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

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Contract Number: DE-FC36-05GO15075

Project Start Date: February 1, 2005
Project End Date: January 31, 2010

Objectives

- Confirm the brief report by Cho et al [1] that approximately 8 wt% (reversible) hydrogen gas storage in doped (metallic) forms of organic conducting polymers (“synthetic metals”), polyaniline and polypyrrole, can be attained.
- Determine optimum polymer preparative methods, chemical composition, polymer electrode potential, polymer crystallinity and morphology to give quantitative optimum conditions of hydrogen gas adsorption and desorption.
- Investigate hydrogen storage by the many known types of organic conducting polymers in their semiconducting and metallic forms, and in selected oxidation states.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(Q) Reproducibility of Performance

Technical Targets

Values reported are material-based. Two types of materials polymerized from aniline (PANI-α-I and PANI-α-II) were used. The highest H₂ uptake values for PANI-α-I and PANI-α-II were 1% and 2.8%, respectively. The gravimetric capacity target for 2010 on a system basis is 6 wt%.

On-Board Hydrogen Storage System Targets (Data is Based on Material Only, Not System Value)

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010 System Target</th>
<th>FY 2006 Result</th>
<th>FY 2007 Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy</td>
<td>kg H₂/kg</td>
<td>(6 wt%)</td>
<td>N/A</td>
<td>2.8 wt%</td>
</tr>
</tbody>
</table>

Accomplishments

- Confirmed by thermogravimetric analysis (TGA) that thermal pre-treatments on PANI (prior to hydrogen uptake measurements) could alter the properties of PANI for subsequent hydrogen uptake studies.
- Comparative studies using two types of PANI materials (PANI-α-I and PANI-α-II) showed that (i) PANI-α series samples exhibited a H₂-dosing-pressure-dependent hydrogen uptake behavior and (ii) with other experimental conditions being equal, PANI-α-II outperformed PANI-α-I in hydrogen uptake.
- Preliminary results indicate gravimetric hydrogen uptake by PANI-based materials up to 2.8 wt%.
- Demonstrated by mass spectrometer (MS) that hydrogen could be released from PANI-α-II pre-dosed with 200 psi H₂ upon gentle heating.

Introduction

Cho et al [1], reported that approximately 8 wt% (reversible) hydrogen gas storage in doped (metallic) forms of organic conducting polymers (“synthetic metals”), polyaniline and polypyrrole, can be attained at room temperature. The conclusions of our research group (at Penn) in collaboration with measurements at the National Renewable Energy Laboratory (NREL) agree with those of Roth et al [2] in that under the incompletely described experimental conditions given by
Cho et al no significant adsorption of H\textsubscript{2} was observed. However, preliminary results (Penn and NREL) have shown an unusual desorption of H\textsubscript{2} up to \(-25^\circ\)C using temperature-programmed desorption (TPD) methods with one of the polyaniline materials synthesized at Penn. As conducting polymers (in doped, non-doped or partially doped forms) could possibly exist at any oxidation state lying within a continuum with no sharp chemical or spectroscopic boundary, it is necessary to systematically conduct hydrogen uptake studies using “unambiguous” conducting polymers for the screening, identification and optimization of the materials for hydrogen storage application.

**Approach**

The Penn group is primarily focused on the synthesis, processing, characterization and selection of PANI-based materials. The Penn group coordinates with project collaborators to carry out H\textsubscript{2} desorption measurements (using NREL TPD facilities and TGA-MS facilities at the University of Houston).

**Results**

The TGA data presented in Figure 1 shows that the change in the composition of doped PANI (PANI-HCl) could occur in different ways during “pre-heating” treatments. (Note: this experiment is not a hydrogen uptake study. The purpose of this study is to show the effect of thermal “pre-treatments” on PANI.HCl.)

Curve A: The method used by us involved commercial polyaniline (emeraldine base) from Aldrich Co. After doping with concentrated HCl, the PANI.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 MS (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 MS (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.

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\textsubscript{2}O) was observed. No weight loss of HCl was observed.

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.

This study shows that previous H\textsubscript{2} sorption study on PANI had not actually used any specific form of PANI. (Note: Cho et al [1] (curve A) preheated at 200°C for an unspecified period of time. Roth [2] (curve C) preheated at 164°C for 3 hours.)

Figure 2 shows the curves of hydrogen uptake (wt%) vs. the pressure of hydrogen dosing for PANI-\(\alpha\)-I and PANI-\(\alpha\)-II. The data in Figure 2 indicates that PANI-\(\alpha\)-I exhibits a H\textsubscript{2}-dosing-pressure-dependent H\textsubscript{2} uptake behavior. The data also show that H\textsubscript{2} uptake by PANI-\(\alpha\)-I becomes saturated (~1 wt%) as the H\textsubscript{2} dosing pressure exceeds 100 psi. Higher H\textsubscript{2} uptake (up to ~2.8 wt%) can be obtained by PANI-\(\alpha\)-II. In general,
with other experimental conditions being equal, PANI-α-II outperforms PANI-α-I in H₂ uptake.

In Figure 3, a comparative MS study shows that H₂ can be released from PANI-α-II (pre-dosed under 200 psi H₂) upon gentle heating.

**Conclusions and Future Directions**

Our research indicates that the properties of PANI-based materials could be affected by thermal pre-treatments. Therefore, ambiguous thermal pre-treatments on PANI-based materials should be avoided in the future H₂ uptake studies. Moreover, we also demonstrated that H₂ uptake by PANI-based materials varied among different sub-species of PANI-based materials. For example, compared to PANI-α-I (~1 wt% H₂ uptake), promotion of H₂ uptake by PANI-α-II (~2.8 wt%) was observed in our study.

Future studies will include:

- Obtain direct atomic and nanoscale information related to H₂ adsorption sites on polyaniline and diffusion mechanisms by neutron scattering measurements at the National Institute of Standards and Technology.
- H₂ TPD studies on polyaniline decorated with traces of metallic Pd, Ni, etc.
- Use the different forms of “Penn PANI” and Professor Ignatiev’s different H₂ adsorption/desorption measurement techniques.
- Integrate the work with Dr. Liu at Argonne National Laboratory.

**FY 2007 Publications/Presentations**


**References**