Midwest Optoelectronics

Project ID # PD056

DOE Hydrogen Program

Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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THE UNIVERSITY OF TOLEDO 1872

NREL National Renewable Energy Laboratory

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Innovation for Our Energy Future

Xunlight CORPORATION

Overview

Timeline

- *Project start date: 10/13/2004*
- *Project end date: 12/31/2013*
- *Percent complete: 85%*

Budget

- *Total project funding*
  - *DOE share: $2,113,888*
  - *Contractor share: $760,492*
- *Funding received for FY11: $200,000*
- *Funding received for FY12: $87,887*
- *Funding planned for FY13: $212,388*
- *Funding was reduced during FY11 Go-No-Go review– Tasks 2 & 5 down-selected from scope.*

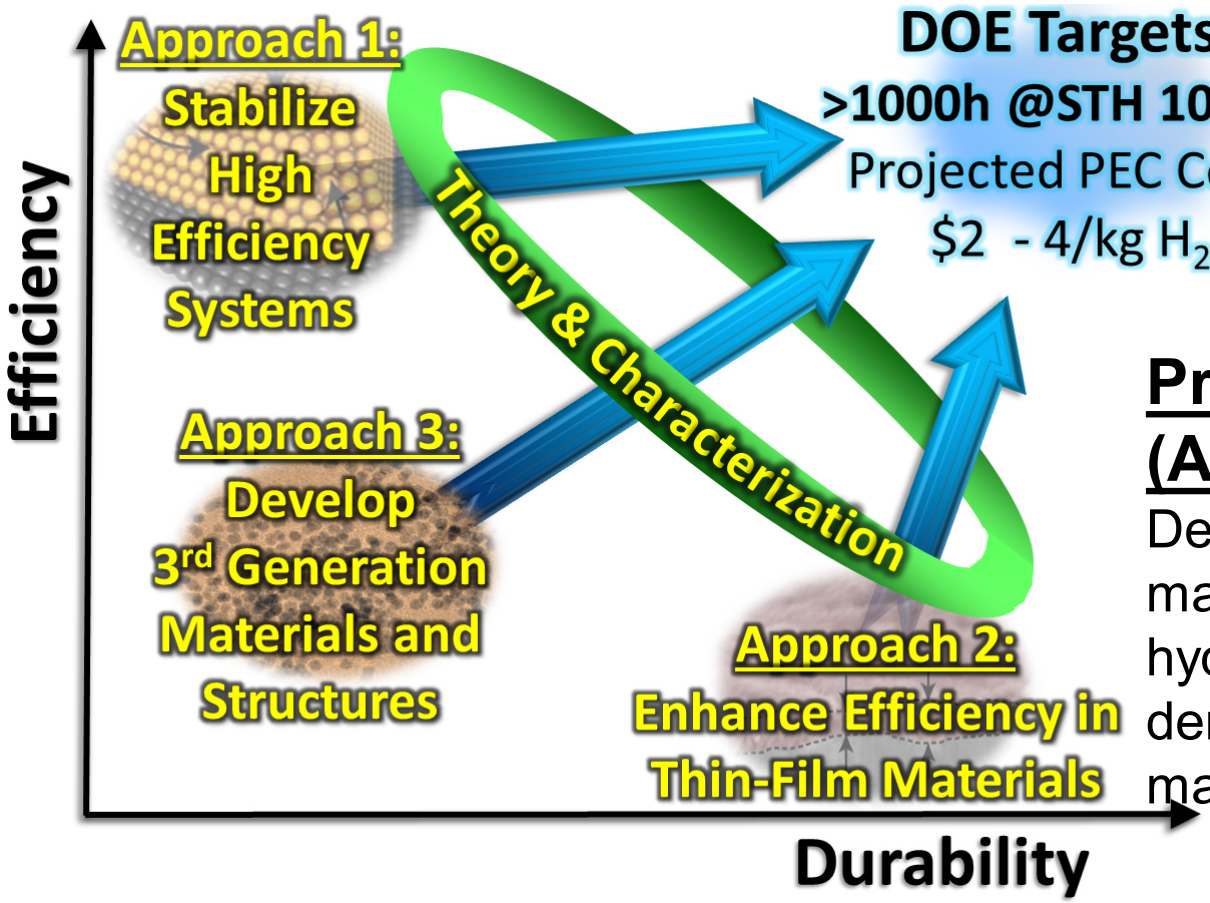
Partners

- *Xunlight Corporation (Xunlight)*
- *University of Toledo (UT)*
- *National Renewable Energy Lab. (NREL)*
  - *Dr. John Turner*

Barriers

- *DOE MYPP Objective for Photoelectrochemical (PEC) hydrogen generation:.*
  - *By 2020, develop advanced renewable photoelectrochemical hydrogen generation technologies to produce hydrogen with a projected cost of $4.00/gge at the plant gate.*
  - *By 2020, demonstrate plant-scale-compatible photoelectrochemical water-splitting systems to produce hydrogen at solar-to-hydrogen energy conversion efficiencies ≥15%*
- *Technical Targets:*
  - *2015: STH Eff > 15%; Durability >0.5 year;*
  - *2020: STH Eff > 20%; Durability >2 year;*
- *PEC Hydrogen Production Barriers - MYPP 3.1.5 Addressed:*
  - *AE. Materials Efficiency*
  - *AF. Materials Durability*
  - *AG. Integrated device configuration*
  - *AI: Auxiliary Material*
  - *AJ. Synthesis and manufacturing*

The US DOE PEC Working Group approach towards efficient and durable solar H_2 production



DOE Targets:

>1000h @STH 10-25%

Projected PEC Cost:

$2 - 4/kg H_2

Project Focus (Approach 2)

Develop scalable thin-film materials devices for PEC hydrogen production, and demonstrate a pathway to manufacturability

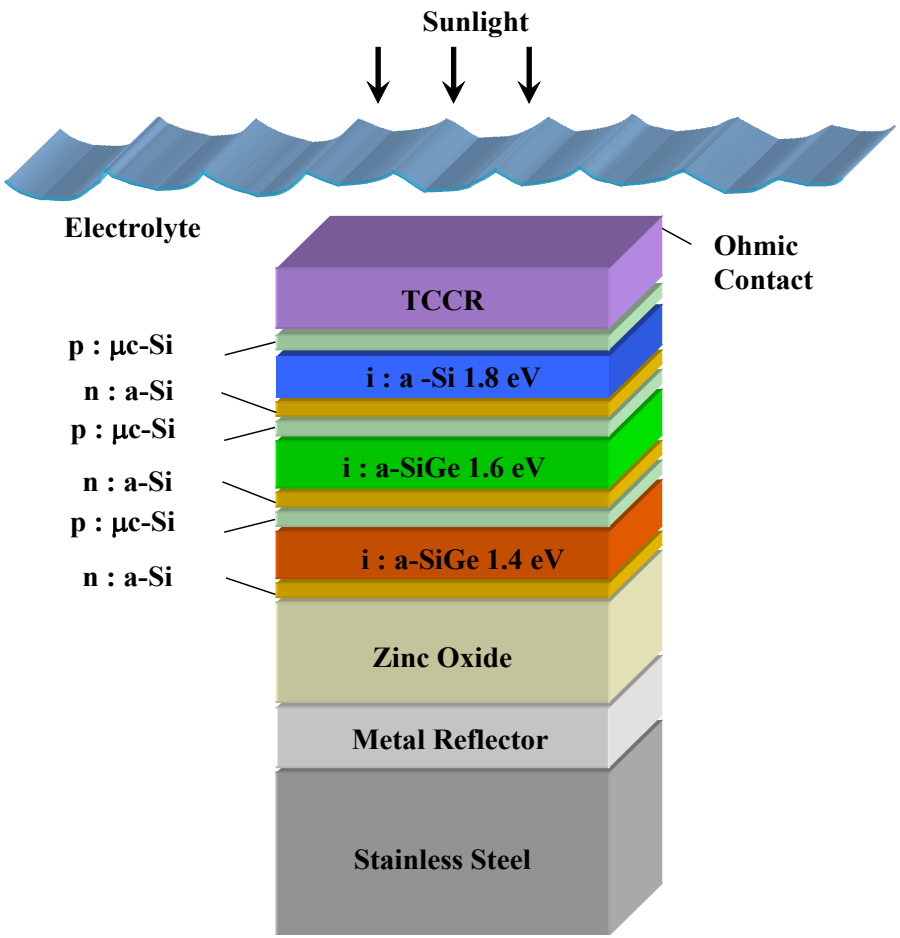
Relevance

Most critical goal: Cost, Cost and Cost! <**$4/gge**

MWOE/Xunlight's Triple-junction Thin Film Photoelectrode

MWOE/Xunlight's triple-junction a-Si/a-SiGe/a-SiGe photoelectrodes have the following key features:

- *V_{oc} ~ 2.3V and operating voltage around 1.6V – ideal for water splitting.*
- *Deposited on a conducting stainless steel substrate which can serve as an electrode.*
- *Produced in large rolls of 3ft wide and up to 5000 ft long SS web in Xunlight's 25MW line – leading to extremely low cost.*



Relevance

Xunlight 25MW Line Producing Triple-junction cells/Photoelectrode

- *1400 m^2 per run in 21 hours*
- *Durable solar cells good for over 20 years*
- *7% stable efficiency in production*
- *12% small area initial efficiency in R&D scale*
- *Var. Mfg Cost: <$25/$m^2$*

Triple-Junction TF PEC Cost Analysis

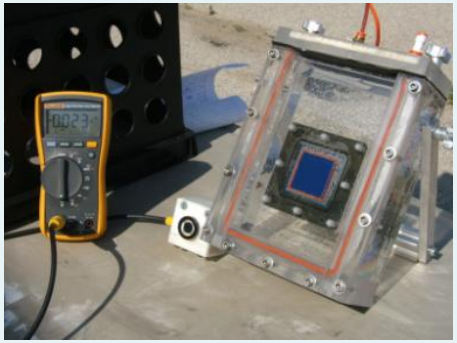
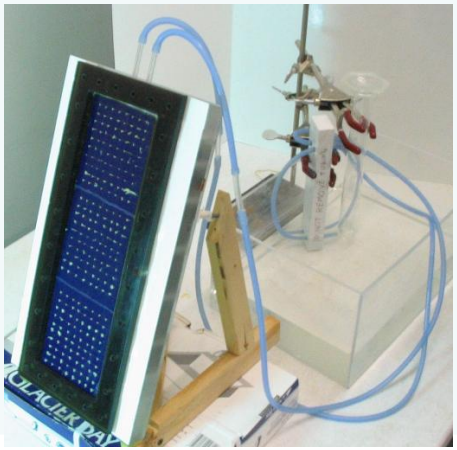
- *DOE 2020 Goal: $4.00/gge*

  ➔ *$47/m^2 PEC system* *assuming 2yr life, 8% STH eff, 6hr/day ave sunlight*

- *Var Mfg Cost for triple-junction photoelectrodes: ~$25/m^2*
- *Leaving ~$20/m^2 for*
  - *Catalyst layers* ➔ *main subject of this research*
  - *PEC housing: durable item*
  - *Balance of system: durable item*

  ➔ *8% TF PEC is a workable option*

Two Main Approaches:

Types	PEC Panels	Electrode in Contact with electrolyte	STH Efficiency Achieved	Major Challenges	
Immersion -type PEC cell		Front and back side	5.7%	TCCR Materials	Main subject of this research
Substrate-type PEC cell		Only back-side	5.0%	Cost reduction	Down-selected due to budget reduction

Research Tasks (Approaches)

The goal of this project is to develop critical technologies required for cost-effective production of hydrogen from sunlight and water using triple junction thin film-Si based photo-electrodes.

Tasks	Task Descriptions	Status
1	Transparent, conducting and corrosion resistant (TCCR) coating for triple-junction tf-Si based photo-electrode.	Third round materials were identified. Co_3O_4 has been fully characterized. More work is being performed on In_2O_3-Co_3O_4. [Phase I: 100%; Total: 90%]
3	Understanding and characterization of photo-electrochemistry.	Various hydrogen and oxygen generation catalysts have been studied. Successful in identifying some promising catalysts for O_2 and H_2 generation and in making production size PEC electrodes with TCCR layers. [Phase I: 100%; Total: 85%]
4	Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems.	Multiple PEC module designs have been built to optimize the solar to hydrogen (STH) conversion efficiency, extend the lifetime and reduce the cost . [Phase I: 100%; Total: 85%]
2	Hybrid multi-junction PEC electrode having semiconductor- electrolyte junction.	Various materials have been studied and Phase I work completed. [Phase I: 100%; Phase II: down-selected at Go/No-Go Decision Point , Dec 2010)]
5	Development of device designs for large-area, substrate-type PEC panels.	Substrate-type PEC modules have been built and optimized. 5% STH conversion efficiency has been achieved. [Phase I: 100%; Phase II: down-selected].

Milestones (Approaches)

- *Develop high quality TCCR materials with stability up to 1,000 hours. Completion date: Quarter 4, 2013. —Co_3O_4 has been identified as both an effective oxygen generation catalyst and a TCCR material. Effective hydrogen generation catalysts have also been identified. Large area photoelectrodes with triple junction a-Si solar cells and Co_3O_4 as TCCR coating have been successfully fabricated and integrated into a PEC system.*
- *Demonstrate 5.5% and 750 hours for an integrated immersion type PEC system using the developed high quality TCCR material. Completion date: Quarter 4, 2013. — Integrated PEC module cases have been designed, built and tested to resolve various issues that we have encountered. 5.7% STH efficiency and reasonable lifetime have been achieved. Further improvements are underway.*
- *Complete a preliminary techno-economic analysis of the immersion-type PEC system. Completion date: Quarter 4, 2013. — Preliminary analysis shows PEC using 8% Triple-junction TF Si photoelectrodes is a viable option to achieve $4/gge.*

Part I: TCCR Materials for PEC Electrodes and Understanding of the Photo-electrochemistry

1. *Different TCCR materials under investigation*
2. *Co_3O_4 as TCCR and oxygen evolution catalyst*
3. *Role of ITO underneath Co_3O_4 TCCR*
4. *Fabrication of Co_3O_4 coating on a-Si solar cells in a large scale roll-to-roll deposition system*
5. *Hydrogen evolution catalyst development*

1. Different TCCR materials under investigation

- ***Third Round of Tested Materials:***

➢ Co_3O_4 – *Excellent current density and stability;*

Large-area deposition process using sputtering was developed & optimized (AMR 2011-2012);

- *good transparency except the UV region;*
- *can be made at below 300°C.*

➢ In_2O_3-Co_3O_4 – *Excellent current density and stability;*

- *good transparency except in the UV region;*
- *can be made at below 300°C;*
- *promising results, but still needs further evaluation.*

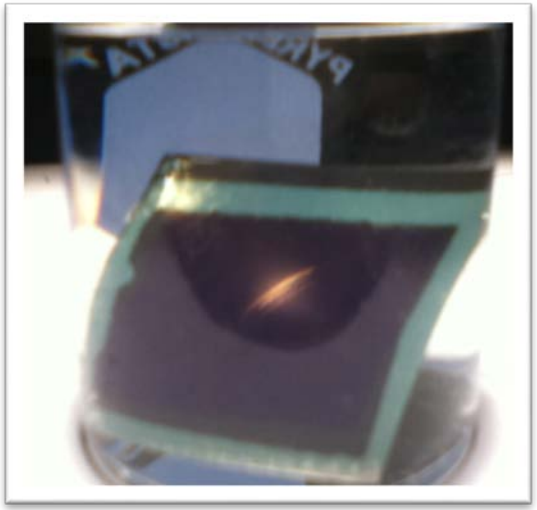
- *Other material studied: TiO_2, Fe_2O_3, W_2O_3, In_2O_3-Fe_2O_3 etc.*

2. Cobalt Oxide as a TCCR and oxygen evolution catalyst

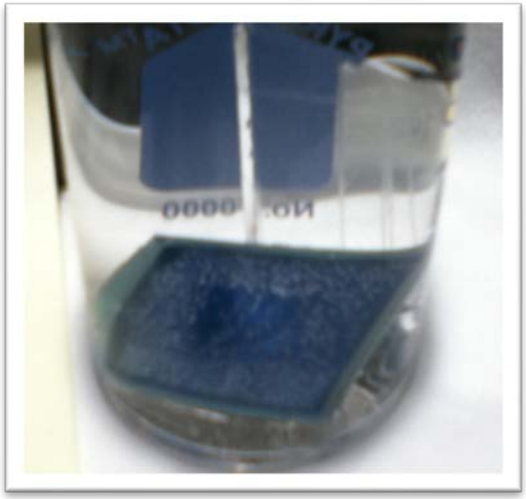
Standard TF Si Photoelectrode; in H_3BO_3/KOH electrolyte; under one Sun

No Co_3O_4 on top of the ITO layer
No O_2/H_2 generation

With Co_3O_4 on top of the ITO layer
With O_2/H_2 generation



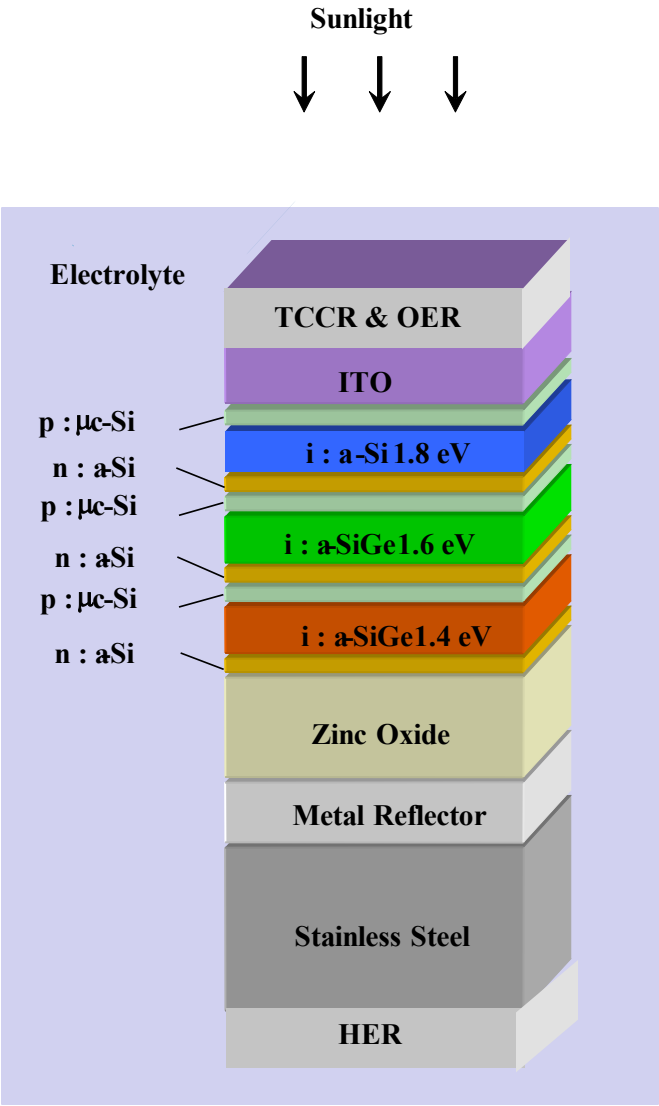
(a) PEC electrode without Co_3O_4 on top of ITO



(b) PEC electrode with Co_3O_4 on top of ITO

- ***Co_3O_4 serves as an oxygen evolution catalyst and as a TCCR layer***

3. Role of ITO layer underneath Co_3O_4 as TCCR



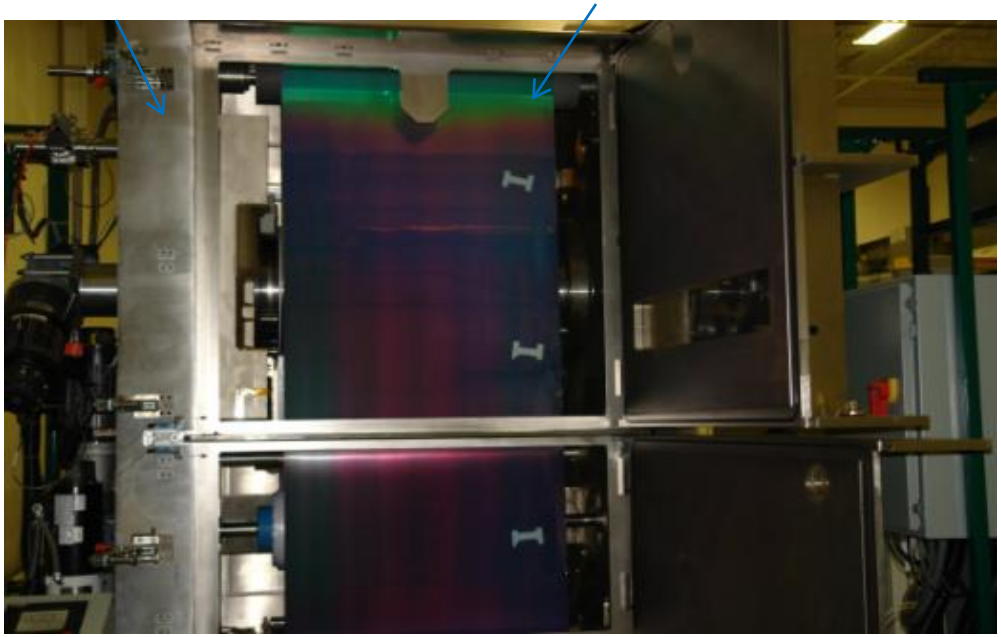
A schematic diagram of our PEC electrode

- *No ITO between Co_3O_4 layer and a-Si layer => no H_2 and O_2 evolution*
- *Thin ITO (0-70 nm) between Co_3O_4 layer and a-Si layer => no H_2 and O_2 evolution if ITO thickness <10nm*
- *Standard a-Si solar cell with ITO coating usually need a shunt passivation process to isolate tiny defect in the Si layer so that the solar cell would not be shunted.*
- *To obtain a PEC electrode which has sufficient voltage for water splitting, the solar cell with ITO needs to go through the shunt passivation first before the Co_3O_4 layer is sputtered on.*

➢ *ITO coating and shunt passivation are necessary for obtaining sufficient PEC device voltage;*

4. Making PEC Electrode with Co_3O_4 TCCR Coating in Large Scale System

- *The 2MW roll-to-roll machine at Xunlight allows the fabrication of triple junction a-Si solar cell, the ITO layer and the TCCR layer to be integrated in one system so that the parameters for each layer can be coordinated and optimized for best photo-electrochemical performance.*
- *The prototype production machine is used to produce large area PEC electrodes (3ft wide and hundreds of feet long) that are more uniform, with less edge effect which exists in a small sputtering system.*
- *Solar cells with ITO were shunted passivated first before the TCCR layer is sputtered.*



Opened pay-out chamber of the 2 MW-line with inserted stainless steel web after sputtering of Co_3O_4:

5.1 Hydrogen evolution catalyst development

Four different types of hydrogen evolution (HER) catalysts are used for PEC electrode development:

- ***Plated Nickel:***

  Fabricated by co-electroplating of Ni and Zn from a $NiCl_2/NiSO_4/ZnCl_2$ solution; Zn is leached from the deposit in order to increase the surface roughness of the Ni-catalyst;

- ***Sintered Nickel:***

  Fabricated by annealing packed Ni-powders at 300°C for 3 hours;

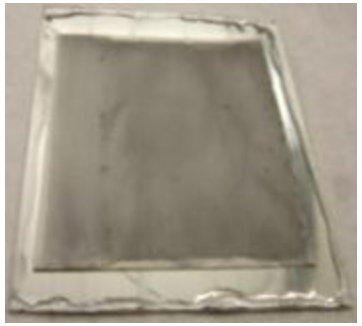
- ***Plated Platinum:***

  Electroplated from H_2PtCl_6 solution;

- ***Plated Ruthenium:***

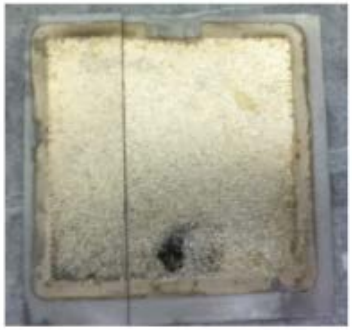
  Electroplated from $RuCl_3$ solution;

Plated Pt



Plated Ru

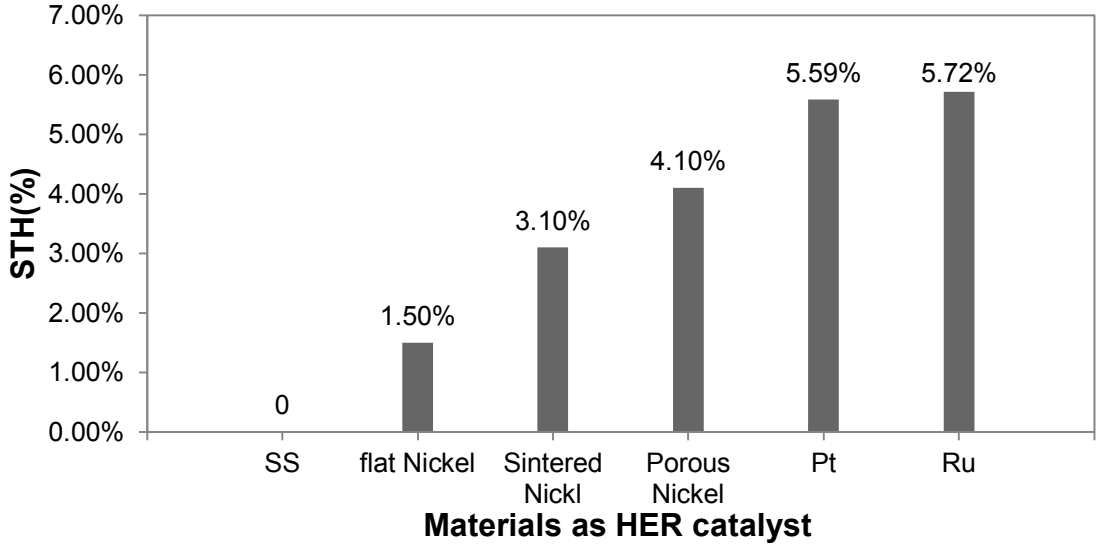
Plated Ni



Sintered Ni

5.2 Tested various materials as HER catalyst

Five Materials have been developed as HER catalyst. The initial STH efficiency corresponding to each of them is shown below



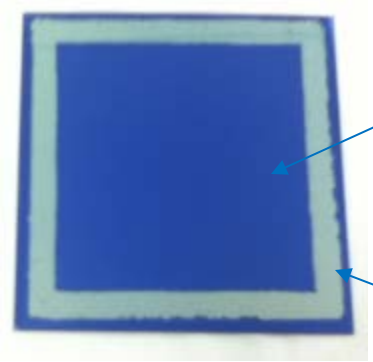
HER Catalyst	Description of the materials
SS	Stainless steel, substrate of the tf-silicon-based cells
Flat nickel	Electrochemical deposition, relatively flat surface
Sintered nickel	Fabricated by annealing packed Ni-powders
Porous nickel	Electrochemical deposition with Zn being leached-out
Platinum	Electrochemical deposition
Ruthenium	Electrochemical deposition

Part II: Development of Low-cost, Durable and Efficient Immersion-type PEC Systems

1. Determination of Solar-to-Hydrogen efficiency
2. STH efficiency obtained using PEC prototype system
3. Development of PEC module case designs
4. Outdoor testing of PEC prototype system

1. Determination of Solar-to-hydrogen Efficiency

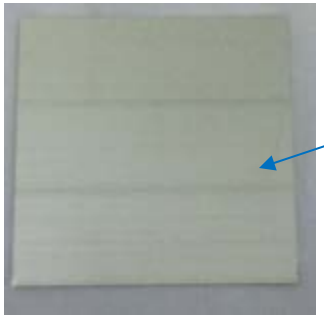
PEC electrode



Co_3O_4/ITO/ a-Si layers

Edge isolation (Co_3O_4/ITO on the edge is etched off with acid)

Front-side



Stainless steel substrate

Back side

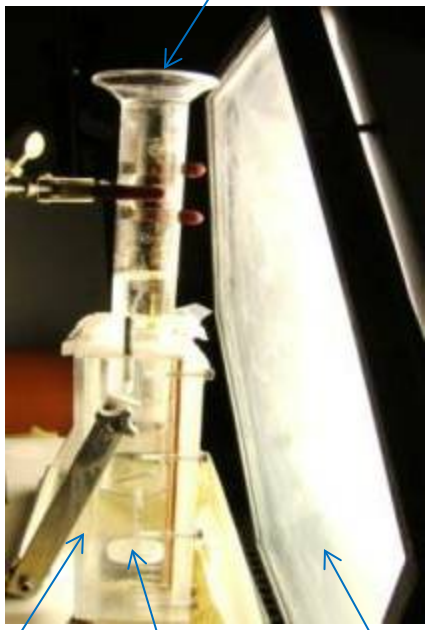
Hydrogen generation catalyst materials deposited onto stainless steel sheets are attached to the back-side of the device;

$$STH = \frac{(\text{mol of } H_2/\text{sec}) \quad (237 \text{ kJ/mol } [\Delta G \text{ for } H_2])}{(P_{total} \text{ mW/cm}^2) \quad (\text{Area of Cell cm}^2)}$$

2.1 STH efficiency obtained using PEC prototype system

A prototype PEC system was used to determine the STH efficiency indoors using a stadium lamp set-up;

- *PEC electrodes tested have an active area of ~1.5”x1.5”;*
- *The light intensity at the container surface is ~77% of one-sun intensity;*
- *A volumetric cylinder is placed above the sample for collecting hydrogen and oxygen generated;*
- *The PEC electrodes are tested during each test day for 4-8 hrs for many days;*
- *The electrolyte temperature increases during each test run from room temperature up to ~56°C, similar to the temperature increase which is observed in the outdoor testing.*

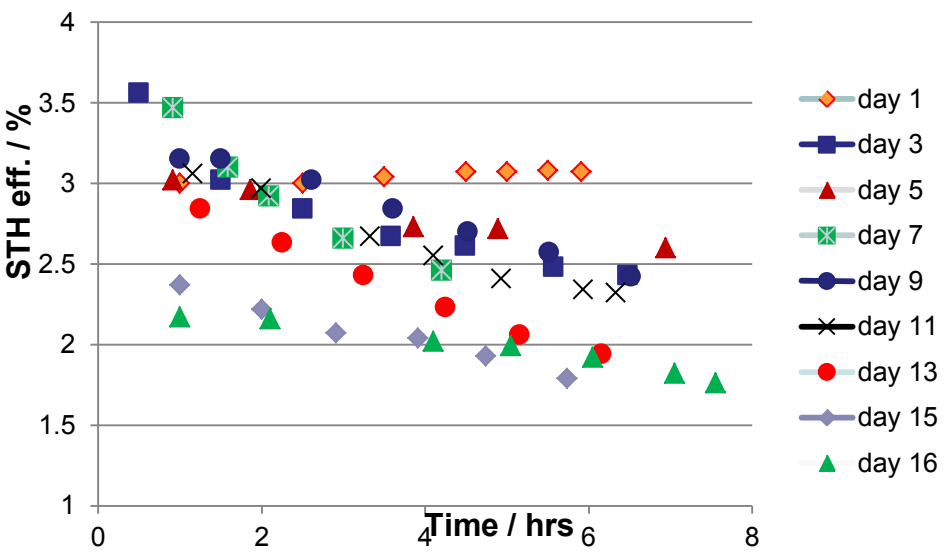


2.2 STH efficiency obtained using PEC prototype system

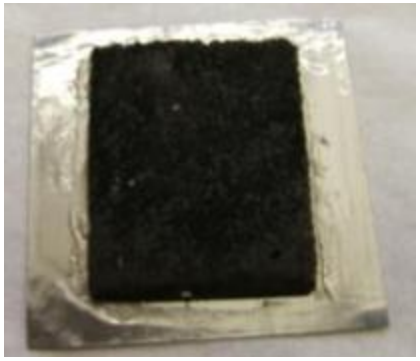
Sintered Ni was attached as HER catalyst to the backside of the PEC electrode;

- *Initial STH eff. values are ~3.5%;*
- *The STH eff. decreases during each testing day, likely due to the increase in electrolyte temperature;*
- *The STH eff. recovers to almost initial values at the beginning of each test day for days 1 to13;*

STH eff. (accumulated) vs runtime



Sintered Ni-catalyst

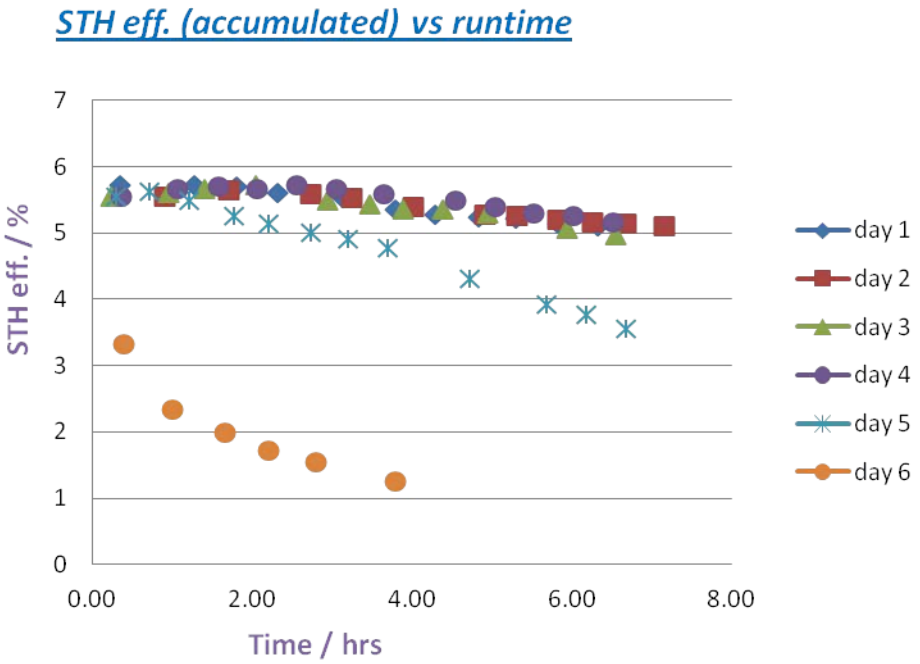


- *A significant decrease in STH eff. is observed for test days 14-16 due to corrosion of the Co_3O_4 and solar cell surface;*

2.3 STH efficiency obtained using PEC prototype system

Electroplated Ru was attached as HER catalyst to the backside of the PEC electrode;

- *The initial STH eff. values are ~5.7%;*
- *The STH eff. shows marginal decrease during test days 1-4; At the beginning of each test day, the STH eff. would recover to 5.7%.*
- *Significant decrease in STH eff. observed during test day 6;*

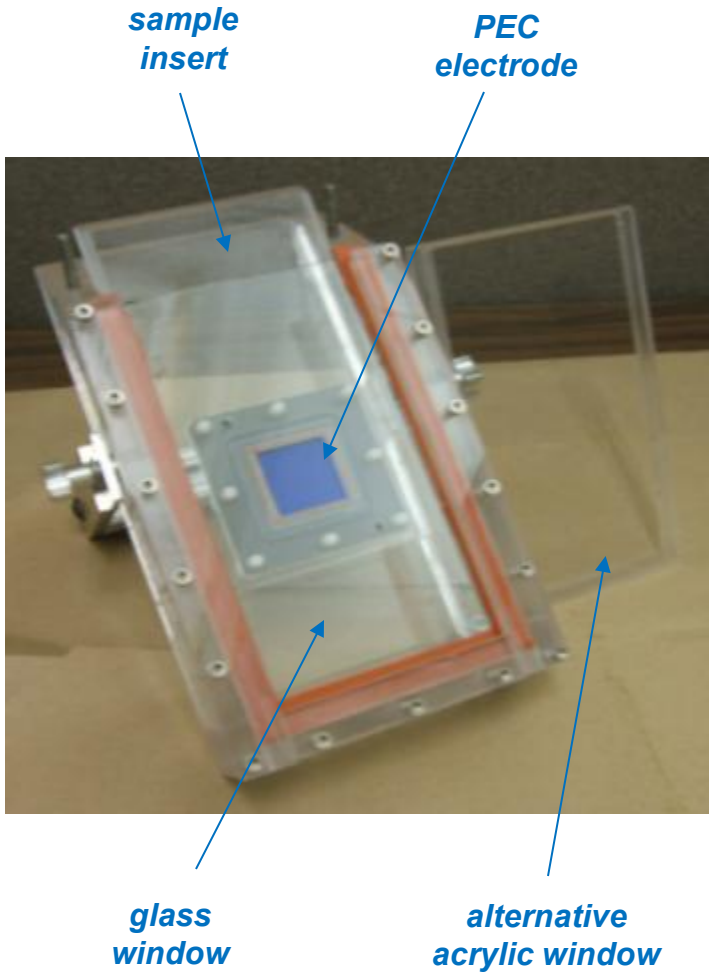


- ***The PEC electrode with 15.2 cm² aperture area generated ~29.3 cc of hydrogen in 77 min under a stadium lamp with 77.4 mA/cm² intensity at the PEC electrode.***

➔ ***Achieved initial Solar-To-Hydrogen efficiency of 5.7%***

3.1 Development of PEC module case designs

Different design options for low-cost PEC prototype system were developed and tested under indoor and outdoor conditions;



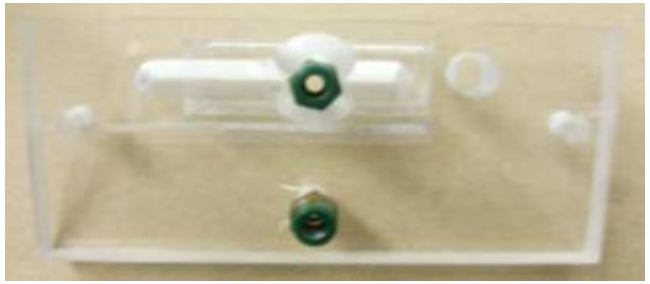
- *A sample insert holds the PEC electrode.*
- *This insert allows exchanging the PEC electrode material using different sizes for the active PEC electrode area (e.g. 4"x4", 1.5"x1.5") for experimentation purposes.*
- *Electrolyte movement is provided at the bottom of the electrolyte container.*
- *The lid (top) provides outlets for collecting H_2 and O_2 and an inlet for refilling the electrolyte during system operation.*
- *The PEC container allows using different window materials such as glass and durable, low cost polymer materials.*
- *The PEC system can be operated under indoor and outdoor operating conditions;*

3.2 Development of PEC module case designs

The gas collection was improved by developing a hydrogen collection system attached underneath the lid of the PEC prototype system

Side view of PEC prototype system lid

Top view of PEC prototype system lid

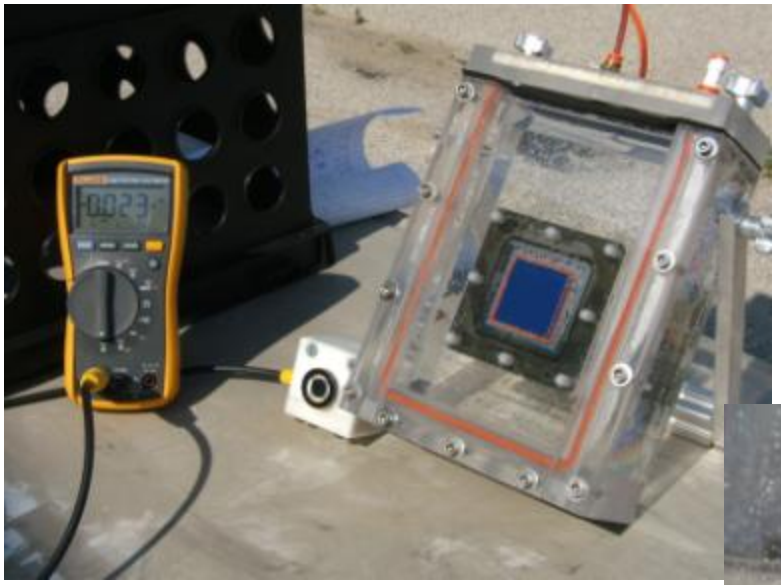


Top view of PEC prototype system

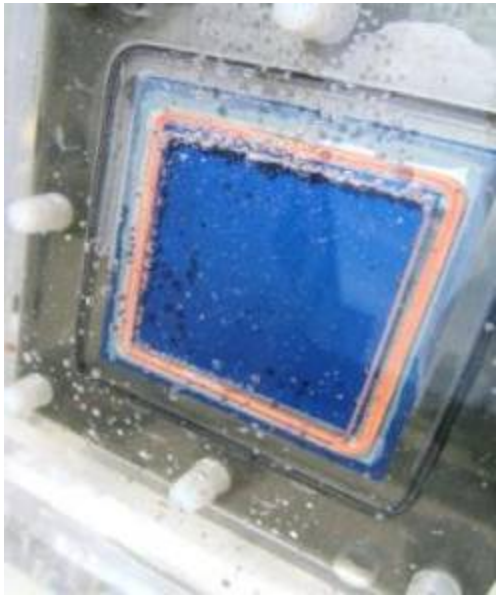
PEC prototype system

4.1 Outdoor testing of PEC prototype system

The PEC prototype system uses a glass window;



O_2 evolution:

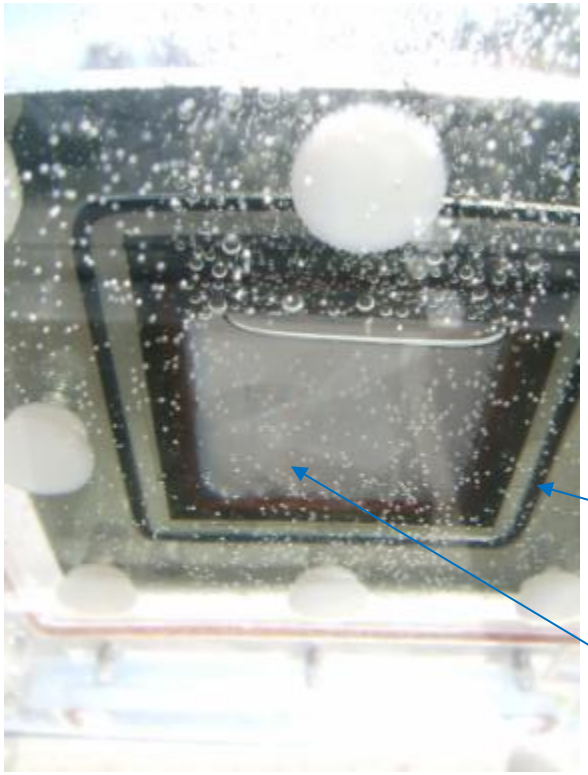


H_2 evolution:

On the backside of the PEC electrode vigorous H_2 evolution was observed;

On the TCCR coated front side vigorous O_2 evolution was observed;

4.2 More Outdoor testing of PEC prototype system

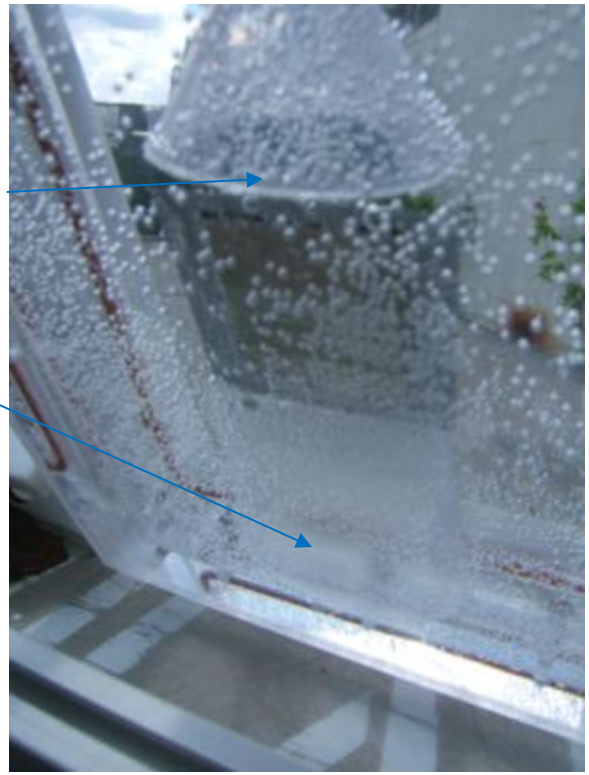


H_2 and O_2 collection

PEC electrode holder

sample holder

H_2 evolution catalyst



Collaborations

Partners:

- ***Xunlight Corporation (Industry):***
  - *Xunlight provides the triple junction solar cells and helps with depositing Co_3O_4 in the large area roll-to-roll machine for PEC electrodes (Tasks 4).*
- ***University of Toledo (Academic):***
  - *UT helps with characterization of TCCR material, and hydrogen generation measurement. (Tasks 1 and 4)*
- ***NREL (National Lab):***
  - *NREL is working on improving the understanding of PEC process for a-Si based photoelectrodes (in collaboration with Dr. John Turner). (Task 3)*

Technology Transfer:

- ***University of Toledo (UT):***
  - *UT and MWOE/Xunlight signed a license agreement for technology transfer for the commercialization of PEC technology.*

Collaborations

- *MWOE/Xunlight's triple-junction photoelectrode converted into "Artificial Leaf" at MIT—published in SCIENCE Magazine and featured as one of Top 50 Innovations of Year 2011 by Time Magazine.*
- *MWOE/Xunlight triple-junction photoelectrodes have the following key features:*
  - *V_{oc} ~ 2.3V and operating voltage around 1.6V – ideal for water splitting.*
  - *Deposited on a conducting stainless steel substrate which can serve as an electrode.*
  - *Produced in large rolls of 3ft wide and up to 5000 ft long SS web in Xunlight's 25MW line – leading to extremely low cost.*
- *Received many requests for collaboration on PEC hydrogen generation research projects from multiple research groups including MIT and Sun Catalytix, University of Texas at Austin, Toyota Technical Center in Ann Arbor, University of California at San Diego, Energy Research Institute at Nanyang Technological University in Singapore, Imperial College London in England, and Tsinghua University and Nanjing University in China.*

"Artificial Leaf" by Dr. Nocera's MIT lab made use of MWOE/Xunlight's triple junction a-Si solar cells

Proposed current and future work

- *Fabricating PEC electrodes with an entirely new design concept (this design is currently under patent filing process) which could extend the durability of the PEC electrode extensively.*
- *Focus on measures which can slow the decay of the STH efficiency and improve durability.*
- *Experimenting with different fabrication methods for PEC electrode preparation with respect to solar cell and ITO deposition, different catalyst and fabrication process, and different conditions for applying TCCR coating both in the lab and in the large scale roll-to-roll deposition system.*
- *Continue to develop different module designs to optimize the STH efficiency, extend lifetime and reduce cost.*
- *Develop large area commercial size PEC system and carry out test in real life conditions.*
- *Complete concept design of large-area low-cost PEC system;*
- *Perform preliminary techno-economic analysis of the immersion-type PEC system based on the concept design;*
- *Collaborate with different research groups around the world to further PEC hydrogen generation research and development.*
- *This project is approaching its final phase and one of the priorities is to document progress made and lessons learned to position for further research and commercialization in the future.*

Project Summary

- **Relevance:** *Addresses DOE MYPP program objectives, specifically low-cost production of hydrogen using photoelectrochemical methods to achieve $4/gge.*
- **Approach:** *Develop immersion-type photoelectrochemical (PEC) system using a multi-junction solar cell device with TCCR layer or PAS material which can generate hydrogen using sunlight at low cost, good efficiency and durability. Second approach is to develop substrate type PEC system using multi-junction solar cell device for renewable hydrogen generation.*
- **Technical Accomplishments and Progress:**

  Have met Phase I go/no-go criteria on time; Continued with the development of the immersion type PEC system.

  Have carried out extensive research with many different material classes for application as TCCR materials and obtained very promising results. Developed various catalyst material. Successfully transferred the lab research recipe to large area deposition of cobalt oxide on a-Si solar cell devices in a 2MW roll-to-roll system. Developed different immersion type PEC modules and achieved good STH efficiency (5.7%) and lifetime results both in the lab and real life outdoor conditions.
- **Technology Transfer/Collaborations:**

  Active collaboration with multiple PEC Hydrogen groups around the World.

  Active collaboration among the project collaborators, MWOE, Xunlight, UT and NREL on material research and characterization, and on scale up of lab results to large scale system.
- **Proposed Future Research:**

  Further improve the STH efficiency and durability of the PEC system by explore different module designs, electrode fabrication processes, catalysts and electrolyte compositions. Continue the collaborate work with other PEC groups around the world to develop advanced PEC systems.

  Design and build commercial size immersion-type PEC system and study the performance, efficiency, cost and durability in real time conditions.

  Carry out the preliminary techno-economic analysis of the immersion-type PEC system.

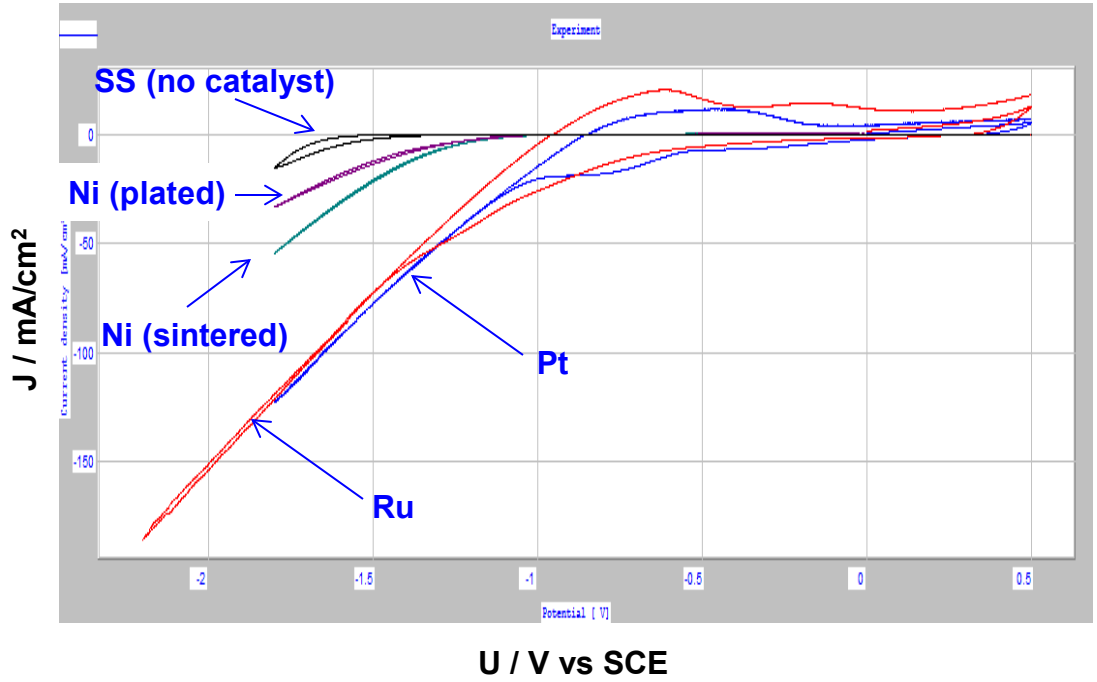
Technical Backup slides

1. Hydrogen evolution catalyst development

Procedures for fabricating electroplated Pt, Ru, Ni and sintered Ni catalysts were developed. These materials were characterized regarding their catalytic activity using Cyclic-voltammetry (CV) measurements in H_3BO_3/KOH electrolyte solution;

- *The catalyst was attached to the back side (which is stainless steel) of the PEC electrodes.*
- *All four catalysts show better catalytic performance compared with the PEC electrodes without any catalyst attached;*
- *In the CV measurements, plated Pt and Ru show stronger catalytic behavour for hydrogen generation than plated Ni and sintered Ni;*

CV-measurements for HER catalyst materials:



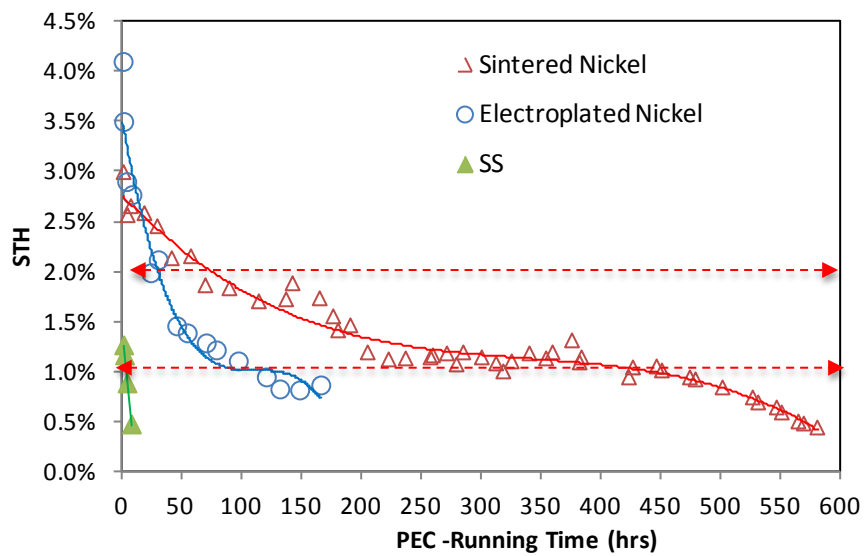
➢ ***Electroplated Pt, Ru are superior but costly hydrogen evolution catalysts; electroplated and sintered Ni are viable low-cost options;***

2. Effect of HER catalyst on STH efficiency

Three PEC electrodes were made: a) with sintered nickel attached to its stainless steel side, b) with electroplated Ni attached to its SS side, and, c) with no catalyst attached, just SS substrate.

- *The PEC electrode, c) just stainless steel, shows very low STH efficiency and durability.*
- *The electrodes with a) sintered Ni and b) with electroplated Ni show much improved STH efficiency and durability.*
- *The PEC electrode with sintered Ni as HER catalyst shows the longer runtime of the PEC electrode (~600hrs);*

STH eff. (accumulated) vs runtime

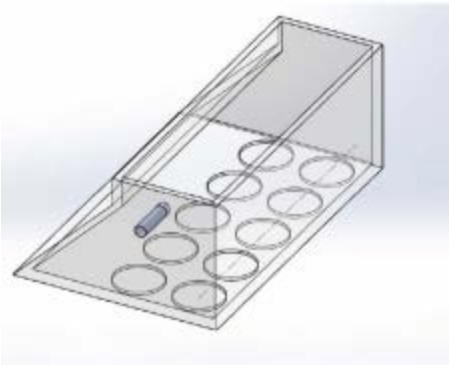


Cathode material		SS	Electroplated nickel	Sintered Nickel
Initial STH		1.27 %	4.1%	3.1%
Running Time	STH>2%	0	35 hrs	60 hrs
	STH>1%	< 4hrs	120 hrs	480 hrs

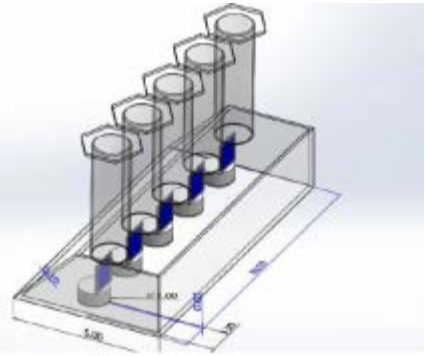
➢ ***HER catalysts have a significant effect on the STH efficiency and on the lifetime of PEC electrodes***

3. Development of set-up for testing multiple samples

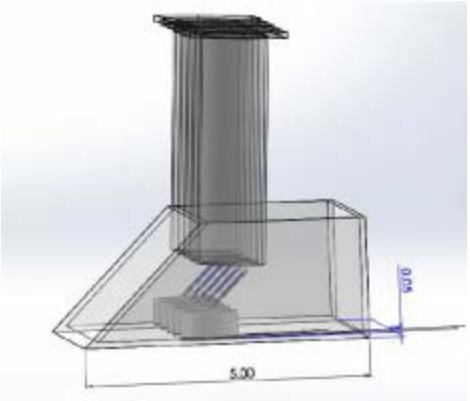
A set-up for testing multiple PEC electrodes at the same time was developed; the set-up can be used under indoor or outdoor conditions;



Design of a setup for testing multiple PEC samples



Design for horizontal incident light source



Design for incident light source with angle to the horizon (sunlight)

Set-up under outdoor operating conditions

Set-up under indoor operating conditions

Presentations

- *Xu, L., "Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen", DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation, Crystal Gateway Marriott, Arlington, VA.,* ***2008, 2007, 2006, 2005*** *(Poster or Oral Presentations)*
- *Ingler Jr., W.B., Attygalle, D., Deng, X. "Properties of Rf Magnetron Sputter Deposited Cobalt Oxide Thin Films as Anode for Hydrogen Generation by Electrochemical Water Splitting" Abstracts of Papers, 210th Meeting of the Electrochemical Society, Inc., Cancun, MX, October 29-November 3,* ***2006****. (Poster)*
- *Ingler Jr., W.B., Sporar, D., Deng, X. "Sputter Deposition of In-Fe_2O_3 Films for Photoelectrochemical Hydrogen Production" Abstracts of Papers, 210th Meeting of the Electrochemical Society, Inc., Cancun, MX, October 29-November 3,* ***2006****. (Poster)*
- *Ingler, Jr., W.B., "Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen", DOE Photoelectrochemical Working Group Meeting, Lee Suite, Crystal Gateway Marriott, Arlington VA, May 18,* ***2006****. (Oral Presentation)*
- *Ingler, Jr., W.B.,"Production of Hydrogen for Clean and Renewable Sources of Energy for Fuel Cell Vehicles", DOE Photoelectrochemical Working Group Meeting, Lee Suite, Crystal Gateway Marriott, Arlington VA, May 18,* ***2006****. (Oral Presentation)*
- *Hunley, D.P.; Ingler, W.B.; Price, K.; Deng, X. "Sputter Deposition on Indium-doped Iron Oxide Films for Photoelectrochemical Hydrogen Production" 5th Annual Posters-at-the-Capitol, Frankfort, KY, February 2,* ***2006****. (Poster)*
- *Ingler Jr., W.B., Sporar, D., Deng, X. "Sputter Deposition of Fe_2O_3 Films for Photoelectrochemical Hydrogen Production" Abstracts of Papers, 208th Meeting of the Electrochemical Society, Inc., Los Angeles, CA, October 16-21,* ***2005****. (Poster)*