

## Hydrogen Storage in Metal-Modified Single-Walled Carbon Nanotubes

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### Objectives

- Alter adsorption enthalpy of hydrogen on single-walled nanotubes (SWNTs) by use of a potassium intercalant.
- Increase number of adsorption sites in SWNTs by increasing the surface area through the use of intercalant.
- Improve the hydrogen storage capacity of SWNTs.

### Technical Barriers

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

- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Approach

- Investigate potassium intercalation synthesis procedures and measure sorption behavior of flaked graphites.
- Apply synthesis "recipes" to SWNT intercalation.
- Measure hydrogen sorption isotherms using Sieverts apparatus

### Accomplishments

- Optimized synthesis procedures for KC24 and KC8 intercalated graphites.
- Determined synthesis procedures for K intercalated SWNTs, including CNI HiPco synthesized SWNTs.
- Determined purification routes for commercial Carbolex SWNTs.
- Carried out initial single point isotherm measurements and Raman and x-ray diffraction measurements for structural characterization.
- Produced K-intercalated SWNTs with room temperature sorption comparable to activated carbons.

### Future Directions

- Further purification and intercalation of SWNTs.
- Optimization of K intercalation into SWNTs.
- Complete volumetric hydrogen adsorption measurements of SWNTs.

## **Introduction**

The abundance of carbon and its relatively low molecular weight make it an attractive possibility as a hydrogen sorbent for fuel tank applications, where a high gravimetric density (mass ratio of hydrogen to carbon) is required. Graphite is the most commonly available form of carbon and consists of stacked graphene sheets. However, the interaction of graphite with hydrogen molecules is very weak, and the carbon layers are stacked too closely together for hydrogen molecules to fit between the layers, a necessity if a high density of hydrogen molecules is to be absorbed by the graphite.

The addition of potassium as an “intercalant” improves the ability of graphite to absorb hydrogen. When processed under controlled conditions, potassium atoms can separate the graphite layers and form an open hexagonal structure.

It has been known for over thirty years that  $KC_{24}$  potassium-intercalated graphite can readily absorb and desorb hydrogen but that this occurs most readily at 77 K [1]. The overall level of absorption in  $KC_{24}$  is ~1.2 wt% at this temperature. The limitation of 1.2 wt% can be understood on the basis of a space filling argument. Potassium atoms form an open hexagonal structure on alternating graphene layers, and four hydrogen molecules can fit within the open hexagon, defining the upper absorption limit. The lattice separation that potassium atoms induce within the graphitic layers can better accommodate the size of molecular hydrogen.

Adopting the approach of increasing the adsorption enthalpy for graphites should have a similar effect for SWNTs, and also have the effect of increasing the surface area of SWNTs. SWNTs have effectively high surface areas (~1600 m<sup>2</sup>/gm outer surface area and ~1000 m<sup>2</sup>/gm inner surface area) that are well beyond normal graphitic carbon. However, nanotubes typically form rope structures due to van der Waals interactions which promote rope formation, limiting the surface area to ~300 m<sup>2</sup>/gm (interior and exterior surface areas for a SWNTs should be above 2600 m<sup>2</sup>/gm). Potassium intercalation of SWNTs will separate the individual tubes. Computational work on SWNTs shows that under certain conditions, increasing the van der

Waals gap will increase the amount of hydrogen that can be adsorbed [2].

## **Approach**

We have been exploring 2-zone furnace procedures for the synthesis of  $KC_{24}$  and  $KC_8$  and nanotube materials. Following 35-year-old synthesis techniques, we have used Madagascar graphites (from Superior Graphite in Chicago), which are generally recognized as the best graphites for intercalation. We have also used Carbon Nanotechnologies (CNI) HiPco nanotubes in addition to nanotubes originally acquired from the group at Rice University.

We have also obtained SWNTs from Carbolex. CNI no longer manufactures laser-oven synthesized SWNT material, which tends to have a narrower size distribution (typically with a 13 Å diameter) than the HiPco material (8-13 Å diameter range) that they presently synthesize and sell. Part of our goal in this work is to synthesize a well-defined structure on the basis of the well-packed rope structure we have seen previously in laser-oven material from Rice.

Our structural characterization tools include x-ray diffraction, transmission electron microscopy (TEM) and Raman spectroscopy.

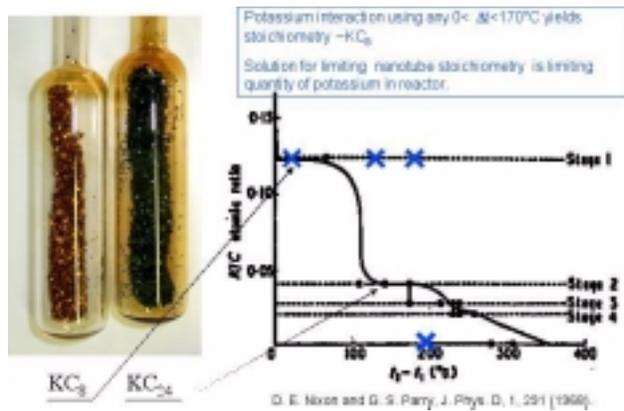
We are having a 2<sup>nd</sup> generation Sieverts apparatus constructed at the Jet Propulsion Laboratory (JPL) that will enable us to obtain both adsorption and desorption isotherms. In the meantime, we have been collaborating with Dr. John Vajo of HRL Laboratories, who has been measuring single point adsorption isotherms for us.

## **Results**

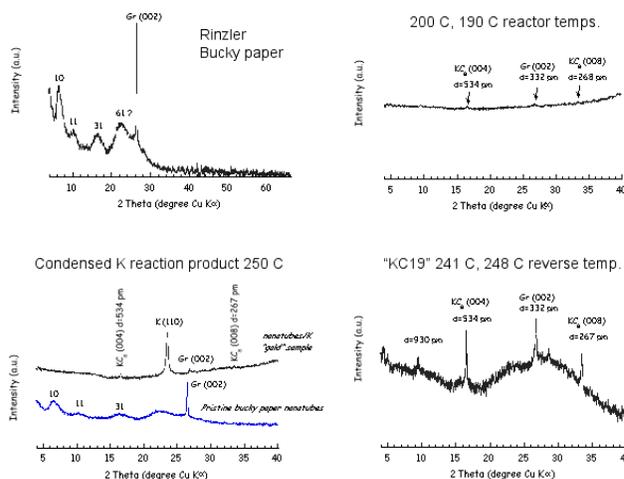
Figure 1 shows an overlay of intercalation synthesis behavior for stage formation of graphite compared to staging behavior for SWNTs. At  $\Delta t$  values of 0 to ~100°C, we can expect Stage 1 compounds to appear, while  $\Delta t$  values of 110 to 150°C are required to form Stage 2 compounds. For SWNTs, values of  $\Delta t$  up to 170°C only yield compounds of between  $KC_8$  and  $KC_9$  stoichiometry.  $\Delta t$  values above 170°C indicate no compound formation occurs. The solution to the problem of yielding the correct stoichiometry is to limit the

amount of potassium in the reactor assembly to match the desired final stoichiometry.

X-ray data is shown in Figure 2. The trace in the upper right shows low angle data from a laser over synthesized nanotube from Rice and shows the periodic structure associated with tube packing to form ropes. The lower left trace shows the result of condensing potassium onto this material as part of our initial attempt to induce intercalation into nanotubes. The upper right trace shows that we have been able to disrupt the periodicity of the rope structure by using a  $\Delta t$  of 10°C. The lower right trace shows our processing attempts to de-intercalate the sample onto which potassium had been condensed.



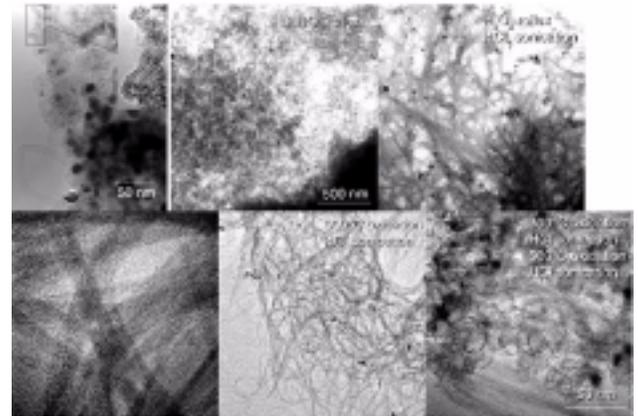
**Figure 1.** Phase Diagram for Staging in Graphite Overlaid with Our Observed Uptake of Potassium in Nanotube



**Figure 2.** X-ray Data for Unprocessed and Intercalated "Bucky" Paper Using Processing Conditions as Noted

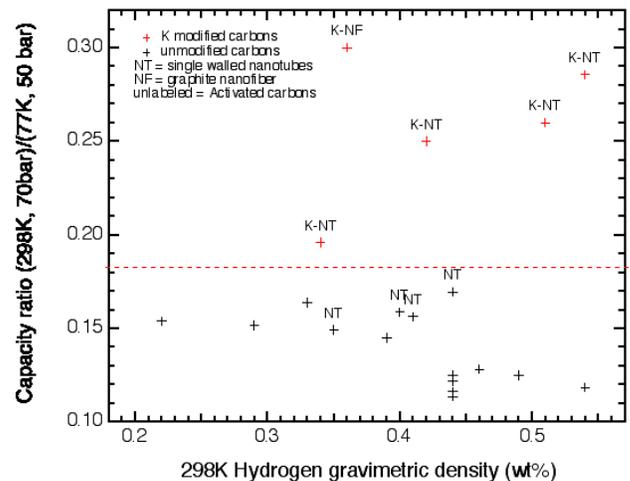
Transmission electron micrographs summarizing our processing procedures for purification of an alternative laser-oven synthesized material from Carbolex are shown in Figure 3.

In Figure 4, a summary of the improvements to room temperature sorption behavior of potassium-modified nanotubes is plotted. We can clearly see



**Figure 3.** TEM micrographs showing the microstructural evolution as a function of processing for as-prepared Carbolex nanotubes. Starting from the upper left and going clockwise is the as-prepared material, HNO<sub>3</sub> refluxed, H<sub>2</sub>O<sub>2</sub> refluxed and HCL sonicated, 2-step oxidation treated and high temperature oxidation treated and a high magnification micrograph.

Single point adsorption isotherm data for pure carbons and K-modified nanotubes



**Figure 4.** Ratio of Room Temperature to Liquid Nitrogen Temperature Gravimetric Densities for Pure and Potassium Intercalated Carbons

that unmodified carbons in the lower part of the plot have room temperature sorption that is 1/6 to 1/8 of the 77 K gravimetric density. Potassium intercalation can improve this ratio by nearly a value of two, indicating that the adsorption enthalpy is being altered. Even though the absolute values for gravimetric density are ~0.5 wt%, we have been able to effect improvements to the room temperature adsorption of nanotubes so that they are now comparable to the best activated carbons, which also have hydrogen gravimetric densities of ~0.5 wt%. We have accomplished this, even though we have not yet optimized the processing or structure of the intercalated nanotubes.

### **Conclusions**

Our potassium modification to carbon nanotubes yields room temperature hydrogen gravimetric densities that are now comparable to the best activated carbons. This indicates that we have now succeeded in altering the chemical potential for hydrogen physisorption in nanotubes. We plan to continue to optimize the structure of these materials by expanding or swelling the structure, to improve the surface area in a way that preserves the packing or rope symmetry. We anticipate that this will further improve the room temperature hydrogen storage capacity of these materials.

### **References**

1. M. Colin and A. Herold, Bull. Soc. Chim. Fr., 6, 1982 (1971).
2. V. V. Simonyan, J. K. Johnson, J. Alloys Comp., 330-332, 659 (2002).

### **FY 2003 Publications/Presentations**

1. Hydrogen storage in carbon nanostructures, C. C. Ahn, Invited Presentation, European Materials Research Society Annual Mtg., Strasbourg (2003).