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Potassium Intercalation of Nanotubes

Anne Dailly[1,2], Channing Ahn[1], Rachid Yazami[1,2] and Brent Fultz[1],
[1]Division of Engineering and Applied Science, California Institute of Technology,
1200 E. California Blvd., Pasadena, California 91125
[2]LEPMI-INPG/CNRS, BP75, 38402 St Martin d'Heres, France

Unlike lithium-based systems that require electrochemical or more extreme means of intercalation into nanotubes, potassium can be intercalated into carbon nanotubes using two bulb reactor techniques, similar to those used for graphites. While graphites display staging phenomena over well-defined temperature ranges in the presence of excess potassium however, single wall nanotubes appear to form stoichiometries near KC_8 (Stage 1) over all values of Δt (difference in reactor bulb temperatures) that would normally form Stage 1 and Stage 2 graphitic intercalated compounds. In order to limit the stoichiometry of a potassium intercalated nanotube, it is necessary to limit the amount of potassium in the reactor to a quantity that is consistent with the final desired value.

We have performed a series of intercalation experiments on "bucky-paper" single wall nanotubes, as well as "HiPco" prepared nanotubes over varying conditions designed to define the temperature and processing regimes that are appropriate to sub-Stage 1 intercalation.

Initial conditions for intercalation were established by using the conditions of Nixon and Parry [1] on Madagascar graphite and result in the characteristic gold color for the KC_8 intercalate, and blue color for the KC_{24} intercalate, phases that were also identified via x-ray diffraction using a Philips PW3040-Pro diffractometer using Cu Kα radiation, with a holder appropriate for air-sensitive samples as shown in Fig. 1.

Depending on their preparation conditions, single wall nanotubes pack into ropes that are held together by van der Waals forces This rope structure can itself yield x-ray diffraction peaks at low angle, with reflections that are consistent with a close-packed rope structure as shown in the lower trace (a) of Fig. 2 for the pristine "bucky paper" sample.

While we are uncertain as to the origin of the graphite (002) reflection in this pattern, our attempts at intercalating this material show two effects as discerned in the upper trace (c) of Fig. 2. The first is a diminution of the (002) peak with a concomitant appearance of weak KC_8 reflections. Second is the disappearance of the low angle peaks. Presumably, the long-range order associated with a well-packed rope structure, is disrupted by intercalation by the conditions used for this material, when intercalated to a stoichiometry of KC_{19}. While "unzipping" of nanotubes into nanostrips by reaction with lithium has been observed [2], the nanotube structure is preserved when reacted with potassium under these conditions.

Upon de-intercalation via cleaning with ethanol, evidence for the reformation of the regular rope structure can be seen in the x-ray diffraction data as shown in the middle trace (b) of Fig. 2.

Results for nanotubes that have been prepared by the HiPco process show similar behavior although this material shows no graphite (002) reflection. Furthermore, intercalation to a stoichiometry of $\sim KC_{25}$ shows that some of the rope structure is still preserved and that expansion of the tube periodicity has increased.

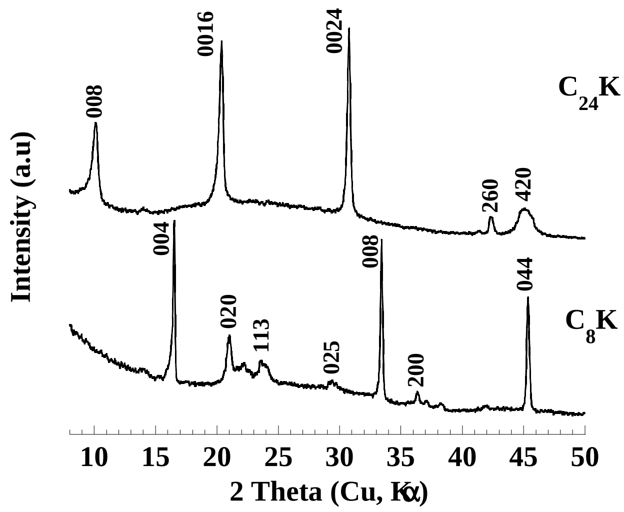

Fig. 1: X-ray diffraction patterns of Madagascar graphite powder after potassium intercalation. The potassium temperature was held constant at 250°C and graphite temperature was maintained at 255°C for C_8K and at 400°C for $C_{24}K$.

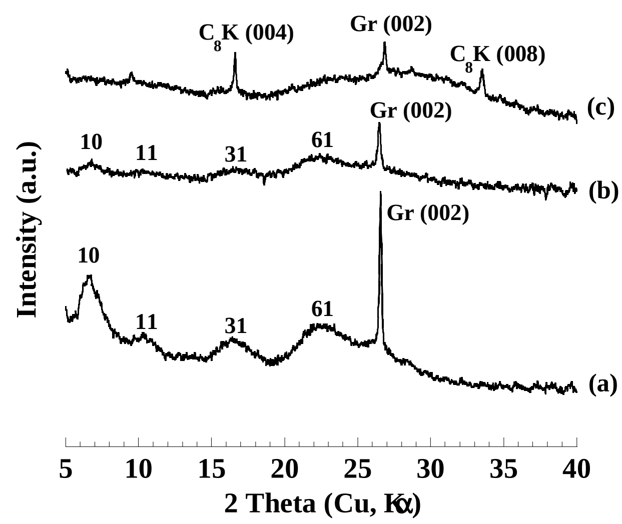

Fig. 2: X-ray patterns of SWNT material before (a) and after (c) potassium doping and (b) chemically K-de-doped SWNT by washing with ethanol.

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References:

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