Low Permeation Liner for Hydrogen Gas Storage Tanks

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Objectives

- Develop a polymer liner that greatly limits hydrogen losses from commercial, light-weight, composite, high-pressure hydrogen tanks

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 R,D&D Plan:

- A. Cost
- B. Weight and Volume
- C. Durability
- I. Materials

Approach

- Select and fabricate polymeric materials with the necessary electron and proton conducting properties to form an electrochemical tri-layer barrier to hydrogen permeation through polymer tank-liners
- Fabricate "bench-top" models of the tri-layers on polymer substrates
- Demonstrate the successful functioning of the bench-top model devices at low and high pressures
- Demonstrate a successful prototype of an active, electrochemical hydrogen barrier system within a high-pressure, polymer-lined, composite hydrogen storage tank

Accomplishments

- Filed U.S. Patent Application on concept (# 10,253,265 in Sept. 2002)
- Negotiated and signed Cooperative Research and Development Agreement (CRADA) (No. 03-CR-07) with a major manufacturer of composite, high-pressure gas storage tanks
- Fabricated initial tri-layer coatings, overcame wetting problems, and began electrical characterization of the individual layers and tri-layers
- Synthesized Pt/Au nanoparticle catalyst that will be added into the poly-3,4-ethylenedioxythiophene (PEDOT) electrodes

- Designed and built a low-pressure hydrogen permeability device at UCLA
- Designed a high-pressure hydrogen permeability device at INEEL

Future Directions

- Test tri-layers on coupons of polymers within low-pressure permeability device
- Conduct further electrical characterization of the tri-layers
- Test tri-layers with various catalysts at electrode interfaces using the low- pressure permeability device and select successful combinations
- Fabricate the high-pressure permeability device
- Test successful tri-layers on coupons within the high-pressure permeability device
- Test perfected tri-layers within commercial high-pressure composite gas storage tanks

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Introduction

State-of-the-art high-pressure gas storage tanks consist of an inner liner, made from a polymer such as cross-linked polyethylene or nylon, overlaid with a continuous graphite fiber/epoxy reinforcement layer. These tanks have successfully stored high-pressure methane gas. It is desired to extend the application of this type of tank to high-pressure hydrogen. However, hydrogen has a significantly higher permeability rate through these polymer liners than methane. Permeation not only leads to a gradual loss of hydrogen pressure, but the hydrogen is thought to damage and weaken the reinforcement layer which could lead to cyclic fatigue or other failures of the tank.

This project was recently begun to develop a hydrogen diffusion barrier that can be applied to the interior of the polymer liner. The barrier will have the following attributes: (1) low permeability of hydrogen, (2) adhere well to the polymer liner, (3) stiffness (modulus) of the coating should match the underlying polymer to avoid cracking when the tank is pressurized, (4) the application method should allow for coating inside a tank with a narrow neck and result in hermetic (gas-tight) coatings that are devoid of pin-holes, (5) the material and coating method should not appreciably add to the overall cost or weight of the tank.

Approach

An electrochemically "active" hydrogen barrier, fabricated from polymers, is being developed. A schematic of this barrier is shown in Figure 1. The hydrogen partial pressure established by the voltage is extremely low at the underlying polymer interface. The hydrogen partial pressure can be calculated using the Nernst equation, as shown in Figure 1. An appropriate level of voltage will be calculated and experimentally verified.

The development plan includes the following:

1. The barrier is to be constructed of three layers of polymers consisting of a proton-conducting electrolyte (electronic insulator) sandwiched in-between electronically conductive polymer electrodes. Candidate polymer compositions were selected based upon existing knowledge. If this

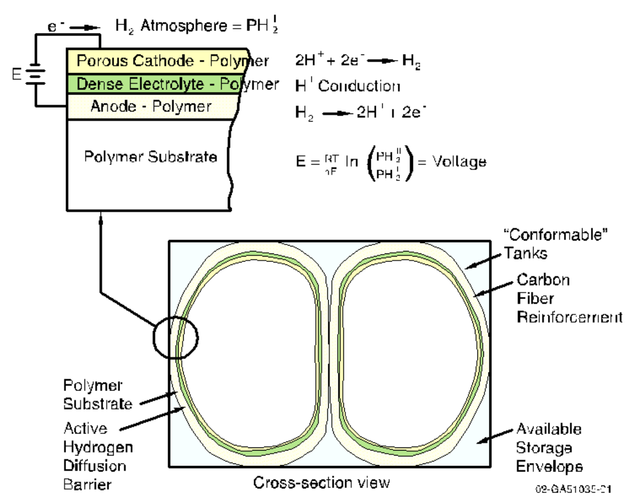

Figure 1. Schematic Showing Tri-layer Hydrogen Barrier Concept

knowledge is not sufficient, new or modified compositions will be developed. Appropriate catalyst materials will be added at the electrolyte/electrode interfaces.

2. The methods to manufacture the layers are being adapted from existing techniques or developed during the project. This could include dip coating or spraying of monomers followed by polymerization. Other possibilities will be explored, and successful manufacturing technologies will be developed.

3. The device is designed as a galvanic-type device that functions to prevent hydrogen permeation through application of a small direct current (dc) voltage using small currents. Methods to provide attachment of the dc voltage are being developed.

Results

Significant progress was made in all four task areas: selection of materials, fabrication of tri-layer coatings, characterization of coating layers, and experimental verification of hydrogenation protection.

The first set of candidate materials were fabricated as a tri-layer prototype barrier. The material selected for the electrodes was highly-conductive H-PEDOT polymer (PEDOT + a small amount of alcohol). The addition of an alcohol (e.g., ethylene glycol) has been shown to increase the electronic conductivity of ordinary PEDOT by up to three orders of magnitude. The material selected for the electrolyte layer was PAMPAS [Poly (2-acrylamino-2-methyl-1-propanesulfonic acid-co-styrene)]. Tri-layers of these materials were first made by spin-coating on glass. Later, the layers were spin-coated on polymer substrates. However, the non-polar surface of the PAMPAS electrolyte resulted in a high contact angle while spin-coating the second layer of PEDOT. To avoid this problem, the PAMPAS film was subjected to an ultraviolet-ozone treatment to modify the surface. The contact angle was greatly reduced, and a good second layer of PEDOT was then obtained.

Electrical characterizations were then conducted on the tri-layer devices shown as a schematic diagram in Figure 2. These included I-V (current/voltage) characteristics of the device and complex impedance measurements. Aluminum layers of 100 nm thickness were evaporated on the two H-PEDOT layers to form electrical contacts. I-V tests showed that the device was a good electronic insulator because of the insulating PAMPAS electrolyte. The device showed a very low current (< 10^{-8} mA) under an applied bias (0-3 Volts), as shown in Figure 3. The complex impedance results will be reported in later reports or papers.

Figure 4 shows the completed low-pressure permeability apparatus. Figure 5 shows an initial permeability test without a barrier and with a barrier (biased and unbiased). Significant reduction in permeation was shown with addition of the tri-layer

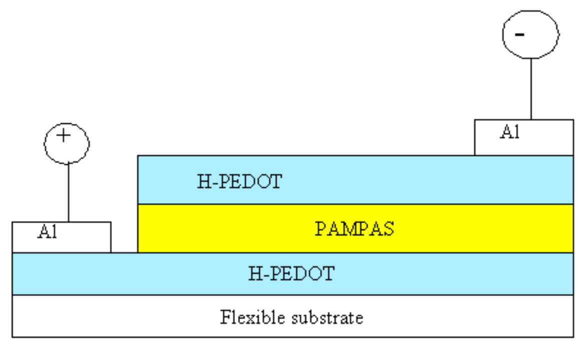

Figure 2. Schematic of Fabricated Tri-layer

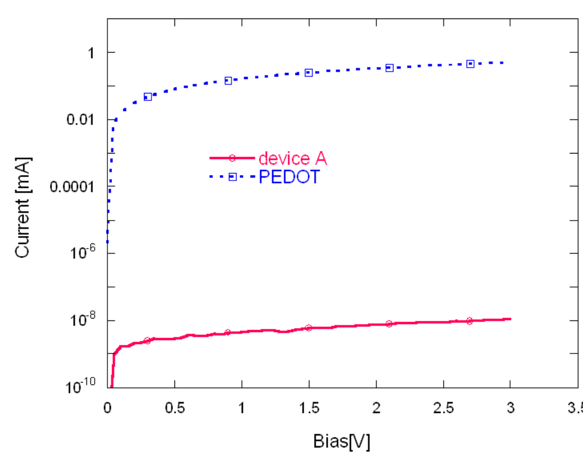

Figure 3. I-V Characteristic Plot for the Tri-layer Barrier

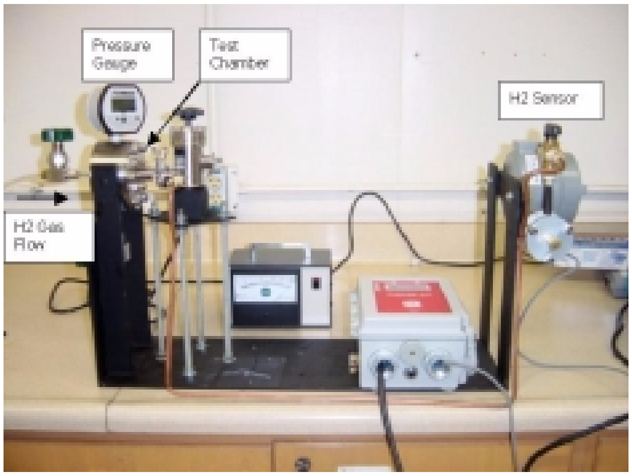

Figure 4. Low-pressure Hydrogen Permeability Apparatus Fabricated at UCLA

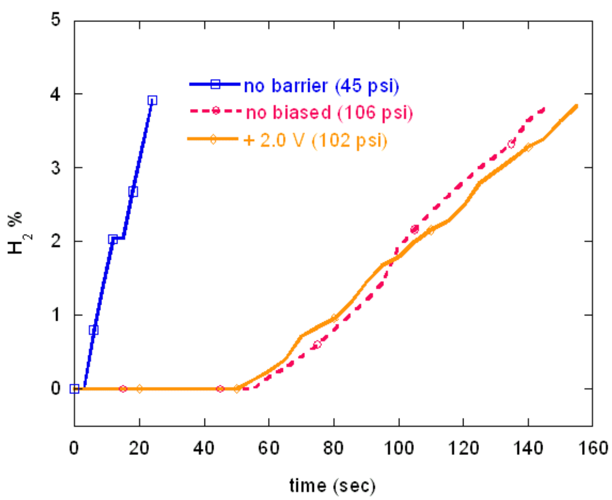

Figure 5. First Permeability Tests Using Low-Pressure Hydrogen

barrier. However, there is little difference between the biased and unbiased cases. Therefore, as previous planned, a catalyst will be necessary (as with proton exchange membrane type low-temperature fuel cells) to enable hydrogen reduction/ oxidation at the electrode/electrolyte interfaces.

Platinum/gold (Pt/Au) is being investigated as a catalyst. This material was synthesized as nano-particles in our laboratories. The material shows good catalytic reduction of hydrogen as shown in Figure 6. The nano-catalyst will be incorporated into

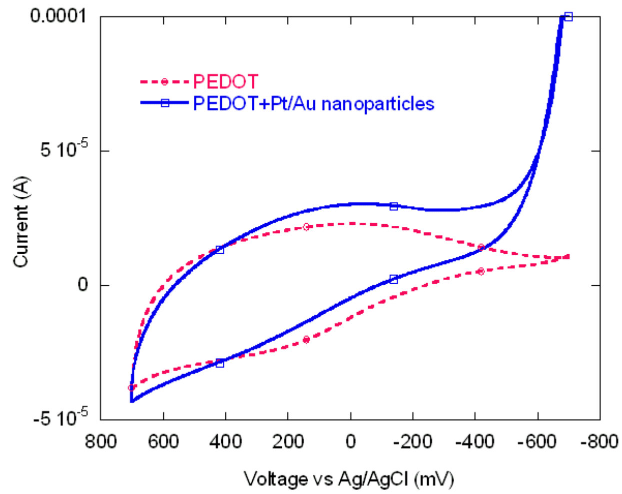

Figure 6. Cyclic Voltammetry of PEDOT Electrodes plus Pt/Au Nano-particles (Electrodes in 1 M HCl + 1 M NaCl solution)

PEDOT electrodes to enable the hydrogen reduction and oxidation reactions at the electrolyte interface, and additional hydrogen permeability tests will be conducted.

Conclusions

- Good progress has been made toward the final goal of developing a polymer liner that greatly limits hydrogen losses from commercial, light-weight, composite, high-pressure hydrogen tanks.
- All of the milestones that were set for this time period have been achieved. Materials were selected, and prototype tri-layer electrochemical barriers have been fabricated and characterized for electrical properties.
- Preliminary testing indicated that fine catalyst particles will be necessary at the electrode/electrolyte interfaces to reduce the high free energy of the hydrogen oxidation and reduction reactions.
- Nanoparticles of Pt/Au catalyst have been synthesized, and good catalytic reduction of hydrogen has been observed. Therefore, we are well positioned to test the tri-layer barriers (with catalyst) in the low-pressure permeability apparatus that was designed and fabricated.

FY 2003 Publications/Presentations

1. "Low Permeation Liner for H_2 Gas Storage Tanks", Paul A. Lessing, Y.Yang, L.P. Ma, F.C. Chen, V. Shrotriya, N. Sirosh, M.J. Warner, Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2003 Merit Review and Peer Evaluation Meeting, May 19-22, 2003, Berkeley, California.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent Application: Paul A. Lessing, "Polymeric Hydrogen Diffusion Barrier, High-Pressure Storage Tank so Equipped, Method of Fabricating a Storage Tank, and Method of Preventing Hydrogen Diffusion", September, 2002.