INVESTIGATIONS ON THE CARBON NANOFORM : ALIGNED GRAPHITIC NANOFIBRES AS A HYDROGEN STORAGE MATERIAL

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Introduction

Although it is generally accepted now that hydrogen (the green fuel) will be the best replacement for oil, the wide ranging use of hydrogen is hampered due to lack of a viable storage technology. The solid state hydride storage route is considered to be an efficient and safe mode of hydrogen storage. However, the present storage capacity for the state of the art hydrides at ambient conditions is ~1.5wt% , which is only marginal, particularly for vehicular applications. The storage capacity of the present hydrides is not enough since the optimum storage capacity should be ~3 to ~6wt% [1]. To achieve this, two approaches are being adopted. One is tailoring of the known state of the art hydrides so that they can achieve higher than 1.5wt% storage capacity. The other approach relates to finding altogether new materials. In this latter approach presently the graphitic nanotubes / nanofibres (GNT/GNF) appear to be one of the most promising candidates. The hydrogen storage characteristic of GNF was first investigated by Chambers et al. [2]. They reported high storage capacity upto ~67wt% which corresponds to storage of 23 litre or 2gm of hydrogen per gram of carbon. However, later reports by other scientists are at variance with initial results of Chambers et al. As for example Ahn et al. reported a low capacity for GNF of about ~2.7wt% [3]. On the other hand Cheng et al. have found storage capacity of ~10 to 13wt% [4]. In another publication the same group (Cheng et al.) has reported a storage capacity about two times lower than the earlier value [5]. Some recent review papers e.g. Cheng et al. [6], Schlapbach [1] and Hirscher et al. [7], Atkinson et al. [8]and D.V. Schur et al. [9] have reported a summary of all the works on hydrogen storage in carbon nano-materials including GNFs. It may be pointed out that graphitic (carbon) nanotubes (single walled and multiwalled) and graphitic nanofibres are two distinctly different nano-forms of graphite. In the former (GNT), the graphitic sheets which are rolled up have very large extents, in the latter (GNF) the graphitic planes have finite extents and are arranged regularly about the axis perpendicular (or parallel or inclined) to the fibre axis. However, in several papers while discussing the hydrogen storage characteristics of nanoforms of carbon, the GNT and GNF have not been distinguished. In our earlier studies on GNF, we have found hydrogen storage capacities of ~10 to ~15wt% [10,11]. It may be pointed that a storage capacity between ~10 to ~15wt% is about one order of magnitude better than any of the metal hydrides. Therefore, there is significant interest in further studies on finding improved synthesis and growth conditions and hydrogenation behaviours of GNF in order to establish it as a new hydrogen storage material. The aim of the present paper is to report improved synthesis and growth of GNF by utilizing Pd sheets as the catalyst. The yield of GNF employing this growth mode is about three times as much as that obtained from the earlier synthesis route using powders of Cu, Ni (and their mixtures) as catalyst [10,11]. The other advantage of the present method is that unlike the previous formation processes, where catalyst incorporation in GNF is ~20%, the inclusion of catalyst (i.e. Pd) in the resulting GNF is low and hence catalyst (Pd) consumption per synthesis run is small (<2%). Yet, another advantageous feature of the present method is that these GNF, instead of very high charging pressures of ~120 atm. employed so far [10,11], get hydrogenated at comparatively lower charging pressure of ~80 atm.

Results and disscution

The formation of graphitic nanofibres as achieved by various workers so far is through catalyst assisted thermal cracking of hydrocarbon [2]. The catalyst employed are often nickel, copper powder or a mixture of the two (e.g. 98% Ni and 2% Cu by weight) [2]. The hydrocarbons employed by us are acetylene (C_2H_2), ethylene (C_2H_4), benzene (C_6H_6) [10,11]. The yield of GNF obtained through these catalyst assisted cracking process is rather poor and also the resulting GNFs are randomly oriented [10]. In order to improve upon this, in the present investigation, we employed Fe, Co, Ni, Mo, Pd catalysts in the form of films and sheets. It has been found that Pd sheets give optimum results in regard to the yield and orientation of the as grown GNFs. The hydrocarbon employed in the present investigation is acetylene (C_2H_2). The thermal cracking was done by taking the gases in a silica tube (80 cm long, 3.5 cm diameter). The tube contained inlet ports for hydrogen and helium gases. The catalyst palladium sheet was in the form of small pieces which were 8 x 2mm and 0.12mm thick with total weight of 200 mg. The growth tube containing Pd sheets, was evacuated to 1.32×10^{-7}atm. and then filled with Helium at 2.63×10^{-2}atm. . The tube containing Pd sheets (catalyst) and Helium was heated to ~600°C for 1 hour. This treatment was done to passivate the Pd sheet surface. The tube was cooled to room temperature and Helium was removed. The tube was evacuated again to 1.32×10^{-7}atm. and then filled with hydrogen at ~4.21×10^{-2}atm. and then acetylene at a total pressure of ~0.22 atm. The cracking of the gases was achieved in stationary mode by heating these in the presence of Pd catalyst at a temperature of 640±10°C for 1½ hrs in a resistance heated furnace. After this the tube was allowed to cool at a rate of 5°C/min. At this stage the carbon got deposited on the catalyst pieces. Before taking out the carbon deposits, the tube was flushed with 2% He and Air. The deposited carbon, as will be shown later, was identified as GNF. The total quantity of GNF grown in one run (the tube was recharged with acetylene seven times in each run) was ~800mg.

The structural characterization of the as-synthesized dehydrogenated/ hydrogenated GNF has been carried through X-ray diffraction technique employing Philips PW-1710 X-ray diffractometer equipped with graphite monochromator. The microstructural characterizations have been carried out through transmission electron microscopy (EM-CM 12) in diffraction and imaging modes and also through scanning electron microscopy (XL-20). The hydrogenation of the as-synthesized aligned GNF was carried out in Sievert’s equipments fabricated in our laboratory. Hydrogenation and dehydrogenation cycles on several other GNF samples synthesized in the present investigations employing Pd catalyst revealed that the storage capacity of ~17wt% could be reproducibly obtained.

Conclusion

The synthesis of GNF through thermal decomposition of acetylene when carried out employing Pd sheets as catalyst, leads to the formation of aligned GNF bundles. The typical bundle length and width of cross-section are ~50μm, ~25μm and the individual GNF length ~50μm, and width ~250nm.

1. The growth of aligned GNF has been shown to result due to the formation of GNF on textured juxtaposed dense away of grains in the palladium sheets.
2. The aligned GNF bundles get hydrogenated at lower hydrogen pressures of ~80 atm. as compared to the coiled GNFs which undergo hydrogenation at higher pressures of ~120 atm. This is thought the result due to ease of adsorption of hydrogen on straight linear aligned GNF as against coiled GNFs which hydrogenate at pressures of ~120 atm. The reproducible hydrogen storage capacity of the GNF grown in the present studies is ~17wt% which is one of the high reproducible hydrogen storage capacity for GNFs.

References

1. L. Schlapbach, A. Zuttel, Nature 414 (2001) 353.
2. A. Chamber, C. Park, R.T.K. Baker, N.M. Rodriguez, J. Phys. Chem. B. 102 (1998) 4253.
3. C.C. Ahn, Y. Ye, B.V. Ratnakumar, C. Witham, R.C. Bowman, B. Fultz, Appl. Phys. Letters., 73 (1998) 3378.
4. Y.-Y. Fan, B. Liao, M. Liu, Y.-L. Wei, M.-Q. Liu, H.-M. Cheng, Carbon 37 (1999) 1649.
5. H.M. Cheng, C. Liu, Y.Y.Fan, F., Li, G. su, L.L. He, M. Liu, Z. Metallkd 91 (2000) 306.
6. H-M Cheng, Q-H. Yang, C. Liu, Carbon, 39 (2001) 1447.
7. M. Hirscher, M. Becher, M. Haluska, A. Quintel, V. Skakalova, Y.-M. Choi, U. Dettlaff-Weiglikowska, S. Roth, I. Stepanek, P. Bernier, A. Leonhardt, J. Fink, J. Alloys and Compounds, 330-332 (2002) 654.
8. K. Arkinson, S.Roth, M. Hisrcher, W. Grunwald, Fuel Cells Bulletin, 38 (2002) 9.
9. D.V. Schur, B.P. Tarasov, S. Yu. Zagi-naichenko, V.K. Pishuk, T.N. Veziroglu, Yu. M. Shul’ga, A.G. Dubovoi, N.S. Anikina, A.P. Pomytkin, A.D. Zolotarenko, Int. J. Hydrogen Energy, 27 (2002) 1063.
10. B.K.Gupta, O.N.Srivastava, Int. J. Hydrogen Energy, 25 (2000) 825.
11. B.K.Gupta, O.N.Srivastava, Int. J. Hydrogen Energy, 26 (2001) 857.