

Hydriding of nitrogen containing Carbon nanotubes

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Hydriding of nitrogen containing carbon nanotubes yields ammonia under mild experimental conditions.

In the concept of hydrogen economy, hydrogen storage is an important component. There have been attempts in the last 20 years to achieve an energy efficient method of hydrogen storage in the form metal hydrides [1,2] as well as in the recent times in carbon nanomaterials. [3-5] In the former case, storage capacity is always controlled by the stoichiometry of the hydride formed and storage capacities greater than 3 wt % could not be achieved employing conventional intermetallics except in the case of alanates [6,7]. However, the exploitation of alanates as hydrogen storage medium has limitations due to difficulties with synthesis and the ease of release of hydrogen. In the case of carbon nanomaterials, there are various claims varying from 0 to 68-wt% [8-11] of hydrogen, though most of these reports could not be successfully reproduced by others.

Ruthenium supported on multi-wall carbon nanotubes have been shown to be potential system for the production of ammonia when conventional systems at atmospheric pressure and 673 K. It is also observed that promotion of such system with potassium enhances the activity [12]. Similarly hydrogen-absorbing intermetallics containing rare earth and Fe, Co or Ru have been examined as catalytic systems for the synthesis of ammonia. However, it has been shown that these catalytic systems underwent decomposition to give rise to Fe supported rare earth nitride systems. Hence essentially they were similar to the conventional supported with catalysis employed in ammonia synthesis. [13] The confinement in carbon nanotubes has been shown to reduce the activation energy and reaction

endothermics for the Menshutkin S_N2 reaction compared to those in the gas phase. [14]

Against this background, we have examined heteroatom containing single walled carbon nanotube as one another alternative material for hydrogen storage. In the present study, two different single walled carbon nanotubes (CNTs) were prepared by employing polymer precursors polypyrrole and polyphenyl acetylene as carbon source, which were polymerized in a templated alumina membrane. The polymers formed were carbonized and then the alumina membrane was dissolved in HF. Details of the synthesis procedure adapted are given in our earlier communications [15,16]. The formation of the carbon nanotubes was clearly seen from the electron microscopic images shown in (Fig.1). The diameter of nanotubes produced is equal to the pore size of the template, alumina membrane, which is around 200 nm. The nitrogen content of the carbon nanotubes prepared from polypyrrole ascertained from the elemental analysis was found to be greater than 2 %.

Hydrogen absorption characteristics were evaluated by evolved gas analysis technique (EGA). In a typical experiment, the sample was loaded in the EGA chamber and was evacuated to 10^{-6} torr by heating the sample to 400K. Hydrogen was then admitted into the chamber while the sample was heated at a rate of 20 K/min to 673 K. The chamber was then cooled to room temperature and the chamber was again evacuated to 10^{-6} torr. The sample was then heated at the same heating rate up to 693 K while simultaneously monitoring the gas evolved by mass spectrometer. The evolved gas traces for the two samples of carbon nanotubes are shown in Fig. 2. It is seen that the carbon nanotube containing nitrogen gave a trace corresponding to mass 17, indicating ammonia formation. The

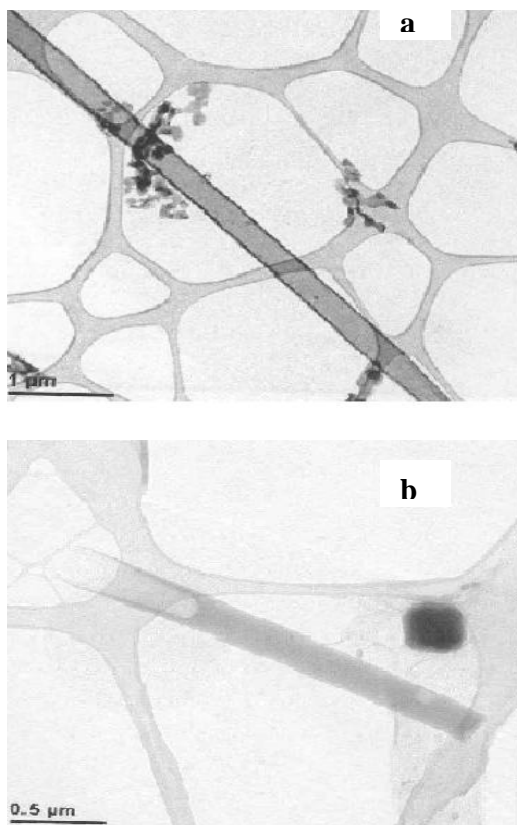


Fig.1 Transmission electron microscopic images of CNTs: - (a) PPy (b) Ppa

evolution of ammonia was pronounced above 473 K. However, in the case of carbon nanotubes obtained from polyphenyl acetylene gave only back ground signal corresponding to mass 17.

In order to ascertain this observation, a second hydriding of the nanotube prepared from polypyrrole was carried out in EGA unit and it was observed that the amount of ammonia evolved considerably decreased (Fig. 2). The cyclic voltammetry [17,18] was recorded in 6 N KOH using carbon nanotubes mounted on a glassy carbon as a working electrode, platinum as a counter electrode and Ag/AgCl as reference electrode with scan rate of 25 mV/sec in the potential range 0 to -1.3 V. It was observed (Fig. 3) that the glassy carbon electrode loaded with CNT from polypyrrole alone showed a peak at -1.05 V corresponding to hydrogen desorption, thus showing CNT from polypyrrole source alone is capable of activating and absorbing hydrogen.

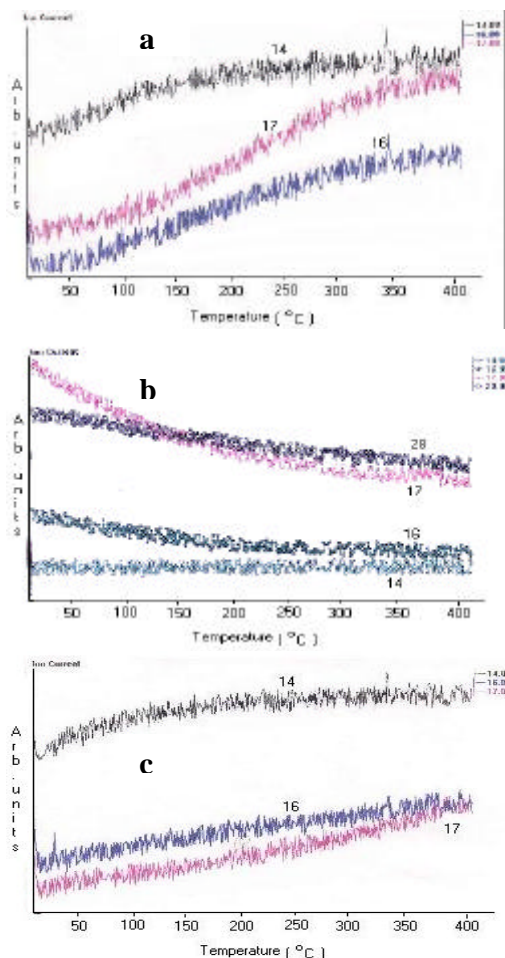


Fig. 2 EGA profile of (a) CNY PPy (b) CNT PPa (c) CNT PPy recycled

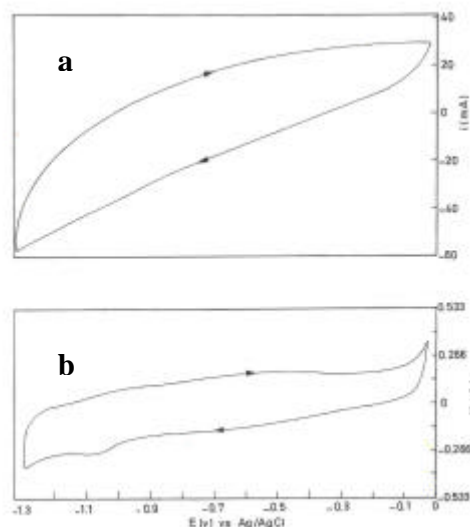


Fig. 3 Cyclivoltammograms (a) CNT PPa (b) CNT PPy

By independent method, the evolution of ammonia was ascertained by spectrophotometry using Nessler's reagent. From the amount of ammonia evolved it is estimated that CNTs containing 20 wt% of nitrogen is capable of taking up about 1 wt % of hydrogen. If this hydrogen could be transported to the carbon skeleton, it may be possible to achieve DOE standards of (6.5 wt %) [19] hydrogen storage capacity in heteroatom containing CNTs. This possibility as well as the effect of hetero-atoms in the reactivity of carbon nanotubes is to be exploited in future.

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