

IV.C.1m Conducting Polymers as New Materials for Hydrogen Storage

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Partner Approach

Cho et al. [1] reported approximately 8 wt% (reversible) hydrogen gas storage in doped (metallic) forms of organic conducting polymers (“synthetic metals”), polyaniline and polypyrrole. Polyaniline is a unique type of conducting polymer in which the charge delocalization can, in principle, offer multiple active sites on the polymer backbone for the adsorption and desorption of hydrogen, involving weakening of the H-H bond followed by “spillover” adsorption of this hydrogen onto the adjacent nano-fibrous network.

The critical information gained to date during this study (see Partner FY 2006 Results in next section) is that the composition of the conducting polymers actually used in all previous H₂ adsorption/desorption studies is unknown. The very recent UPenn studies have shown conclusively that the different, vague, preheating “degassing” procedures used in the past by all groups lead to major modification in the chemical composition of the polymer, hence presumably in the type and number of active sites available for H₂ absorption. The key focus of the UPenn group will now be to show conclusively once and for all whether the products formed in the previously described [1,2] preheating, “degassing” treatment of the conducting polymers result in materials which can, or cannot absorb/desorb H₂.

Thus, the University of Pennsylvania (UPenn) group will first investigate the use of polyaniline in which the active sites are no longer occupied by water molecules. This study will then be continued to polyaniline in its different oxidation states (doped and non-doped forms) and other conducting polymers (especially polypyrrole) for optimization of hydrogen storage applications. Specific activities to optimize the fundamental absorption processes and to determine the hydrogen sorption performance include investigation of the partly deprotonated polyaniline formed in some [1,2] preheating “degassing” procedures (see Partner FY 2006 Results in next section) to ascertain whether the new material formed by the “degassing” procedure results in more active sites related to H₂ sorption/desorption.

Partner FY 2006 Results

- The UPenn group in collaborative work with NREL has presented strong evidence that adsorbed H₂O in the polyaniline affects its interaction with H₂. In Figure 1, we give the results of our TGA studies in collaboration with Dr. Andrew R. McGhie at University of Pennsylvania.
- Together with the data in the next bullet below, it is concluded that H₂ absorption does not occur when the polyaniline contains strongly absorbed water which occupies the active sites on the polymer needed for H₂ absorption.
- The UPenn group observed that camphorsulfonic acid (HCSA)-doped polyaniline nanofibers [3] showed reversible electronic interactions with hydrogen, which could be further exploited for hydrogen storage. It has been reported that electronic interaction with hydrogen is completely stopped by the presence of water [3]. Figure 2 shows the results on the reversible and reproducible electronic interactions between HCSA-doped polyaniline nanofibers and 1% H₂ carried by a N₂ flow.
- Synthesized and characterized polyaniline nanofibers in the emeraldine oxidation state.
- Conducted ¹H-NMR studies in collaboration with Dr. Y. Wu's group at the University of North Carolina, Chapel Hill, NC, on samples of polyaniline nanofibers that did not show significant hydrogen adsorption. However, consistent with our collaborative studies on H₂ desorption with M. Heben's group (NREL), the ¹H-NMR results

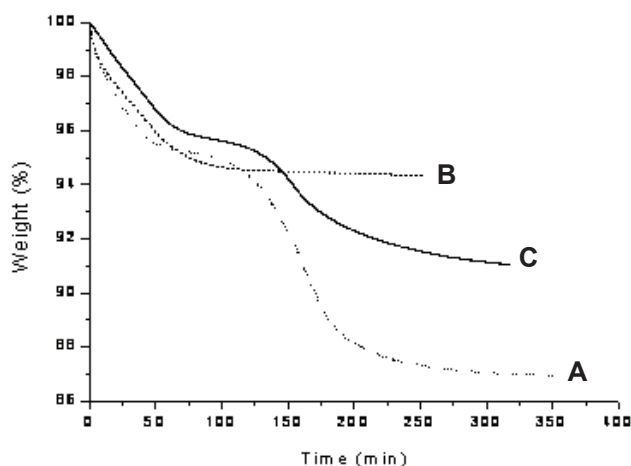


FIGURE 1. TGA studies on polyaniline (emeraldine.HCl).

Curve A (Figure 1): The polyaniline used by us, its HCl treatment, and heat treatment followed, as best as we could, the somewhat incompletely described method given by Cho *et. al.* [1]. The method used by us involved commercial polyaniline (emeraldine base) from Aldrich Co. After doping with conc. HCl, the polyaniline. HCl was dried at 87°C (dynamic vacuum) for 24 hours and was used to obtain curve A by the following procedure: the sample was heated in an Argon stream at 1°C/min to 200°C and then held at 200°C for 3 hours in our TGA study. At the point of inflection, there was a total weight loss of 4.9%. The gas evolved was proven by mass spec (NREL) to be water. The second weight loss (from the point of inflection) to the termination of the study was 8.2%. The gas evolved was proven by mass spec (NREL) to be HCl. Thus, even after the initial drying process, the polyaniline still contained strongly absorbed water. It should be stressed that Cho *et. al.* [1] did not give their time of heating. Moreover, the presence of 4.9% water could reduce H₂ adsorption greatly [3]. If the material on which the actual H₂ sorption studies were performed, i.e. preheating “degassing” time between ~125 min. and ~190 min, during which HCl was evolved, the Cho *et. al.* studies [1] would have been performed on partly decomposed polyaniline.HCl.

Curve B (Figure 1): The experiment was performed on part of the original sample as prepared for curve A except that after reaching 100°C, the temperature was held at 100°C for 3 hours. Approximately 5.8% weight loss (of H₂O) was observed. No weight loss of HCl was observed.

Curve C (Figure 1): The experiment was performed on part of the original sample as prepared for curve A except that after reaching 164°C, the temperature was held at 164°C for 3 hours as described by Roth *et. al.* [2] in their H₂ adsorption studies. We found that the weight losses were similar in kind to curve A.

showed unusual features during the hydrogen *adsorption* process, which seems to depend on the amount of water previously adsorbed by the polyaniline sample.

- The UPenn group developed a new electrochemical method for determining the *actual* oxidation state of samples of polyaniline. Determination of actual quantitatively discrete oxidation states of several spectroscopically indistinguishable polyaniline samples was demonstrated using this novel method.

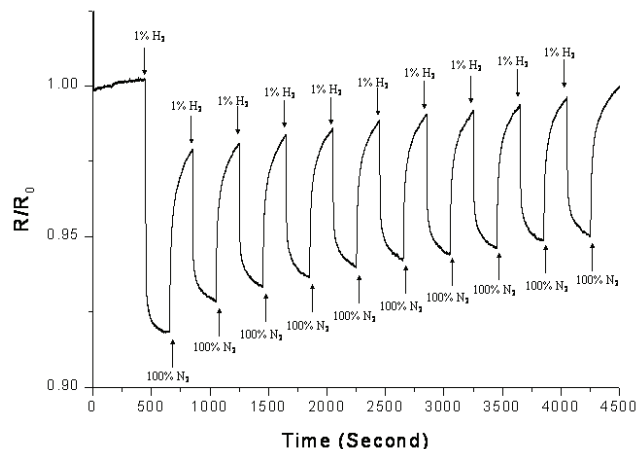


FIGURE 2. The plot of response current as a function of time when HCSA-doped polyaniline (synthesized at UPenn) nanofiber mat bridging two isolated parallel gold electrodes deposited on a silicon wafer upon exposure to several cycles of 1% hydrogen carried by a N₂ flow (applied voltage: 0.1 V). This result is consistent with that reported by B.H. Weiller [3].

Partner FY 2007 Plans

- Collaborate with NREL (M. Heben group) on H₂ absorption/desorption studies on emeraldine forms of polyaniline which have been shown by the UPenn group by TGA to have had all absorbed water removed from active sites in the polymer.
- Supply samples to NREL group of polyaniline decorated with traces of metallic palladium which have already been prepared by UPenn group and which have been shown by UPenn group to be free of water absorbed on active sites.
- Supply samples of water-free polyaniline to Y. Wu (U. of North Carolina) to continue on-going collaborative NMR studies on the interaction of gaseous H₂ with polyaniline.
- Obtain direct atomic and nanoscale information related to H₂ adsorption sites on polyaniline and diffusion mechanisms by neutron scattering measurements at NIST.
- Prepare isomeric forms of emeraldine base formed on heating emeraldine base at or below 300°C [4].
- Use pernigraniline base (most highly oxidized form of polyaniline) in H₂ absorption/desorption studies on pernigraniline polyaniline base in collaboration with NREL.

University of Pennsylvania FY 2006 Publications/Presentations

1. “Conducting Polymers as New Materials for Hydrogen Storage,” A.G. MacDiarmid, DOE Annual Merit Review, Arlington, VA, May 16-19, 2006.

References

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3. S. Virji, J.D. Fowler, C.O. Baker, J. Huang, R.B. Kaner, B.H. Weiller, *Small*, 1 (2005) 624; B.H. Weiller. Poster, MRS Meeting, San Francisco, April 17-21, 2006.
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