HYDROGEN STORAGE IN CARBON NANOTUBES

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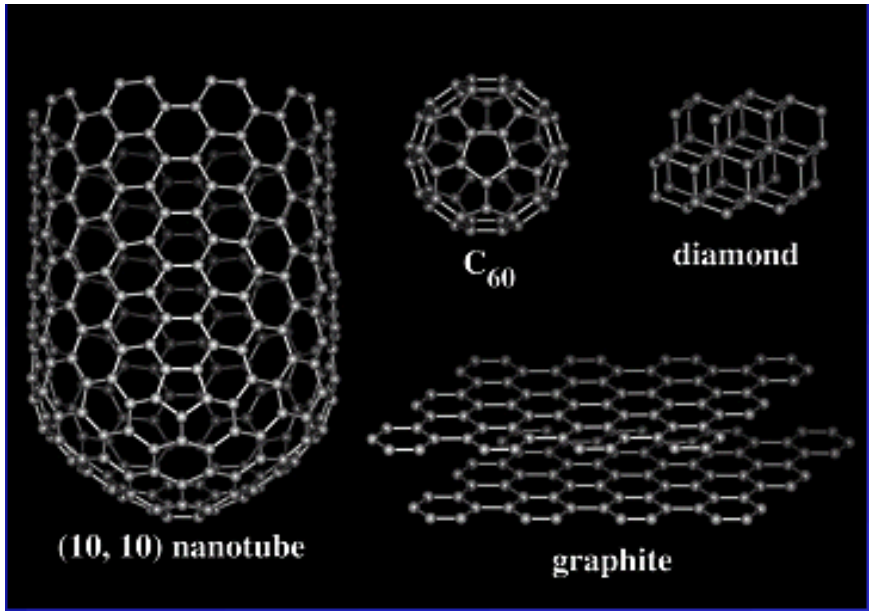
* **SOME BASIC NOTIONS**
* **BINDING SITES AND ENERGIES**
* **PROCESSING TO ENHANCE CAPACITY:**

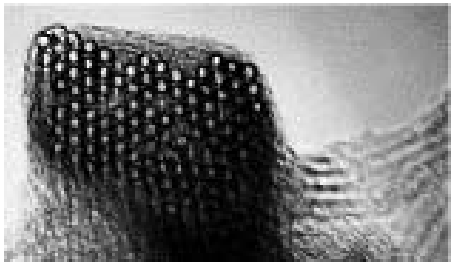
  EX: ELECTROCHEMICAL Li INSERTION
* **PHYSISORPTION vs. CHEMISORPTION**
* **MOLECULAR vs. ATOMIC HYDROGEN**
* **CONCLUSIONS**

Allotropes of Carbon

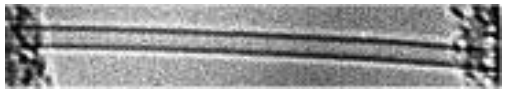


DENSITIES

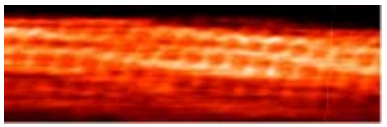
diamond	3.3
graphite	2.2
fullerite	1.7
“rope”	1.3



TEM of SWNT rope:
typical tube D ~ 1.4 nm
http://cnst.rice.edu

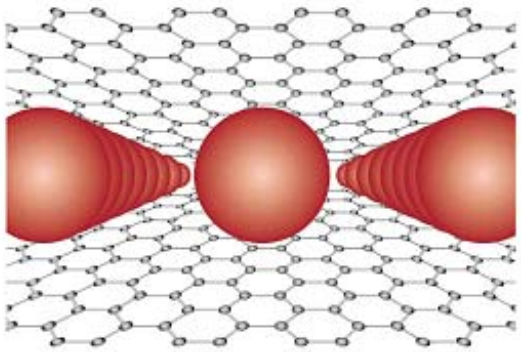


Cross-section of individual SWNT
B.W. Smith, Penn

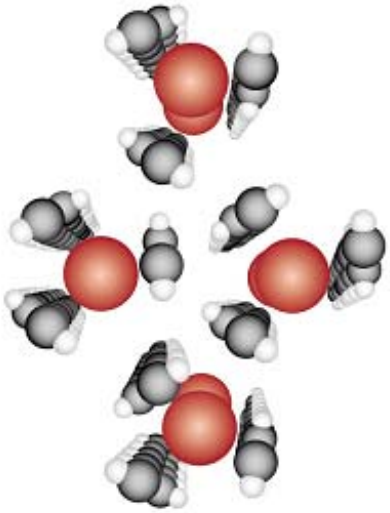


Atomic Resolution STM
W. Clauss, Penn

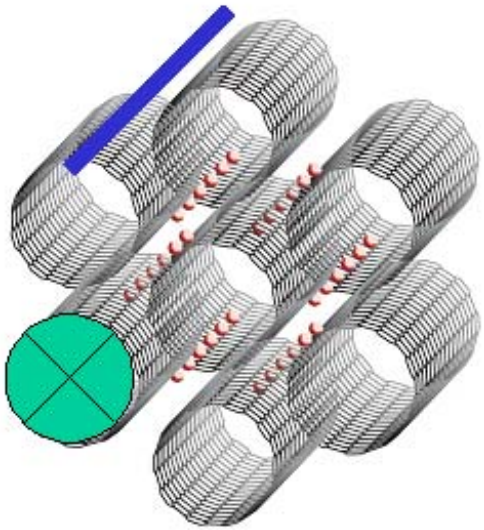
INCLUSION COMPOUNDS OF CARBON HOST MATERIALS



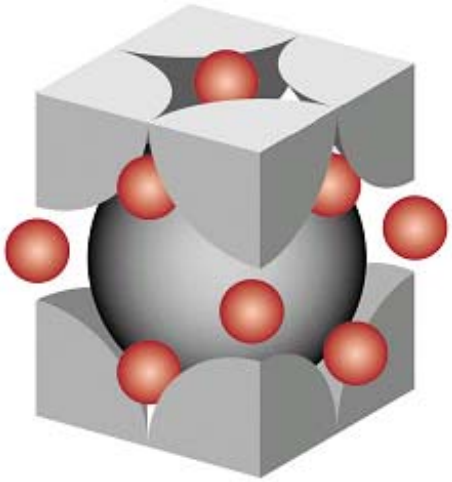
KC_8



$[Na_Y(CH)]_x$



DOPED NANOTUBES



K_3C_{60}

graphite intercalation compounds

doped conjugated polymers

alkali metal fullerides

SWNT ropes:

- interstitial
- endohedral
- surface channels or "groove sites"

OCTANE: C_8H_{18} - 15.8 wt.% HYDROGEN

or 1.12 H_2 MOLECULES per C ATOM

CLEAN CAR PROJECT REQUIREMENT:

6.5 wt.% or 1 H_2 per 2.4 C ATOMS

WHAT DO WE KNOW ABOUT LIMITING COMPOSITIONS FOR OTHER SWNT INCLUSION "COMPOUNDS"?

EXAMPLE: electrochemical insertion of Li into cut SWNT bundles

1 Li^+ per ~2 CARBONS

BUT: kinetic diameter of H_2 >> diameter of Li^+.

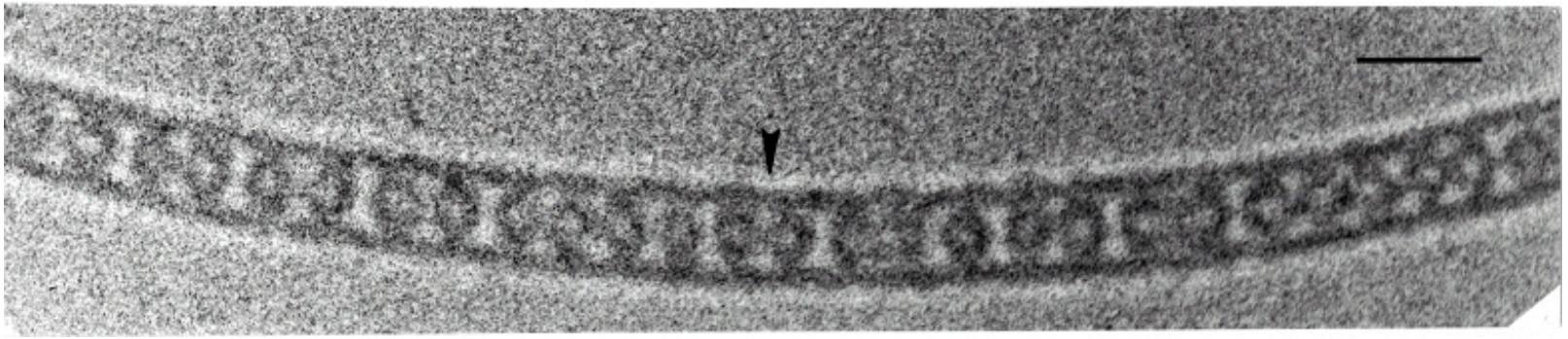
AND: *van der Waals* interaction << ionic bonding.

FILLING NANOTUBES

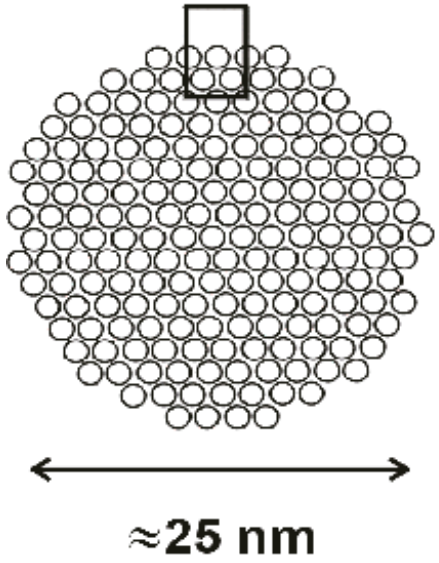
CAPILLARITY: metals and oxides, large diameters
(Ebbesen, others)

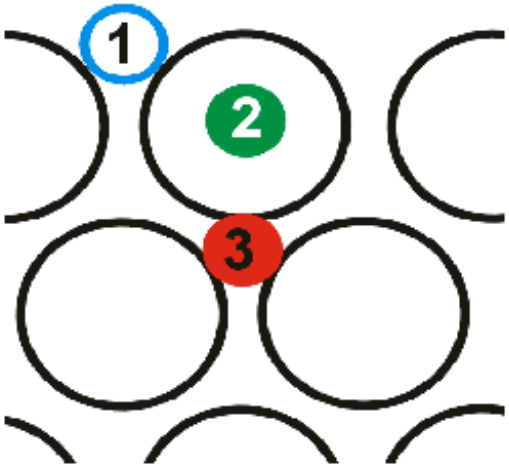
IMMERSION IN MOLTEN SALTS: MWNT
(Sloan, others)

GAS PHASE: fullerene peapods (Luzzi, others)



DIRECT PROOF OF ENDOHEDRAL ACCESS AND FILLING
(PENN 1998)



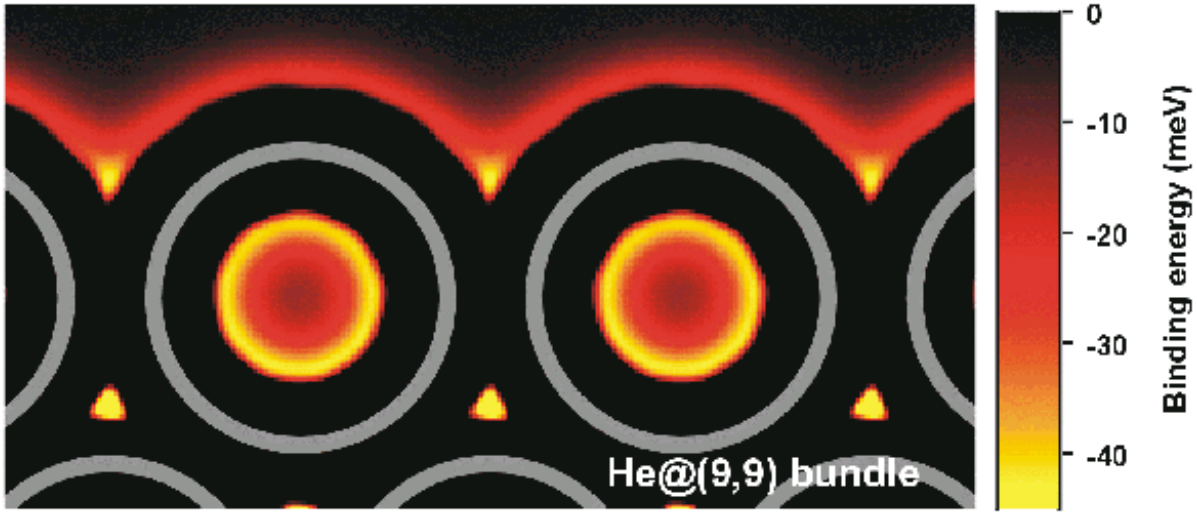


1 groove-site

2 endohedral-site

3 interstitial channel

A 25 nm diameter rope of (9,9) tubes. The number of surface tubes is an appreciable fraction of the total, and the "groove sites" form 1-D channels with significant binding energy for neutral molecules.



2-D potential energy surface for helium. The channel sites are well localized; the endohedral "site" is actually a ring of He density while the groove-site is quite dispersed on the surface. This suggests the possibility for novel dynamical behavior in the groove sites.

Thanks to Tobias Hertel

BINDING ENERGIES AND RELATIVE ABUNDANCES OF THE 3 SITES VS. TEMPERATURE AND ROPE DIAMETER

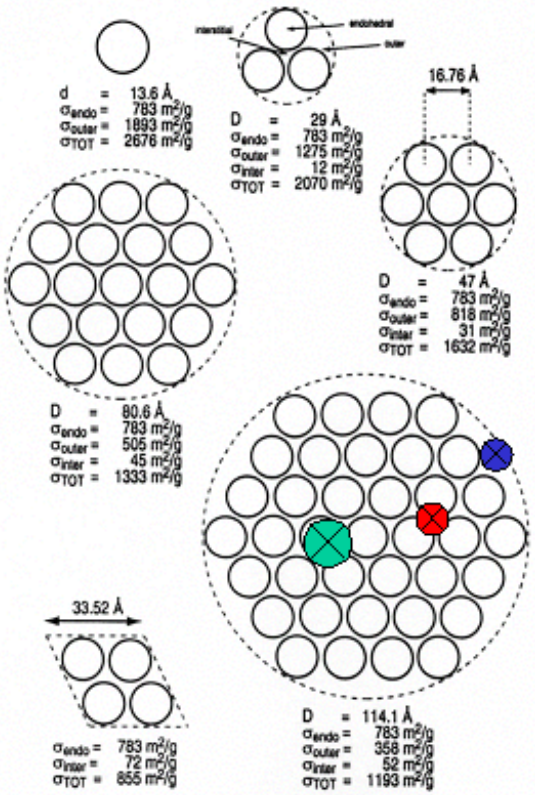


Fig. 1. Rope geometries considered in this work, with computed specific surface area contributions indicated for the endohedral (σ_{endo}), interstitial (σ_{inter}), and outer (σ_{outer}) adsorption sites. The total specific surface area is indicated by σ_{TOT}.

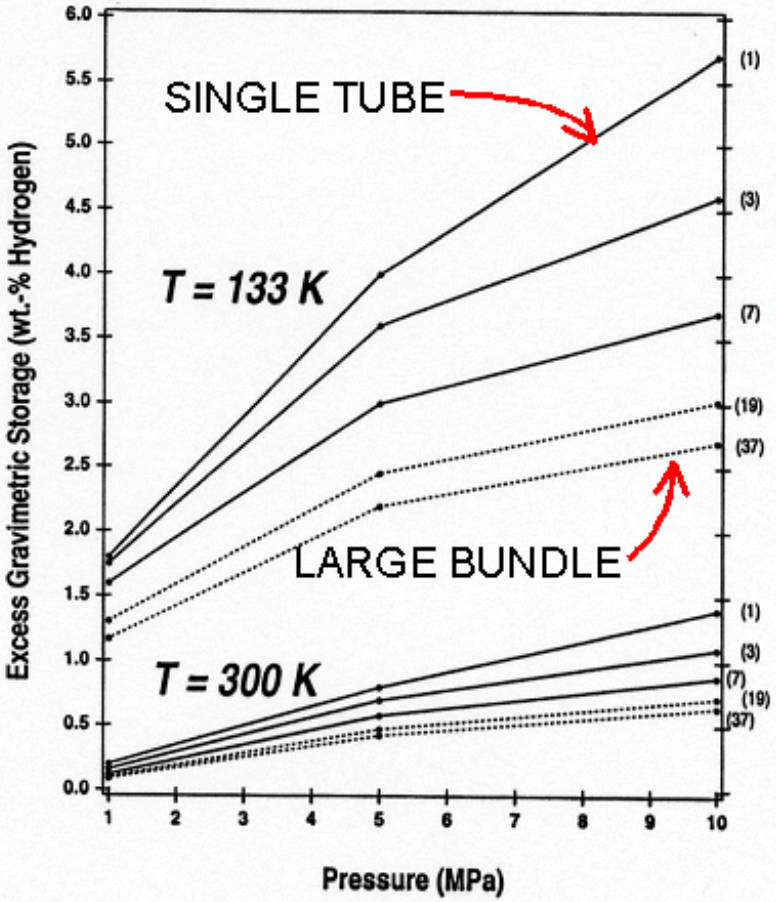


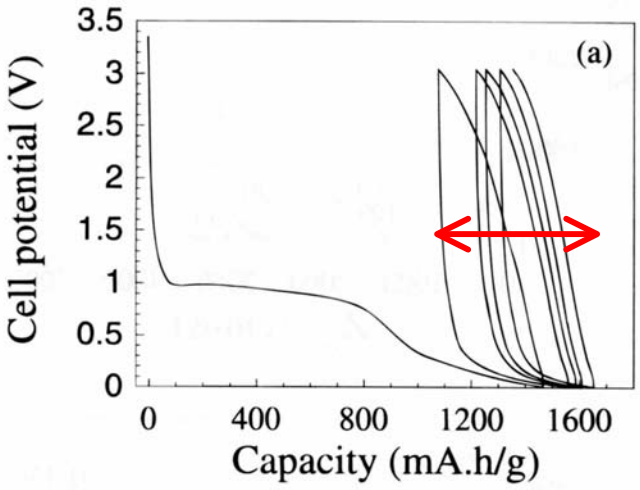
Fig. 4. Excess gravimetric storage isotherms at temperatures of 133 and 300 K for ropes containing 1–37 individual nanotubes.

Williams & Eklund 2000

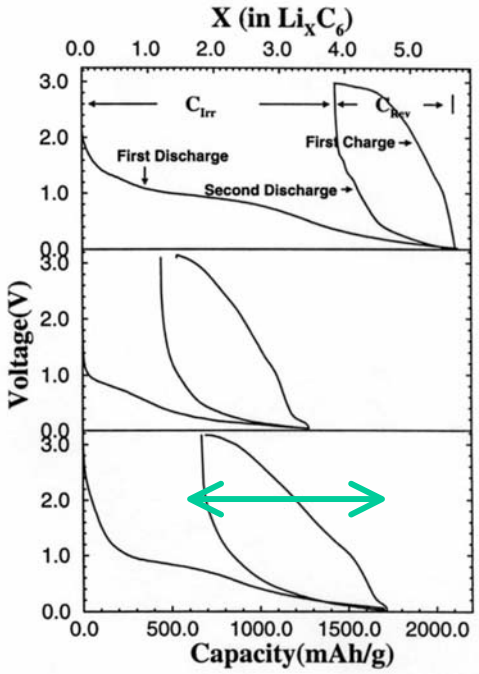
GOAL CAN BE MET AT 133 K and 10 MPa
(~ gas cylinder) WITH ISOLATED SWNT

ENHANCED Li STORAGE BY OPENING AND CUTTING

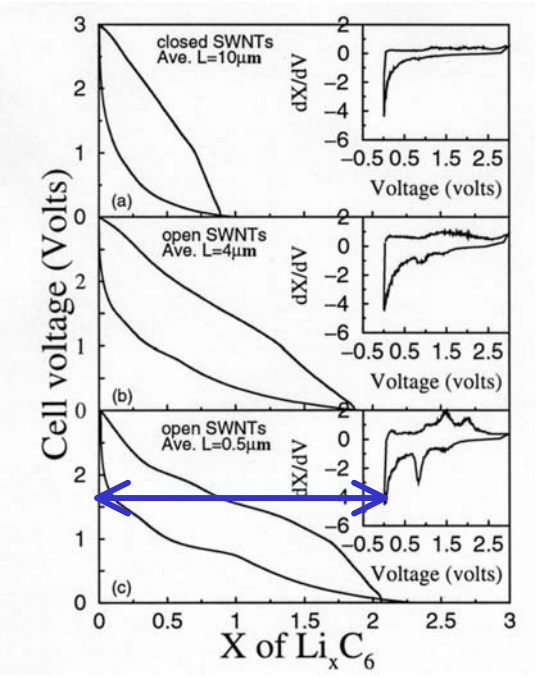
Purified/annealed PLV tubes: well-ordered ropes, long tubes, closed ends (PENN 2000).



Ditto, then ball-milled for different times (UNC 2000).



Ditto, then sonicated in 3:1 sulfuric/nitric for 10-24 hours (UNC 2002).



Reversible capacities:

LiC_5 **$LiC_{2.2}$ @ 10 min** **LiC_3 @ L = 0.5 mm**

WHERE ARE WE SO FAR?

- PHYSISORPTION WON'T MEET THE GOAL AT PRACTICAL TEMPERATURES OR PRESSURES – WE NEED SOME INTERACTION STRONGER THAN *van der Waals* BETWEEN H_2 AND SWNT.

- ACCESS TO TUBE INTERIOR IS AN ABSOLUTE REQUIREMENT; NEED TO CONTROL AND OPTIMIZE POST-SYNTHESIS PROCESSING.

- Li^+ PROBABLY FILLS SWNT, AND DIFFUSES FAST AT 300K. WHAT ABOUT THE MUCH LARGER H_2?

MD SIMULATION: DISTORTED TUBES -> WEAK COVALENT BOND BETWEEN H_2 and CARBON (JACS **2001,** 123, 5845)

J. Am. Chem. Soc. **2001,** *123,* 5845−5846

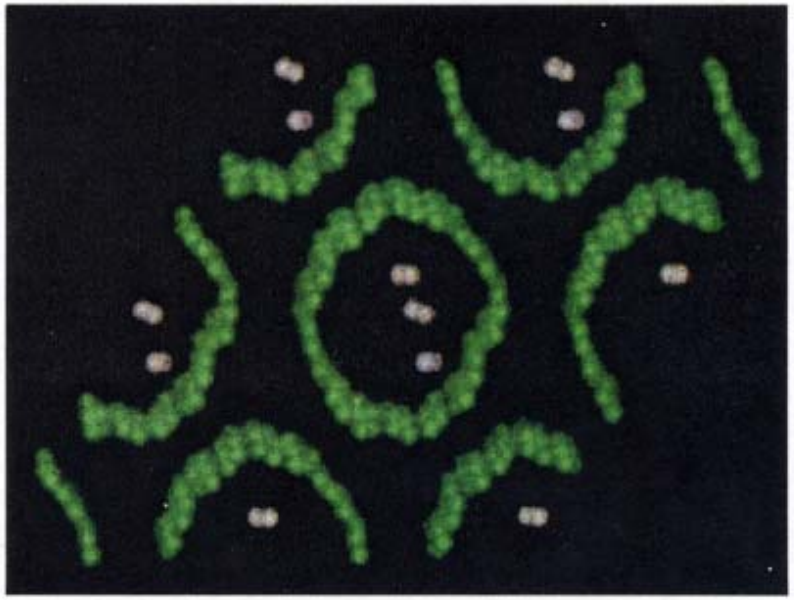
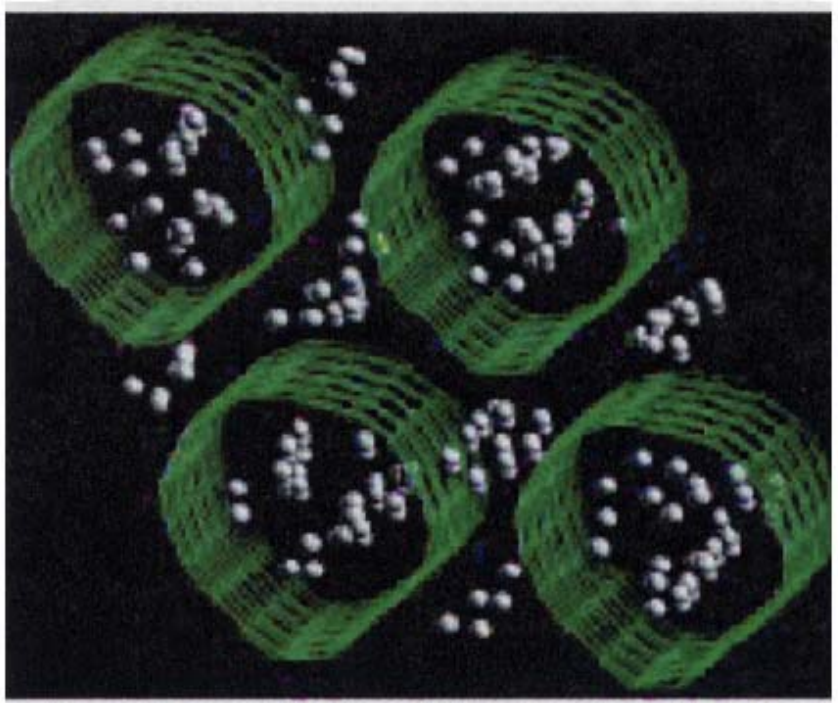


Figure 1. A representative time step during the MD simulation of endohedral H_2 adsorption at 300 K. The radial deformation of the SWNT wall and orientation of the H_2 molecules are illustrative of the dynamics observed throughout the simulation.

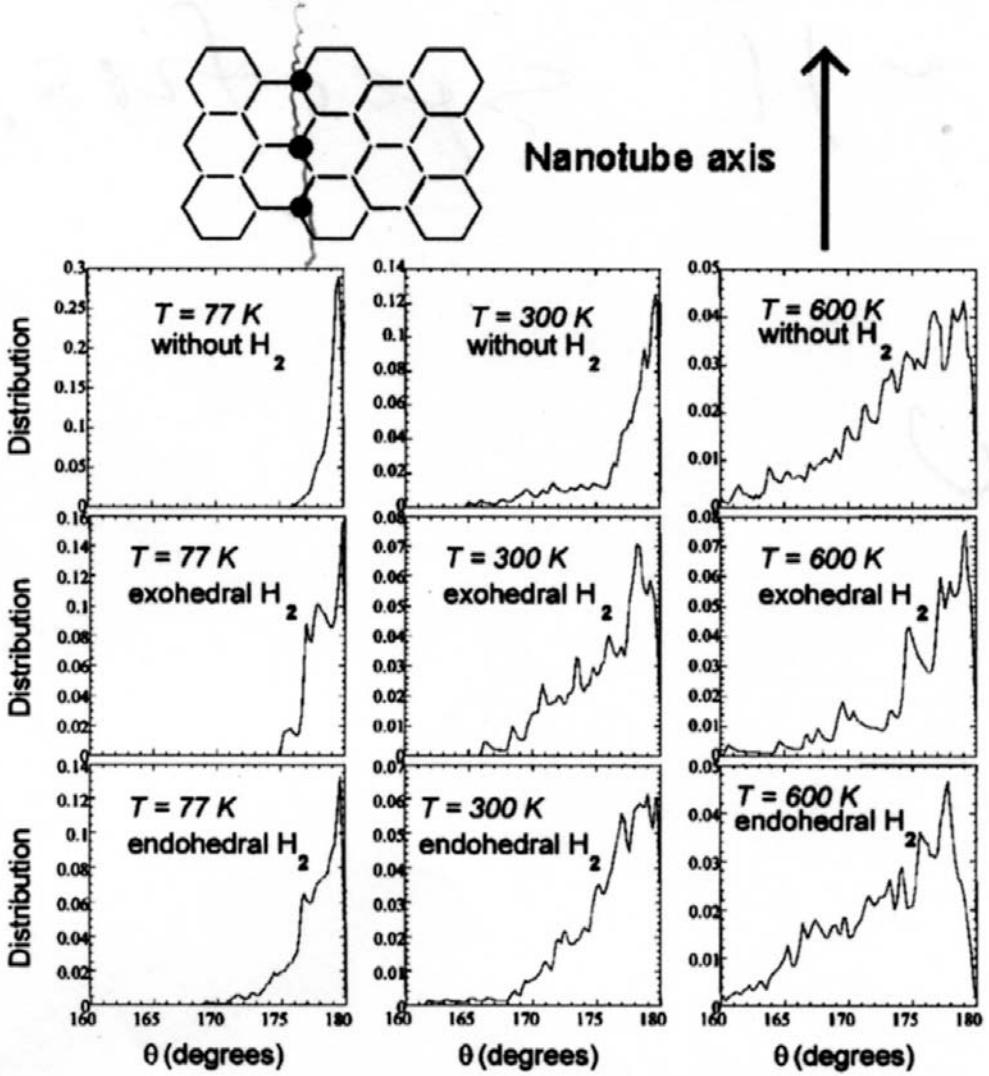
Table 1. The Energies (kcal mol^{-1}) of Adsorption of H_2 in SWNT's

temp, K	endohedral	exohedral
77	−3.94	−4.79
300	−7.51	−6.75
600	−3.86	−10.91

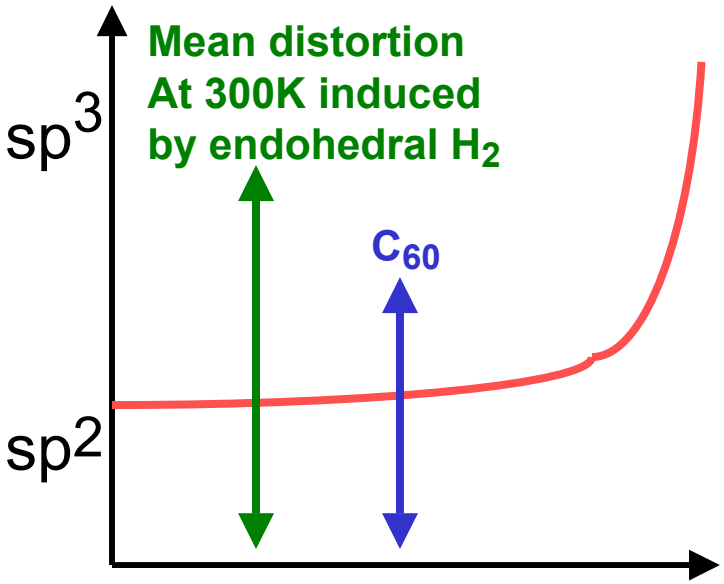


MOLECULAR HYDROGEN ACTS AS A WEAK ACID, EXTRACTING ELECTRON DENSITY FROM THE SWNT. BUT ….

AT HIGH LOADING MOST H_2's DON'T FEEL THE TUBE WALLS.



EFFECT IS QUITE WEAK; REHYBRIDIZATION TOWARDS SP^3 IS SMALL. AT HIGH T THE DISTORTIONS ARE JUST THE ON-TUBE VIBRATIONS, UNAFFECTED BY H_2



90° ~94° 109°

graphite diamond

BY THIS ARGUMENT, SOLID C_{60} SHOULD BIND H2 MORE STRONGLY THAN SWNT, ESP. ON THE OUTSIDE.

ROBERT HADDON

EXPERIMENTAL TESTS OF PARTIAL COVALENT BONDS

PERTURBED TUBE SYMMETRIES and RAMAN SCATTERING:
RADIAL BREATHING MODES SHOULD BE GONE;
TANGENTIAL MODE FREQUENCIES WILL CHANGE,
DUE MOSTLY TO MODIFIED BOND BENDING FORCE CONSTANTS.

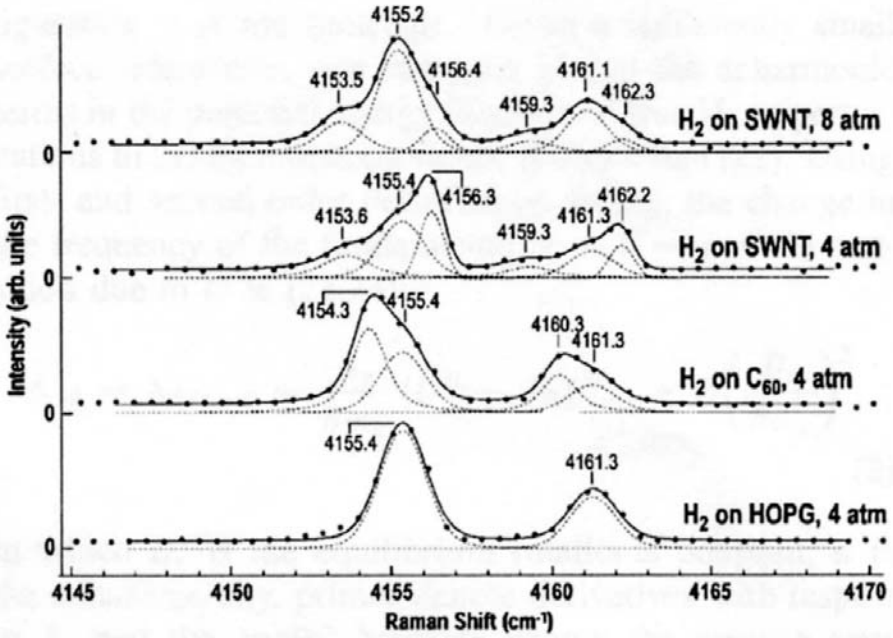
NEGATIVE CHARGE ADDED TO H_2 SIGMA ORBITALS:
EXPANDED H – H BOND from RAMAN, IR, NEUTRON VIBRATIONAL SPECTROSCOPY.

p-DOPING THE SWNT BY DEPLETING pseudo-PI ORBITALS:
RAMAN G_2 BAND SHOULD BLUESHIFT;
RESISTIVITY SHOULD DECREASE,
THERMOPOWER SHOULD REVEAL E_F DOWNSHIFT.

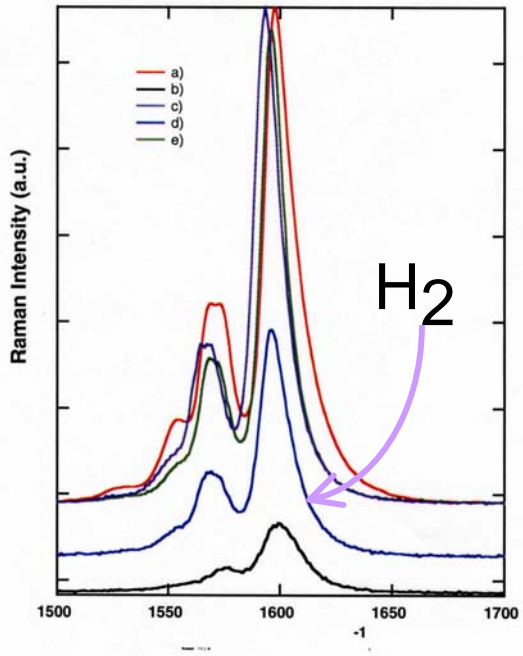
^{13}C and proton NMR *in situ* : SENSITIVE AND DIRECT PROBE.

RAMAN SPECTROSCOPY RESULTS

H_2 S and Q branches (Penn State 2002)



SWNT G-band (NREL)

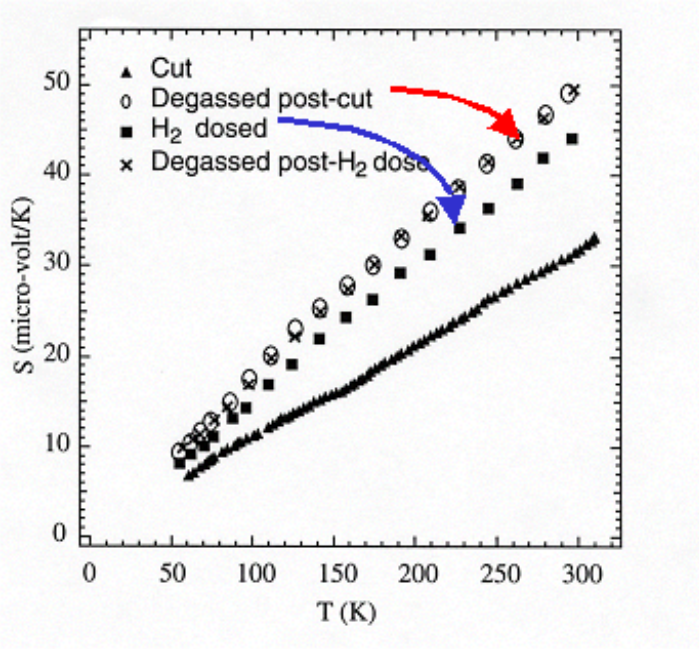


Q-branch: BOTH RED - and BLUESHIFTED COMPONENTS AFTER *in situ* EXPOSURE; MAXIMUM REDSHIFT 2 cm^{-1}; ".. no transfer…..".
0.008 hole / C .

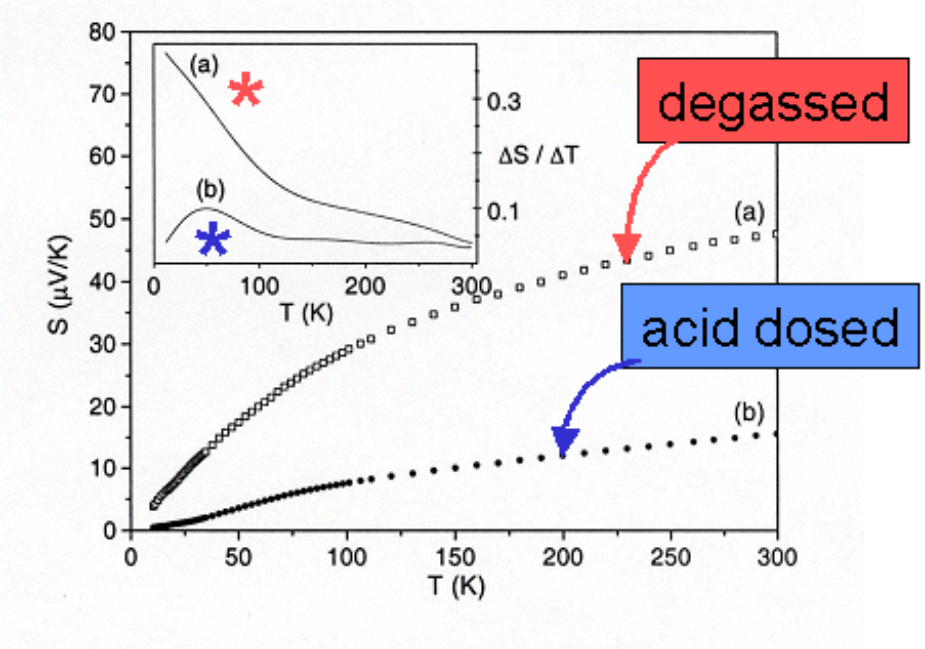
3 cm^{-1} BLUESHIFT CORRESPONDS TO 0.08 e^{--} / H_2 , and evidence for charge

THERMOPOWER AS A PROBE OF FERMI ENERGY DEPRESSION BY ACCEPTOR DOPING: DIFFUSION vs. PHONON DRAG CONTRIBUTIONS

H_2 as acceptor dopant (NREL)

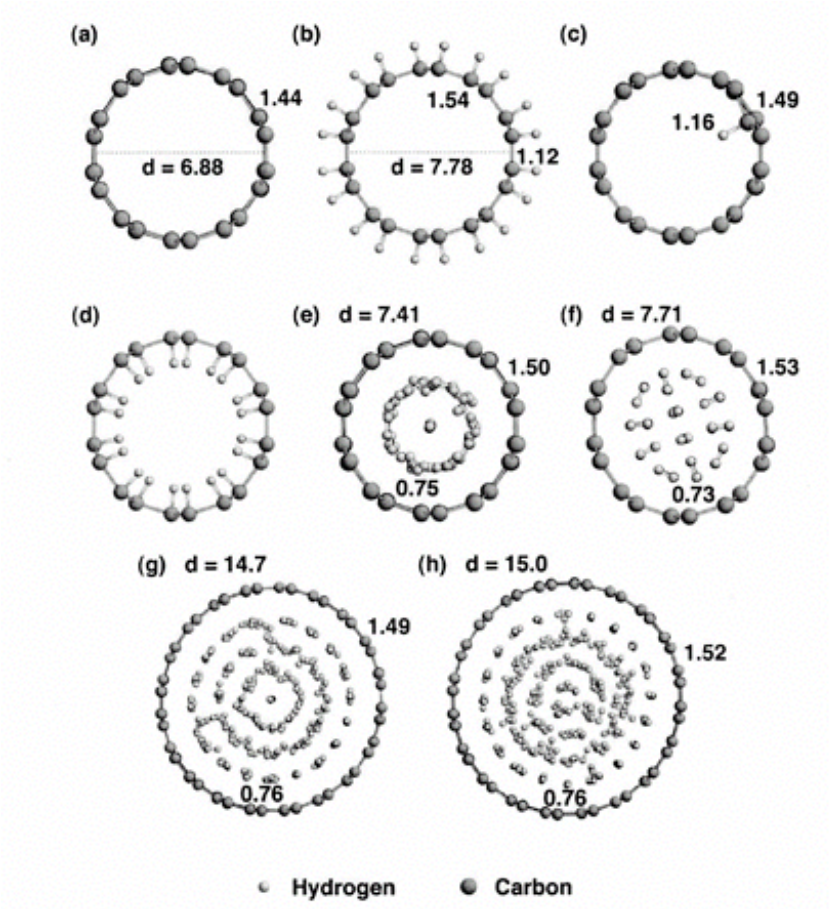


Strong acids (PENN,RICE)



TEP IN DEGASSED SWNT DOMINATED BY DIFFUSION TERM: EXTRINSIC HOLE DOPING BY DEFECTS and/or RESIDUAL OXYGEN. E_F IS DEPRESSED BY p-DOPING; THIS CUTS OFF ELECTRON-PHONON INTERACTION BELOW A CUTOFF TEMPERATURE RELATED TO PEAK IN DERIVATIVE CURVES. E_F DEPRESSION BY H_2 IS MINIMAL.

ANOTHER MODEL STARTING WITH ATOMIC HYDROGEN (Lee and Lee, 1990x)



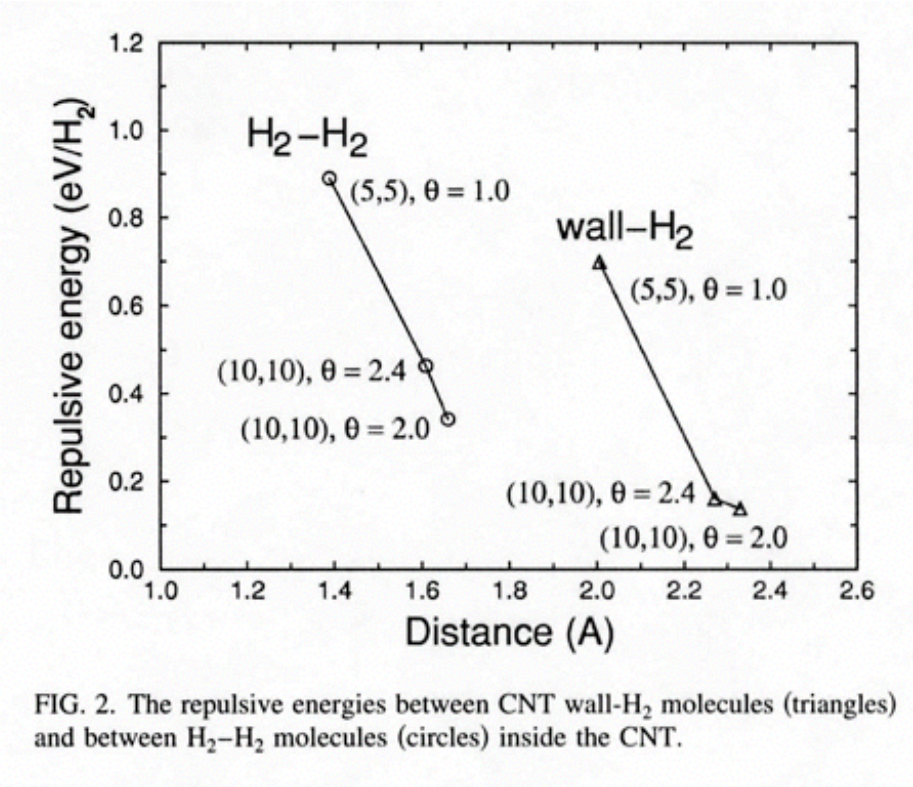


FIG. 2. The repulsive energies between CNT wall-H_2 molecules (triangles) and between H_2–H_2 molecules (circles) inside the CNT.

AT HIGH COVERAGES, EXO-H "FLIPS" INSIDE TO FORM H_2 – MAX CAPACITY 16.7 wt.% for (10,10) @ T = 0, ENDO ONLY!

IN THIS MODEL, C-H_2 INTERACTION IS <u>NIL OR WEAKLY REPULSIVE</u>

ELECTROCHEMICAL STORAGE OF ATOMIC H in Li-SWNT (CHONBUK UNIVERSITY, KOREA 2001)

SWNT LITHIATED SWNT

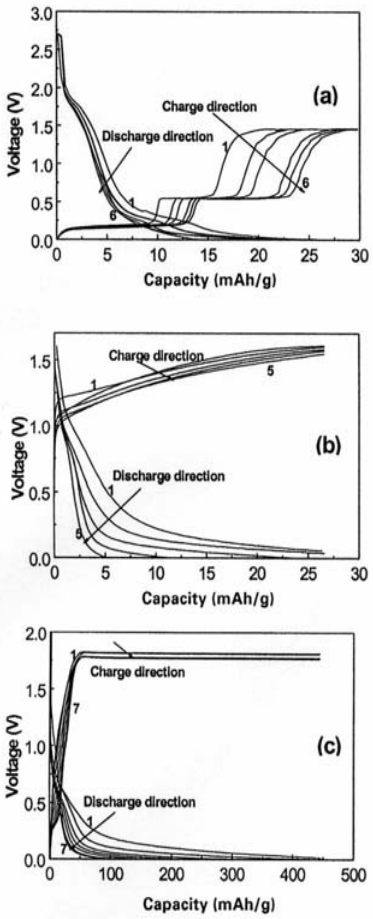


Fig. 3. Charge–discharge capacities of (a) CVD, (b) AD, and (c) LA grown CNT electrodes in 6 M KOH electrolyte.

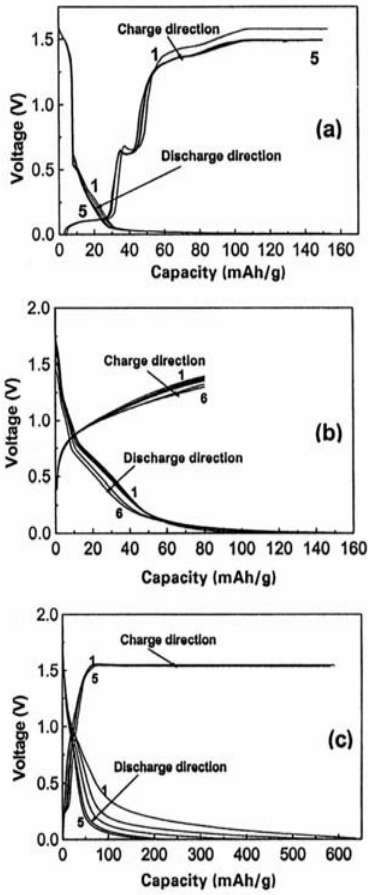


Fig. 4. Charge–discharge capacities of (a) CVD, (b) AD, and (c) LA grown Li- doped-CNT electrodes in 6 M KOH electrolyte.

CVD

ARC

LASER

LASER ABLATION

SWNT:

1.6 wt.% neat

2.3 wt.% lithiated @ 300 K

CONCLUSIONS

CONFIRM THE POSSIBILITY OF *INTRINSIC* 6.5% CAPACITY:
- COMPLEMENTARY THEORETICAL APPROACHES
- INCISIVE MICROSCOPIC EXPERIMENTS
- REPEATABILITY and REPRODUCIBILITY:
  - ROUND-ROBIN OF SAMPLES
- MORE *IN SITU* EXPERIMENTS

MATERIALS NEED TO BE OPTIMIZED:
- SINGLE TUBES SEEM TO BE THE BEST
- OPTIMUM DIAMETER:
  - TOO BIG – ENDOHEDRAL LH_2
  - TOO SMALL – DENSITY ⇧ FASTER THAN # SITES/TUBE
  - CUTTING MECHANISM AND PROCESSING

IF STORAGE IN SWNT ISN'T *INTRINSIC*, FIND A CHEAPER FORM OF CARBON AND ENGINEER THE DEFECTS/IMPURITIES!

HYDROGEN-SPECIFIC PROBES

- TPD with MASS SPECTROMETRY
- *in situ* PROTON NMR (UNC)
- *In situ* SPECTROSCOPY (RAMAN, IR): H_2 molecular vibrations (Penn State)
- ELASTIC NEUTRON SCATTERING w/D_2 SUBSTITUTION: locate molecules in the structure
- INCOHERENT INELASTIC NEUTRON SCATTERING: identify binding sites; molecular dynamics/diffusion (NIST, Penn State, ANL, Karlsruhe)
- ELECTROCHEMICAL CHARGE/DISCHARGE