hydrogen is stored and distributed as a compressed gas, cryogenic liquid or adsorbed/absorbed phase
- 3) Molecular hydrogen extracted from storage is oxidized in a combustion engine or fuel cell

Steps 1 and 3 (and sometimes step 2) involve conversions between molecular and atomic (bound) hydrogen. These material transformations are always accompanied by efficiency penalties. Taking the molecular hydrogen out of the fuel chain can improve significantly the conversion of resource energy to useful work.

It has been shown [1] that atomic hydrogen can be stably and repeatedly adsorbed onto appropriately sized single walled carbon nanotubes (SWCNTs). The energy contained in the bond between the hydrogen atoms and the nanotubes would be available as work if the hydrogen could be reversibly desorbed and combined with oxygen. Electrochemistry may provide a pathway to reversible desorption.

An electrolyte solution surrounding carbon nanotubes provides an environment where hydrogen can be desorbed without recombining into  $H_2$  molecules. In this system, the kinetic barriers to phase change may be far lower than in the SWCNT- $H_2$  (gas) system. For example, if the nanotubes were surrounded by an acidic aqueous medium, hydrogen would desorb from the surface as  $H^+$  (or  $H_3O^+$ ) ions which could be oxidized from solution at a cathode.

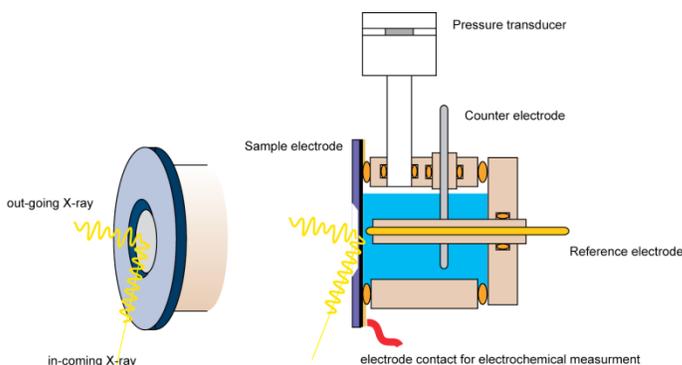
### Approach

There is little quantitative information available regarding the structure of the SWCNT-H/electrolyte system. Through electrochemical measurements, spectroscopic analysis and molecular modeling, the suitability of different types of SWCNT and electrolytes for energy storage will be determined.

The diameter and chirality of SWCNTs affects significantly the energy of the C-H bond. It is critical to reproducible results that nanotube size be well controlled during this investigation. Samples of nanotubes with narrow diameter distributions will be grown in the Dai and Clemens laboratories for use in these experiments. Nanotubes produced from ethanol gas on  $SiO_2$  with FeCoMo catalysts will be

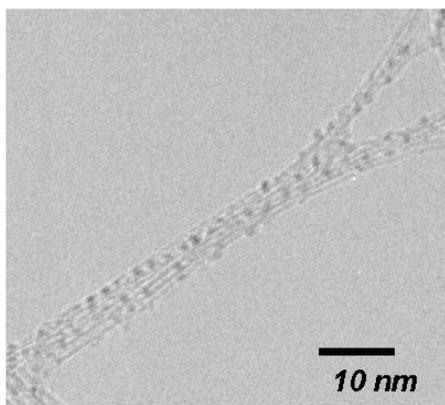
used in the first experiments, as these tubes have been shown in previous work to reach close to 100% hydrogenation.

The degree of hydrogenation that takes place will be evaluated both via current-voltage (I-V curve) measurements and x-ray photoelectron and absorption measurements by the Nilsson group (see Figure 1). The I-V curve data measures directly the amount of electrical energy that is consumed by the SWCNT-electrolyte system, while the spectroscopic measurements can detect directly the presence of C-H bonds. These preliminary measurements will be made on minimal surface-area samples of SWCNTs immersed in both acidic and alkaline solutions under high partial pressures of hydrogen gas.



**Figure 1:** Back illumination x-ray spectroscopy cell with a three-electrode set-up. An ultra thin carbon nanotube film on a thin film of  $\text{Si}_3\text{N}_4$  serves as a working electrode. Both the  $\text{Si}_3\text{N}_4$  and carbon nanotube films are thin to provide sufficient transparency to soft x-ray light. The setup allows simultaneous voltammetric and x-ray spectroscopic measurements of electrochemical reactions on the surface of the working electrode.

Two types of modifications to the nanotubes will be investigated which may increase the efficiency of hydrogen adsorption and desorption: (1) Addition of metal catalyst particles to the nanotube surface (see Figure 2) may provide specific sites where adsorption reactions can take place. These nanoparticles will be fabricated separately and applied to the nanotube samples. (2) Dopants such as nitrogen or boron intentionally grown into the nanotubes might also provide sites that catalyze adsorption. In either case, it has been shown that hydrogen atoms adsorbed at a catalytic site may migrate to unoccupied carbon atoms in a "spill-over" mechanism.



**Figure 2:** Transmission electron microscopy images of ~2.4 nanometer diameter platinum nanoparticles sputter-deposited onto SWCN.

This project will also examine the dehydrogenation process by reversing the electrical potential on the nanotube anode and performing more I-V measurements. The difference between electricity consumed in hydrogenation and electricity produced during dehydrogenation is a measure of the inefficiency of the system. Effects of temperature, pH, nanotube size and catalysts on efficiency will be measured.

Finally, molecular modeling of the SWCNT-H system in aqueous medium will be performed to corroborate experimental results and to guide hydrogen storage system design in future research efforts.

## References

[1] A. Nikitin, H. Ogasawara, D. Mann, R. Denecke, Z. Zhang, H. Dai, K. Cho, A. Nilsson, *Phys. Rev. Lett.* 95, 225507 (2005).