

Production of Hydrogen for Clean and Renewable Source of Energy for Fuel Cell Vehicles

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Project ID #
PDP 39

Timeline

- Project start date: May 1, 2005
- Project end date: July 31, 2007
- Percent complete: 70%

Budget

- Funding for FY07: \$0 Total project funding
 - DOE share: \$992,000
 - UT share: \$451,000
 - ODOD share: \$204,000
- Funding received in FY05: \$992,000
- Funding received in FY06: \$0 (\$450,000 spent)
- Funding for FY07: \$0

Barriers

- **DOE MYPP Objective for Photoelectrochemical Production of Hydrogen**
 - **By 2015, demonstrate direct PEC water splitting with a plant-gate hydrogen production cost of \$5/kg projected to commercial scale.**
- **Technical Targets:**
 - **2010: STH Eff >9%; Durability >10,000 hours; Cost < \$22/kg**
 - **2015: STH Eff >14%; Durability >20,000 hours; Cost < \$5/kg**
- **PEC Hydrogen Generation Barriers -- MYPP 3.1.4.2.3**
 - **M. Materials Durability**
 - **N. Materials and Systems Engineering**
 - **O. PEC efficiency**

Partners

- Bowling Green State University
- Ohio Department of Development
- Midwest Optoelectronics, LLC

Objectives

- To expand a research program directed to the development of clean and renewable domestic methods of producing hydrogen. This program will provide industry with ways to produce hydrogen in an environmentally sound manner to support the use of fuel cells in vehicles and at stationary locations.

Approach

- **Task 1: Integrated hydrogen facility [82% Complete]**
 - Demonstration of a solar-powered fuel cell vehicle. While this task involves some research elements, this is largely a demonstration of technologies. The task includes
 - 12 kW PV array installation (First Solar thin-film CdTe on glass modules)
 - Integration of the solar array with a pressurized electrolyzer (or an integrated electrolyzer plus compressor)
 - DC voltage regulation system for direct PV-to-electrolyzer power feed
 - Hydrogen storage options include storage in carbon fiber cylinders or nickel metal hydride
 - Retrofit of an electric vehicle, envisioned to be of a GEM-style, with a Ballard 5 kW liquid-cooled fuel cell, including all balance of plant components
- **Task 2: Development of substrate-type PEC cells [77% Complete]**
 - Development of improved encapsulation materials and process
 - Optimization of grid configuration and installation process
 - Investigation of effect of various cell dimensions in the oxidation and reduction compartments
 - Design of improved membrane holder to prevent hydrogen and oxygen from intermixing, and
 - Study of various electrolyte inlet and gas/electrolyte outlet configurations
- **Task 3: Development of advanced materials for immersion-type PEC cells [77% Complete]**
 - Deposition of a transparent, conducting and corrosion resistant coating for PEC photoelectrode.
 - Deposition of photoactive semiconductor as the top component cell absorber layer in a multi-junction PEC photoelectrode
 - Characterization and modeling of PEC materials and photoelectrodes

Approach – Cont.

- Task 4: Hydrogen production through conversion of biomass-derived wastes [77% Complete]
 - Identify the products of fermentation
 - Catalytic reforming
 - Direct conversion of biomass derived resources to hydrogen
 - Low temperature (< 300°C)
 - Pressurized, aqueous phase
 - Evaluate: Feedstock opportunities; Reaction conditions; Catalyst stability
- Task 5: Economic analysis of integrated system [0% Complete]
 - Economic analysis of different types of PEC cells
 - Operating and equipment cost at each step
 - Cost projections considering

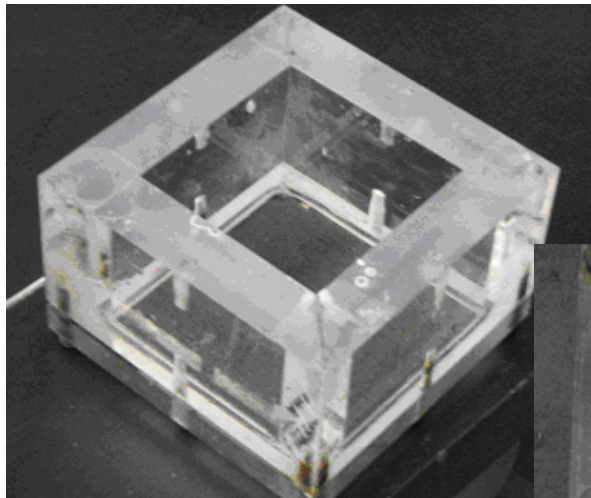
Task 1: Integrated Hydrogen Facility

- Demonstration of a solar-powered Fuel Cell vehicle.
 - While this task involves some research elements, this is largely a demonstration of technologies.
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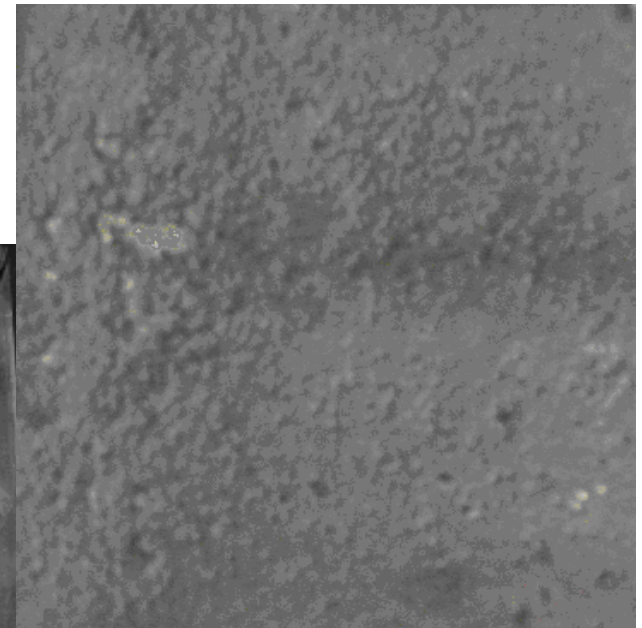
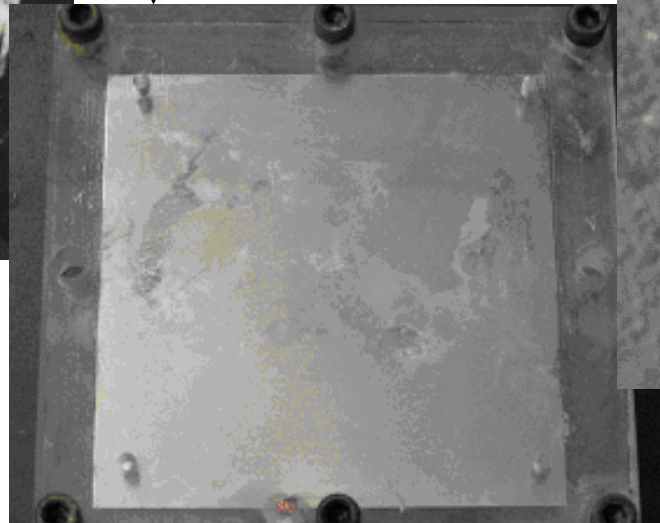
- Matching funds were received from the Ohio Department of Development to support this demonstration activity.
- Complete bench testing of the Ballard 1.2 kW Nexa Fuel Cell in preparation for installation on a GEM electric vehicle.
- Determined satisfactory method for mounting two hydrogen tanks on the GEM.
- Initiated testing of the 2 kW Zahn DC-DC converter that interfaces the 26 V Fuel Cell with the 72 V battery on the GEM.
- Completed plans and work order for installation of utility connections for the solar driven 2 kW Avalence electrolyzer for producing hydrogen.

Task 2: Development of substrate-type PEC cells

- A three dimensional open top cell with inner dimensions of 3"×3"×2.5" was fabricated, to electroplate porous nickel on stainless steel substrate with a-Si solar cells on the reverse side.

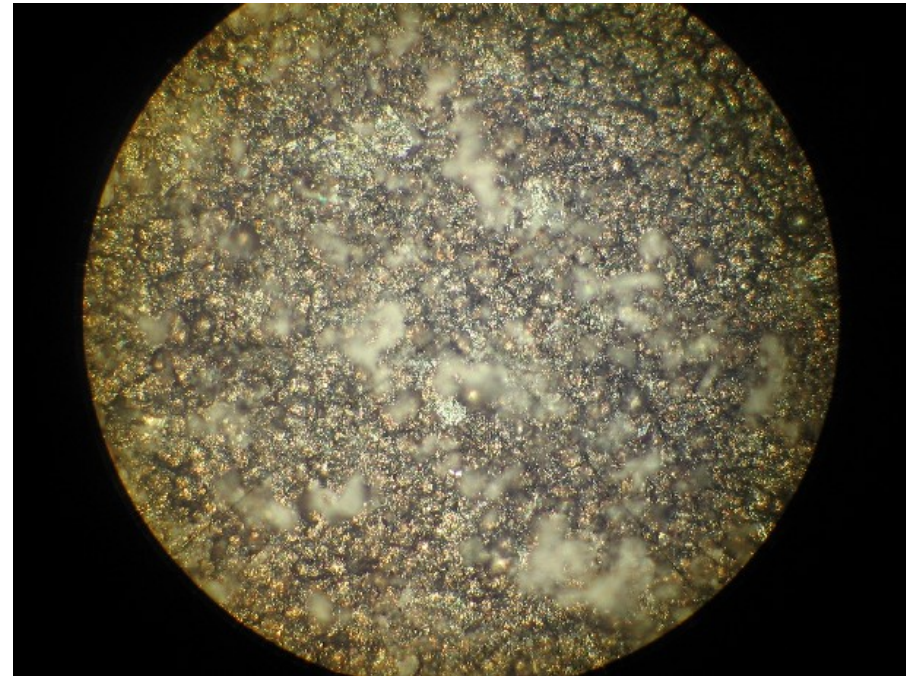


↓
Stainless Steel
Substrate



↑
Electroplated
Nickel

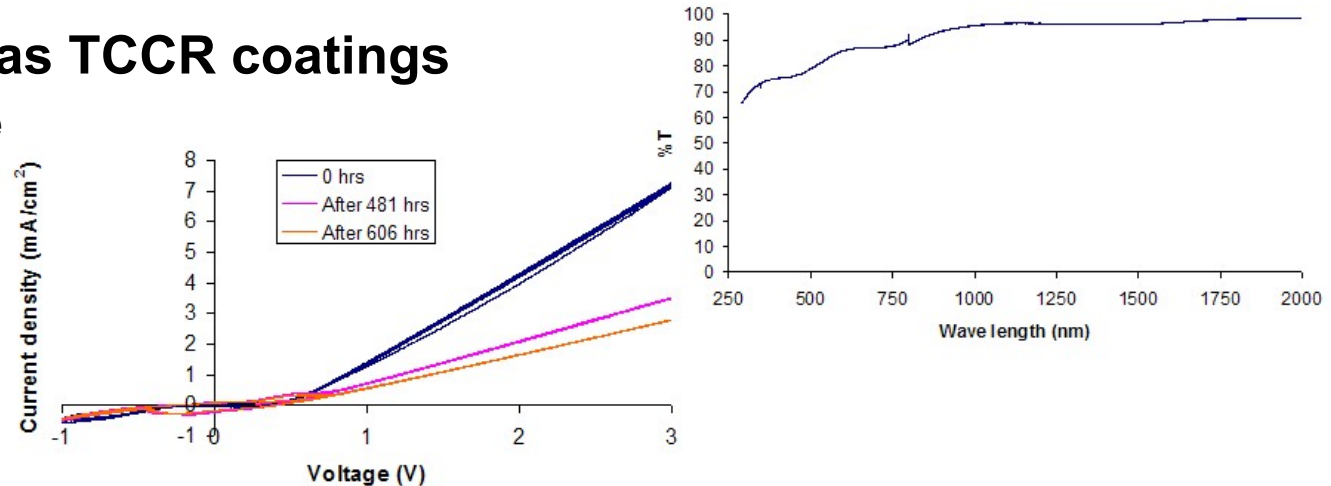
Task 2: Development of substrate-type PEC cells



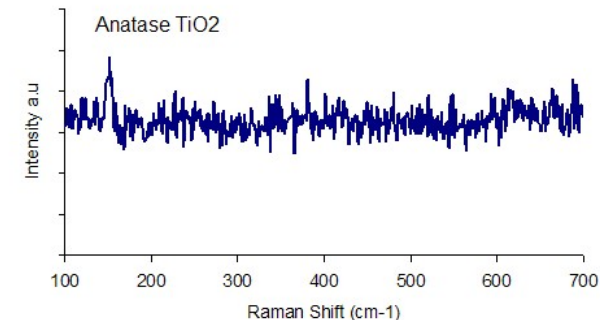
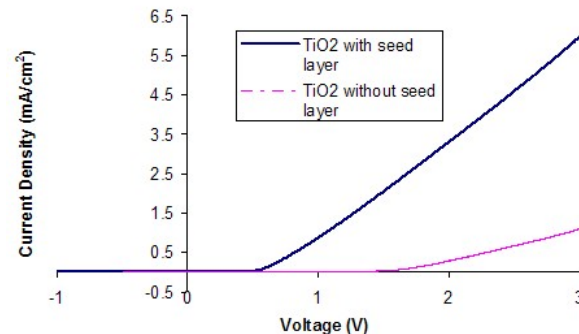
- Left – Pulsed DC-Power Supply with electroplating bath for electrodeposition of porous nickel.
- Right – 20× magnification of porous nickel substrate.

Task 3: Development of advanced materials for immersion-type PEC cells

- Metal oxides as TCCR coatings
 - Cobalt oxide



- Titanium dioxide (~70 to 100 nm)
- Zirconium oxide was used as a seed layer to promote crystalline formation

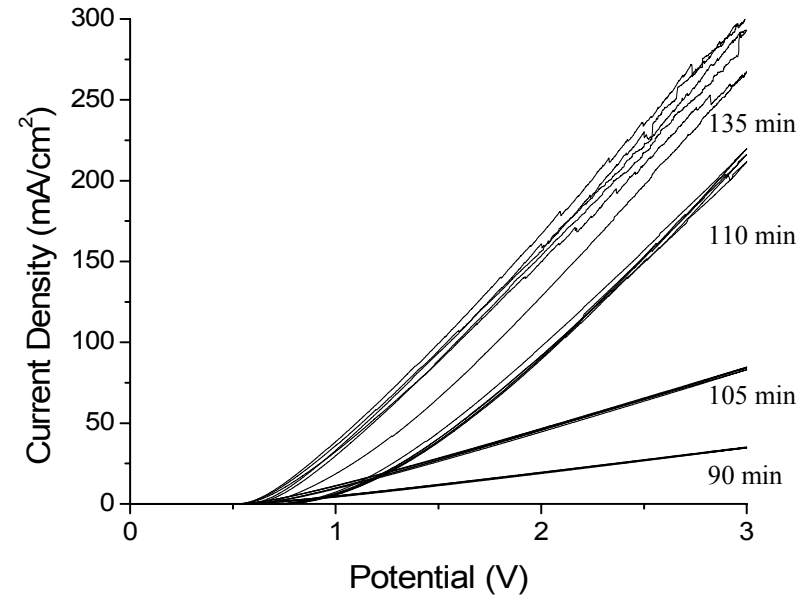
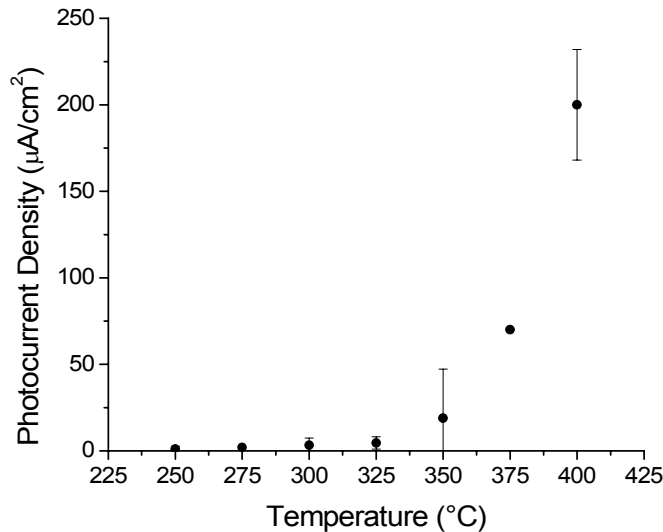


Raman spectroscopy of TiO₂ 75 W for 60 min on ZrO₂ 50 W at 30 min seed layer.

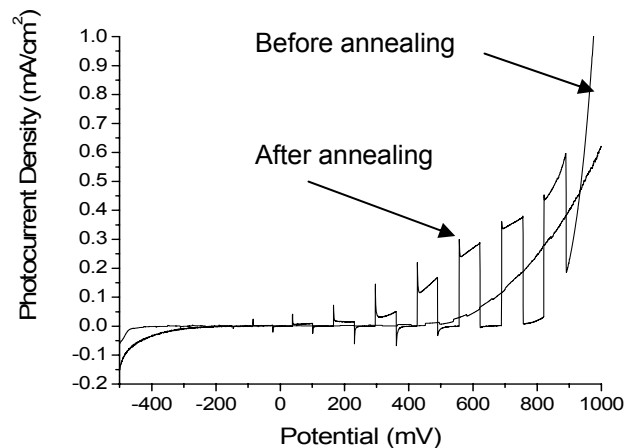
Task 3: Development of advanced materials for immersion-type PEC cells

- Metal oxides as Photoactive Semiconductor (PAS)**

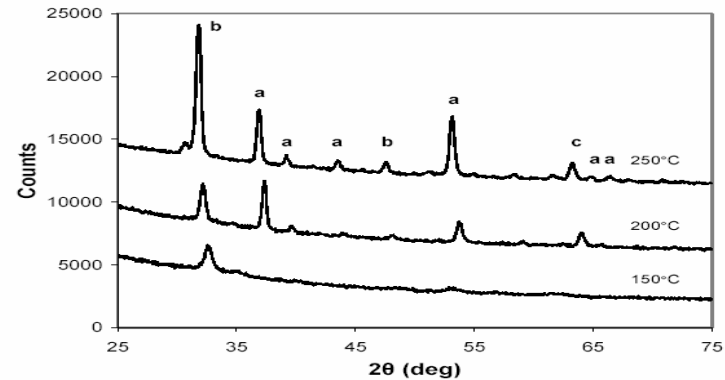
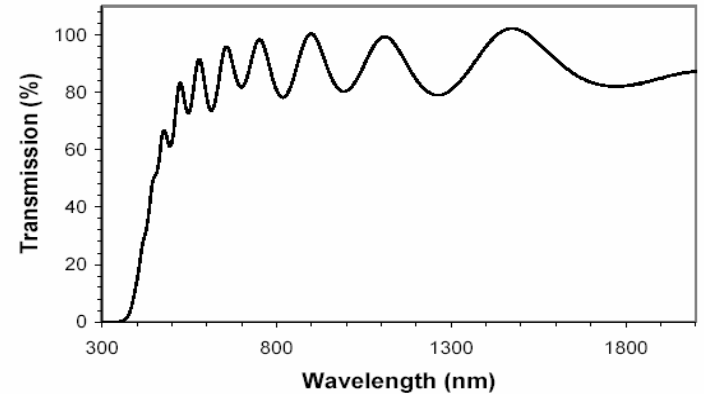
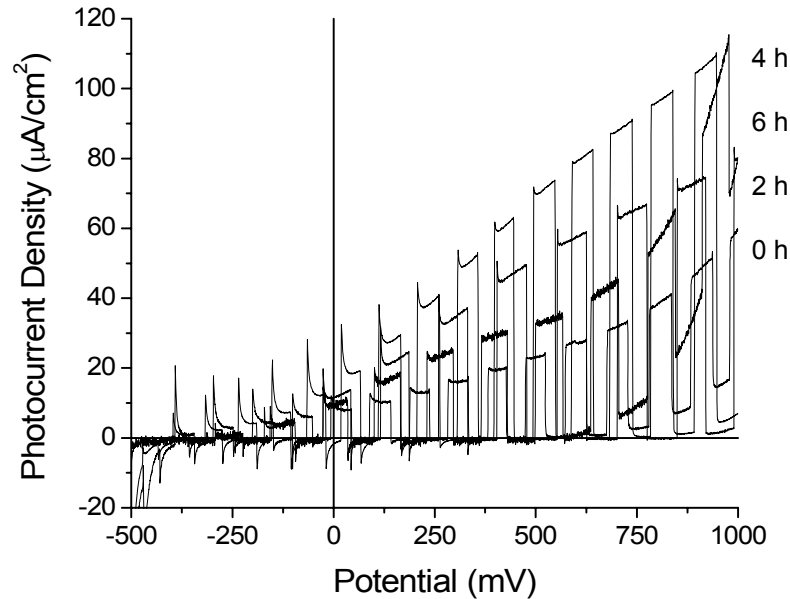
- Iron Oxide**



- Antimony-Doped Iron Oxide**

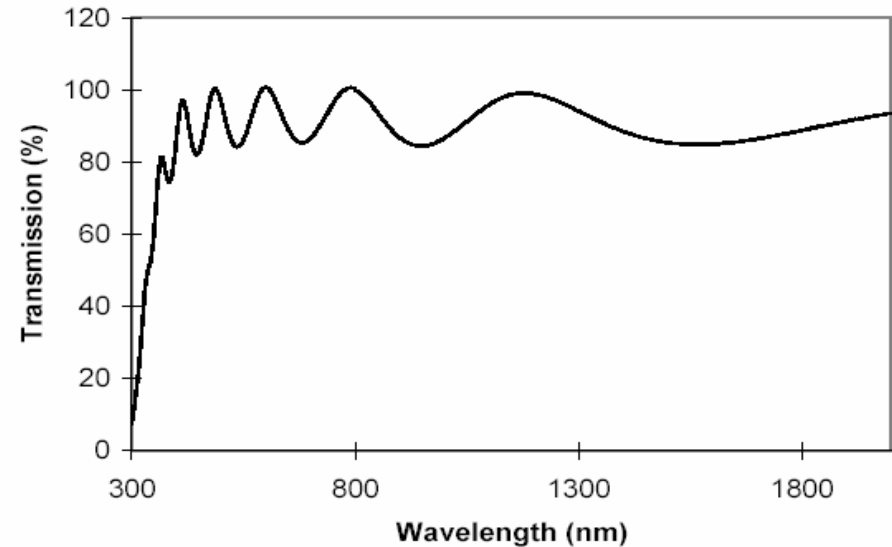
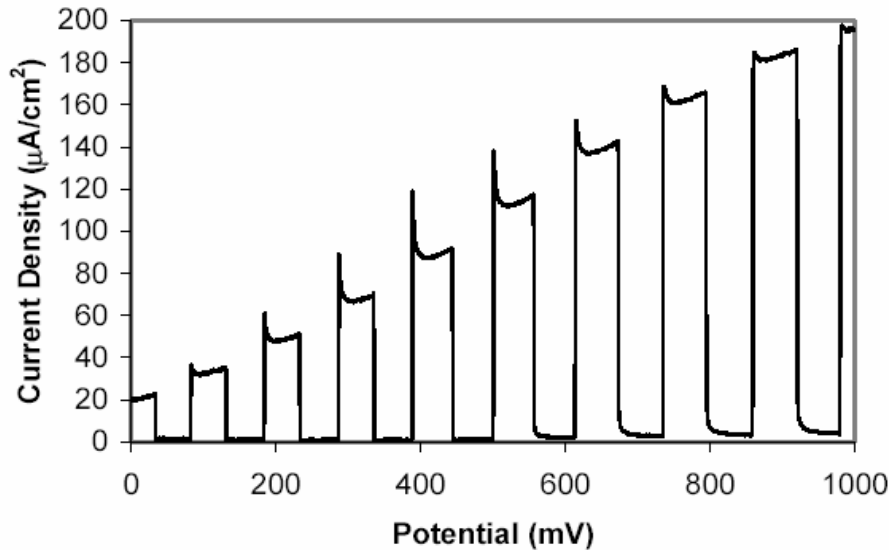


- **Metal oxides as Photoactive Semiconductor**
 - **Indium-Doped Iron Oxide**



Task 3: Development of advanced materials for immersion-type PEC cells

- **Metal oxides as TCCR coatings**
 - **Fluorine-Doped Tin Oxide**



- **Tin Oxide**

- Deposited on various substrate materials, including Tec15, glass, and amorphous silicon devices.
- A sample of a solid mix of MnO , RuO_2 , Co_2O_3 deposited on Tec15 glass ran for 3 days and it needed 2.9 V to reach $0.008 \text{ mA}/\text{cm}^2$ compared to 2.3 - 2.7 V range needed to reach the same current density with the RuO_2 , or MnO-RuO_2 .

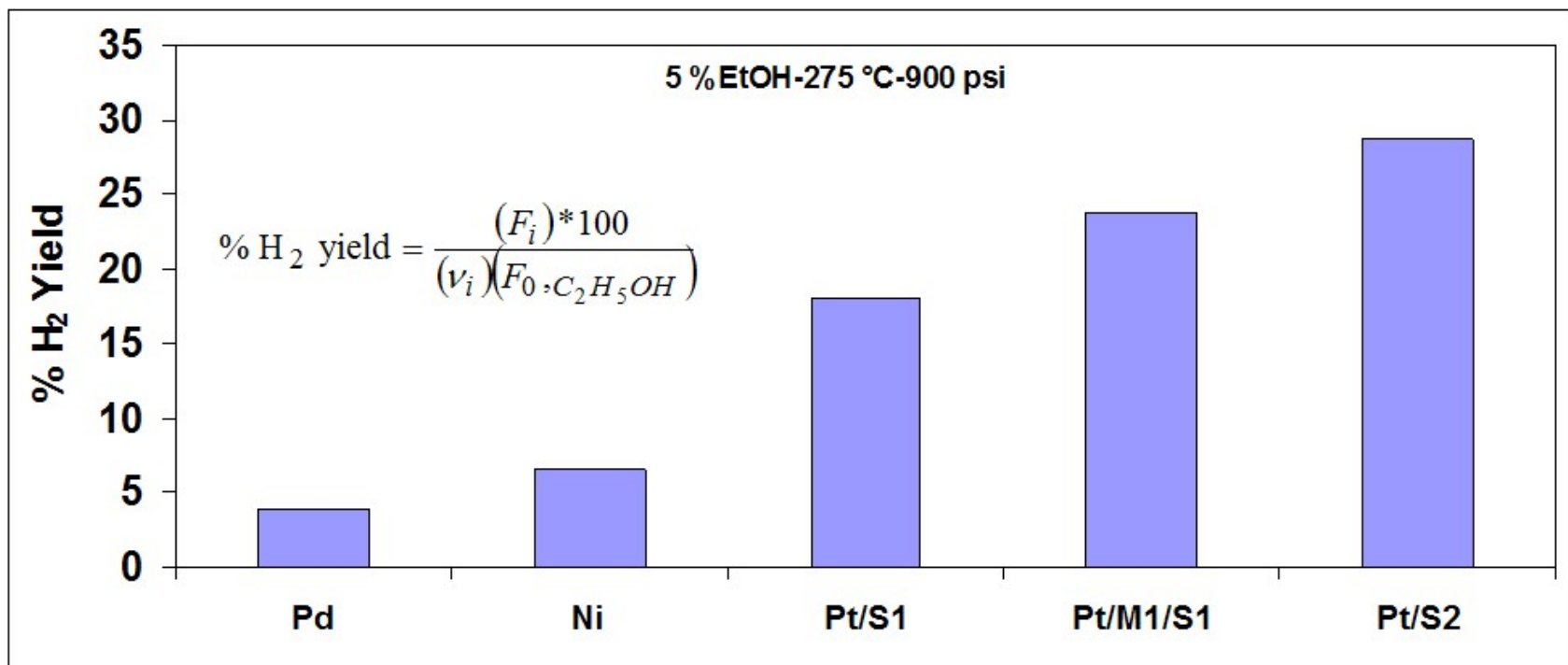
Task 3: Development of advanced materials for immersion-type PEC cells

- **Development of transparent, conductive and corrosion resistant polymer nanocomposite coating**
- Silane-NH₂ and silane-vinyl treatments under the appropriate condition improved the adhesion between polymer nanocomposite and solar cell so that no degradation of polymer nanocomposite coating was observed after the solar coated with polymer nanocomposite Flexbond-ATO had been immersed in 2 N KOH for 5 days at room temperature.
- However, the polymer nanocomposite film was still observed to peel off from the solar cell that was treated with either silane-NH₂ or silane-vinyl first and coated with Flexbond-ATO polymer nanocomposite after the coated solar cell had been immersed in 2N KOH to generate gases under halogen light for about 3 hours. This might be because polymer nanocomposite film has larger thermal expansion coefficient than the solar cell.
- One approach is to add negative thermal expansion (NTP) nanomaterial into the Flexbond-ATO mixture to fabricate the Flexbond-ATO-NTP composite coating.
- One approach is to choose the ceramic conducting as coating, such as single nanotube thin films.
- Additionally, we can fabricate a free-standing conducting polymer nanocomposite film, which can be directly used to wrap the solar cell, such as polyimide-single carbon nanotube composites of very low loading.

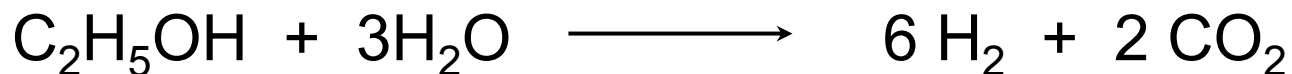
Task 4: Hydrogen production through conversion of biomass-derived wastes

- Development of the stable, active, inexpensive catalyst for aqueous phase reforming (APR) of fermentation broth
- Understanding of the catalyst deactivation mechanism for APR
- Study the effects of different reaction parameters on the hydrogen productivity
 - Temperature, pressure, pH, ionic strength, concentration, residence time

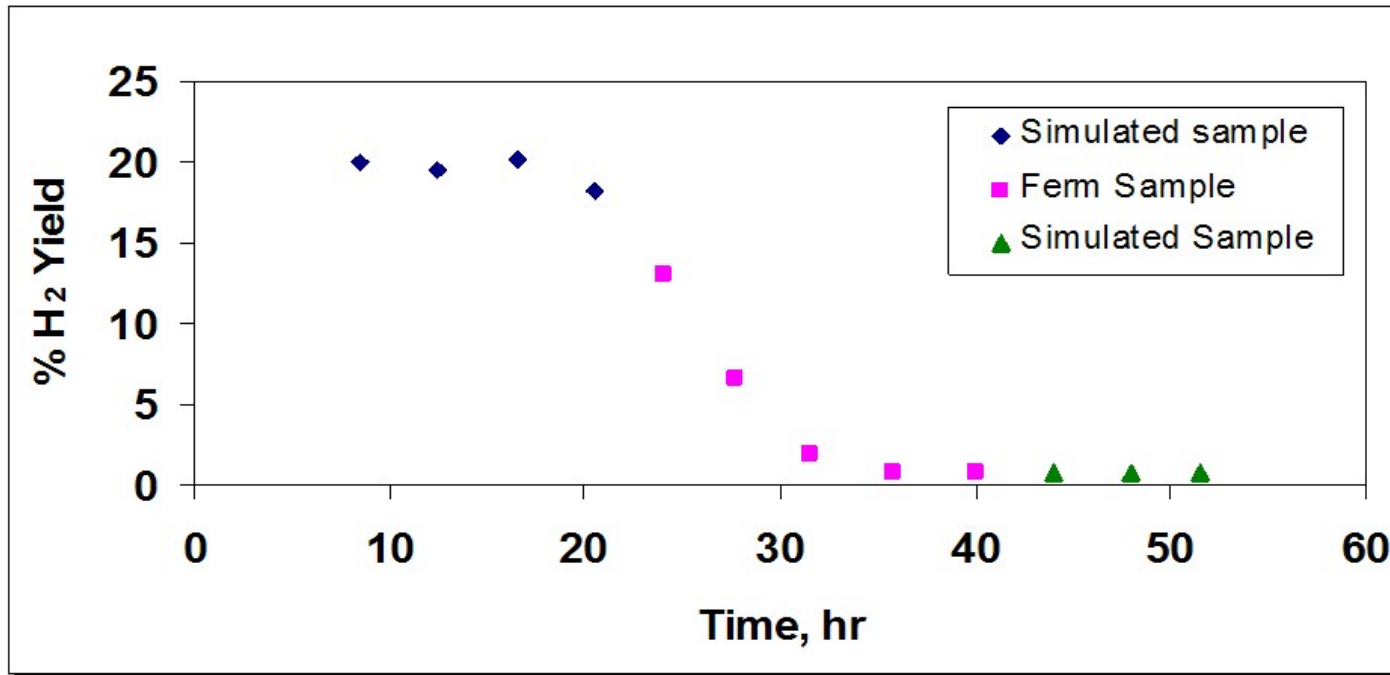
Catalyst development for APR of ethanol



Reaction:

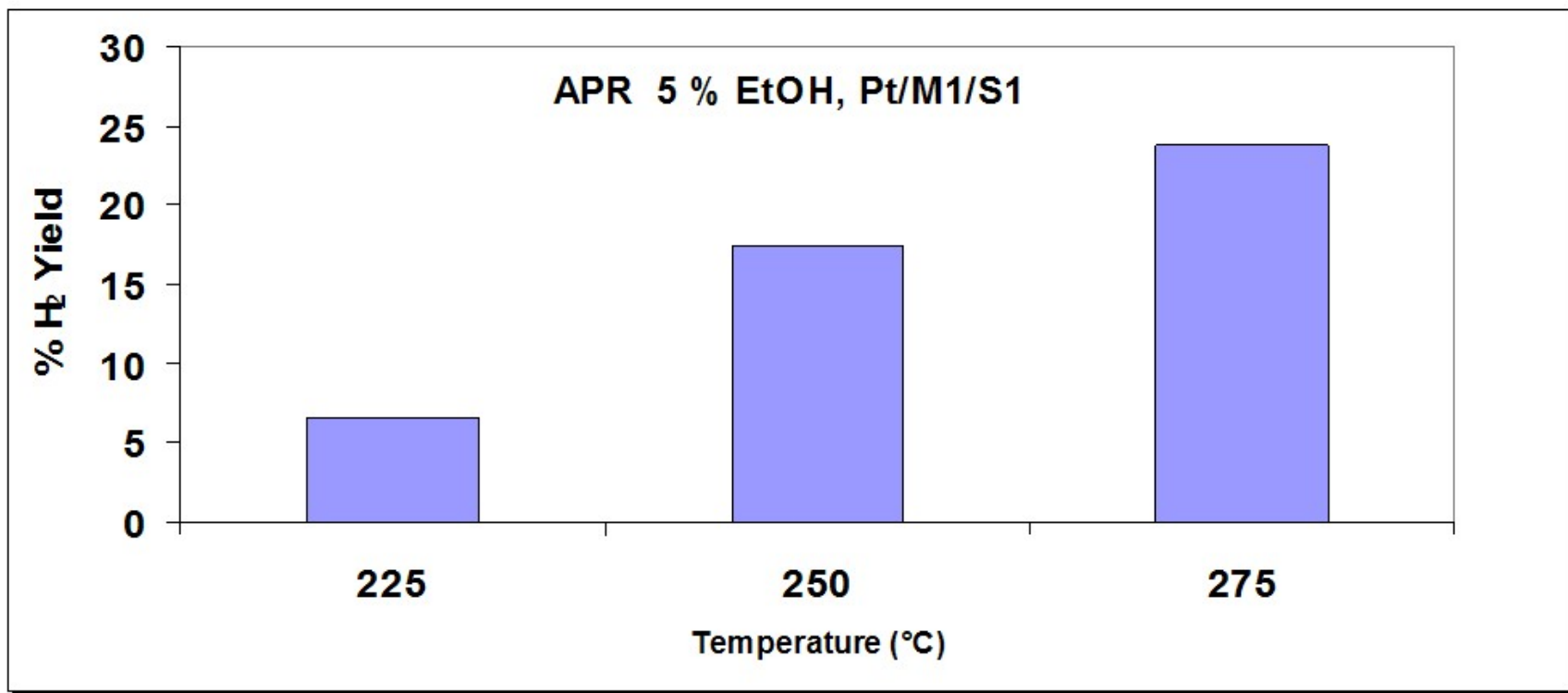


Catalyst Pt/S2 is not stable for APR of fermentation broth



- Catalyst deactivation in case of the fermentation broth is suspected due to fermentation impurities
- ~ 10 ppm of both S and P was observed in the fermentation broth
- Effect of S and P will be studied using amino acids (Containing S) and ATP as model compounds

Effect of temperature on H₂ productivity during APR of ethanol



Task 5: Economic analysis of integrated system

- The start of Task 5 was delayed due to the delayed development of PEC systems and manufacturing process at collaborating organization (caused by delayed funding).

Future Work

- Task 1: Integration of fuel cell vehicle to solar array power supply.
- Task 2: Production of final module design with electroplated nickel on back of stainless steel with triple junction a-Si on front.
- Task 3: Continued study into optimization of present oxide materials.
- Task 3: Deposition of oxides under higher power and with metallic targets to improve stability and oxide structure.
- Task 4: Understand the catalyst deactivation mechanisms.
 - Use nano- and ultra-filtration to separate the fermentation impurities.
 - Study the effect of S and P on APR of the ethanol.
- Task 4: Study the kinetics of aqueous phase reforming of ethanol.
- Task 5: Begin economic analysis in the next quarter.

Project Summary

- **Relevance:** Addresses DOE program objectives, specifically high-efficiency and low-cost production of hydrogen using photoelectrochemical methods.
- **Approach:** An immersion-type photoelectrochemical cells where the photoelectrode is immersed in electrolyte and a substrate-type photoelectrochemical cell where the photoelectrode is not in direct contact with electrolyte.
- **Technical Accomplishments and Progress:** Demonstrated a PV-electrolysis system that has separate PV system and electrolysis unit and the hydrogen generated is to be used to power a fuel cell based vehicle in the near future.
- **Technology Transfer/Collaborations:** Active collaboration with MWOE towards commercialization of research done at UT
- **Proposed Future Research:** Integrate fuel cell car into PV system. Further develop TCCR coatings for immersion and substrate-type cells.