INVESTIGATION ON THE CARBON SPECIAL FORM GRAPHITIC NANOFIBRES AS A HYDROGEN STORAGE MATERIALS

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INTRODUCTION

The depleting and polluting fossil fuel makes it imperative to find renewable and clean 21st century fuel. Decades of R&D efforts have revealed that hydrogen is indeed such a fuel. The harnessing of hydrogen as a 'Green Fuel' on a massive scale is held up largely due to lack of a viable storage system. The state of the art storage media, the hydride are too heavy and have a storage capacity at ambient conditions of only about ~1.5wt% [1]. Therefore, there is an ever on going search for new storage materials,. In this search recently some new carbon materials in the form of graphitic nanofibres and ball-milled carbon with very high storage capacity have been found

The exotic hydrogen storage characteristics of graphitic nanofibres prepared by catalyzed decomposition of ethylene over Ni:Cu catalysts was first reported by Chambers of et al. (1999). They claimed storage of about 23.1 or 2g of hydrogen per gram of carbon corresponding to a storage capacity of ~67wt% [2]. This hydrogen storage capacity is an order to magnitude higher than that of the conventional hydrogen storage material, i.e. metal hydrides. However, later in a similar effort Ahn et al. (1998) did not get as high storage capacity from GNF. They in fact obtained a storage capacity of only ~2.7wt% [3] and concluded that the earlier results of Chambers et al. may not be valid. In their further work the Boston group (Park et al., 1999) suggested that careful pretreatment of GNF to remove chemisorbed gases is a critical step for obtaining high storage capacity of GNF [4]. In view of these two early contradictory results, there has been interest to find out the real position regarding the hydrogen storage capacity of GNF. In another recent study of GNF, hydrogen storage capacity of ~6.5wt% has been found [5].

We have carried out studies on GNF grown in a manner similar to that of the above said earlier studies [6,7]. In our studies we have found reproducible storage capacity of ~15wt% [7].

RESULT AND DISCUSSION

In the studies carried out so far by other workers on hydrogenation of GNF, it has been found that the amount of hydrogen desorbed is always less than that which is absorbed. It has been conjectured that some hydrogen even after discharge is still left within the GNF. The feasible mechanism of hydrogen storage corresponds to adsorption of hydrogen molecules between graphitic sheets. It has been suggested that as a result of expansion multilayer coverage takes place within the mobile pore walls formed from graphitic sheets. It is further suggested that under these conditions mobility is suppressed and hydrogen molecules get agglomerated in a liquid like configuration. In order to visualize whether lateral expansion of graphitic sheet takes places, we have carried out detailed microstructural characteristics of the as synthesized as well as hydrogen desorbed GNF employing the technique of transmission electron microscopy.

X-ray diffraction studies of the as-synthesized, hydrogenated and dehydrogenated GNFs' samples revealed some curious characteristics. These are listed in the following :

(a) The (002) peak which manifests the graphitic layers was invariably poorly defined in the XRD patterns of the as synthesized GNFs'. On the other hand, the (101) peak and other non (00l) peaks were found to be sharp and of high intensity. These features are brought out by the as synthesized sample.

(b) The (002) peak of the hydrogenated samples (upto ~120 atm. of H$_2$) which were taken out from the reactor after hydrogenation for 24 hrs. and then dehydrogenated is better defined than that of the as grown GNF.

(c) It may be pointed out that for GNFs' even on repeated dehydrogenation some amount of hydrogen is always present. The hydrogenation leads to lateral expansion of graphene sandwich layers and hence an increase of the interlayer spacing. This is clearly borne out by the estimates of d$_{002}$ which is 3.46Å for the as synthesized and the average d$_{002}$ on hydrogenation/dehydrogenation.

For graphitic nanofibres, the (00l) layers are of finite extent (100 to ~1000Å) arranged nearly perpendicular or inclined to the fibre axis. In all the firbres which will be arranged randomly the (00l) planes in GNF have finite extents. Therefore, the XRD peak profile for (00l) planes including (002) will be broadened in as-synthesized sample. The other planes like (h0l) e.g. (101) or (hk0) e.g. (110) do not have finite extents like (00l) planes and therefore, the peaks corresponding to these will not be broadened but comparatively sharp. This is what is actually observed in hydrogenated sample. Now when hydrogen goes in between the graphene planes, later expansion of graphene planes will take place. Transmission electron microscopic investigations reveal that the hydrogenated/dehydrogenated GNF samples show expansion of the graphene planes through the existence of gaps between graphene planes. As is easily discernible, hydrogenation has led to lateral expansion of the graphene planes as brought out by the void like spaces. The TEM micrograph of hydrogenated samples.

The P-C-T desorption curves were evaluated for several hydrogenation/dehydrogenation cycles. The P-C-T desorption curves correspond to the first, third, seventh, ninth and fifteenth cycle. The highest hydrogen storage capacity as brought out by the P-C-T desorption curves from the 9th cycle is ~15wt.%. Several runs carried out on different lots of GNF's confirm the storage capacity of ~15wt.%. After the ninth cycle hydrogen concentration did not increase upto 15th cycle. Besides the hydrogen storage capacity, we have also investigated desorption kinetics of GNF sample studies in the present investigations and we had found the average rate of hydrogen desorption ~57ml^3/min. The highest desorption kinetics of GNF sample ~90ml^3/min was obtained for hydrogen concentrations ranging between ~6.0 to 8.0wt%.

CONCLUSIONS:
Based on the present investigations, the following conclusions can be drawn: The present investigation forms furtherance of our earlier result on hydrogenation behaviour of graphitic nanofibres. Some results are enumerated in the following :

(i) The actual hydrogen storage capacity will depend on the activation treatments imparted to GNF. In the present case through suitable activation, it was possible to increase, the storage capacity from 10 to 15wt.%. The storage capacity may get raised to still higher values.

(ii) The small extents and dispositions of (00l) planes makes (00l) X-ray diffraction peaks e.g. (002) broadened unlike the (h0l), (hk0) peaks which are comparatively sharp.

(iii) The XRD and TEM investigations suggest that hydrogen enters between the (00l) graphene layers, leads to lateral expansion of these layers creating void like space and turning the (00l) planes curved and lengthened. The periphery of the void space may be special favoured sites of adsorption of hydrogen molecules in further hydrogenation cycles.

(iv) The present investigation on desorption kinetics of GNF sample shows that the average rate of hydrogen desorption ~57ml^3/min. The highest desorption kinetics of GNF sample ~90ml^3/min was obtained for hydrogen concentrations ranging between ~6.0 to 8.0wt%.

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