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

Xunming Deng (PI), Martin Abraham, Maria Coleman, Robert Collins, Alvin Compaan, Dean Giolando, A. H. Jayatissa, Thomas Stuart, Mark Vonderembse, and William B Ingler Jr.
University of Toledo

Felix Castellano, Bowling Green State University
6/11/2008

Project ID #
PDP 24

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: May 1, 2005
- Project end date: Jan 31, 2008
- Percent complete: 100%

Budget

- Funding for FY08: $0 Total project funding
  - DOE share: $992,000
  - UT share: $337,551 (Revised)
- Funding received in FY05: $992,000
- Funding received in FY06: $0
- Funding received in FY07: $0
- Funding for FY08: $0 ($992,000 Spent)

Barriers

- DOE MYPP Objective for PEC
  - Develop advanced renewable PEC hydrogen generation technologies.
  - By 2018, verify the feasibility of these technologies to be competitive in the long term.
- Technical Targets:
  - 2013: STH Eff > 8%; Durability >1,000 hours;
  - 2018: STH Eff > 10%; Durability >5,000 hours;
- PEC Hydrogen Generation Barriers -- MYPP 3.1.4
  - Y. Materials Efficiency
  - Z. Materials Durability
  - AA. PEC Device and System Auxiliary Material
  - AC. Device Configuration Designs
  - AD. Systems Design and Evaluation

Partners

- Bowling Green State University
- Midwest Optoelectronics, LLC
- Xunlight Corporation

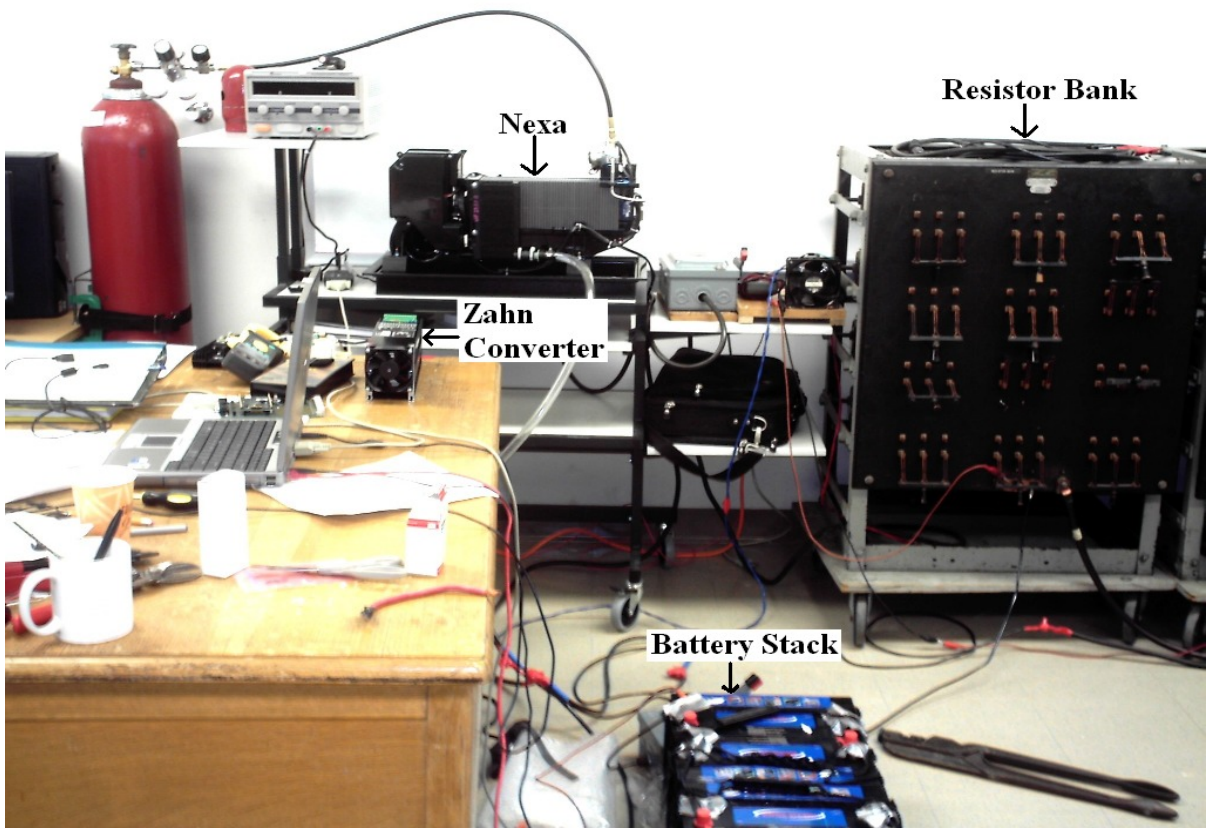
Objectives

- 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: Design and analysis of DC voltage regulation system for direct PV-to-electrolyzer power feed [100% Complete]
  - Design strategy for integrating a solar array with a pressurized electrolyzer (or an integrated electrolyzer plus compressor), including pressurized hydrogen storage.
  - Analysis of the DC voltage regulation system required for direct PV-to-electrolyzer power feed
- Task 2: Development of substrate-type PEC cells [100% 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 [100% 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
- Task 4: Hydrogen production through conversion of biomass-derived wastes [100% 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 1: Design and analysis of DC voltage regulation system for direct PV-to-electrolyzer power feed

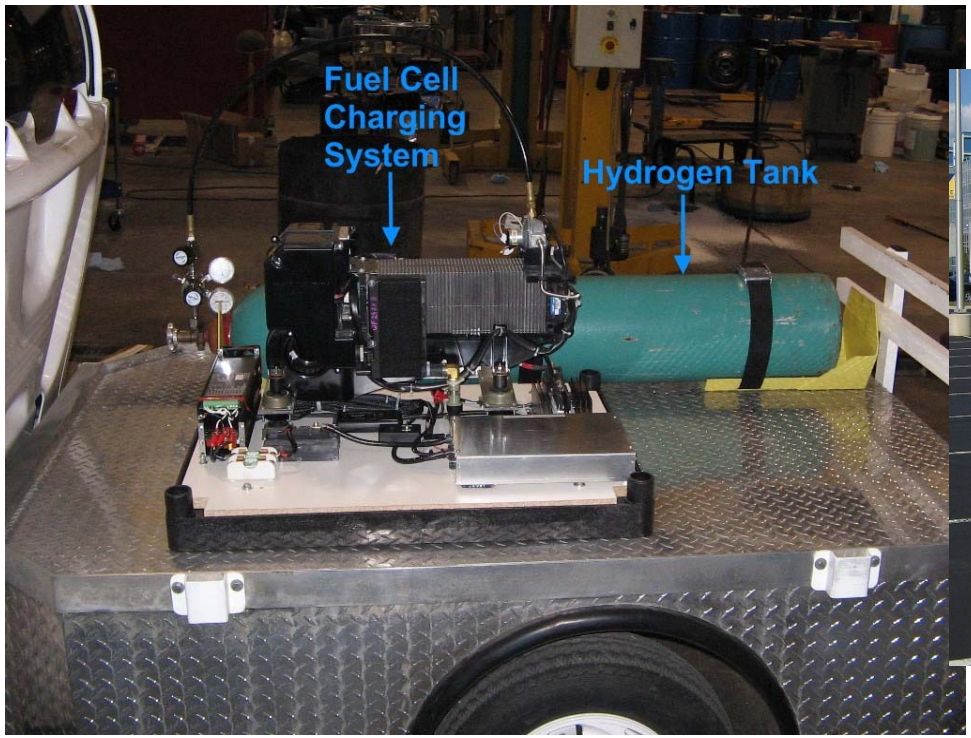


- Design strategy for integrating a solar array with a pressurized electrolyzer (or an integrated electrolyzer plus compressor), including pressurized hydrogen storage.
- Analysis of the DC voltage regulation system required for direct PV-to-electrolyzer power feed.

Nexa®-Zahn Laboratory Test Setup

Task 1: Continued

- GEM vehicle provided by plant operations at University of Toledo.
- Cooling fans were added to casing for fuel cell, since it was over-heating and shutting down.



Task 1: Continued – Initial results from operation of GEM vehicle with fuel cell and hydrogen storage tank.

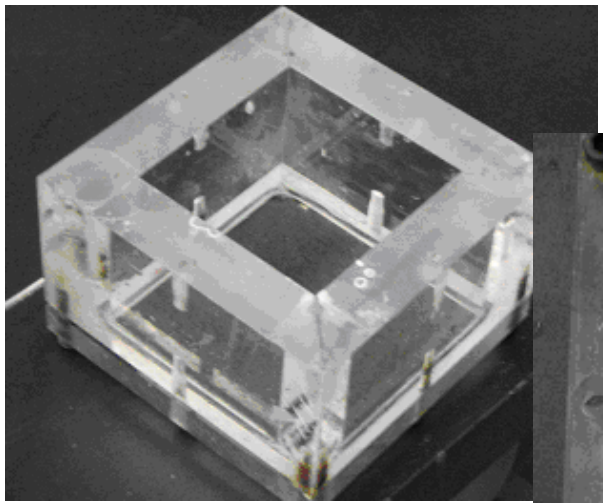
Odometer (mile)	Mileage Δ (mile)	Pressure Δ (psi)	H2 used (g)
1008	0	0	0
1018	10	190	53.15
1021	3	20	5.59
1025	4	90	25.17
1029	4	100	27.97
1038	9	110	30.77
1043	5	100	27.97
1048	5	170	47.55
1053	5	100	27.97
1057	4	100	27.97
1063	6	100	27.97
1068	5	110	30.77
1075	7	140	39.16
1079	4	100	27.97
1085	6	100	27.97
1090	5	110	30.77
1096	6	140	39.16
1103	7	100	27.97
1109	6	150	41.96
SUM	**101**	**2030**	**567.83**

FCH GEM Test Using the Battery and FCCS

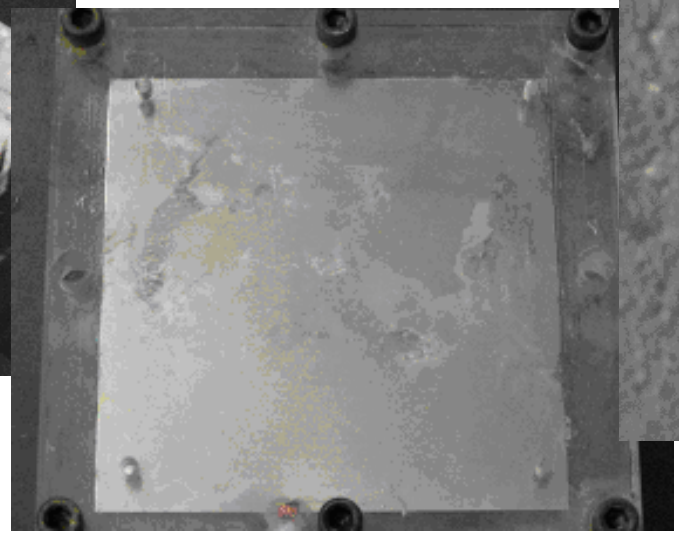
Date	9/22/2007
Mileage Start	1008
Mileage Stop	1109
Delta Mileage	101
H2 Consumed (g)	567.83
Duration (Minutes)	352
Speed (MPH)	17.2
Air Temperature	70

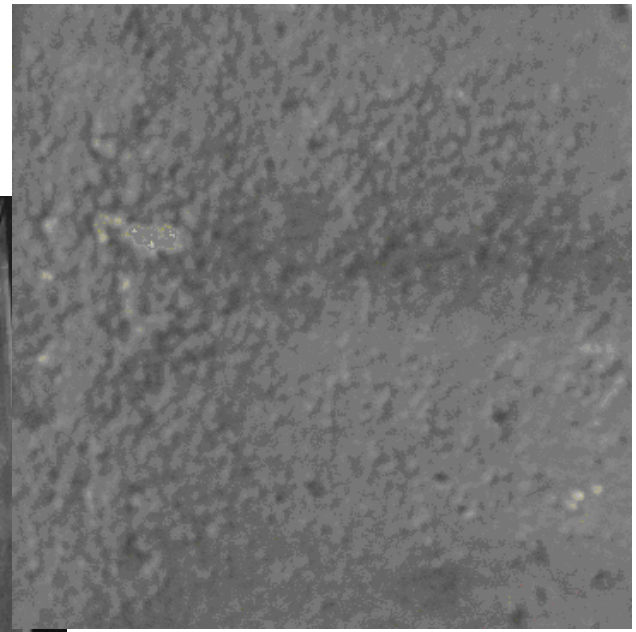
Task 2: Development of substrate-type PEC cells

- 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



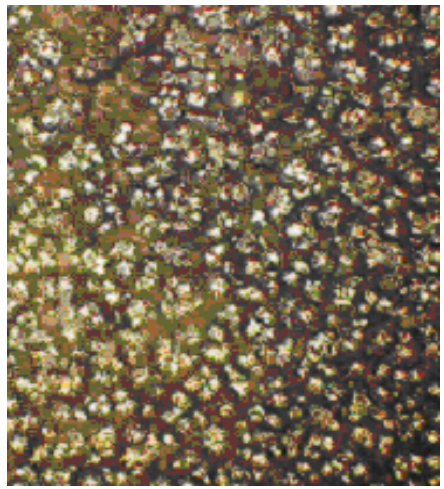


Electroplated Nickel

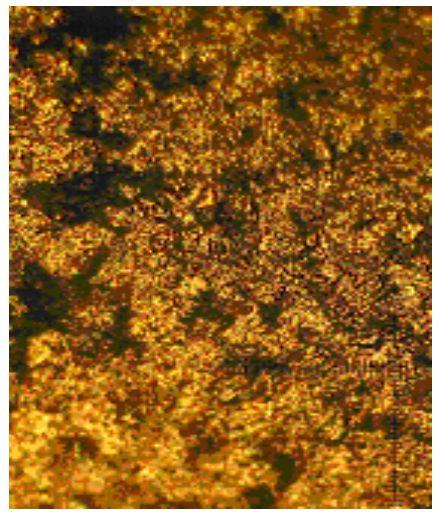
Currently fabricating 12” × 12” nickel plating set-up.

- Step 1: Electroplating of pure Nickel on the substrate.
- Step 2: Co-deposition of Nickel and Zinc on the substrate.
- Step 3: Enhanced co-deposition of Zinc.
- Step 4: Leaching of Zinc and producing porous Nickel structure.

Task 2: Development of substrate-type PEC cells



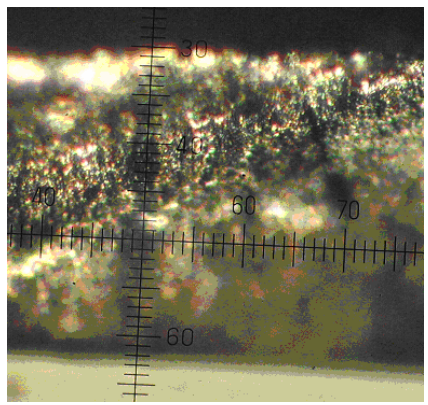
20 kHz



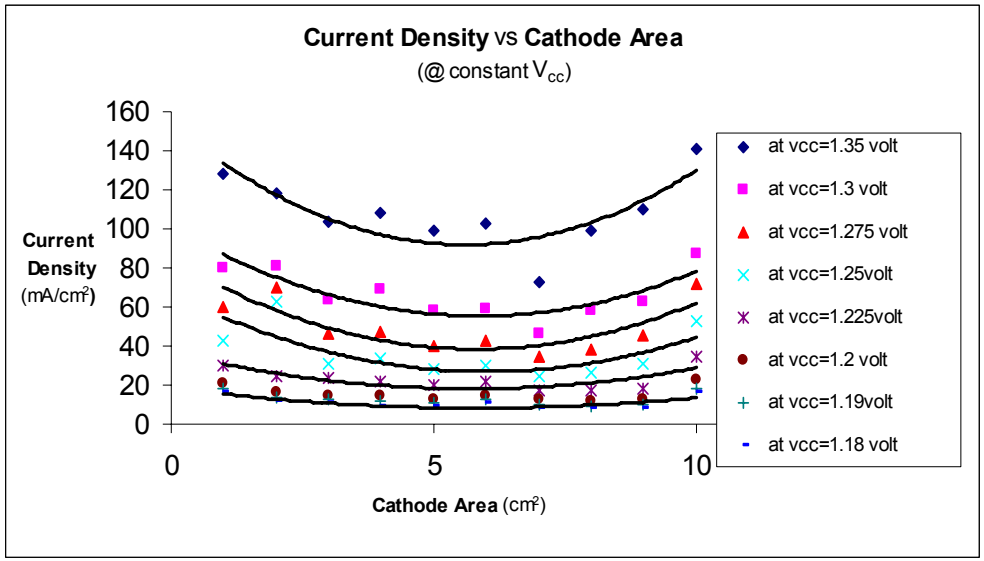
100 kHz

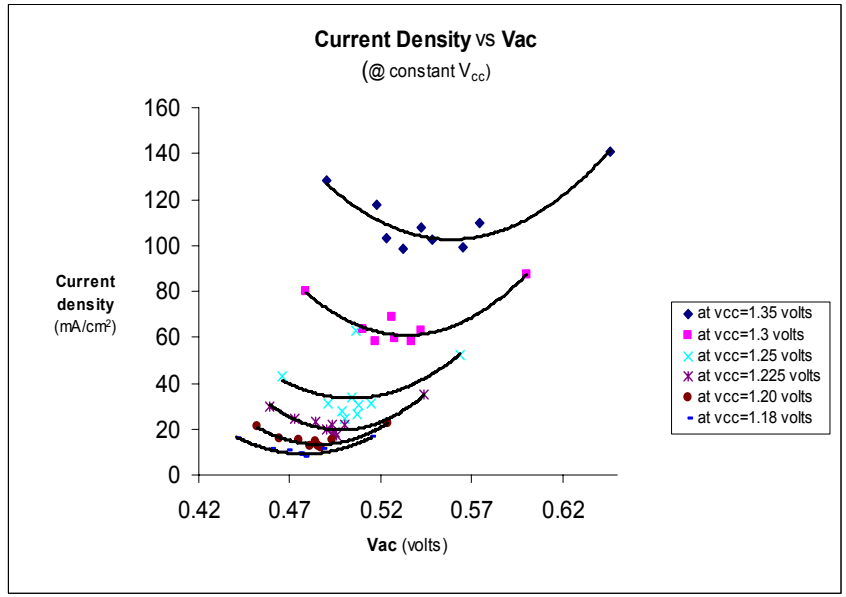
- Left – Pulsed DC-Power Supply with electroplating bath for electrodeposition of porous nickel.
- Right – 20× magnification of porous nickel substrate.

100 kHz – Cross-section



Task 2: Electroplated Nickel Results



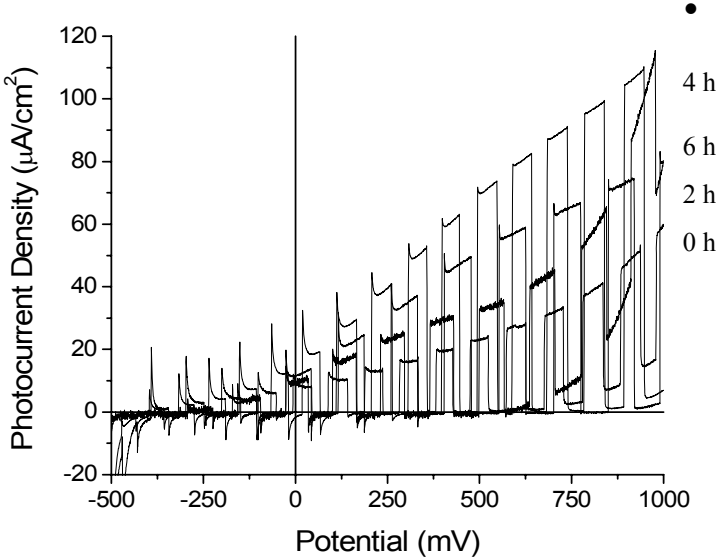


- Left – Plot of the current density versus the area of the DC pulsed electroplated cathodes .
- Right – Plot of current density with the voltage of the cathode (Vac) with reference to saturated calomel electrode when the voltage at the anode with reference to saturated calomel as constant .
- Bottom - Cathodic over-potentials determined from Tafel plots.

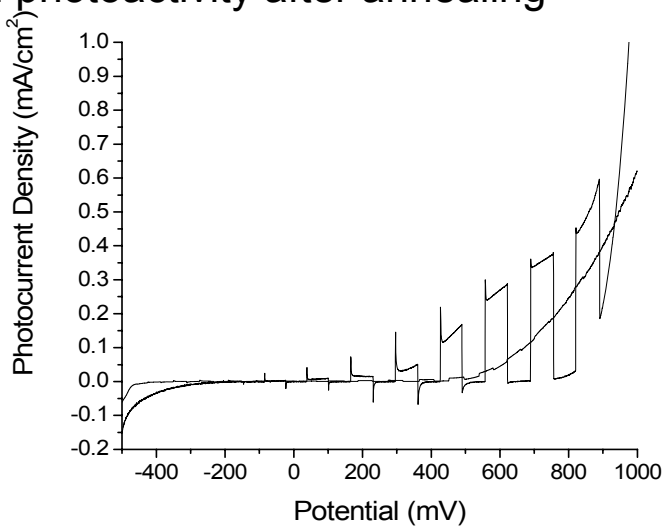
Sr. No.	Frequency (kHz)	Over-Potential (mV)
1	10	-99.3
2	20	-88.6
3	100	-113.1

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

- Metal oxides as TCCR coatings
  - Down-selected Materials:
    - Cobalt oxide – UV Absorption High
    - Titanium dioxide – Not very stable – Have not revisited zirconium oxide seed layer as reported earlier
    - Iron oxide – Only fully stabilizes and increases in photoactivity after annealing
    - Antimony Iron oxide – Same as Iron Oxide



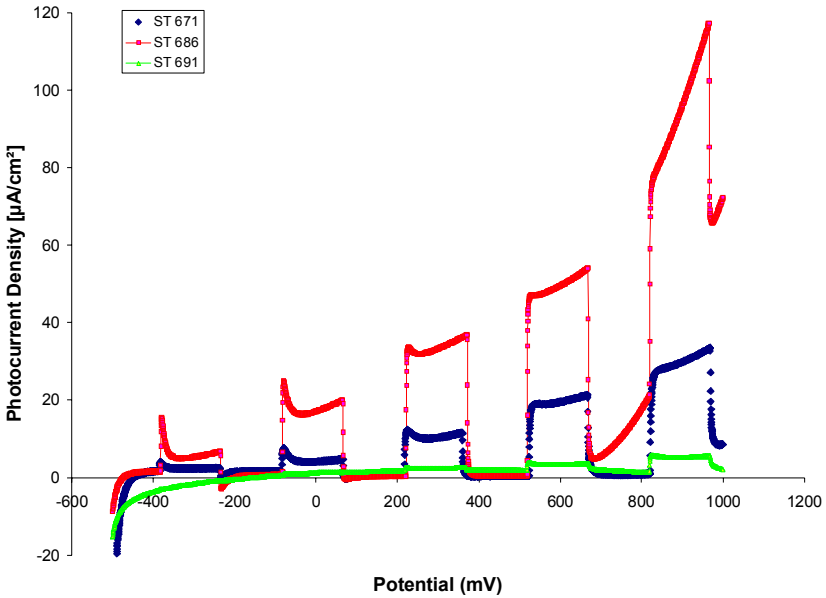
- Left: In-Fe_2O_3 thin film using a 100 W xenon arc lamp. Annealing time up to 4 hours at 550°C, after which any annealing provided no benefit

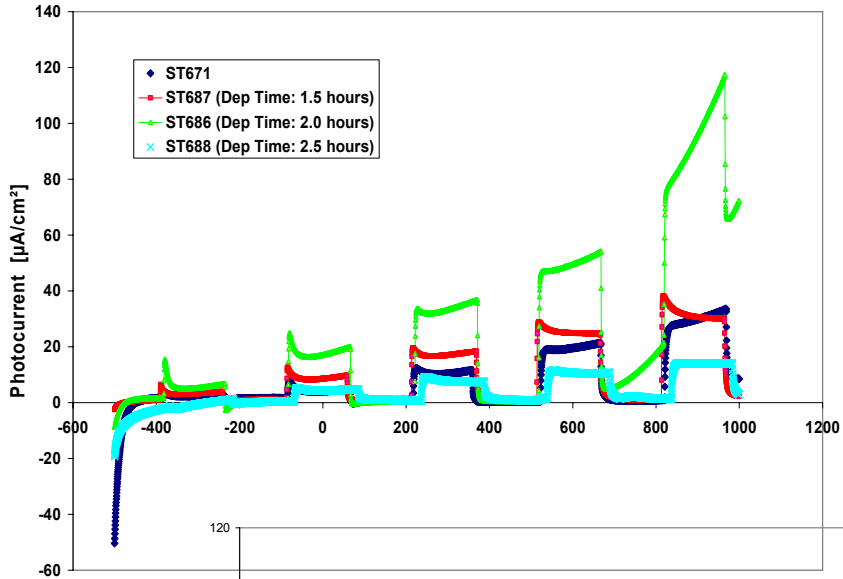


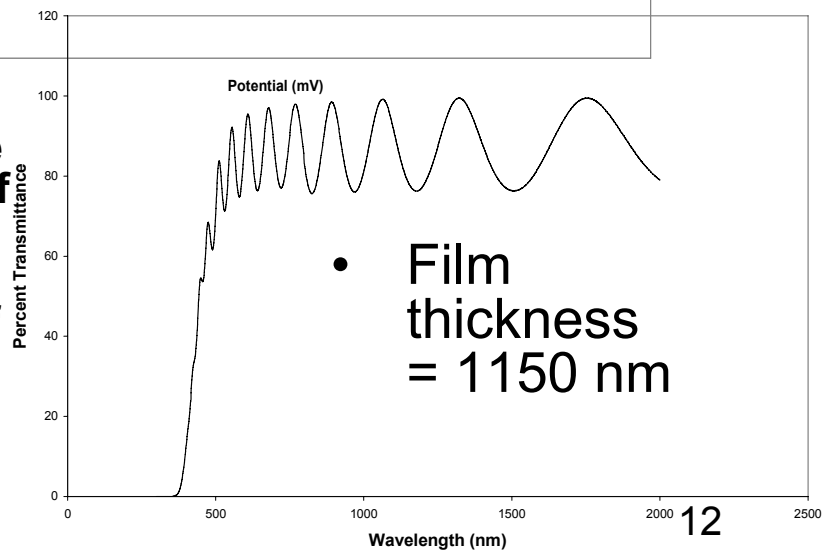
- Right: Chopped scan of Sb-Fe_2O_3 thin film using a 100 W xenon arc lamp. Film performance improved with an annealing time of two hours at 550°C.

Task 3: Continued

- **Metal oxides as Photoactive Semiconductor (PAS)**
  - **Indium Iron Oxide**



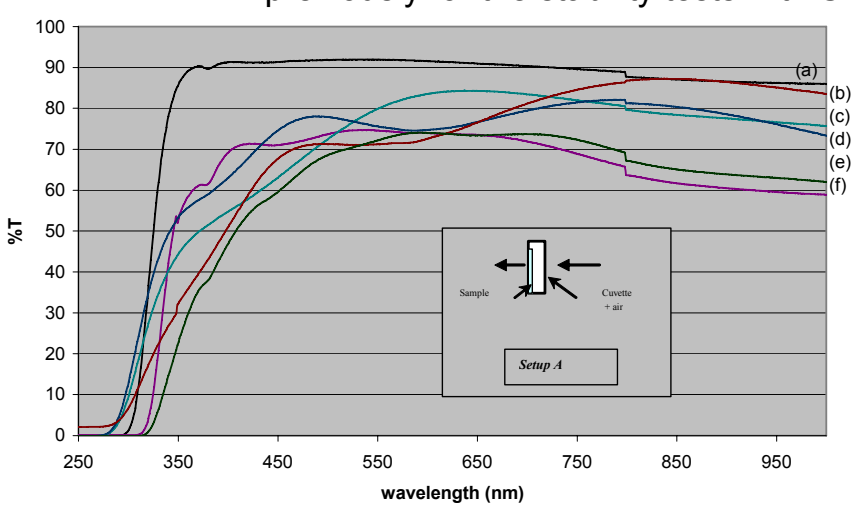


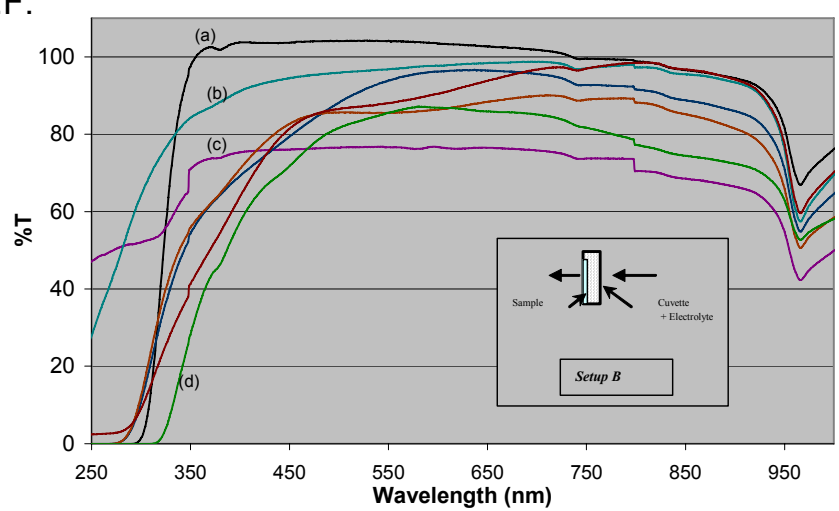


- Film thickness = 1150 nm

- **Top Left: Photocurrent of all samples that were made at the best conditions of: 228° C, 30 W of indium, 100 W of iron oxide, 2 hour sputter deposition period.**
- **Top Right: Samples made at best conditions of 228°C with 30 W of indium and 100 W of iron oxide. The graph shows the relationship between photocurrent and film thickness.**
- **Bottom Right: Optical Absorption measurements from UV/vis.**

- **Metal oxides as TCCR coatings**
  - **Tin Oxide (F-Doped)**
    - SnO_2:F thin films were deposited on stainless steel and on Tec 15 (commercially available highly conductive SnO2:F) at a low temperature between 200°C and 250°C by spray pyrolysis.
    - When connected as an anode in the electrolysis cell, the low temp SnO_2:F thin films lasted for up to three months while maintaining a current density of 0.008 A/cm^2, using 3.5 V for coated Tec15 and around 2.2 V for those deposited on stainless steel.
    - Samples coated with an undoped tin oxide thin film failed to last for even a few hours under the same conditions in a highly concentrated KOH electrolyte solution.
  - **Tin Oxide (Sb-Doped)**
    - Antimony doped tin oxide (SnO_2:Sb) thin films were deposited on Tec 15, where the solution was prepared from a solution of tin tetrachloride dissolved in a mixture of water and ethanol.
    - The resulting films, which exhibited a sheet resistance of circa 500 Ω, were connected to the electrolysis cell where they lasted for barely a few hours under the same conditions stated previously for the stability tests with SnO_2:F.





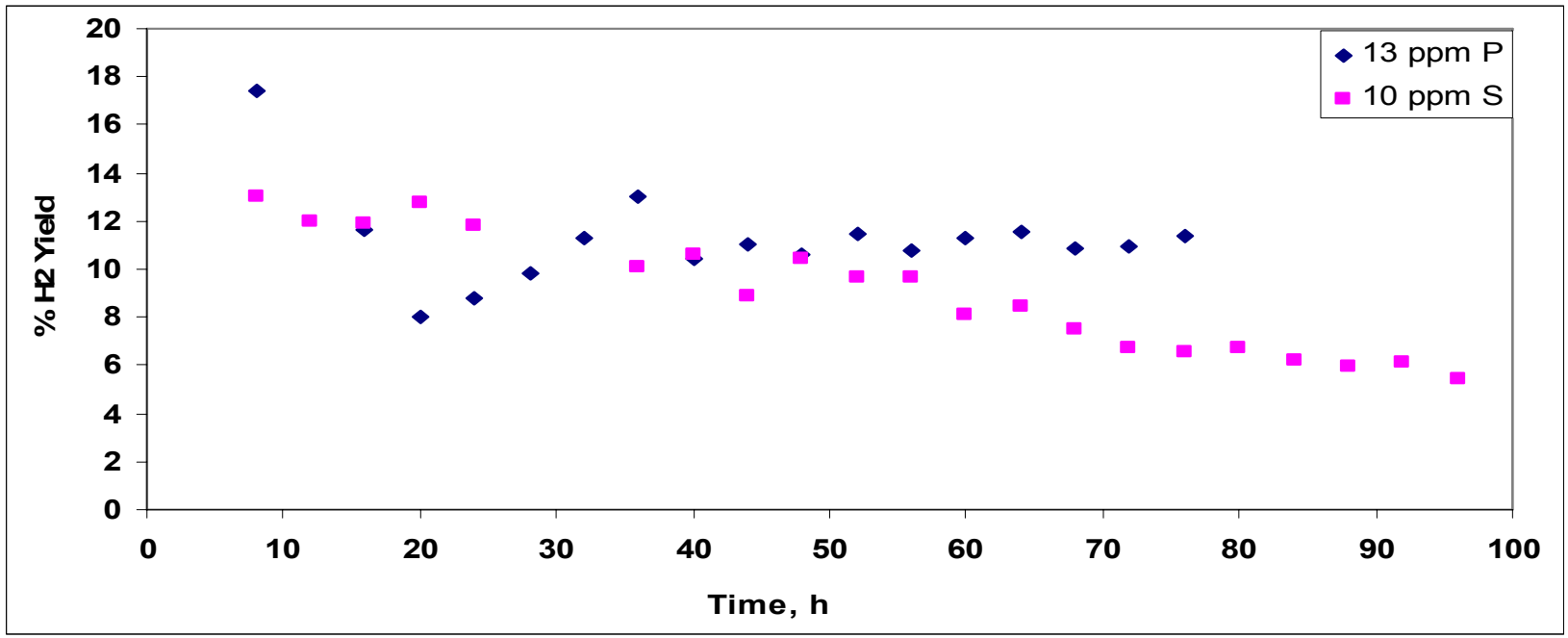
(a) glass, (b), (c), (d) glass/TCCR, (e) TEC15/TCCR, (f) TEC15

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

- Production of hydrogen from biomass for its use in fuel cells for transportation and stationary applications
  - Choice of appropriate method for biomass conversion to hydrogen
  - Demonstrate the feasibility of proposed process
  - Optimization of the process parameters in order to enhance the hydrogen productivity

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

The performance of the Pt-Co catalyst supported on activated carbon when exposed to different impurities

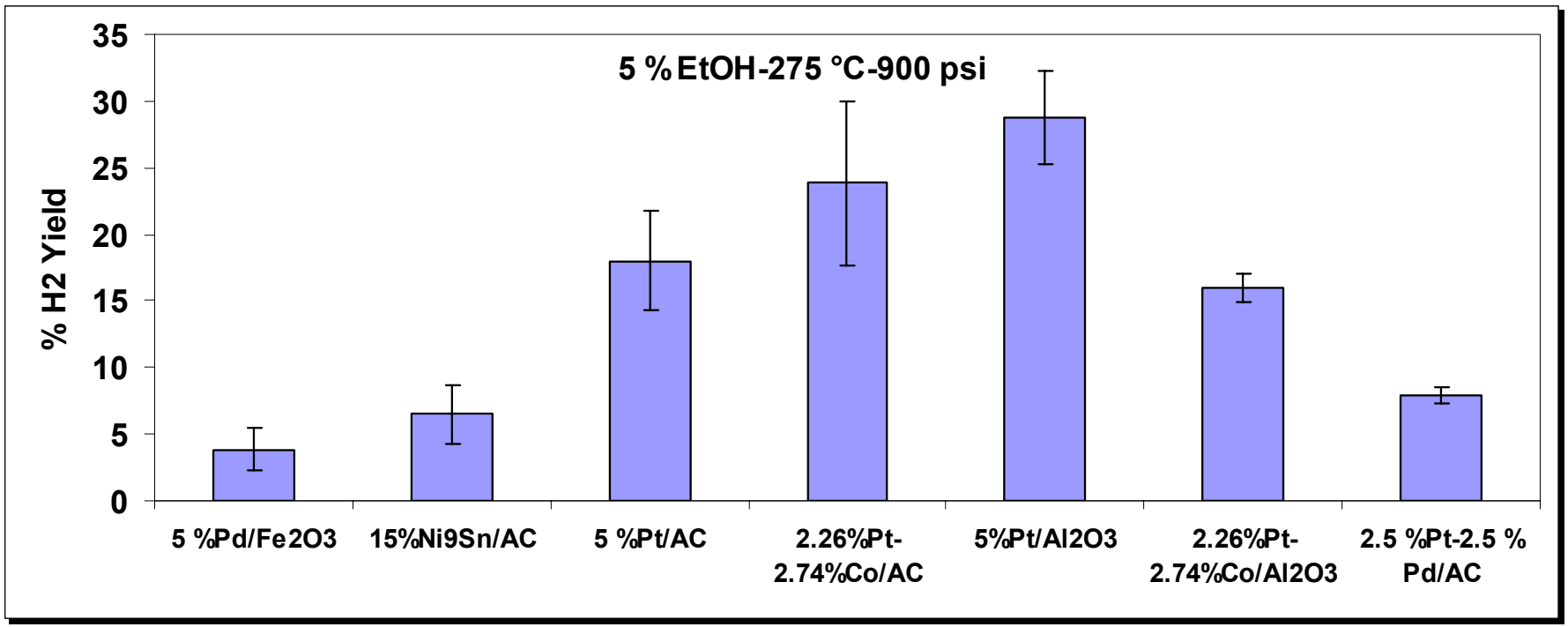


Reaction:

$$C_2H_5OH + 3H_2O \longrightarrow 6\,H_2 + 2\,CO_2$$

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

Activity of the different catalyst for hydrogen production in APR of ethanol



Future Work

- 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.

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 and Xunlight towards commercialization of research done at UT
- Proposed Future Research: Further develop TCCR coatings for immersion and substrate-type cells.