Midwest Optoelectronics

Project ID # PD056

DOE Hydrogen Program

Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

Liwei Xu (PI, Presenter)
Midwest Optoelectronics, LLC, Toledo, Ohio
William B. Ingler Jr.
University of Toledo, Toledo, Ohio
Anke Abken
Xunlight Corporation, Toledo, Ohio
John Turner
National Renewable Energy Lab, Golden, CO

05/16/2012 6:30 to 8:30 PM

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

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: 6/30/2013*
- *Percent complete: 85%*

Budget

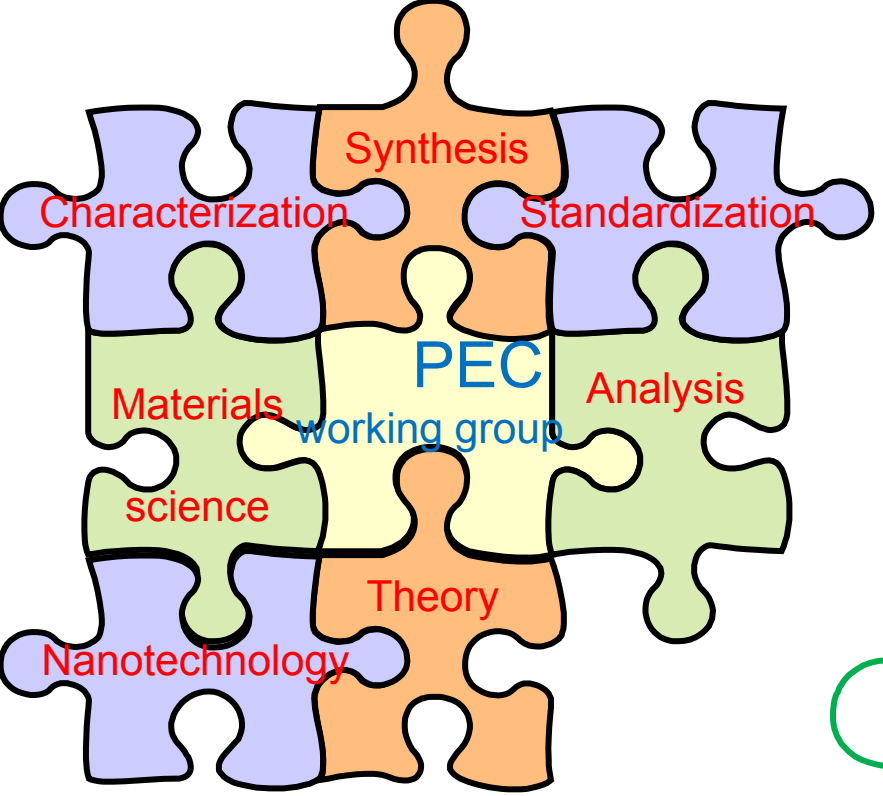
- *Total project funding*
  - *DOE share: $2,351,500*
  - *Contractor share: $760,492*
- *Funding received for FY10: $413,613*
- *Funding received for FY11: $200,000*
- *Funding projected for FY12: $87,887*
- *Funding reduced for FYs11 & 12 – Tasks 2 & 5 down-selected from scope – during Go-No-Go review*

Barriers

- *DOE MYPP Objective for Photoelectrochemical (PEC) hydrogen generation:*
  - *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 Production 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

- *Xunlight Corporation (Xunlight)*
  - *Dr. Anke Abken*
- *University of Toledo (UT)*
  - *Dr. William B. Ingler Jr.*
- *National Renewable Energy Lab(NREL)*
  - *Dr. John Turner*

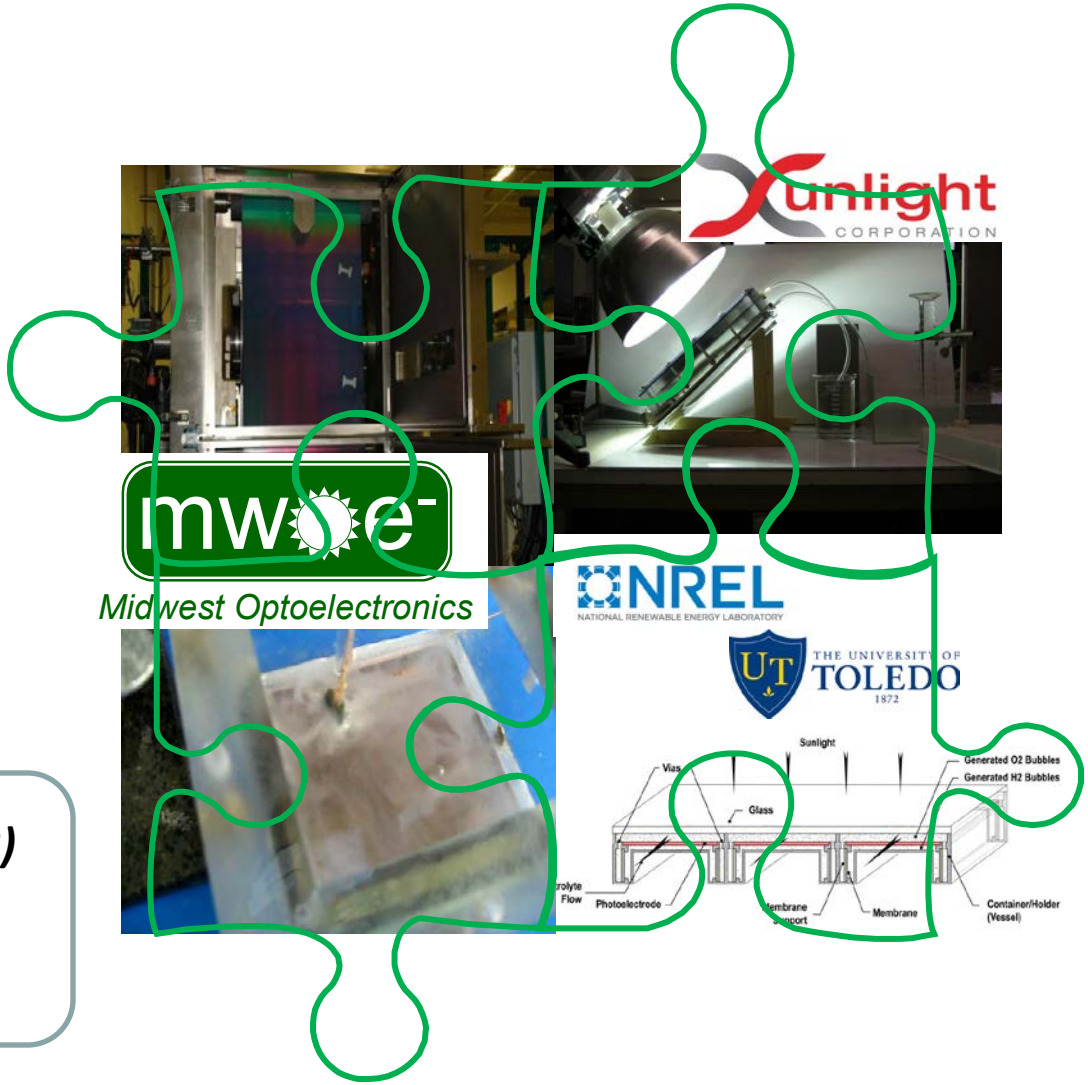


PEC Working Group:

Evaluating working directions
Sharing and building-up knowledge
Accelerating research progress

Integrated Systems for PEC Hydrogen Production

DOE Targets: >1000h @STH > 8% (2013)
$2 - 4/kg H_2 projected PEC cost
(beating >$10/kg H_2 for PV-electrolysis)



Research Tasks (Approach)

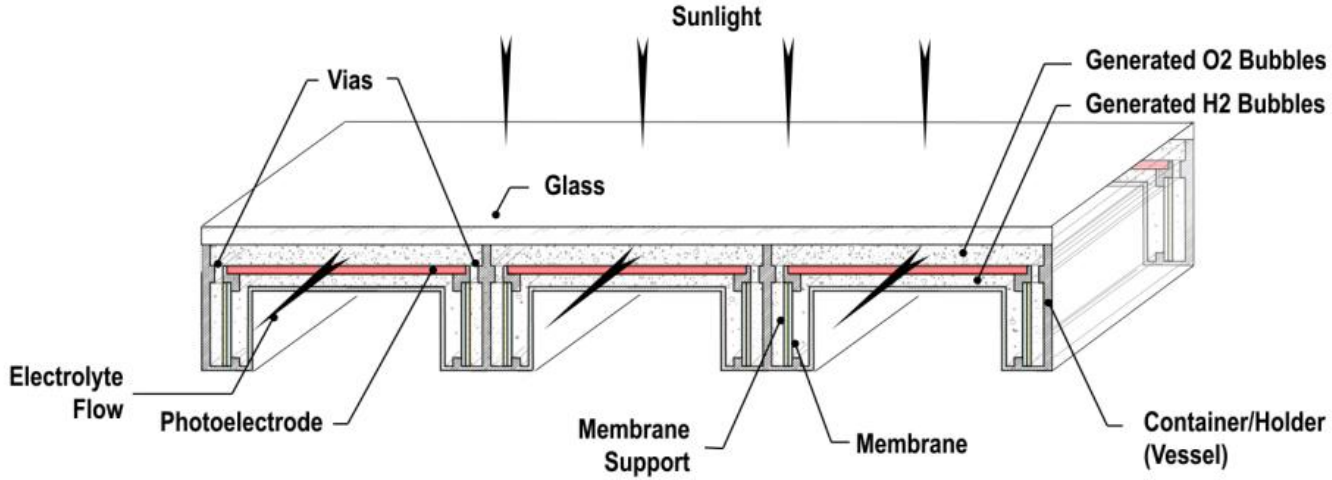
The goal of this project is to develop critical technologies required for cost-effective production of hydrogen from sunlight and water using triple junction thin film-Si based photo-electrodes.

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: 85%]
3	Understanding and characterization of photo-electrochemistry.	Different approaches have been explored, and successful in making production size PEC electrodes with TCCR layers. [Phase I: 100%; Total: 80%]
4	Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems.	Various PEC module designs have been built to optimize the STH conversion efficiency, extend the lifetime and reduce the cost . Optimum design parameters are being identified. [Phase I: 100%; Total: 80%]
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 (Approach)

- *Develop high quality TCCR materials with stability up to 1,000 hours. Completion date: Quarter 4, 2012. — The third round materials have been identified as Co_3O_4 and In_2O_3-Co_3O_4. Co_3O_4 materials have been successfully integrated into tf a-Si solar cells in a prototype production machine.*
- *Demonstrate an integrated immersion type PEC device using the developed high quality TCCR material. Completion date: Quarter 4, 2012. — Integrated PEC module cases have been designed, built and tested to resolve various issues that we have encountered. 4.0% 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, 2012. — we plan to engage in this task after good STH efficiency and lifetime are achieved.*

An immersion-type PEC



MWOE/Xunlight's Triple-Junction Photoelectrode Converted into "Artificial Leaf" at MIT—Published in SCIENCE Magazine

- *MWOE/Xunlight's triple-junction a-Si/a-SiGe/a-SiGe photoelectrodes used by MIT/Sun Catalytix Groups for "Artificial Leaf".*
- *Work published in Science (4 Nov 2011:645-648)*
- *Title: Wireless Solar Water-Splitting using Silicon-Based Semiconductors and Earth-Abundant Catalysts*
- *S. Y. Reece et al.*

Collaboration, Accomplishment and Progress

SCIENCE

Volume 334, Nov. 4, 2011

Title:
Wireless Solar Water-Splitting Using Silicon-Based semiconductors and Earth-Abundant Catalysts

By Dr. Nocera's group at MIT and Sun Catalytix

Volume 334, Page 645-648, Nov. 4, 2011

MWOE/Xunlight's Triple-Junction Photoelectrode Converted into "Artificial Leaf" at MIT—Featured in TIME Magazine

- *MWOE/Xunlight's triple-junction a-Si/a-SiGe/a-SiGe photoelectrodes used by MIT/Sun Catalytix Groups for "Artificial Leaf"*
- *Work recognized in TIME Magazine Best Invention Issue (Nov 28, 2011 Vol 178 No. 21)*
- *The Artificial Leaf -- a thin silicon solar cell with low cost catalytic materials bonded on both sides — can split water into hydrogen and oxygen when exposed to sunlight, with the gases usable later to power a fuel cell.*

Collaboration, Accomplishment and Progress

TIME

Volume 178, Nov. 28, 2011

The invention Issue

THE ARTIFICAL LEAF

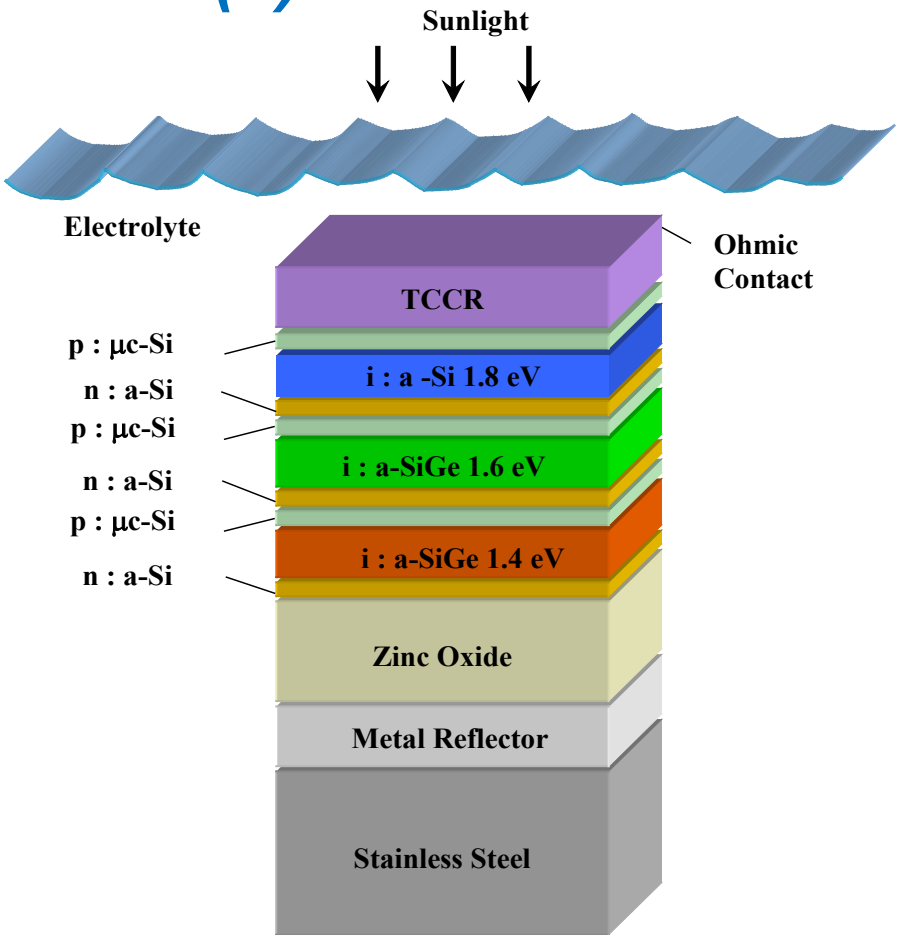
…The Artificial Leaf -- A thin silicon solar cell with cheap catalytic materials bonded on both sides can split water into hydrogen and oxygen when exposed to sunlight, with the gases useable later to power a fuel cell…

Volume 178, Page 58-59
Nov. 28, 2011

Key Material for "Artificial Leaf" – MWOE/Xunlight's Triple-junction photoelectrode (1)

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

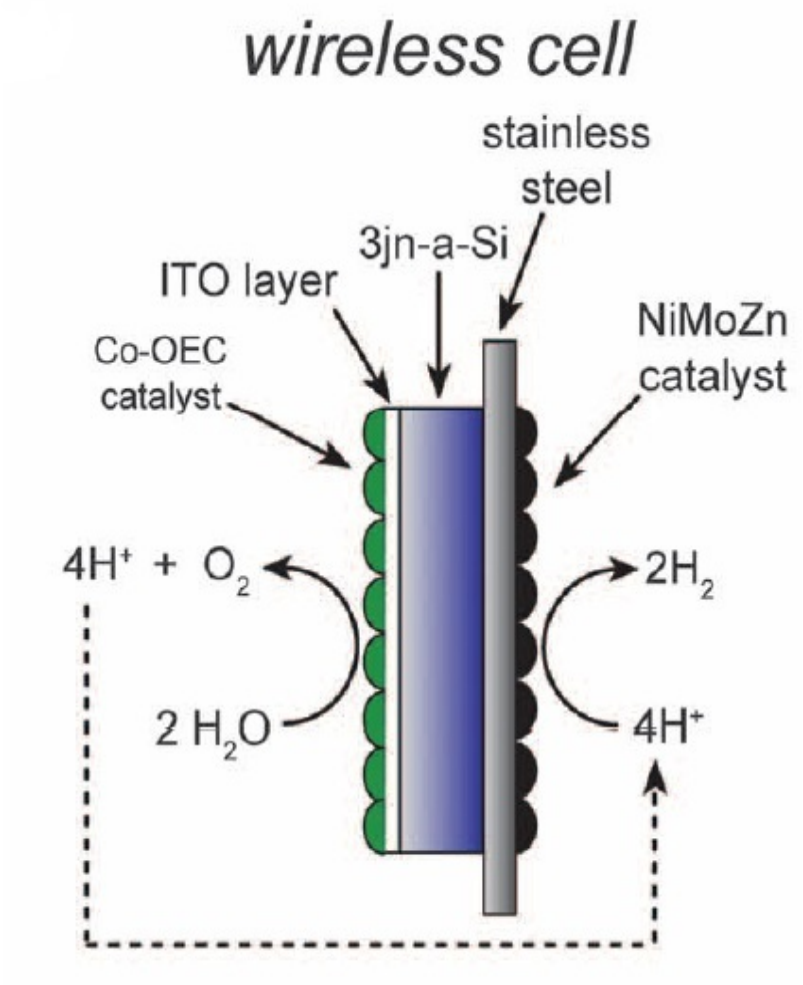
- *V_{oc} ~ 2.3V and operating voltage around 1.6V – ideal for water splitting.*
- *Deposited on a conducting stainless steel substrate which can serve as an electrode.*
- *Produced in large rolls of 3ft wide and up to 5000 ft long SS web in Xunlight's 25MW line – leading to extremely low cost.*



Key Material for "Artificial Leaf" – MWOE/Xunlight's Triple-junction photoelectrode (2)

Some key features of MIT/Sun Catalytix work:

- *Oxygen evolving catalysts with Cobalt (PSII) as the anode.*
- *Hydrogen evolving catalysts NiMoZn, as the cathode.*
- *Effective water splitting in near PH-neutral electrolyte.*



Performance Metrics for Immersion-Type PEC system using TCCR materials (Relevance)

DOE Barriers	Performance Measure	Units	DOE 2013 Targets	2010 Go/No-Go	MWOE current Status	References
Y. Materials Efficiency	Solar-to-Hydrogen efficiency	% Efficiency	8	N/A	4.0	slide 21A.
Z. Materials Durability	Durability	Hours	≥1000	≥700	1000 hr (Co_3O_4) 330 hr(PEC)	slide 13. Slide 21A.
	Cost	gge	$2-3	N/A	TBD	
	Deposition temperature	°C	≤250 (MWOE Target)	≤300	200	slide 17.
	Transparency of TCCR	% Trans-mission	≥90 (MWOE Target)	≥85	95	slide 13.
	Voltage drop across TCCR layer	V	≤0.15	≤0.35	0.086	slide 15.

DOE Barriers	Project Progress
AA. PEC Device and System Auxiliary Materials	Third round materials for TCCR coatings were identified.
AC. Device Configuration Designs	Co_3O_4 is being deposited on tf-a-Si solar cells in large scale prototype production machine and optimized conditions obtained.
AD. Systems Design and Evaluation	Multiple PEC module designs are being evaluated to identify possible problems and to optimize performance.

Technical Accomplishments and Progress

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

1. *Summary of different TCCR materials that we studied*
2. *Performance of Cobalt Oxide as TCCR material under operating conditions of a PEC cell assembly*
3. *Development of TCCR material on large scale roll-to-roll deposition system*

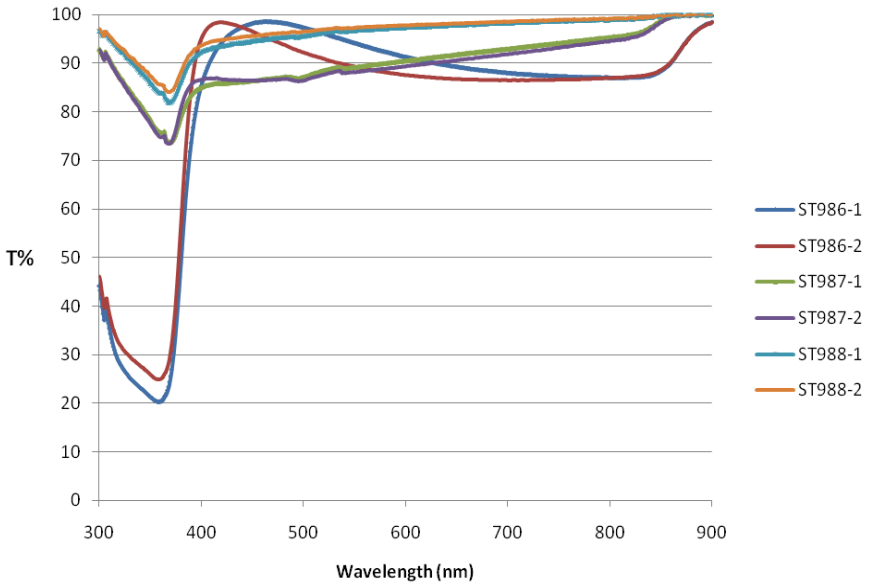
1. Different TCCR material we studied

- **Third Round Tested Materials:**
  - *Cobalt oxide – Excellent current density and stability; good transparency except the UV region; can be made at below 300°C. Very promising results.*
  - *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. Very promising results, but still needs further evaluation.*
- **Other Tested & Down-Selected Materials:**
  - *Fluorine-doped tin oxide – Little to no stability.*
  - *In_2O_3-Fe_2O_3 – Short-term stability, excellent conductivity, transmission needs improvement.*
  - *In_2O_3-$InFe_2O_4$ – Very stable under initial trials, excellent conductivity, transmission needs improvement.*

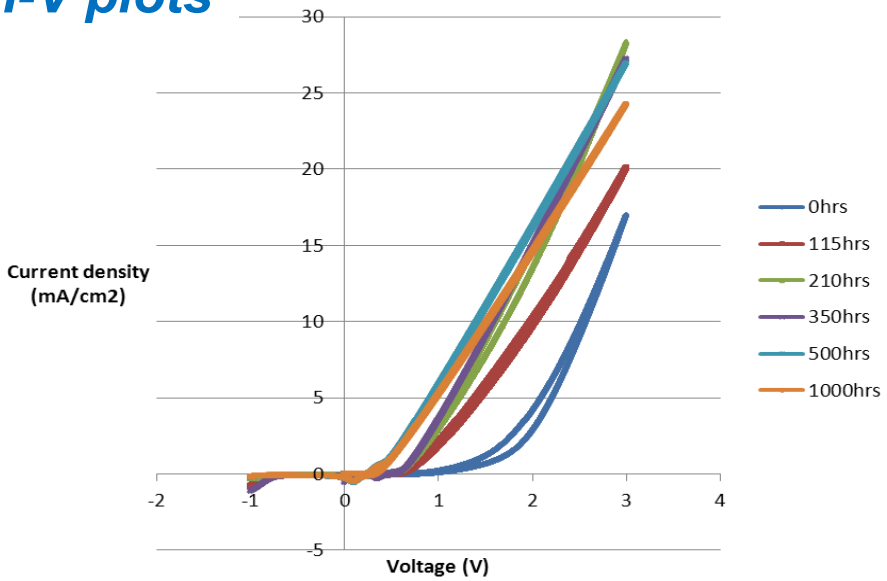
2A. Cobalt Oxide as a TCCR material

- *Co_3O_4 was deposited by sputtering onto TEC15 glass. Optimized Co_3O_4 layer show transmission in UV-visible up to 95%.*
- *The Co_3O_4 samples were biased in electrolyte at ~1.8V which reassembles the operating conditions of the PEC electrode.*
- *The following I-V measurement shows that the Co_3O_4 is stable and does not change its characteristics during biasing in electrolyte for up to ~1000hrs.*

Transmission of Co_3O_4 Optimized to 95%



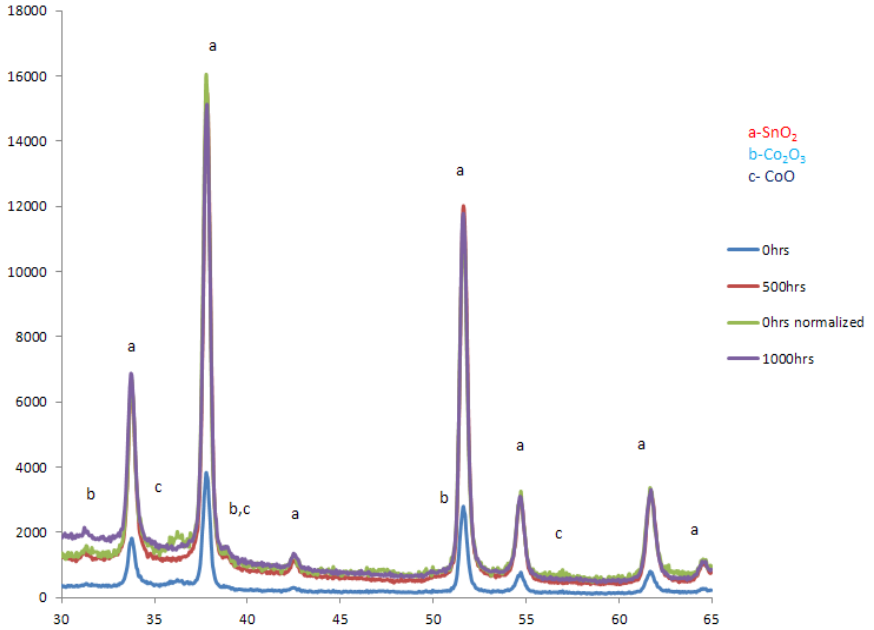
I-V plots



IV-plots show little to no change after biasing in electrolyte (115hrs-1000hrs); the drift between initial and 115hrs measurement is caused by oxidizing residual metallic Co in the film;

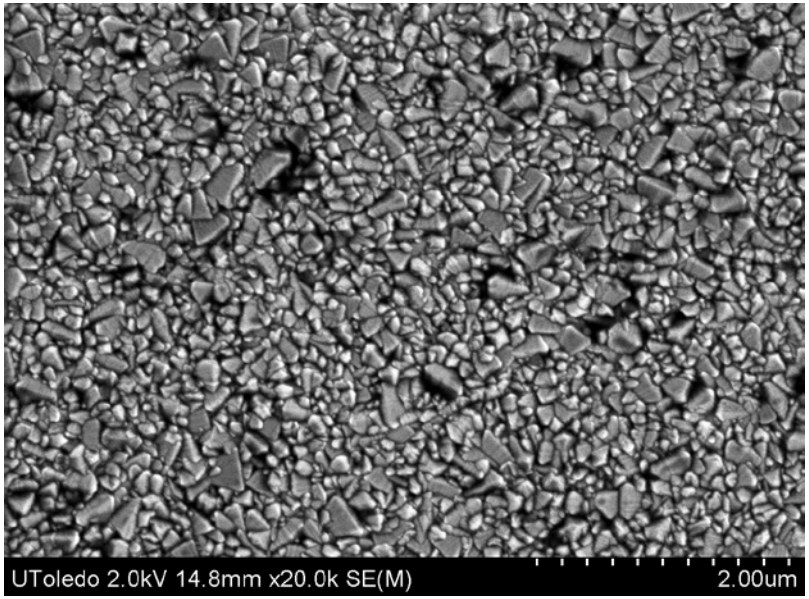
2B. Stability of Co_3O_4 as TCCR material

XRD



XRD spectra show the reflection peaks of CoO and Co_2O_3, the components of Co_3O_4 before and after biasing the sample in electrolyte; Both the XRD and SEM shows no degradation of Co_3O_4 occurred after 1000 hrs of biasing in electrolyte.

SEM



SEM after 1000 hrs of biasing.

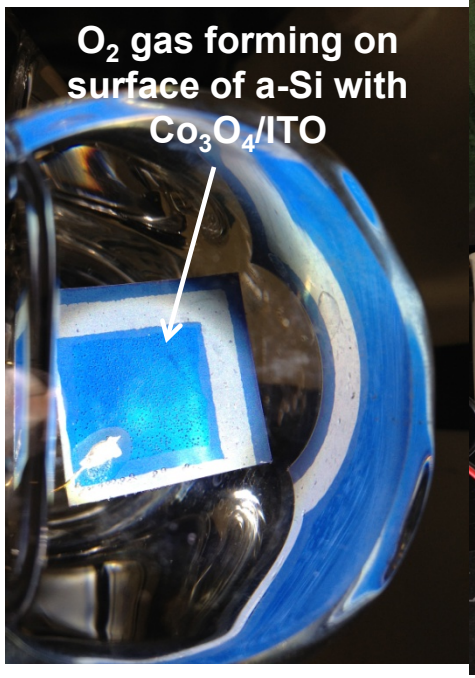
2D. Voltage drop across TCCR layer in the PEC electrode

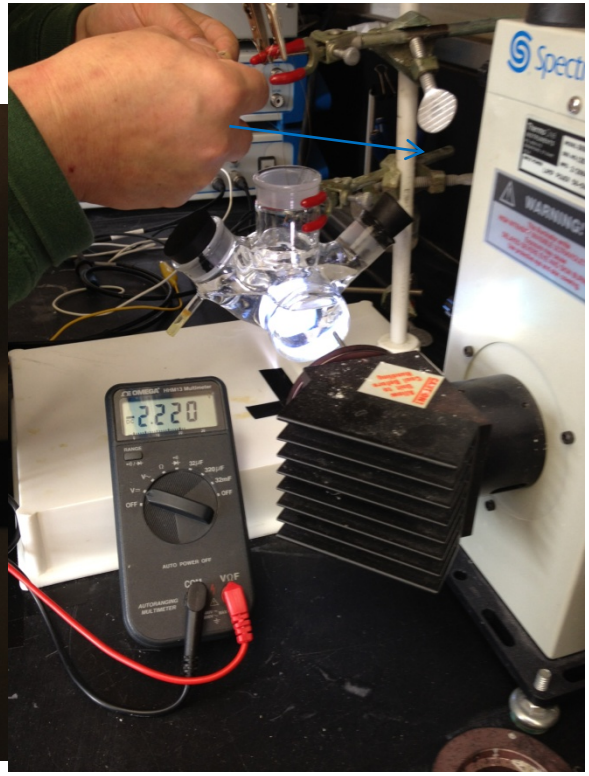
- *Co_3O_4 TCCR layers were sputtered onto a-Si solar cells; The voltage drop across the TCCR layer is determined by the difference between the open circuit voltages of an a-Si with ITO and an a-Si with Co_3O_4/ITO layer sample measured in electrolyte under 1 sun from 150 W Xenon lamp.*
- *The open circuit voltages are measured in electrolyte (pH 9 buffer soln.) using a 2-electrode set-up:*
  - *Working electrode: (1) a-Si with ITO, (2) a-Si with Co_3O_4 / ITO*
  - *Counter Electrode: (1) Stainless steel back of solar cell; (2) Platinum Gauze*

Using Stainless Steel	open circuit voltage
a-Si with ITO	2.156 V
a-Si with Co_3O_4/ITO	2.220 V
difference	No voltage drop within experimental error

Using Platinum Mesh	open circuit voltage
a-Si with ITO	0.822 V
a-Si with Co_3O_4/ITO	0.736 V
difference	0.086 V

- *The data indicate a voltage drop of ~ 0.086 V or less across the Co_3O_4 TCCR layer, which satisfies the Go/no-go target (2010) of 0.35V for TCCR/PV-layer stack;*





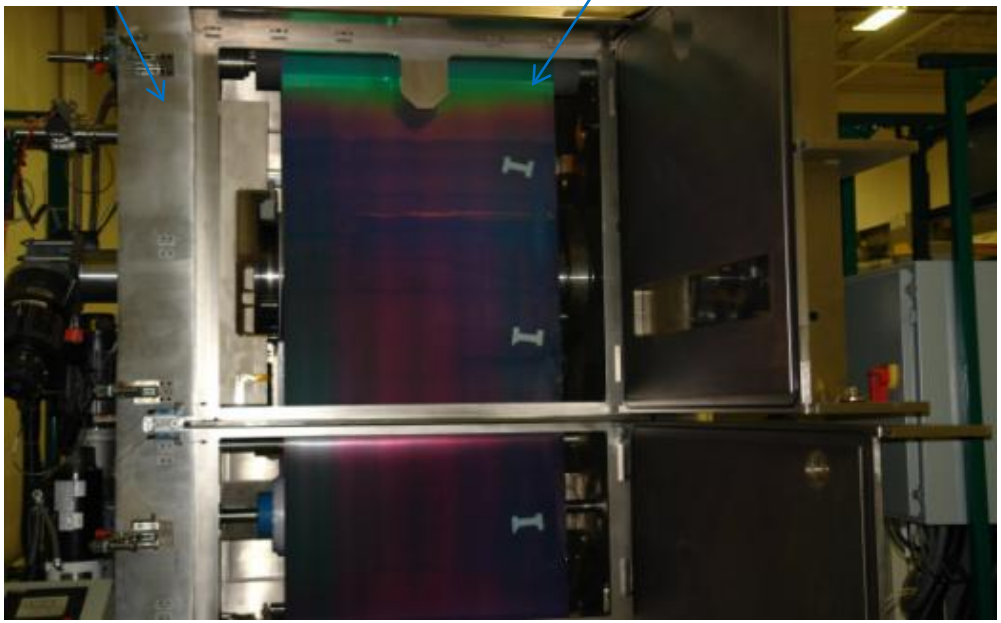
Volta-lab setup with 2 electrode set-up; *Electrochemical cell*

3A. Making Co_3O_4 on Large Scale System

- *The 2MW roll-to-roll machine at Xunlight allows the fabrication of triple junction a-Si solar cells, the ITO layers and the TCCR layers 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 also produce large area PEC electrodes (3ft wide and hundreds of feet long) that are more uniform, with less edge effect which exists on a small sputtering system.*
- *Solar cells with ITO were passivated first before the TCCR layer is sputtered.*

Pay-out chamber of 2MW line

3 ft wide SS web coated with Co_3O_4



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

3B. Making Co_3O_4 on Large Scale System

- *Process parameters such as sputtering temperature, line speed, oxygen flow rate, and sputtering power are fine-tuned for optimum TCCR performance. The deposition condition in Run 5 (Table 1) is one example of optimized conditions which gives a good transparency and uniformity of the Co_3O_4 layer (Fig. 1) with a thickness of about 30 nm (Fig. 2), at the same time provides good corrosion resistance and electrical conductivity.*

Co_3O_4 layer were sputtered using pulsed DC power at a line speed of ~ 6"/min; The sputtering power was varied between 0.8kW and 1.5kW

The O_2 flow was varied between 100-140 sccm;

The substrate temperature was kept at ~200°C.

Table 1, Some sputtering conditions for Co_3O_4

Run, experiment #	*sputtering power*	*Ar/Ar-O_2 flow*
Run 4, exp. 13	*1.5kW*	*40 sccm / 100 sccm*
Run 4, exp. 14	*1.5kW*	*20 sccm / 120 sccm*
Run 4, exp. 15	*1.5kW*	*10 sccm / 130 sccm*
Run 4, exp. 16	*1.5kW*	*0 sccm / 140 sccm*
Run 5, exp. 17	*0.8kW*	*40 sccm / 100 sccm*
Run 5, exp. 18	*0.8kW*	*20 sccm / 120 sccm*
Run 5, exp. 19	*0.8kW*	*10 sccm / 130 sccm*
Run 5, exp. 20	*0.8kW*	*0 sccm / 140 sccm*

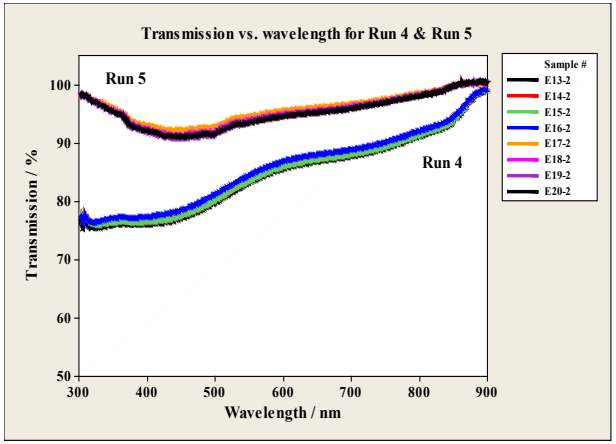


Fig. 1: Uv-vis measurements:

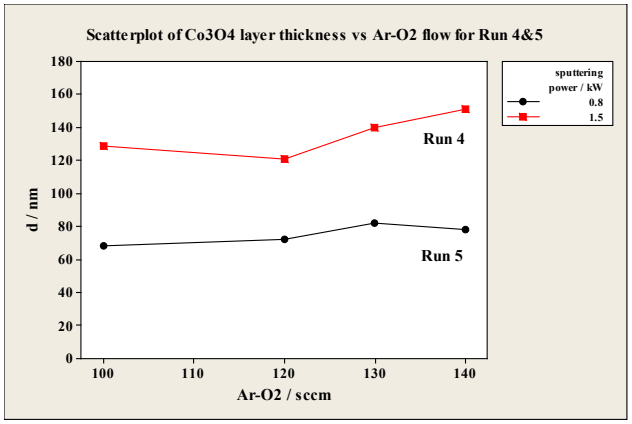


Fig. 2: Co_3O_4 thickness vs. Ar-O_2 flow:

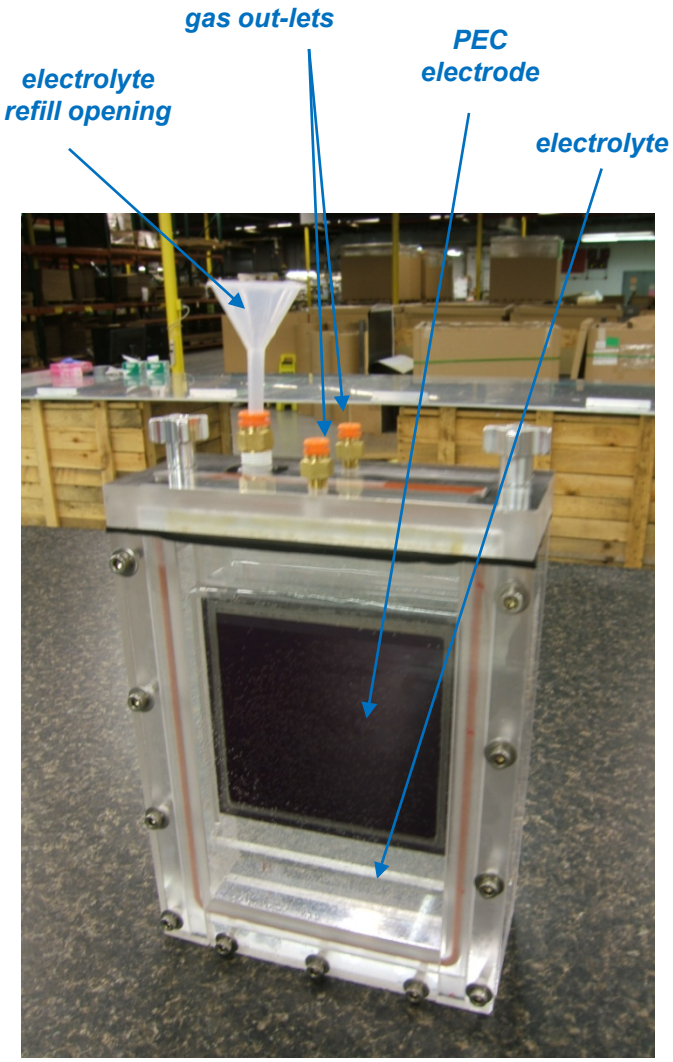
Technical Accomplishments & Progress

Part II: Development of low-cost, durable and efficient immersion-type PEC systems

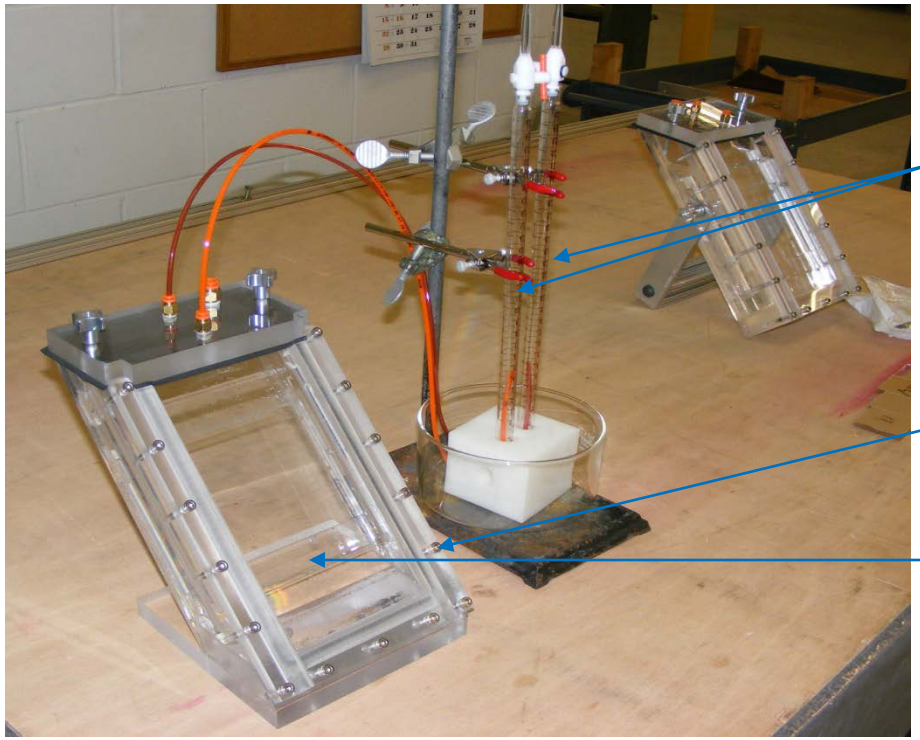
1. *Development of different PEC module case designs*
2. *Fabrication of PEC electrode with TCCR layer*
3. *Solar to hydrogen conversion efficiency for immersion type PEC system*
4. *Durability and lifetime of PEC system*

1. Development of PEC Module Case Designs

Prototype PEC modules:



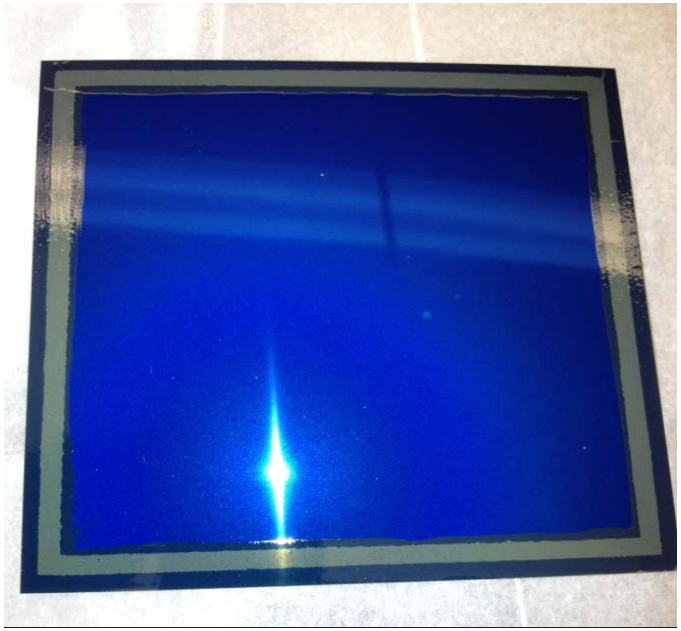
- *Designed and fabricated various PEC module cases.*
- *Tilted modules were designed for maximum light intake and reduced shadowing effect.*
- *An insert holds the PEC electrode which allows for easy replacement of different PEC electrode materials.*
- *Electrolyte movement is provided at the bottom with an 1" opening.*
- *Experimented with different electrolyte composition and PH conditions.*

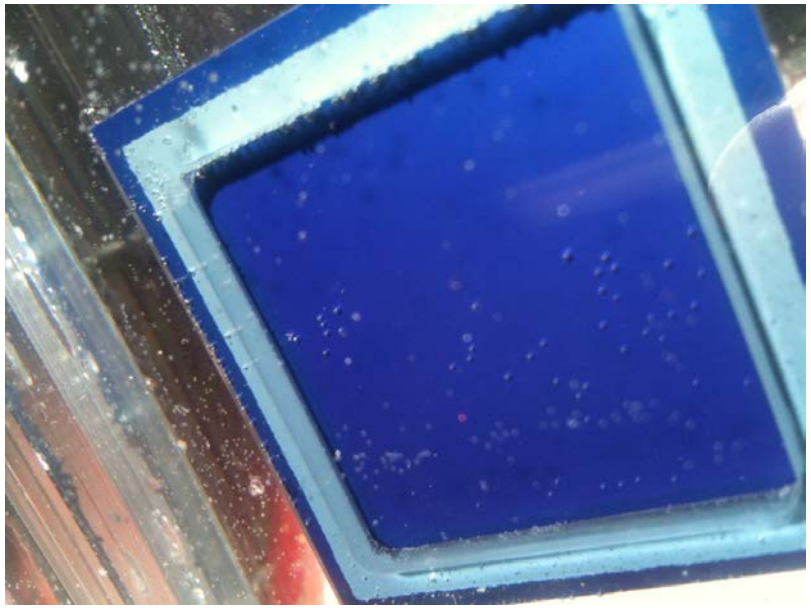


2. Fabrication of PEC electrode with TCCR layer

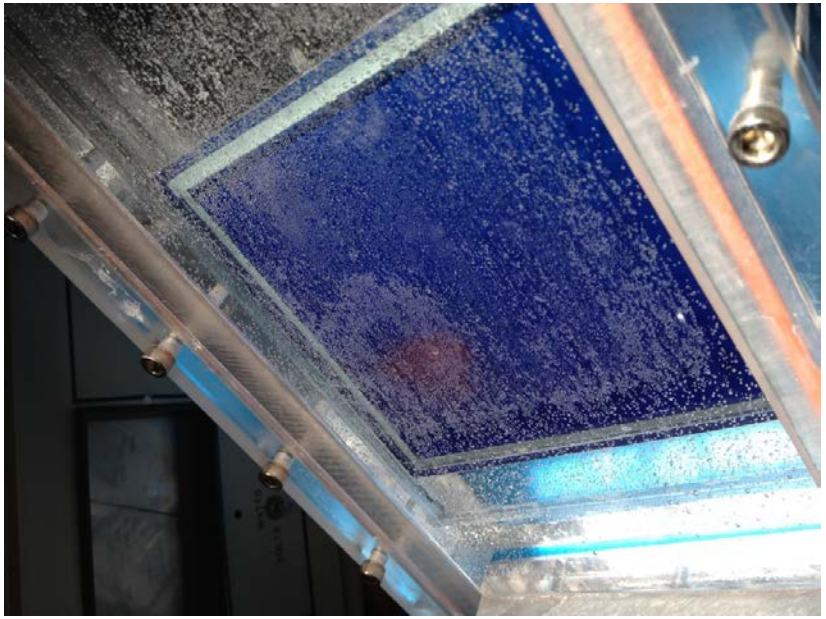
Experimented with various methods to prepare the PEC electrode. The following method seems to yield the best results so far:

1. *Start with triple junction a-Si solar cells with standard ITO coating.*
2. *Edge isolation with acid to isolate the positive and negative electrodes of the solar cell.*
3. *Shunt passivation to isolate any potential defect in the solar cell.*
4. *Sputtering of TCCR layer, currently Co_3O_4.*
5. *Apply a special clear coat to the edge of the cell or use a special gasket to protect the edge from the electrolyte .*
6. *Experiments indicated that the ITO layer is still needed for good PEC performance.*





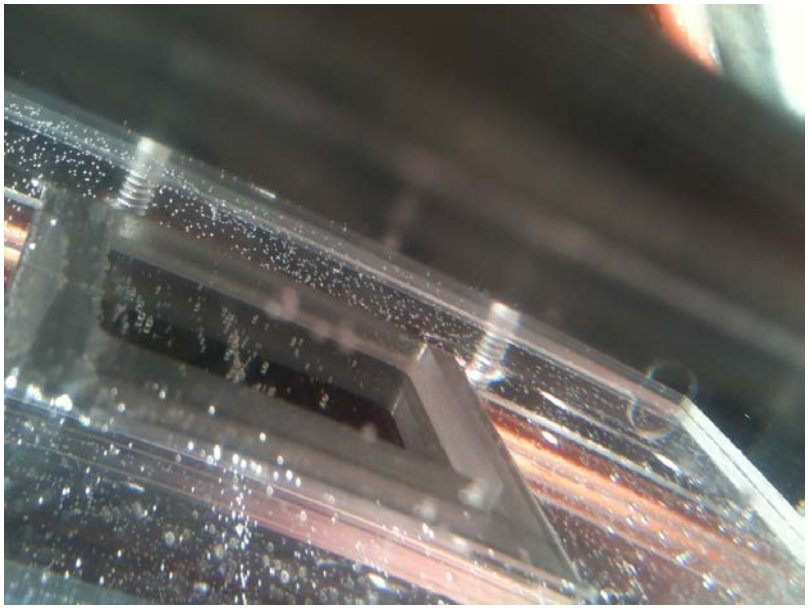
2. Solar to Hydrogen conversion efficiency for immersion type PEC system



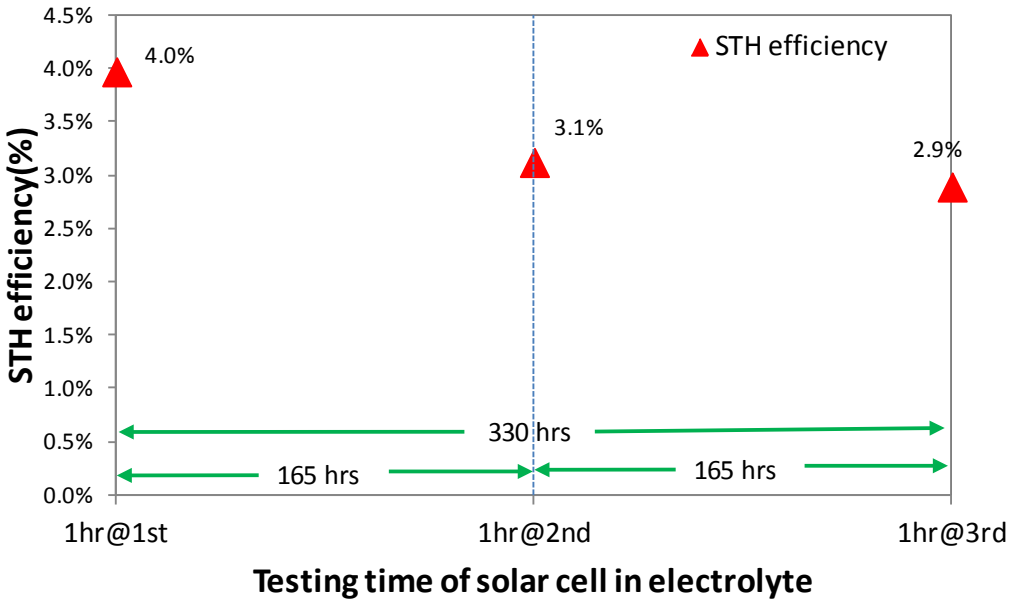
A PEC module with a 1.5"x1.5" electrode produced 4 ml of O_2 and 8 ml of H_2 in 90 min. P = 100 mW/cm^2.

This translates to an STH (solar to hydrogen) efficiency of 2.2 %. Further work is underway to improve the STH efficiency.

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

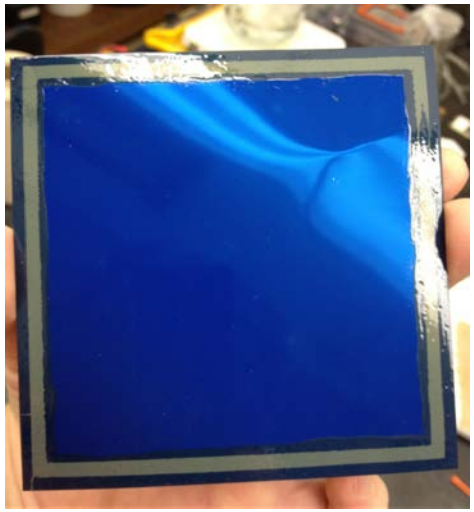


2a. Solar to Hydrogen conversion efficiency for immersion type PEC cell

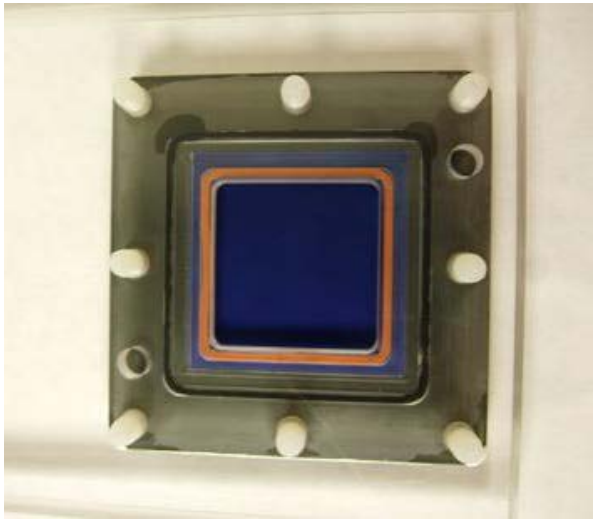


Solar to hydrogen conversion efficiency for PEC electrode with cobalt oxide TCCR coating at the oxygen generation side and platinum coating at the hydrogen generation side. Corrosion of clear coat at edge of the cell likely is the main reason of the STH decrease. The PEC electrode is still under testing…

3. Durability and lifetime of PEC system



Corrosion at the edge



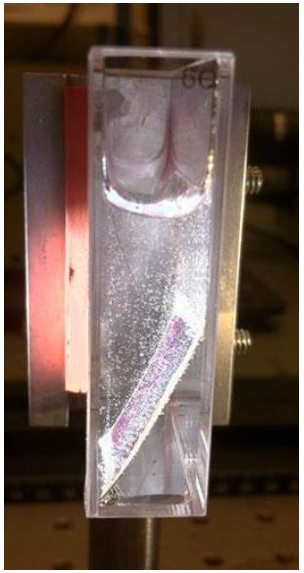
Electrode holder with gasket

- *The hydrogen generation rate seems to decrease with time.*
- *One very likely cause is shorting at the edge when the clear-coat is corroded away by electrolyte. Re-apply the clear coat seems to revive the electrode.*
- *To solve this problem, a few special electrode holders with double gasket are under development.*
- *Smaller electrodes seems have better STH performance and better durability than larger electrodes, experiments are underway to understand causes.*
- *Another possible cause for the decrease of the hydrogen generation rate is possible degradation of the TCCR layer, thus the solar cell material, we plan to study the electrode surface change at different time stages.*

Collaborations (1)

- *Worked with Dr. Nocera's group at MIT and Sun Catalytix on solar water splitting project, by providing triple junction a-Si solar cells. Dr. Nocera's research results were published in Science Magazine and was selected as one of Top 50 Innovations of Year 2011 by Time Magazine ("Artificial Leaf").*
- *Received many requests for collaboration on PEC hydrogen generation research projects from multiple research groups around the World, including 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.*

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



Collaborations (2)

Partners:

- *Xunlight Corporation (Industry):*
  - *Xunlight helps with depositing Co_3O_4 in the large area roll-to-roll machine for PEC electrodes and fabricating module cases. (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 improved 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 had reached a license agreement for technology transfer for the photovoltaic and PEC technology.*
  - *UT had another DOE grant for PEC hydrogen generation basic material research, which complemented this PEC grant project.*

Proposed Current and Future work

1. Large area Immersion-type PEC System

- *Continue to investigate the cause for the low STH conversion efficiency, understand the different factors which could affect the efficiency such as uniformity, optimum operating voltage and current of the solar cell, the effect of the TCCR characteristics on the PEC performance, and the hydrogen generation catalyst, etc.*
- *Experiment with different fabrication methods for PEC electrode preparation with respect to solar cell and ITO deposition, electrode preparation 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 more TCCR materials in additional to Co_3O_4.*
- *While working on improving the STH efficiency, also focus on improving the lifetime of the system, explore different types of electrolyte, different treatment of the electrodes and different module designs.*
- *Develop 1'x1' commercial size PEC system and carry out test in real life conditions.*
- *Collaborate with different research groups around the world to further PEC hydrogen generation research and development.*

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

Project Summary

- **Relevance:** *Addresses DOE MYPP program objectives, specifically high-efficiency and low-cost production of hydrogen using photoelectrochemical methods.*
- **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, and have been approved to proceed into Phase II continuing with the development of the immersion type PEC system.

  Have carried out extensive research with many different material classes for application as TCCR materials. 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 reasonable STH efficiency and lifetime results.
- **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:**

  Develop variousTCCR materials and 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, 1ft x 1ft 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.