

# **Final Technical Report**

**Project Title:** Conducting Polymers as New Materials for Hydrogen Storage

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**Recipient:** University of Pennsylvania (MacDiarmid)

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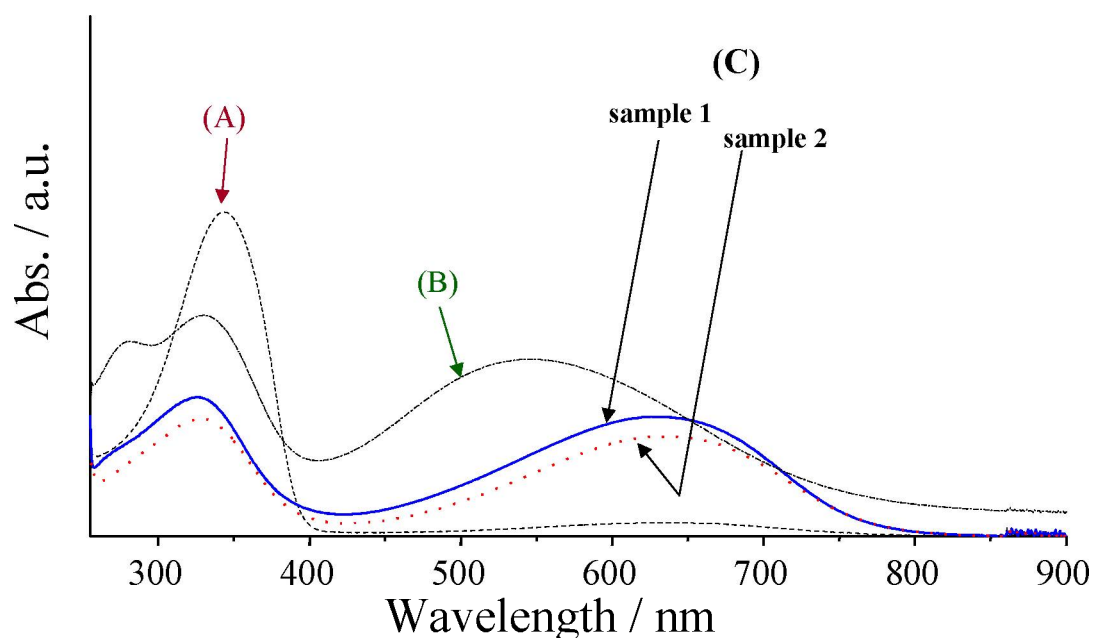
## 1. Background

Since Cho et al. reported up to ~8 wt% room-temperature hydrogen adsorption in HCl-treated polyaniline and polypyrrole [1], the research on the interactions between hydrogen and conducting polymers has become an area of special interest in the hydrogen economy community. However, later studies on hydrogen sorption using conducting polymers gave controversial results, which showed either much lower H<sub>2</sub> uptake [2] or no H<sub>2</sub> uptake at all [3]. As conducting polymers possess some unique “unconventional” and complex characteristics [4], it is highly likely that the controversial results could be attributed to the variation in material characteristics caused by “ambiguous” processing/handling procedures employed in H<sub>2</sub> uptake studies involving conducting polymers. In order to determine whether conducting polymers can be developed into a new type of high-performance media for hydrogen storage applications, the goals of the project were to (i) confirm the brief report by Cho et al. [1] that ~8 wt% hydrogen gas storage in doped (metallic) forms of organic conducting polymers (“synthetic metals”), polyaniline and polypyrrole, can be attained, (ii) determine the optimum polymer preparative methods, chemical composition, polymer electrode potential, polymer crystallinity and morphology to give quantitative optimum conditions of hydrogen gas adsorption and desorption and (iii) investigate hydrogen storage by the many known types of organic conducting polymers in their semiconducting and, metallic forms, and in selected oxidation states.

## 2. Research Results

### (a) UV-VIS and OCP studies

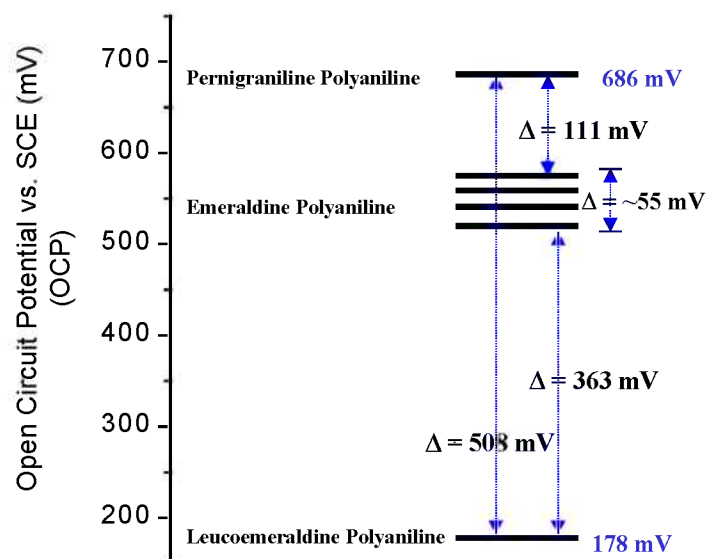
Figure 1 shows the UV-VIS spectra of leucoemeraldine polyaniline (A), pernigraniline polyaniline (B) and emeraldine polyaniline (C) in NMP. The leucoemeraldine (A) and pernigraniline (B) polyaniline samples used in this UV-VIS study were synthesized at PENN, while the two emeraldine polyaniline samples (C) were purchased from Aldrich (same catalogue number with different batch numbers). As can be seen in the Figure, the three different types of polyaniline have completely different UV-VIS spectra, and the spectra of the two emeraldine polyaniline samples (C) obtained from Aldrich are essentially identical.



**Figure 1** UV-VIS spectra of (A) leucoemeraldine polyaniline, (B) pernigraniline polyaniline and (C) emeraldine polyaniline (two different samples purchased from Aldrich: same catalogue number, different batch numbers).

Figure 2 shows the OCP (Open Circuit Potential) values of the four samples described in the UV-VIS study – leucoemeraldine polyaniline (A), pernigraniline polyaniline (B) and two emeraldine polyaniline samples (C) obtained from Aldrich, along with two different batches of emeraldine polyaniline samples synthesized at PENN. As is expected, the pernigraniline polyaniline sample has the highest OCP value (686 mV), the leucoemeraldine polyaniline sample has the lowest OCP value (178 mV) and the four emeraldine polyaniline samples have similar OCP values intermediate between those of pernigraniline polyaniline and leucoemeraldine polyaniline. Although (i) the two emeraldine polyaniline samples from Aldrich are spectroscopically indistinguishable by UV-VIS (Figure 1), and (ii) the total four emeraldine polyaniline samples under investigation in this study have comparable OCP values, their OCP values are, in fact, distributed in a range with 55 mV in difference. This result indicates that the spectroscopically indistinguishable (by UV-VIS) “emeraldine polyaniline” materials, which are commercially available and widely used for many other applications, may not have exactly the same oxidation state.

The combined UV-VIS and OCP studies suggest that the difference in OCP values of nominally identical polyaniline samples could be a latent variable which needs to be dealt with in H<sub>2</sub> sorption studies involving conducting polymers.



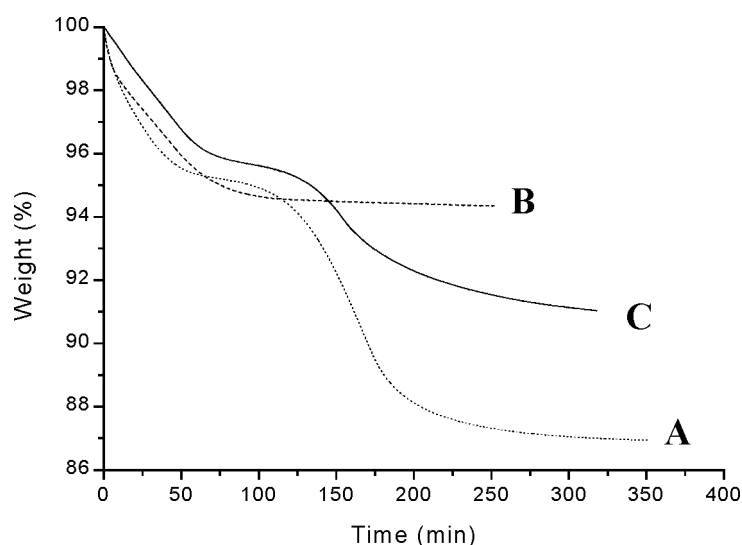
**Figure 2** Measured OCP values for various polyaniline samples with different oxidation states under investigation in this study (see text for details).

### **(b) TGA studies**

The TGA studies using the thermal treatment conditions matching the procedures described by Cho et al. [1] and Roth et al. [3] as closely as possible were carried out at PENN. The TGA profiles are shown in Figure 3.

Specifically, 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 the TGA study. Up to the first 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 first point of inflection) to the termination of the study was 8.2%. The gas evolved was proven by

mass spec (NREL) to be HCl. It can be seen from **curve A** that even after the initial drying process, the polyaniline still contained strongly adsorbed water. For **Curve B**, 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 H<sub>2</sub>O) was observed. No weight loss of HCl was observed. For **Curve C**, 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. We found that the weight losses were similar to **curve A**, but smaller, as might be expected from the heating conditions.



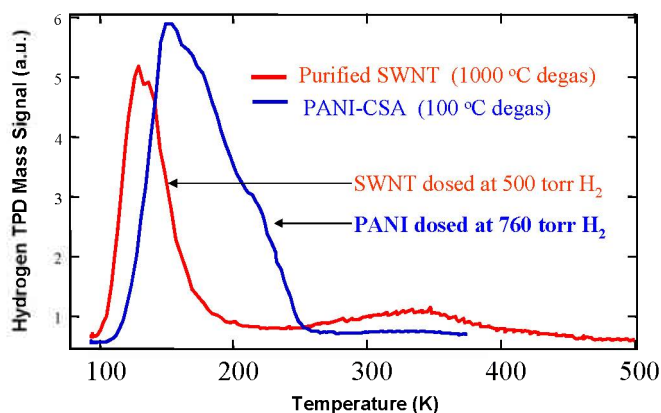
**Figure 3** TGA profiles of the HCl-treated emeraldine polyaniline subject to thermal treatments in Ar at 1°C/min from room temperature to (A) 200°C, (B) 100 °C and (C) 164 °C. For each case, after the specified temperature was reached, the temperature was held constant at the specified temperature for 3 hours.

Our TGA study suggests that previous H<sub>2</sub> sorption studies on polyaniline had not actually used any known form of polyaniline! Polyaniline of a different composition had been used for the H<sub>2</sub> sorption studies as concluded from the above TGA studies carried out under “preheating” conditions. For examples, Cho et al. [1] preheated at 200 °C for an unspecified period of time. Roth et al. [3] preheated at 164 °C for 3 hours. As can be seen from Figure 3, these preheating

processes will result in significant change in composition of the polyaniline first loaded into the sample chambers by previous investigators during their preheating.

### **(c) TPD studies – comparison of conducting polymers to SWNTs**

A comparative TPD study using HCSA-doped polyaniline nanofibers vs. SWNTs was carried out in collaboration with M. Heben at NREL. As can be seen in Figure 4, Polyaniline.HCSA sample gave an extremely broad desorption peak ( $\sim -165$  °C to  $-25$  °C) with a shoulder at  $\sim -60$  °C. This could indicate the presence of a variety of different binding sites for  $H_2$  sorption in HCSA-doped polyaniline and though it is not room temperature, it is quite accessible through standard cooling methods. Moreover, polyaniline materials can be easily produced in large quantities at low cost, and further re-designed via modified synthetic routes to tailor their properties to meet the practical criteria for high-performance hydrogen storage media.



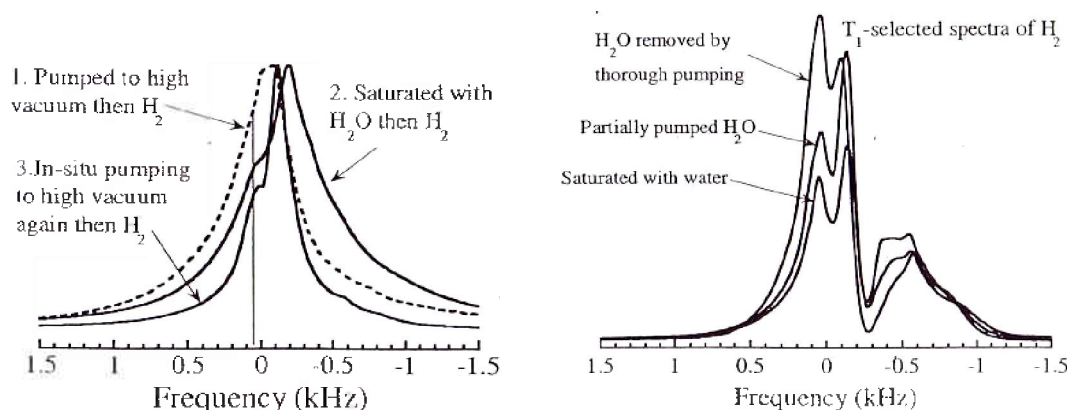
**Figure 4** Temperature Programmed Desorption (TPD) studies by M. Heben Group at DOE labs, Golden, CO, using emeraldine polyaniline nanofibers doped with CSA (i.e. HCSA, camphorsulfonic acid).

### **(d) $^1H$ NMR studies - $H_2O$ Effect on $H_2$ Adsorption**

A  $^1H$  NMR study using HCSA-doped polyaniline was carried out in collaboration with Y. Wu at UNC-Chapel Hill. As can be seen in Figure 5, the study shows that adsorbed  $H_2O$  on polyaniline.HCSA has a pronounced effect on the interaction of  $H_2$  with polyaniline.HCSA.

Polyaniline.HCSA with  $P(H_2) = 70-100$  atm

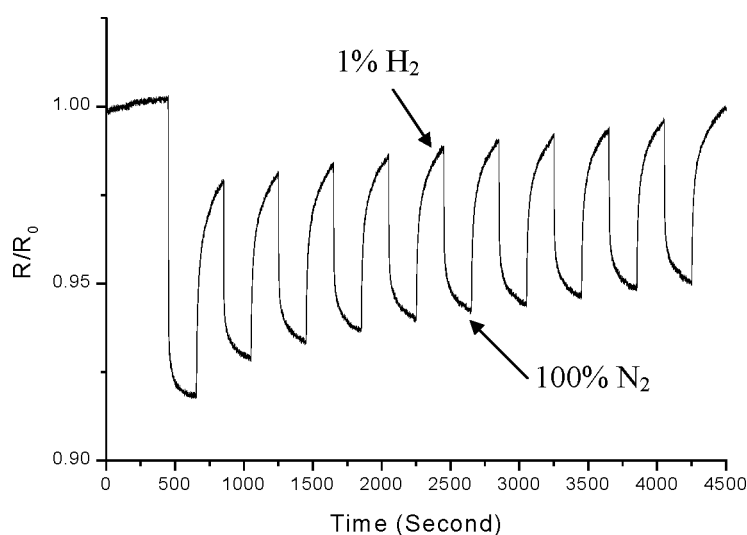
Polyaniline.HCSA with  $P(H_2) = 112$  atm



**Figure 5**  $^1H$  NMR spectra showing the effect of  $H_2O$  on the interaction between polyaniline.HCSA and  $H_2$ .

### **(e) Electrical resistance studies**

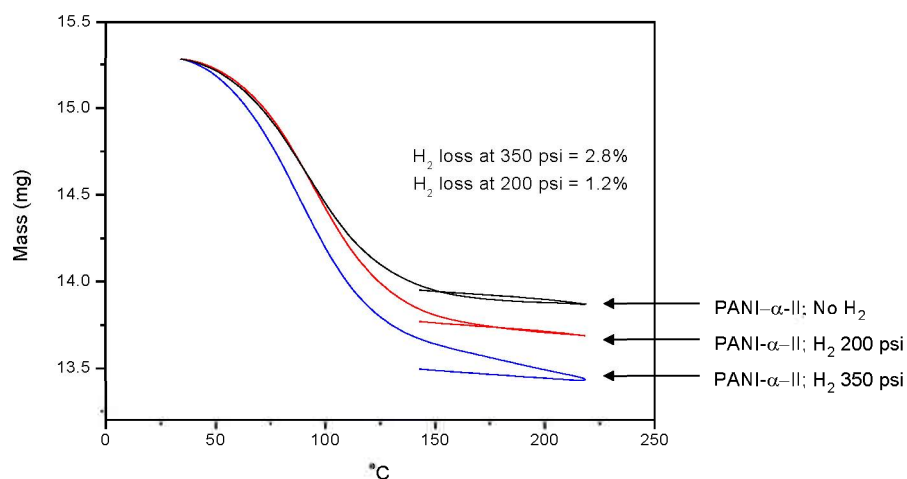
A study on the interaction between HCSA-doped polyaniline nanofibers (synthesized at PENN) and 1%  $H_2$  was carried out in collaboration with A.T. Charlie Johnson, Jr. at PENN. When a HCSA-doped polyaniline nanofiber mat bridging two isolated parallel gold electrodes deposited on a silicon wafer was exposed to several cycles of 1% hydrogen carried by a  $N_2$  flow (applied voltage: 0.1 V), a repetitive response pattern was observed (Figure 6). This result is consistent with that reported by B.H. Weiller [5]. The electrical response of HCSA-doped polyaniline upon exposure to  $H_2$  revealed in this type of measurement indicates that some sort of electronic interaction is involved.



**Figure 6** Electrical response of HCSA-doped (metallic) polyaniline upon exposure to  $H_2$ .

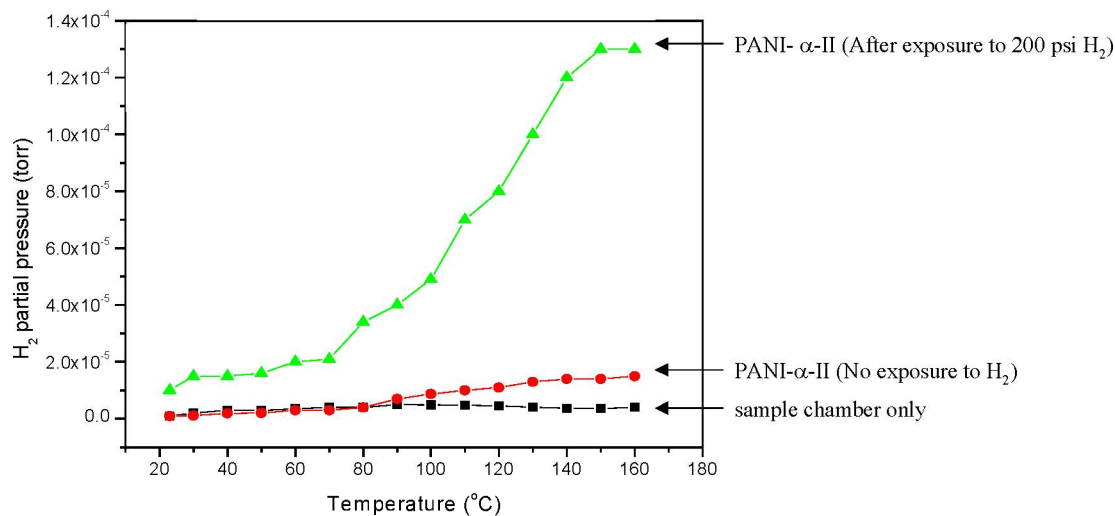
#### **(f) Hydrogen storage studies using “unconventional polymerized aniline”**

A hydrogen storage study using “unconventional polymerized aniline” was carried out in collaboration with Professor A. Ignatiev at University of Houston. In this study, Two PANI- $\alpha$  series samples, PANI- $\alpha$ -I and PANI- $\alpha$ -II, were selected for H<sub>2</sub> uptake studies. The experiments were carried out using TGA (i.e. using PANI- $\alpha$ -II samples as the example; see Figure 7: i. each PANI- $\alpha$ -II sample was dosed with H<sub>2</sub> under a given pressure for 2 hours, ii. Control: PANI- $\alpha$ -II without exposure to H<sub>2</sub>, iii. TGA: room temperature to 225 °C). A mass spectrometric measurement showed that, upon gentle heating, H<sub>2</sub> was liberated from PANI- $\alpha$ -II sample pre-dosed with 200 psi H<sub>2</sub> (Figure 8). Both PANI- $\alpha$ -I and PANI- $\alpha$ -II show a H<sub>2</sub>-dosing-pressure-dependent hydrogen uptake behavior by up to 1.00 wt% and 2.8 wt%, respectively (Figure 9). Compared to PANI- $\alpha$ -I, PANI- $\alpha$ -II outperforms PANI- $\alpha$ -I in H<sub>2</sub> uptake by up to ~180% (Figure 9).

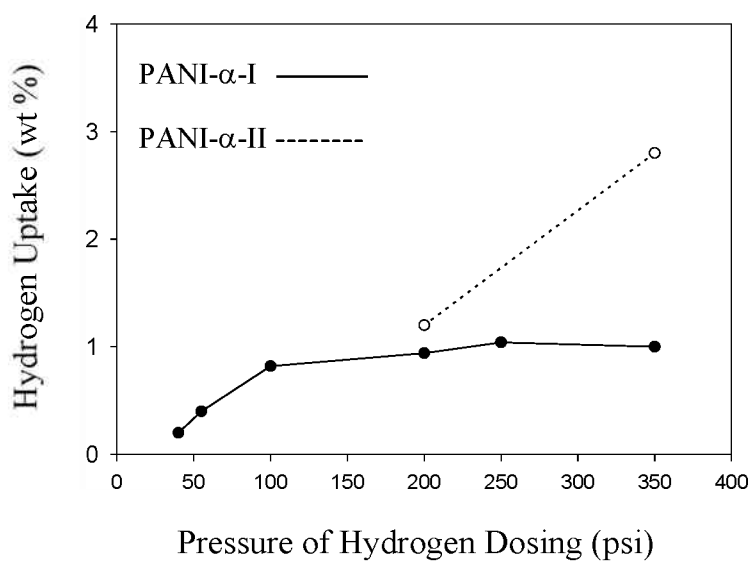


**Figure 7** Examples of H<sub>2</sub> uptake studies by TGA.





**Figure 8** The mass spectrometric measurement showing that, upon gentle heating, H<sub>2</sub> was liberated from PANI-α-II sample pre-dosed with 200 psi H<sub>2</sub>.



**Figure 9** H<sub>2</sub> uptake by PANI-α-I and PANI-α-II.

### 3. Final Conclusions

The results from our H<sub>2</sub> sorption studies show that up to 2.8 wt% H<sub>2</sub> uptake can be obtained by using “unconventional polymerized aniline”. Our highest H<sub>2</sub> uptake value (2.8 wt%) is lower than the highest H<sub>2</sub> uptake value (~8 wt%) reported by Cho et al. in 2002. Our study shows that

adsorbed water can affect the interactions between H<sub>2</sub> and HCSA-doped polyaniline. The TGA study on HCl-treated commercial polyaniline also indicates that “ambiguous” thermal treatments could result in different types of “degraded” materials with compositions different from that of the original HCl-treated polyaniline. The TGA study suggests that systematic screening on conducting polymers subject to various types of thermal treatments be required to identify the materials capable of H<sub>2</sub> storage.

### **Conclusions related to Cho’s work**

Cho et al. recently published a full paper describing the experimental details of their hydrogen studies using conducting polymers [6]. Although the mechanism is still not fully understood, the data presented in the paper show that thermal pre-treatments on conducting polymers can affect the hydrogen storage capacity of conducting polymers.

### **Suggested future work**

- Systematically investigate the effect of thermal pre-treatments on conducting polymers to gain more insights into the relationship between the capability of H<sub>2</sub> uptake and the composition of the “degraded” conducting polymers.
- Obtain direct atomic and nanoscale information related to H<sub>2</sub> adsorption sites on conducting polymers and diffusion mechanisms by neutron scattering measurements.
- Synthesize conducting polymers incorporated with a trace amount of metal nanoparticles (Ni, Pd etc) to investigate whether “spill-over” effect can be exploited to enhance conducting polymers’ H<sub>2</sub> storage capability.

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#### **Published articles generated by this project**

E.C. Venancio, P.-C. Wang and A.G. MacDiarnid, *Synth. Met.*, **156** (2006) 357.

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