

HYDROGEN STORAGE AND NEUTRON POWDER DIFFRACTION OF DEUTERIDED KC_{24} and KC_{48}

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Onboard hydrogen storage for transportation applications is a challenging problem from both scientific and engineering standpoints. Many materials, including carbon nanofibers and single-walled nanotubes (SWNTs), generated initial excitement with claims of high storage capacities, but have ultimately fallen short of the requirements of transportation engineering needs[1]. Our traditional understanding of adsorption in such systems is that high surface area is the key to high adsorption levels—a result of having a high number of adsorption sites. The hydrogen storage capacities of materials such as SWNTs and other novel carbons should thus reflect the high surface area nature of these materials. There has been no credible evidence to suggest that the adsorption enthalpy of hydrogen with respect to any sp^2 carbon varies substantially as a result of being in nanotube rather than graphitic form[2]. Consequently, we expect novel carbons to behave as high surface area graphitic carbons.

We can also consider absorption processes in which the requirements of high surface area are obviated and hydrogen storage depends on the intrinsic nature of the bulk material. Potassium intercalated carbons have long been known to absorb hydrogen[3] and represent an excellent starting point from which to develop insight into the sorption process. While these materials also presently fall short of the engineering requirements for practical hydrogen storage systems, they provide a basis for understanding metal modifications to graphitic surfaces that might change the adsorption enthalpy of high surface area carbons.

We have performed neutron diffraction studies using the Neutron Powder Diffractometer (NPD) at the Lujan Center at Los Alamos National Laboratory (LANL), of deuterided KC_{24} , a Stage 2 intercalation compound, and KC_{48} , a Stage 4 intercalation compound. Unlike hydrogen, deuterium is an effective coherent scatterer for neutrons. In both Stage 2 and Stage 4 compounds, K atoms sit in a dodecal structure within alternating graphene sheets as shown in Fig. 1 for the Stage 2 compound. Alternating graphene planes are assumed to stack in an a-b sequence as shown, with K-containing layers within a-a or b-b graphene sequences. Hydrogen has long been known to physisorb into the K containing planes of Stage 2 material to a value of 1.2 wt% at 77 K, although the precise nature of the interaction between the K, the graphite layers and the hydrogen is poorly understood. From Fig. 1, we might expect 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 would yield information on the nature of the interaction between K and D_2 .

Our initial analysis of the KC_{24} (0 0 6) peak shown by neutron powder diffractometry shows a 0.6% reduction in lattice parameter from 300 K, down to 35 K when the sample is held at vacuum (lower set of traces in Fig. 2). In the presence of ~ 3.8 bar of D_2 , the sample undergoes a lattice expansion of 1.6% at 125 K, and saturates at 3.3% at 35 K, indicating that the maximum number of D_2 molecules has been accommodated by this structure. In the case of the Stage 4 compound which has half as many K-containing planes as the Stage 2 compound, we see that the change in the lattice parameter of the basal plane (0 0 10) reflection is roughly half of that of the Stage 2 compound.

We can conclude then that the deuterium likely occupies only the K containing planes in these intercalated graphites.

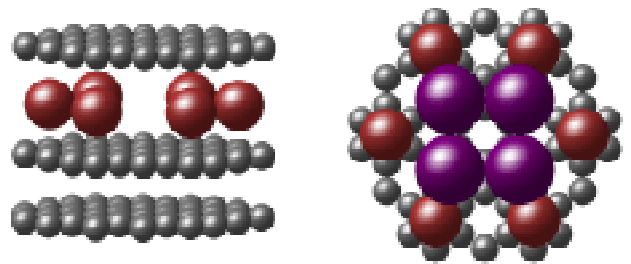


Figure 1: The left figure shows the stacking sequence for KC_{24} . The small atoms represent carbon and the larger atoms show the dodecal structure of potassium atoms. The right figure shows a view down the basal direction of the dodecal K structure atop a single graphene layer. In addition, a possible arrangement for four larger deuterium molecules is depicted.

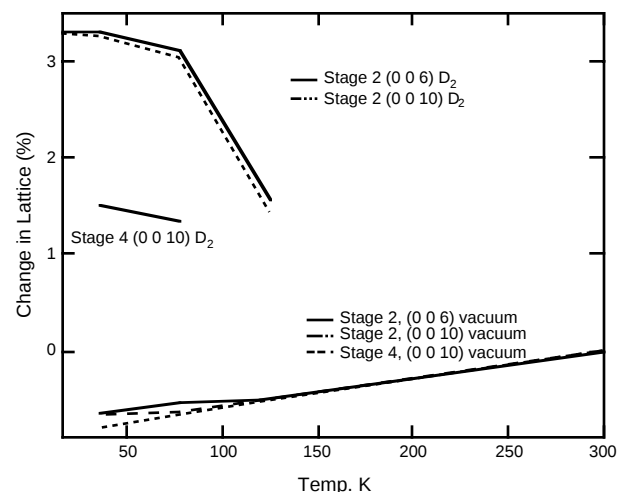


Figure 2: Summary of lattice changes as a function of temperature in Stage 2 and Stage 4 intercalated graphites under vacuum and while deuterided.

- [1] G. G. Tibbetts, G. P. Meisner and C. H. Olk, Carbon, **39**, 2291 (2001).
- [2] C. C. Ahn, Y. Ye, B. V. Ratnakumar, C. Witham, R. C. Bowman, Jr. and B. Fultz, Appl. Phys. Lett. **73**, 3378 (1998).
- [3] M. Colin and A. Hérol, Bull. Soc. Chim. Fr., **6**, 1982 (1971).