DOE Cooperative agreement # DE-FC36-01GO11090
"Hydrogen storage in metal-modified single-walled carbon nanotubes"

Final Report:

Period from: 9/15/01 to 12/15/02 and 9/15/03 to 2/15/04

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Goals and Objectives:

It has been known for over thirty years that potassium-intercalated graphites can readily adsorb and desorb hydrogen at ~1 wt% at 77 K. These levels are much higher than can be attained in pure graphite, owing to a larger thermodynamic enthalpy of adsorption. This increased enthalpy may allow hydrogen sorption at higher temperatures. Potassium has other beneficial effects that enable the design of a new material:

a) Increased adsorption enthalpy in potassium-intercalated graphite compared to pure graphite reduces the pressure and increases the temperature required for a given fractional coverage of hydrogen adsorption. We expect the same effects in potassium-intercalated SWNTs.

b) As an intercalant, potassium separates c-axis planes in graphite. Potassium also separates the individual tubes of SWNTs ropes producing swelling and increased surface area. Increased surface area provides more adsorption sites, giving a proportionately higher capacity.

The temperature of adsorption depends on the enthalpy of adsorption. The characteristic temperature is roughly the adsorption enthalpy divided by Boltzmann's constant, k_B. For the high hydrogen storage capacity of SWNTs to be achieved at room temperature, it is necessary to increase the enthalpy of adsorption.

Our goal for this project was to use metal modifications to the carbon surface of SWNTs in order to address both enhanced adsorption and surface area. For instance, the enthalpy of sorption of hydrogen on KC_8 is 450 meV/H_2, whereas it is 38 meV/H_2 for unmodified SWNTs. By adsorption thermodynamics we expect approximately that the same performance of SWNTs at 77 K will be achieved at a temperature of [450/38] 77 K = 900 K. This is a high temperature, so we expect that adsorption on nearly all the available sites for hydrogen will occur at room temperature under a much lower pressure. This pressure can be estimated conveniently, since the chemical potential of hydrogen is approximately proportional to the logarithm of the pressure. Using 300 K for room temperature, the 100 bar pressure requirement is reduced to exp(-900/300) 100 bar = 5 bar at room temperature. This is in the pressure range used for prior experimental work such as that of Colin and Herold in the late 1960's and early 1970's.

Adsorption enthalpy and surface area are both necessary to consider in designing a practical hydrogen sorbent based on physisorption. The adsorption enthalpy is the driving force required for hydrogen to be attracted to a surface and should be sufficiently high if physisorption will be the operative phenomenon for hydrogen storage applications at ambient temperatures. Geometric constraints will also be required in our analysis if a particular material system is to be suitable. Adsorption enthalpy and surface area are intertwined in a way that can be better appreciated by noting that large surface area activated carbons, that have also long been known as effective physisorbents. van der Waals interactions between adsorbate and adsorbant represent the driving force. Large surface areas of activated carbons between 1600 to 3000 m^2/gm provide numerous sites onto which gases can easily adsorb and desorb with well-understood adsorption enthalpies. Single walled nanotubes (SWNT) represent a class of effectively high-surface area carbons with total surface areas that are comparable to that of a single graphene sheet (2600 m^2/gm). Nanotubes tend to bundle together as ropes however, limiting their effective surface area to several hundred m^2/gm. The overall goal of this work was to use potassium as an "intercalant" to enhance the adsorption enthalpy of hydrogen on carbon as has been seen in Stage 2 intercalated graphite (KC_{24}). Another effect of this intercalation would be to enhance the overall surface area of nanotubes, making areas that are otherwise difficult to access like interstitial sites (not the endohedral sites of the nanotube interiors) readily accessible without having to overcome the van der Waals forces that lead to rope formation.

Our results on this project show that enhanced ambient temperature behavior can be measured in potassium-modified nanotubes. We have however, fallen short of the optimization required to establish practicality as this work was originally meant to be a three-year project, but was interrupted by earmarking of funds that stopped our project after the first quarter of the second year of funding. While the Golden Field office of EERE was able to allocate somewhat less that another quarter of funds for this work, our intended work fell far short of the goals that were called for in the original proposal, as we were able to spend only half of the original allotted time and resources for this work. This final report reflects work that we were able to address given the constraints of our resources and also reflects the shortcomings of completing this work to its logical conclusion.

Neutron Diffraction of Stage 2 and Stage 4 Deuterided K-intercalated Graphite at Los Alamos National Laboratory

This work was begun before the awarding of the contract from DoE. Our initial goal of this work was to establish some expertise at conducting potassium intercalation experiments. While the techniques and phenomena associated hydrogen sorption in Stage 2 materials was first discovered over 50 years ago, our understanding of the limitations of these materials required a re-examination of this system. The 1.2 wt% limitation that had been discussed in the literature could in fact be inferred from simple hard sphere models of hydrogen sorption. While the space limitations set the upper limit, what was less clear was the enhanced driving force for sorption. We were not, and are still uncertain as to whether the additional driving force is controlled by a slit pore effect brought on by the expansion of the potassium containing planes, or by back-donation of electrons from the potassium to the graphene sheets.

The Stage 2 intercalated graphite, KC_{24}, consists of a graphite lattice in which K atoms form a dodecal structured layer between graphene layers as shown in Fig. 1. The stacking sequence is a-K-a-b, in which the a and b designation represent the normal stacking designation

typically used to describe graphite. To define an entire unit cell, the actual sequence would be a-Kα-a-b-Kβ-b…, for a perfect unit cell, where Kα and Kβ are alternating stacking sequences for potassium layers. Each potassium layer of the Stage 2 compound is separated by an a-b graphene stacking sequence.

From Fig. 1, we might appreciate that on the basis of a space filling model, that only a limited number of sites for deuterium (D_2) occupancy exist. A precise determination of these sites however, would yield information on the nature of the interaction between K and D_2.

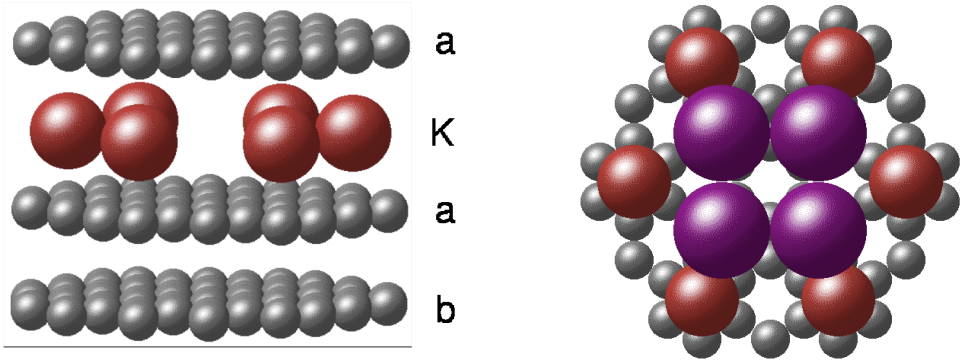


Fig. 1. The left figure shows the stacking sequence for KC_{24}. The gray atoms represent carbon and the larger red atoms show the dodecal structure of potassium atoms. The right figure shows a view down the basal direction of the dodecal K (red atoms) structure atop a single graphene layer. In addition, a possible arrangement for four larger deuterium molecules is depicted in purple. The optimal packing of hydrogen or deuterium into this structure would result in $KC_{24}2H_2$, or 1.2 wt%.

The Stage 2 K-intercalated graphite for this work was prepared using the 2-zone furnace technique. The starting material was a battery anode grade graphite designated G-1 from Diemasters. In addition to this sample, we attempted to synthesize this compound using a battery grade anode designated SL-20 from Superior Graphite. SL-20 has been shown to display excellent cycling and capacity behavior for Li battery applications.

We were able to perform a series of temperature runs on two samples, one designated IC-5, the stage 2 compound, as well as a Caltech stage 4 compound. These runs were performed under both vacuum conditions, and deuterided conditions. A temperature series of experiments of this type has not been performed before.

The temperature series of runs for both samples is summarized below in Fig. 2. For the Stage 2 compound, we measured lattice parameter changes in basal plane reflections using the (0 0 6) diffraction located at 2.9 Å. This value is consistent with 1/6 of the value of the stacking sequence a-Kα-a-b-Kβ-b where the a-Kα-a separation is 5.4 Å and the a-b graphite spacing is 3.35 Å (for a total of 17.5 Å lattice parameter). The lower set of traces represent the temperature series collected under vacuum. For this set, we can see a reduction in the basal plane lattice spacings for the Stage 2 compound as the sample temperature is reduced. Lattice parameter shifts for both (0 0 6) and (0 0 10) reflections were measured as a check for consistency and we observe that both sets of reflections track.

After the vacuum temperature series of data was obtained, we initially attempted to introduce D_2 to the sample at 77 K. No lattice expansion, or other effect of the deuterium could be seen under these conditions. There is a possibility that at this temperature, the lattice is

configurationally frozen and unable to accommodate D_2. There is also a possibility that the ends of the graphitic planes, which serve as conduits for D_2, became contaminated.

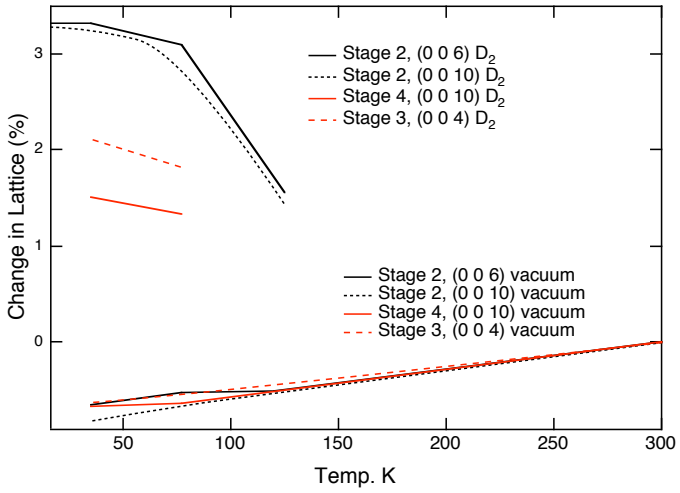


Fig. 2. Basal plane lattice parameter changes as a function of temperature for Stage 2 and Stage 4 compounds under vacuum (lower traces) and deuterided (upper left trace).

The sample was heated back up to 310 K under vacuum and D_2 reintroduced to a pressure of ~4 bar. When the temperature was reduced, an increase in the lattice parameter was then observed as seen in the upper left traces of Fig. 2. Again, both sets of basal plane reflections for the Stage 2 compound tracked and increased, indicating that deuterium was being accommodated by the lattice. We took measurements down to ~16 K but the lattice expansion appeared to saturate at ~35 K.

The NPD data for the 300 K run of the Stage 4 compound synthesized at Caltech is seen in Fig 3. While the synthesis conditions used to make this sample were similar to the conditions used to make the sample IC-5 from HRL Laboratories, we believe that subtle differences in the nature of the starting graphite resulted in slower intercalation kinetics. In fact, this sample also contained a small amount of Stage 3 material. Both the (0 0 10) reflection from the Stage 4 phase as well as the (0 0 4) reflection corresponding to the stage 3 phase can be observed in Fig. 3. Simulated and indexed diffractions for both phases can be seen in the lower traces. For the Stage 4 compound, we used a 200 atom stacking sequence of a-Kα-a-b-a-b-Kβ-b-a-b (30.9 Å thickness) to define the lattice for our simulation. Each potassium layer of this compound is separated by four graphene layers. The stacking sequence for the Stage 3 simulation was a-Kα-a-b (12.1 Å thickness) and each potassium layer is separated by the graphene stacking sequence a-b-a.

The error in the Caltech synthesis that resulted in a Stage 4 and Stage 3 mixed phase compound, rather than a stage 2 compound turned into a fortuitous circumstance from an analysis standpoint. First of all, the lattice contraction of each phase of the mixed phase material (shown in red in Fig. 2), shows that under vacuum, the contraction of each phase is consistent with the lattice contraction of the Stage 2 material.

Of note however, is that an analysis of peak shifts of the basal plane reflections for each deuterided phase is consistent with lattice expansion occuring on the K containing planes. On the basis of the relative distance difference between K layers, in a Stage 4 compound, we would expect the expansion to be roughly half of that as in the Stage 2 material.

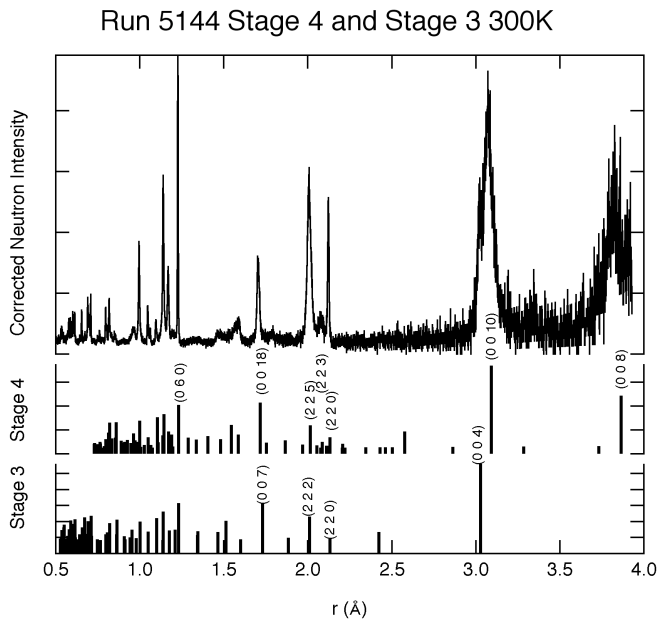


Fig. 3. Neutron diffraction pattern from Caltech Stage 4 intercalated graphite. Indexed simulated peaks appear in the lower traces. Reflections from a Stage 3 phase (0 0 4) at 3.02 Å overlap with the Stage 4 (0 0 10) reflection at 3.09 Å. Lattice spacing measurements were determined by gaussian deconvolution.

In a Stage 3 compound, we would expect the lattice expansion to be roughly 70% of that of the stage two compound. The deuterided traces of Fig. 2, seen in the middle of the left-hand side of the figure, show this behavior. We believe that this is the first time that absorption of D_2 into higher stage intercalated graphites has been observed. We might also infer from this data that the nature of the interaction between D_2 is confined to the K containing layer and that this interaction is independent of the number of intervening graphene layers.

Nanotube procurement, purification and intercalation

The main thrust of our work was the intercalation of nanotubes and the measurement of their hydrogen sorption properties. At the start of this project, we were interested in using a commercial vendor as a source of material for this work. Unfortunately, the limited number of vendors available at the time of the start of this project meant that we were also limited to obtaining as-prepared nanotubes that had a high weight fraction of remnant catalysts and disordered carbons. We procured most of our material from Carbolex. While we had not intended to devote a large time fraction of effort to nanotube purification, this became a necessary step if unambiguous hydrogen storage properties that were solely attributable to nanotubes were to be discerned.

Virtually every procedure described in the scientific literature fell short of our expectations of producing a reasonably pure material and we ended up adopting a variation of the procedure that we had developed for intercalation work, by adding an exfoliation step, in obtaining a material with the requisite purity.

An extensive amount of time was devoted to using “recipes” from the literature and on the basis of thermo-gravimetric analysis (TGA), X-ray diffraction and transmission electron microscopy (TEM), little improvement in reducing the amount of Ni-Y catalyst used for the laser-oven prepared AP grade of nanotube from Carbolex. Fig 4 shows a TEM micrograph highlighting the problem with the starting material. Dark contrast from the globular features results from diffraction contrast from the catalysts and this was confirmed by x-ray flourescence microanalysis.

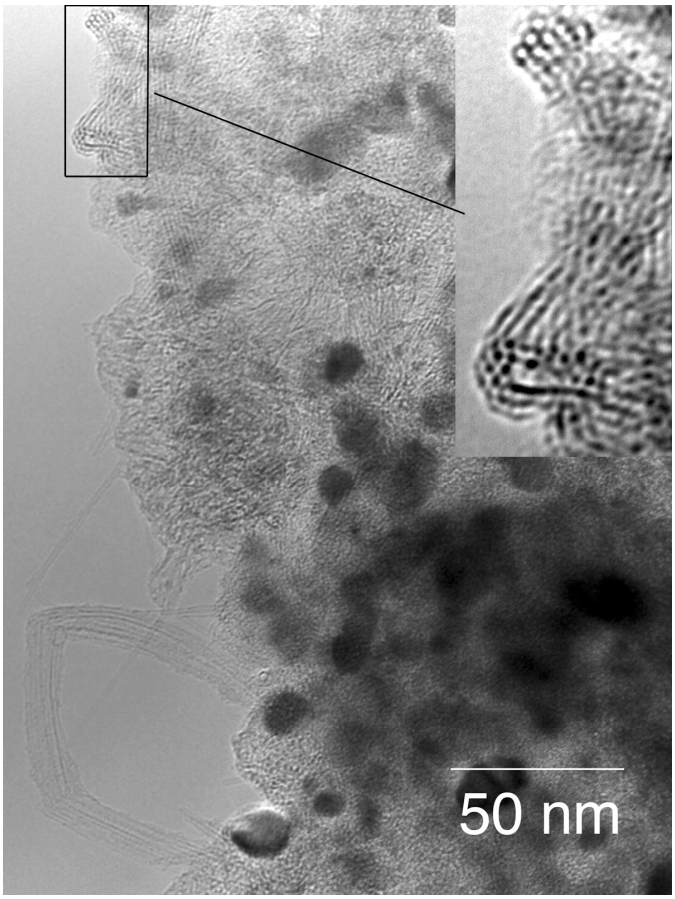
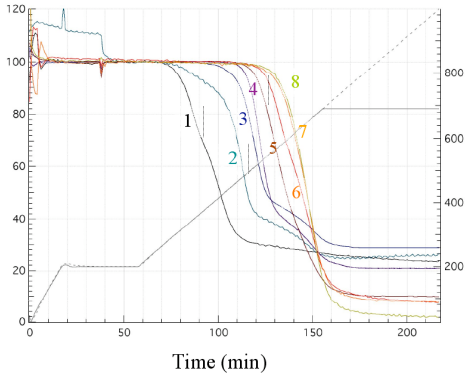


Fig. 4. TEM micrograph showing this as prepared material with 10 to 20nm sized catalyst particles sitting within the carbon matrix. In the upper right inset is a blow-up of the boxed region, showing some of the nanotubes, oriented in a way that the cross-section is apparent. The tube size appears reasonably uniform. The rope structure typical of these materials is more apparent in the lower left of the image.

An analysis of TGA results shows that a number of purification steps are required, with substantial loss of starting material weight (>95%) before AP-Carbolex is free of enough catalyst to begin work on storage properties. The starting material has over 20 wt% residual mass left over in the form of NiO. Our procedure for cutting down on the number of purification steps and for improving the overall materials yield from arc derived nanotubes consists of the following sequence: (a) doping/intercalating the as-prepared SWNTs with potassium (b) washing/exfoliating the resulting powder with ethanol and (c) gas phase oxidation at successively higher temperatures, with each step followed by a reflux in concentrated hydrochloric acid.

Our use of potassium intercalation followed by washing with ethanol causes more complete exfoliation of the intercalated layers, weakening the carbon shell structure covering the metallic particles. These structures are therefore more easily cracked by wet oxidation, more completely exposing the metal catalyst. Each of these steps contributes to the purification, but only a combination of K-intercalation, wet oxidation and hydrochloric acid treatments leads to high-purity material. The effectiveness of this new method will be compared to another process involving more classical purification steps such as a combination of refluxing in HNO_3, centrifugations, refluxing in H_2O_2 and wet oxidations in air at different temperatures (350 to 520°C). The TGA results are shown in Fig. 5.

a)



b)

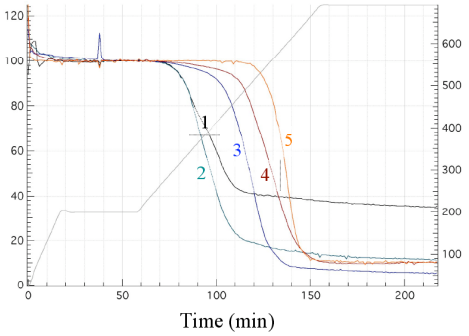


Fig. 5: TGA data of the different levels of Carbolex SWNTs purification
(a) (1) AP Carbolex, (2) after processing in HNO_3 and H_2O_2, (3) after heating at various temperatures in wet air (3) 350°C, (4) 425°C, (5) 480°C, (6) 510°C, (7) 520°C and finally (8) after heat treatment in N_2 forming gas at 750°C.
(b) (1) AP Carbolex, (2) after doping with K, washing with EtOH and HCl reflux, (3) after 350°C wet oxidation step, (4) after 425°C wet oxidation step and (5) after annealing at 750°C in N_2 forming gas. Each oxidation step is completed by HCl reflux.

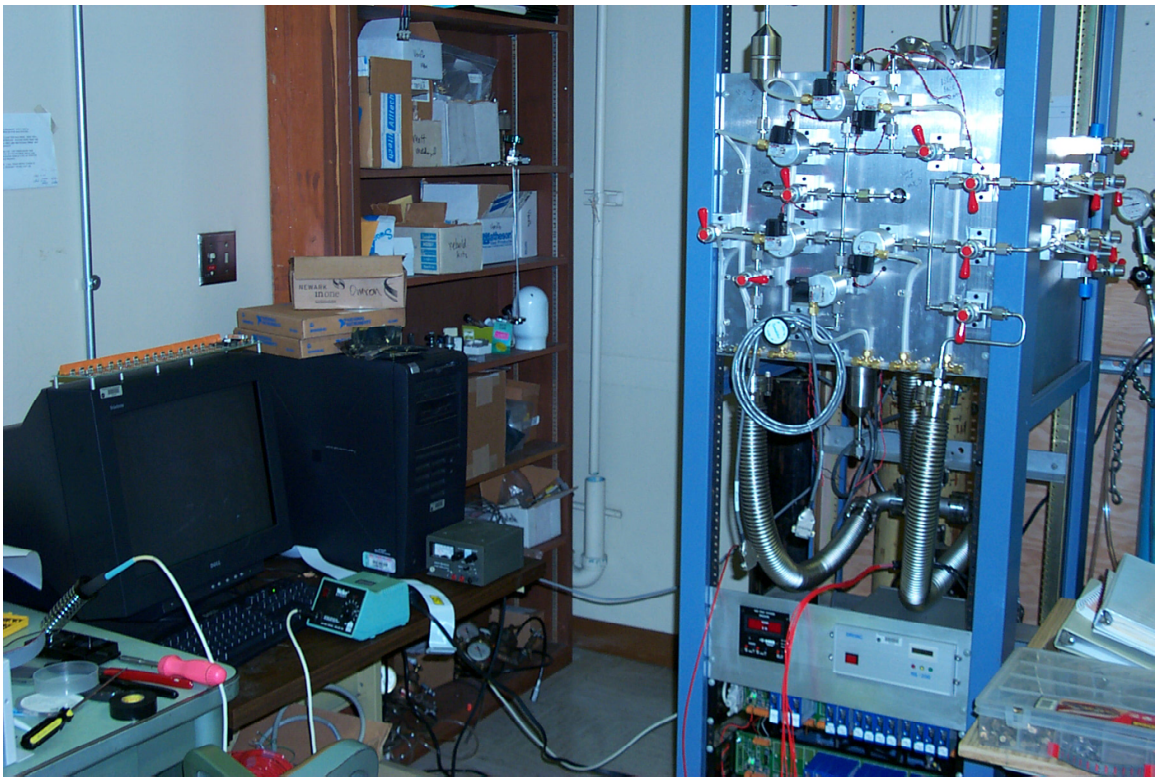
With the completion of the nanotube purification phase of our work, we were able to pursue the real goal of our project, which was to begin intercalation experiments. We hired a post-doctoral fellow from Albert Herold's group in Nancy, France, Dr. Anne Dailly, who had extensive intercalation experience as part of her thesis work. Herold's group has the most experience worldwide in graphite intercalation and Dr. Dailly has made an immediate impact in revamping our synthesis techniques, producing KC_8, KC_{24} and intercalated nanotubes from bucky paper from Rice and purified Carbon Nanotechnologies Hipco material. We've based our initial assessments of the success of this intercalation work on the basis of material color change and on x-ray diffraction measurements. Below is a photograph of KC_8 (above, gold colored) and KC_{24} (blue colored) samples of graphite used to test the furnace temperatures and sample handling procedures.

It was at this time that the funding for this project was earmarked for other purposes. The timing for this was unfortunate as we had made a hiring commitment to Dr. Dailly. We were able to secure a $30,000 gift from the Chemical and Environmental Sci. Lab of General Motors Corporation, which had allowed us to continue with aspects of this work.

Sieverts apparatus and volumetric hydrogen storage measurements

A subsequent $40,000 gift from the Chemical and Environmental Sci. Lab of General Motors Corporation made it possible for us to complete the construction of a He-carbon cryo-cooler Sieverts that was located at the Jet Propulsion Laboratory. This He-carbon cryo-cooler Sieverts represents a >$100k investment on the part of JPL and we were fortunate in being able to locate this equipment in our lab on the Caltech campus.

We have completed initial calibration runs of this unit as of the time of the writing of this report. This unit is performing adequately and we continue to debug some of the baratron readout instrumentation that is yielding pressure resolutions and values at somewhat poorer resolution than specified, and at values that do not correspond with normal non-ideal behavior expected at high pressures. Data for LaNiSn do, however, show sorption behavior that is typical of this material, with values that are comparable to those obtained with the Sieverts apparatus at JPL.



Hydrogen sorption measurements

While the work on our Sieverts apparatus has taken place more slowly than predicted, we have been able to obtain data from Dr. John Vajo of HRL Laboratories of materials that we have processed. Because the material that we had originally intended to use for this work also took a longer than expect time to process, we relied on nanotube material that we had deemed less adequate due to the larger size distribution of tubes. The material we attempted our first sorption measurements of intercalated material were CNI nanotubes that were purified by John Vajo of HRL Laboratories. Our first attempt at intercalating this material resulted in an effective stoichiometry of KC9 and the highly exothermic reaction that took place upon initial hydrogenation led us to believe that KH formation had occurred. The initially high uptake of 0.69 wt% at room temperature and 1.05 wt% uptake at 77K, dropped considerably upon a 2nd attempt, yielding values of 0.043 and 0.22 wt% respectively at the two temperatures, suggesting that some reaction had occurred that no longer made it possible to adsorb hydrogen.

After cleaning of the sample in ethanol, we re-intercalated the material to an effective stoichiometry of KC25 and still obtained a fairly high RT value of adsorption of 0.54 wt% and 77K value of 1.87 wt%. While the 77K data is lower than expected, the RT value is comparable to the highest RT values seen in activated carbon. Our previous attempts at intercalating nanotubes resulted in a total disruption of the tube structure, but for this sample, the x-ray data revealed that some preservation of the original tube packing was preserved, with a 1 Å increase in tube separation. This is the first evidence we have that the rope structure is expanding in a way that we had predicted.

We have summarized the overall extent improvement from single point adsorption isotherms in Fig 6. below. These data compare gravimetric densities of activated carbons with potassium-modified nanotubes and show that there is an increase in the relative amount of hydrogen adsorbed at room temperature with respect to 77K data. In addition, the best data we have obtained so far for K-intercalated nanotubes is comparable to the best activated carbon in yielding >0.5wt% gravimetric storage. We have achieved these results even though we have not yet optimized the processing procedure and attained the desired intercalated nanotube structure. These data indicate that we are beginning to alter the adsorption enthalpy of K intercalated nanotubes as described as part of the original goal of this work.

We hope in the near future to allocate resources for the completion of this work but this will probably depend on funding through one of the Virtual Centers. Completion of this work will consist of complete isotherms of well-characterized, lattice-expanded nanotube rope structures. In any event, we have enclosed a copy of a manuscript that will be submitted for publication within the next few days. This manuscript describes in full detail, the spectroscopic and microscopic analyses of the purification part of this project. In addition, we have submitted a patent application for this part of the project.

We have made good progress into this project and have observed the improvement to adsorption enthalpy that we had anticipated. In addition, we have put together and developed expertise in a number of experimental resources that are necessary for any hydrogen storage project of this type, including, X-ray diffraction, Raman, TEM, TGA and Sieverts volumetric analysis.

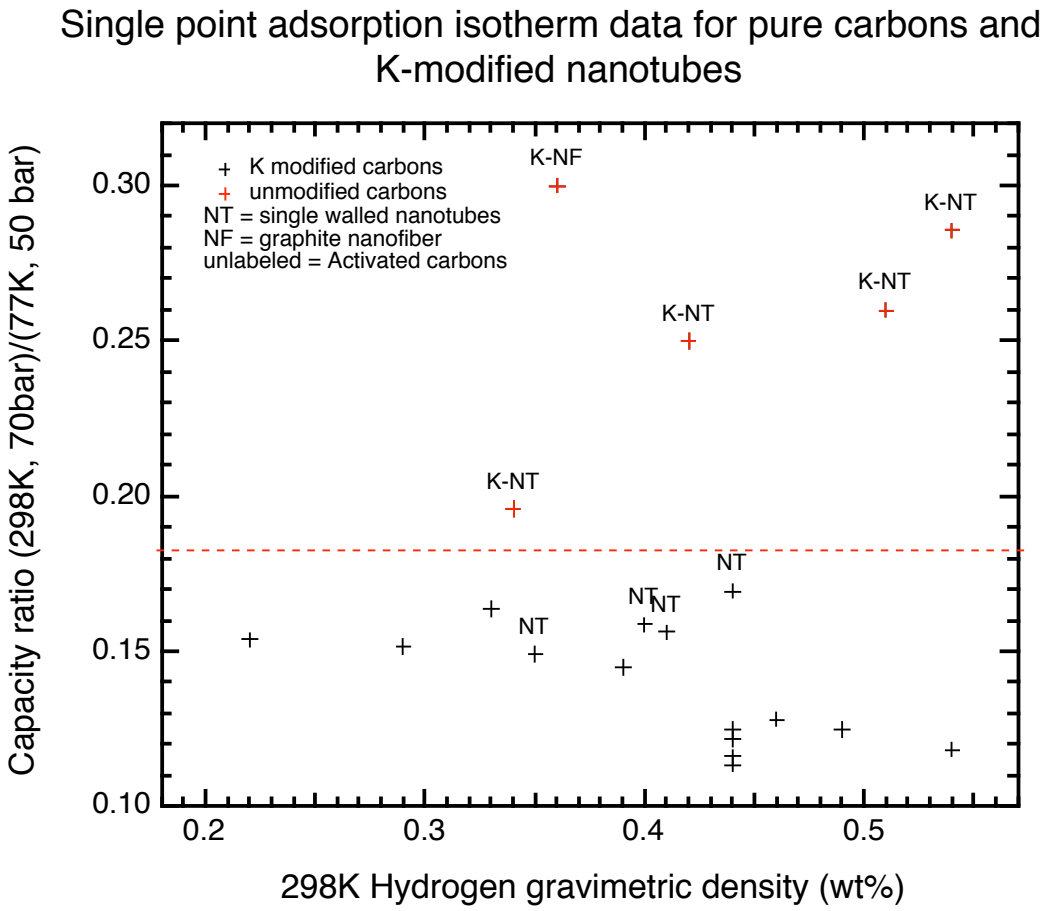


Fig. 6. Comparison of gravimetric densities of activated carbons and potassium-modified nanotubes. The increase in the relative amount of hydrogen adsorbed at room temperature with respect to 77K data show changes to the adsorption enthalpy as a result of potassium modification to the material.

Publications, Patents, and Supported Talks:

Provisional patent application:

Purification of Catalytic Carbons, DOE#60-553,930, 3/17/04, 4057-P
Anne Dailly, Channing Ahn, Rachid Yazami, Brent T. Fultz

Invited Talk, American Nuclear Society
Dr. Channing Ahn, entitled "Hydrogen storage via Physisorption in Carbon Nanostructures"

Manuscript

" A. Dailly, J. Yim, C. C. Ahn, R. Yazami, and B. Fultz , "Purification of Carbon Single-walled Nanotubes by Potassium Intercalation and Exfoliation, submitted to Applied Physics A, 2004.

Residual Funds

The amount of residual funds is estimated to be less than $10.