

Interaction Between Polyaniline and Hydrogen (H₂)

Everaldo Carlos Venancio^{1*} (PQ) and Alan G. MacDiarmid^{1,2} (PQ)

¹Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA. ²Department of Chemistry, University of Texas at Dallas, Richardson, TX 75083, USA. * venancio@sas.upenn.edu

Keywords: hydrogen storage, energy, polyaniline, hydrogen.

Introduction

Cho et al.¹ reported approximately 8 wt% (reversible) hydrogen gas storage in doped (metallic) forms of the organic conducting polymers (“synthetic metals”), polyaniline and polypyrrole. There has been, and still is, some confusion among investigators who are not familiar with polyaniline. Polyaniline does not exist as such. It exists in 3-different discrete oxidation states: (i) the fully oxidized “pernigraniline” oxidation state, (ii) the half oxidized “emeraldine” oxidation state and (iii) the completely reduced “leuco” oxidation state, or in oxidation states intermediate between any two of the above adjacent oxidation states. Each of these different oxidation states can be “doped” i.e. protonated to varying extents, giving at least six different chemical compounds². “Polyaniline” can exist as two different emeraldine classes of compounds², the semiconducting emeraldine base form ($\sigma \sim 10^{-5}$ S/cm) and the metallic, emeraldine conducting form ($\sigma < 1,000$ S/cm). These 2 forms are completely different compounds with their own characteristic chemical and physical properties².

The unique nature of this fascinating class of compounds highlights its potential importance in a new type of H₂ reaction, e.g. adsorption of H₂, especially since it can also be prepared in many different nano/micro morphology^{2,3}.

Results and Discussion

Camphor sulphonic acid-doped polyaniline nanofibers (Polyaniline.HCSA) showed an extremely broad desorption peak (~ -165 °C to -25 °C) with a shoulder at ~ -60 °C (Figure 1). This could indicate the presence of a variety of different binding sites and though it is not room temperature, it is quite accessible through standard cooling methods.

¹H-NMR and electrical resistance measurements, upon exposure to hydrogen and several cycles of 1% hydrogen carried by a N₂ flow stream (applied voltage: 0.1 V), showed that adsorbed water has a pronounced effect on the interaction of H₂ with Polyaniline.HCSA. Previous H₂ sorption^{1,4} studies on HCl-doped polyaniline (polyaniline.HCl) had not actually used any known form of polyaniline! Polyaniline of a different composition from that placed in the TPD apparatus had been used for the H₂ sorption studies as concluded from the TGA studies carried out under “preheating” conditions. It was demonstrated by TGA

measurements that the composition of doped polyaniline (polyaniline.HCl) changed during pre-heating (“pre-conditioning”) carried out at different temperatures (100, 164 and 200 °C).

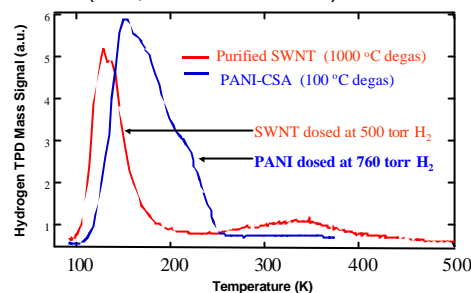


Figure 1. Temperature Programmed Desorption (TPD) studies using emeraldine polyaniline nanofibers doped with camphorsulfonic acid (HCSA). Note: “PANI” is synonymous with “polyaniline”.

Conclusions

There is experimental evidence for an interaction between H₂ and doped polyaniline. This interaction is certainly an electronic interaction as shown in the change of electrical resistance measurements of polyaniline.HCSA in the presence of hydrogen (H₂).

We hypothesize that if heating is done in the presence of H₂ that the H₂ is adsorbed at the sites finally liberated by the H₂O and/or HCl and which had previously been occupied by H₂O and/or HCl.

Cho¹ preheated at 200 °C for an unspecified period of time. Roth⁵ preheated at 164 °C for 3 hours. It was found from the TGA studies that these preheating processes will result in significant change in composition of the polyaniline first loaded into the TPD apparatus by previous investigators during their preheating.

Acknowledgements

Studies described were supported by the Department of Energy (USA) and University of Pennsylvania. TPD studies done by Dr. Michael J. Heben (NREL, USA). ¹H-NMR studies done by Prof. Yue Wu (Univ. North Carolina, USA).

¹ Cho, S.J.; Song, K.S.; Kim, J.W.; Kim, T.H.; Choo, K. *Fuel Chemistry Division, 224th National Meeting of the American Chemical Society*, 2002, 47, 790.

² MacDiarmid, A.G., *Angew. Chem. Int. Ed.*, **2001**, 40, 2581.

³ Venancio, E.C.; Wang, P.C.; MacDiarmid, A.G. *Synthetic Metals*, **2006**, 156, 357.

Sociedade Brasileira de Química (SBQ)

⁴ Panella, B.; Kossykh, L.; Dettlaff-Weglikwska, U.; Hirscher, M.; Zerbi, G.; Roth, S. *Synthetic Metals*, **2005**, *151*, 208.