Midwest Optoelectronics

Project ID # PD056

DOE Hydrogen Program

Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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05/10/2011 6:30 to 8:30 PM

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THE UNIVERSITY OF TOLEDO 1872

Xunlight CORPORATION

Overview

Timeline

- *Project start date: 4/1/2005*
- *Project end date: 12/31/2012*
- *Percent complete: 66%*

Budget

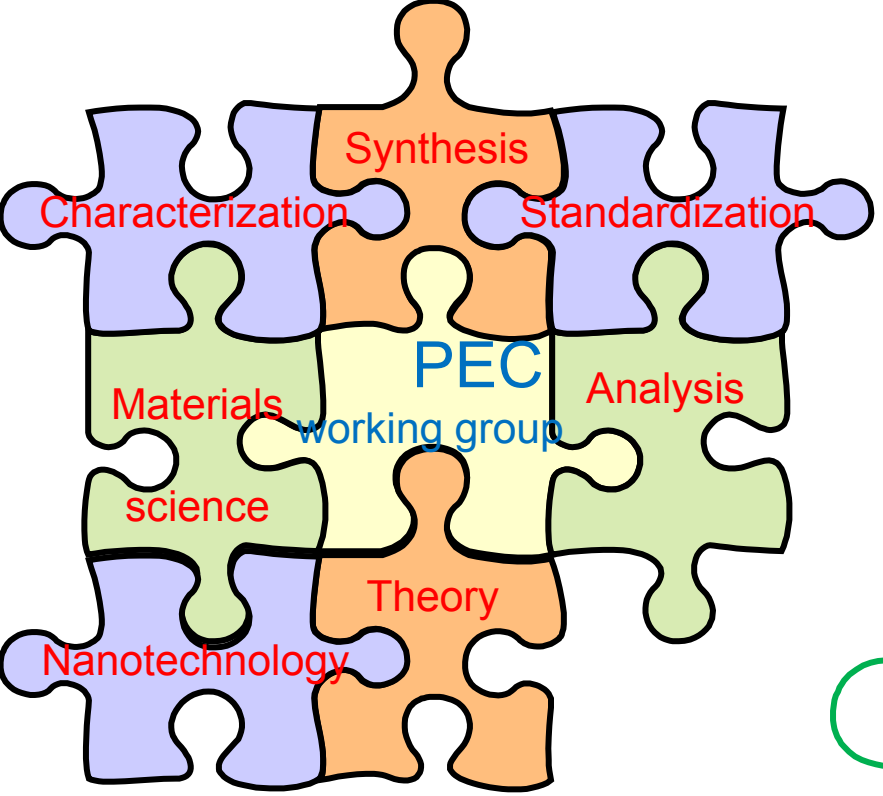
- *Total project funding*
  - *DOE share: $2,351,500*
  - *Contractor share: $760,492*
- *Funding received in FY07: $400,000, $200,000 for NREL*
- *Funding received in FY08: $500,000*
- *Funding received for FY09: $0*
- *Funding received for FY10: $413,613*
- *Funding expected for FY11: $200,000*

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 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

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

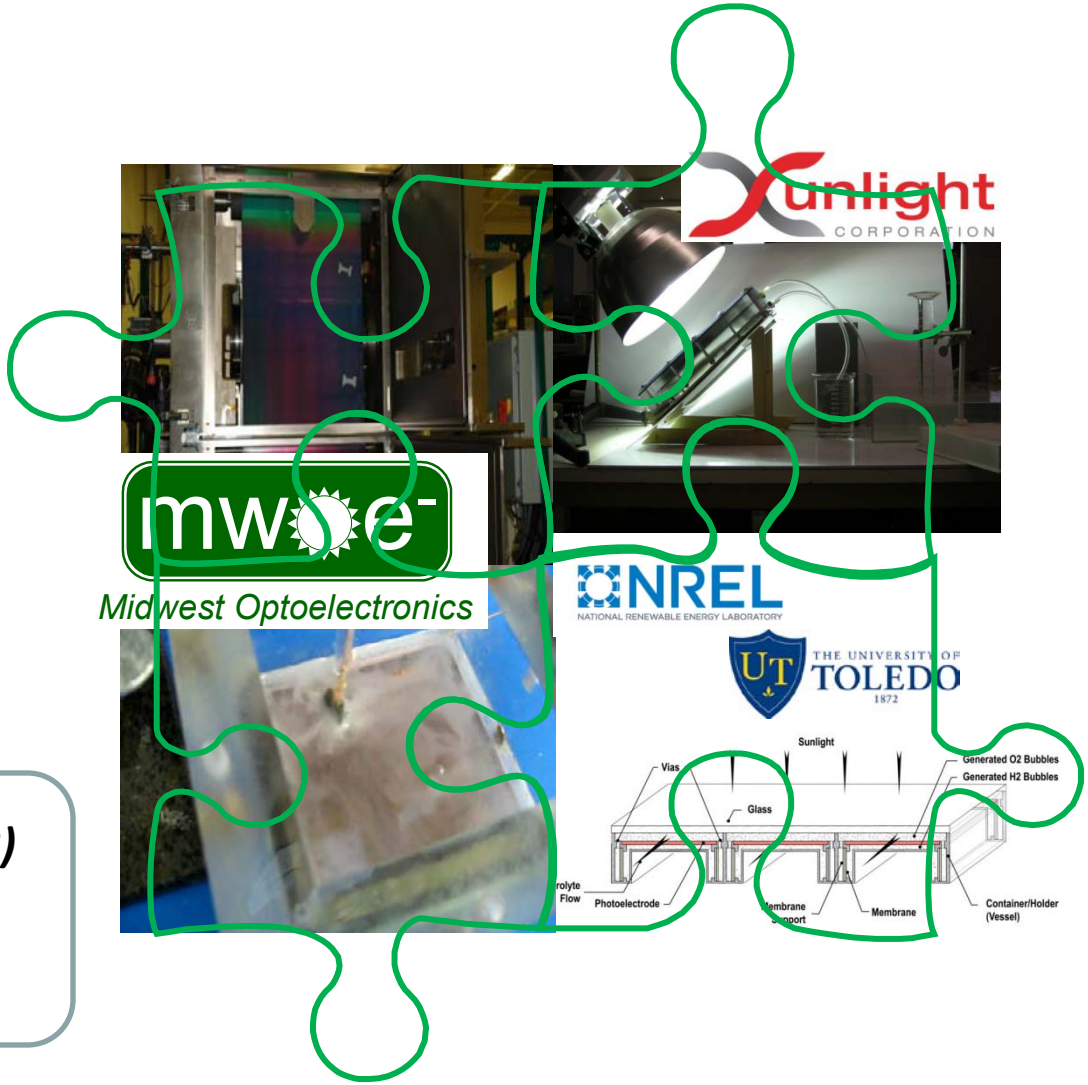


PEC Working Group:

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)

Task 1: *Transparent, conducting and corrosion resistant (TCCR) coating for triple-junction tf-Si based photo-electrode; [Year 1: 100%; Year 2: 100%; Total: 66%]*

Task 3: *Understanding and characterization of photo-electrochemistry; [Year 1: 100%; Year 2: 100%; Total: 66%]*

Task 4: *Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems; [Year 1: 100%; Year 2: 100%; Total: 66%]*

Task 2: *Hybrid multi-junction PEC electrode having semiconductor-electrolyte junction; - Down-Selected (Dec 2010) [Year 1: 100%; Year 2: 100%; Total: 66%]*

Task 5: *Development of device designs for large-area, substrate-type PEC panels; - Down-Selected (Dec 2010) [Year 1: 100%; Year 2: 100%; Total: 66%]*

Project Objectives (Approach)

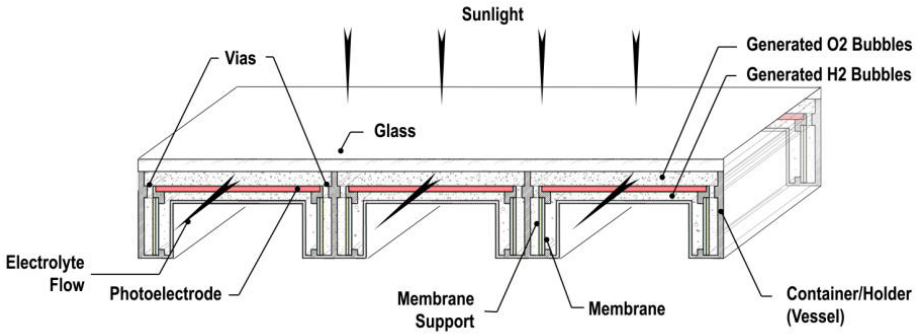
- *To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film-Si based photo-electrodes.*
- *Two approaches are taken for the development of efficient and durable photo-electrochemical cells.*
  - *An immersion-type photoelectrochemical cell in which the photo-electrode is immersed in electrolyte.*
  - *A substrate-type photoelectrochemical cell in which the photo-electrode is not in direct contact with electrolyte.*

- *During the recent Go/No-Go review in Dec 2010, it was decided that the immersion-type PEC work will proceed into the second phase and the substrate-type PEC work (Task 5) would come to an end.*
- *It was also determined the TCCR work will proceed and the PAS work (Task 2) will be halted.*

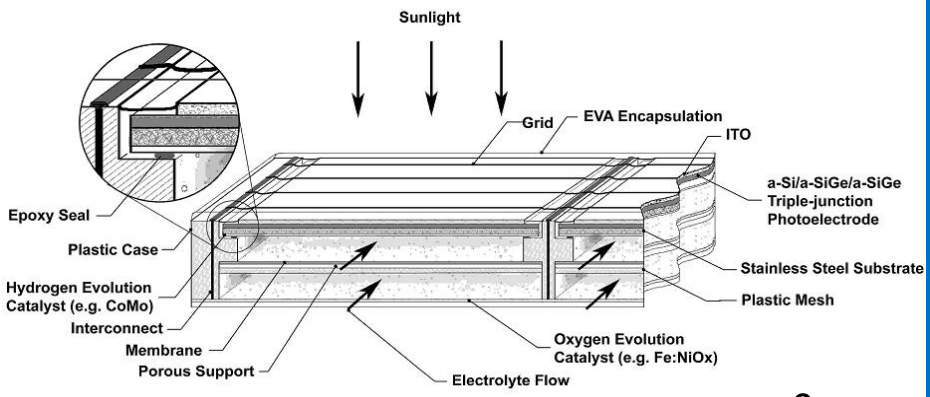
Milestones (Approach)

- *Go/No-Go Decision Point (this decision point will coincide with the end of Budget Period 1): Go/no go decision will be based, in part, on progress toward developing TCCR and/or PAS materials capable of meeting the following performance criteria: ≥700 hours of stability, capable of being fabricated at ≤300°C, 85% or greater transparency, and a voltage drop ≤0.35V across the TCCR layer for the TCCR/PV-cell layer stack under typical PEC device operating conditions (TCCR material); or ≥700 hours of stability, capable of being fabricated at ≤300°C, and ≥5 mA/cm^2 photocurrent (PAS material). Completion date: Quarter 4, 2010*
- *Develop high quality TCCR materials with stability up to 1,000 hours. Third round of TCCR materials to be produced at 250°C or lower with 90% or greater transparency and a voltage drop ≤0.15V across the TCCR layer for the TCCR/PV-cell layer stack under typical PEC device operating conditions. Completion date: Quarter 1, 2012*
- *Demonstrate an integrated immersion type PEC device using the developed high quality TCCR material and complete a preliminary techno-economic analysis of the immersion-type PEC system. Completion date: Quarter 4, 2012.*

An immersion-type PEC cell



A substrate-type PEC cell



Technical Accomplishments --- Part 1:
Development of Substrate-type PEC System

1.1 Electroplating of porous nickel electrodes for hydrogen generation

1.2 Design of substrate-type PEC system

1.3 Summary of the performance metrics of the substrate-type PEC system comparing to the DOE multi-year goals

1.1A Nickel Electroplating Procedure

- *Material combinations for use as catalytic electrodes with micro- and macro-porous structures were developed.*
- *Efforts were made to develop sintered Nickel catalyst for hydrogen generation.*

Porous Nickel electrodes were fabricated using the following procedure:

- *Preparation of Ni electrolyte*
- *Etching of the stainless steel substrate*
- *Electrodeposition of Ni onto the substrate*
- *Leaching of the precursor from the Ni deposit in KOH in order to obtain porosity*
- *Testing the porous Nickel electrodes*

Nickel electrolyte

$NiSO_4 \cdot 6H_2O$ (Nickel Sulfate Hexahydrate)	330g/l
$NiCl_2 \cdot 6H_2O$ (Nickel Chloride Hexahydrate)	45g/l
H_3BO_3 (Boric Acid)	37g/l

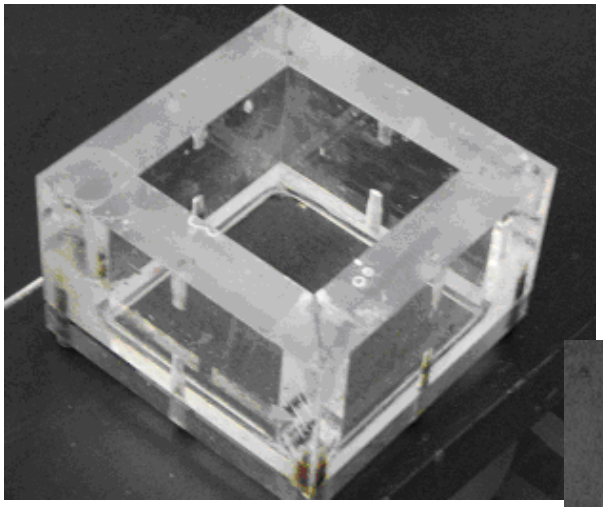
Precursor salts

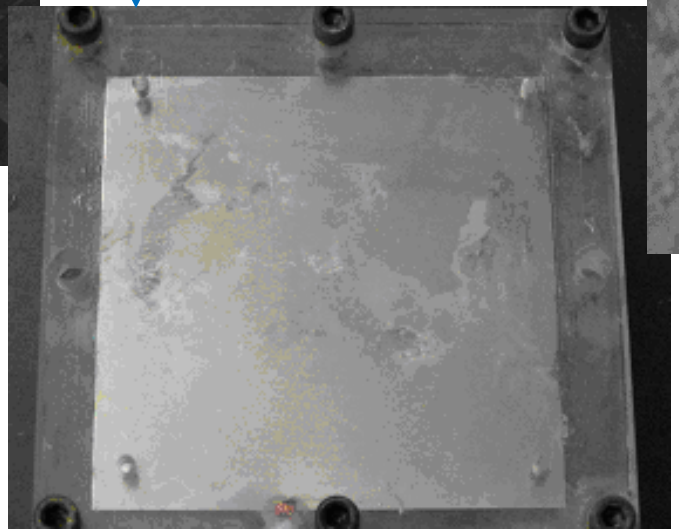
Zinc Chloride (5% $ZnCl_2$)
Copper Sulfate (5% $CuSO_4$)
Zinc Nitrate (5% $Zn(NO_3)_2$)
Ammonium Sulfate (10% $(NH_4)_2SO_4$)
Manganese Chloride (10% $MnCl_2$)

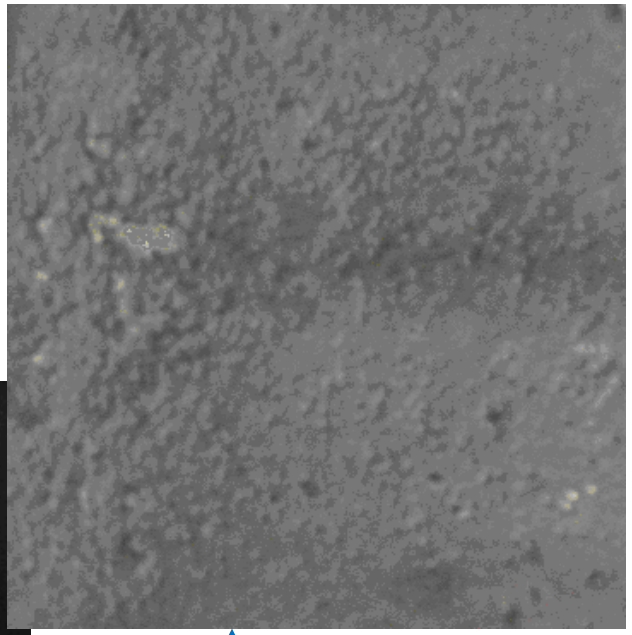
5 precursor salts were tested for their usefulness in obtaining the required micro-porosity for the catalytic Ni electrode; a precursor salt is added to the Ni-electrolyte and the material is embedded into the Ni-deposit during electrolysis; leaching of the electrode after Ni-deposition removes the precursor and leaves a porous electrode structure behind;

1.1B Electroplated Nickel

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

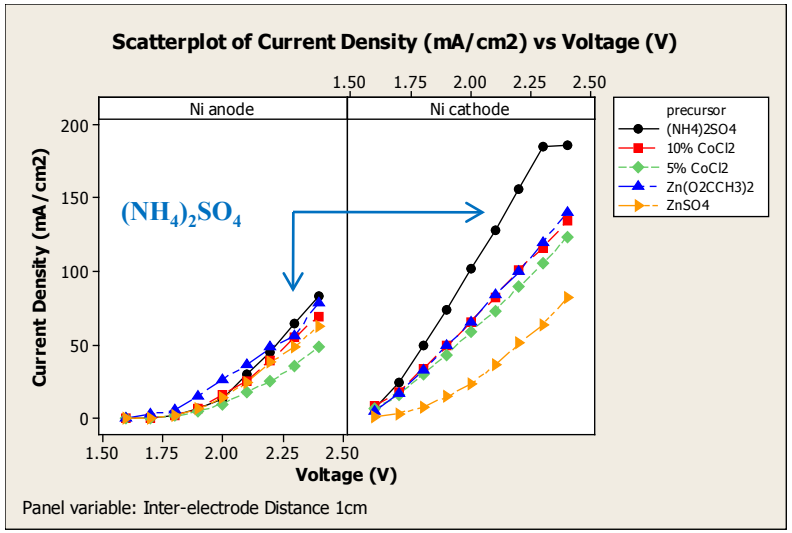


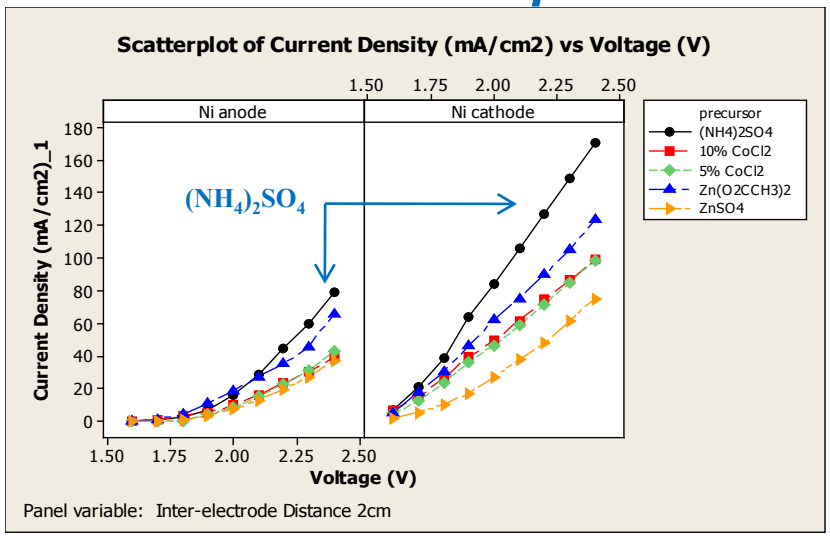




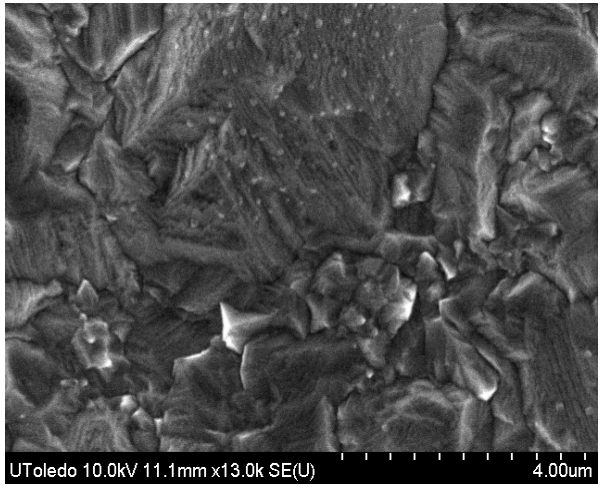
1.1C Study of Various Precursors for Electroplating Porous Nickel

J-V curves for Ni-electrode as anode or cathode for various precursors:





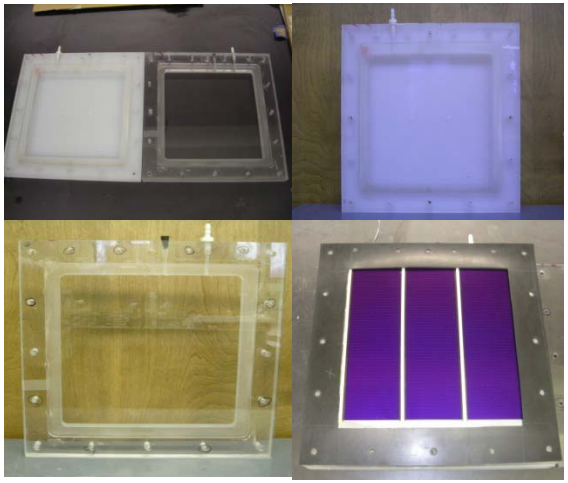
Ni deposit made with $(NH_4)_2SO_4$ precursor:



- *10% $(NH_4)_2SO_4$ used as precursor demonstrated the best results;*
- *Goal of the precursor is to improve porosity of nickel;*
- *Need to pre-treat SS with acid to improve adhesion of nickel deposit;*

1.2 Design of the substrate-type photoelectrochemical cell

- *The unit shown in the right was assembled and tested for leaks. The unit holds the solar cell, membrane, and the electrocatalysts.*
- *Microporous nickel was electroplated on the back side of a triple junction a-Si solar cell, which acts as the anode for the PEC.*
- *Another electroplated nickel on a stainless steel substrate acts as the cathode.*
- *Properties of the electrocatalysts were discussed on the previous slides.*
- *Triple junction solar cells were made at Xunlight Corp. which were shunt passivated and gridded with copper wires.*
- *The triple junction a-Si solar cells produced an open circuit voltage of 2.06 V.*
- *33% KOH is used as the electrolyte for the substrate-type PEC.*



1.3 Performance Metrics for Substrate-Type PEC Systems (Relevance)

Performance Measure	Units	DOE 2012 Targets	MWOE 2010 Status	References
Solar-to-Hydrogen efficiency	% Efficiency	8	5 (4" × 12" module)	Ingler Jr., W. B., Xu, L. "Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen", 2006 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation, Crystal Gateway Marriott, Arlington, VA., May 15, **2006**. (Poster)
Durability	Hours	1000	TBD	
Cost	gge	2-3	TBD	

Technical Accomplishment --- Part 2:
TCCR Material and Immersion-type PEC

2.1 Summary of different TCCR material we studied

2.2 Performance of Cobalt Oxide material

2.3 Development of TCCR material on large scale roll-to-roll deposition system

2.4 TCCR material using Sun Catalytix approach

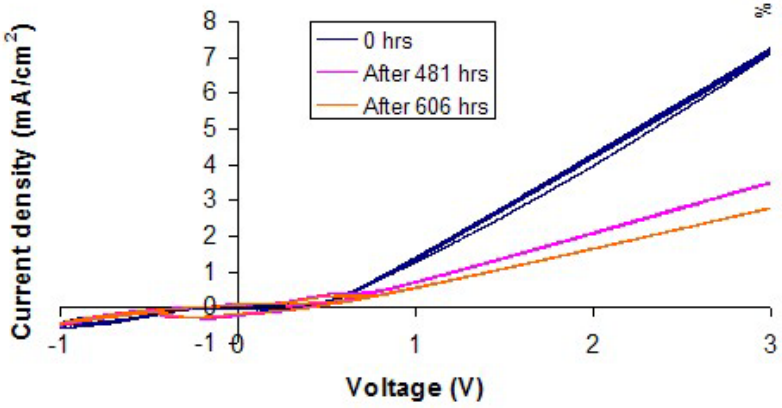
2.5 Performance Metrics for Immersion-Type PEC system using TCCR material

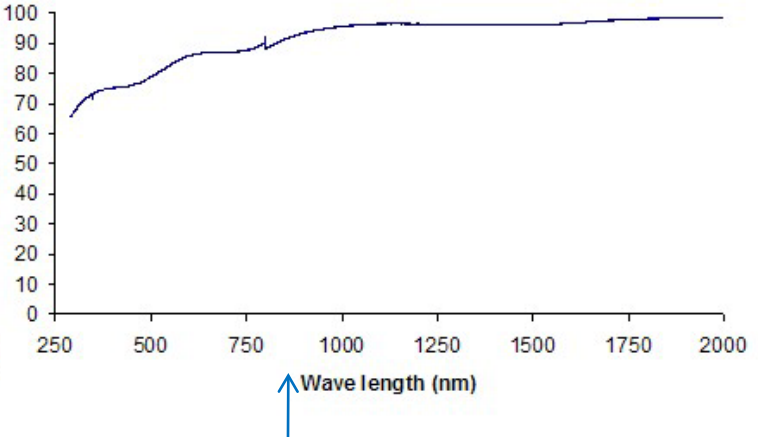
2.1 Present Status of TCCR Material Class Study

- ***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.*
  - *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-$InFe_2O_4$ – Extremely stabile under initial trials, excellent conductivity, transmission needs improvement (or band gap lowered);*

2.2A Cobalt Oxide as a Material Class

JV plots at various times

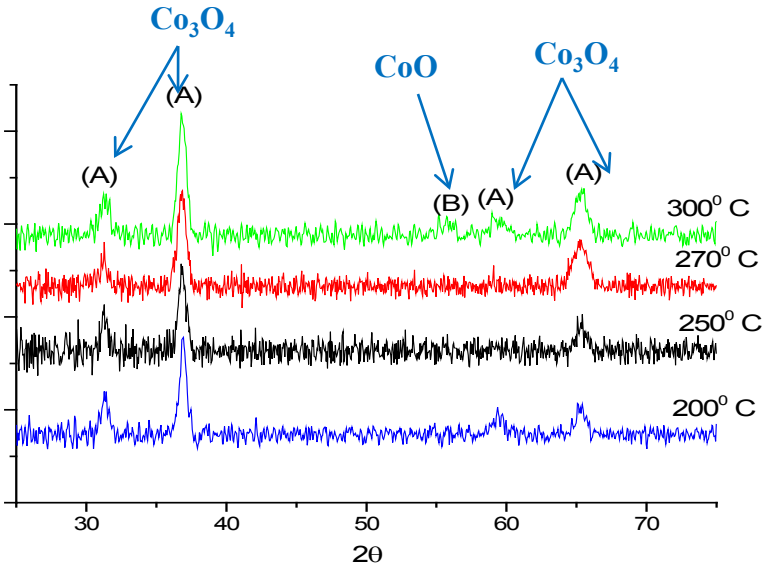




Transmission of Co_3O_4

XRD ⟶

XRD spectra of cobalt oxide thin films deposited at different substrate temperatures. The spectra reveals the films consist mainly of Co_3O_4 (A) with a smaller amount of CoO (B).



2.2B Cobalt Oxide as a Material Class

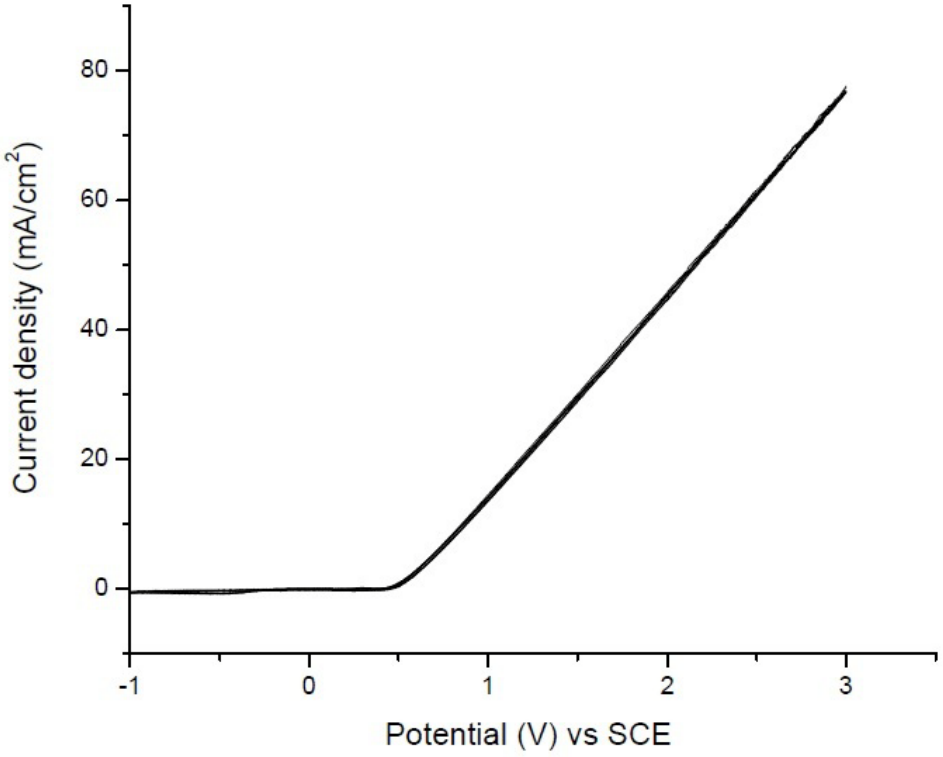


Figure 1. Current density (mA/cm^2) versus applied potential (V) vs SCE for a cobalt oxide thin film electrode (Co 100 W, 270 °C) deposited on TEC 15 glass.

2.2C Cobalt Oxide as a Material Class

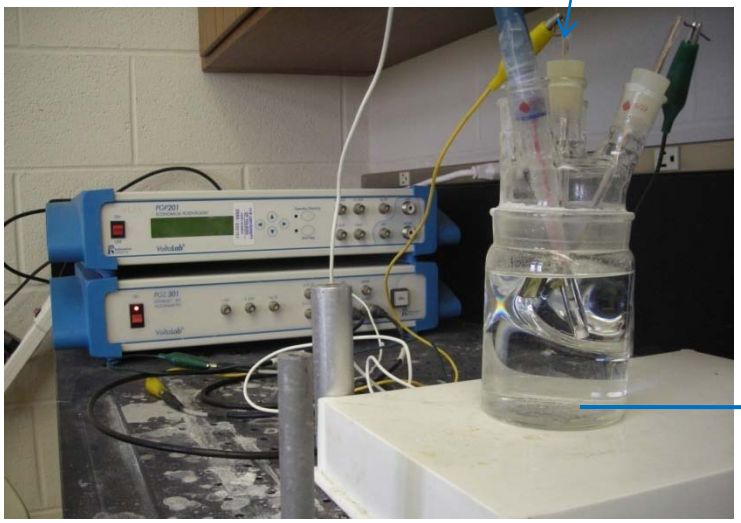
Voltage drop across TCCR layer

- *Co_3O_4 TCCR layers were sputtered onto TEC 15 glass; The voltage drop across the TCCR layer is determined by the difference between the open circuit voltages of a TEC 15 glass sample and a TEC 15 glass/Co_3O_4 layer sample measured in electrolyte.*

- *The open circuit voltages are measured in electrolyte (KOH) using a 3-electrode set-up (Volta-lab):*
  - *Working electrode: TEC 15 glass, Co_3O_4 / TEC 15 glass sample;*
  - *Counter Electrode: Platinum Gauze;*
  - *Reference Electrode: Calomel Electrode (SCE);*

	open circuit voltage
Tec 15 glass	*0.400 V vs SCE*
Co_3O_4/Tec 15 glass	*0.382 V vs SCE*
difference	*0.018 V*

- *The data indicate a voltage drop of ~0.02 V across the Co_3O_4 TCCR layer (on Tec 15), which satisfies the Go/no-go target (2010) of 0.35V for TCCR/PV-layer stack;*



Volta-lab setup with 3 electrode set-up;

Electrochemical cell

2.2D Cobalt Oxide as a Material Class

Voltage drop across TCCR for TCCR/PV-layer stack

- *Co_3O_4 TCCR layers were rf-sputtered onto the ITO top layer of single junction a-Si solar cells; The voltage drop across the TCCR layer is determined by the difference of the open circuit voltage of the ITO/PV-layer stack sample (a-Si solar cell) and the open circuit voltage of same sample covered with Co_3O_4 TCCR layer (Co_3O_4/ITO/PV-layer stack sample);*
- *The V_{OC} measurements (15 samples) were performed using a solar simulator;*

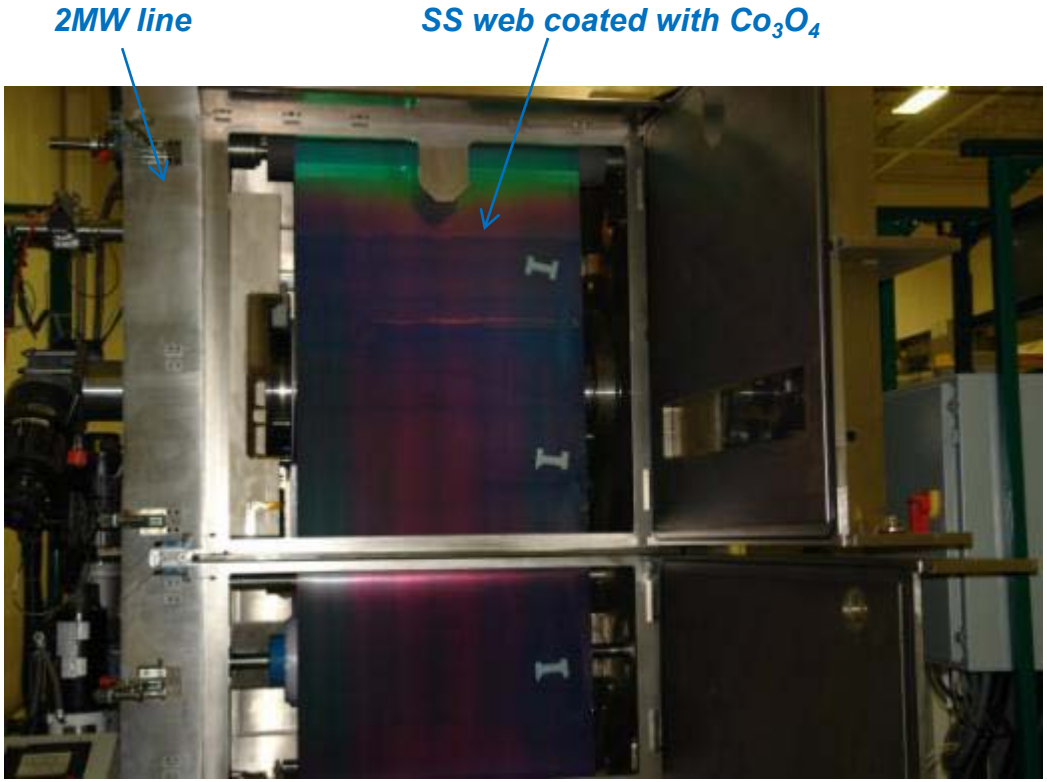
	ITO/a-Si	Co_3O_4/ITO/a-Si	Voltage Drop
Cell ID	VOC (V)	VOC (V)	delta VOC (V)
gd3009-2.12	0.541	0.488	0.053
gd3009-2.13	0.54	0.486	0.054
gd3009-2.14	0.541	0.484	0.057
gd3009-2.15	0.542	0.478	0.064
gd3009-2.21	0.561	0.506	0.055
gd3009-2.22	0.555	0.504	0.051
gd3009-2.23	0.555	0.501	0.054
gd3009-2.31	0.299	0.207	0.092
gd3009-2.32	0.578	0.52	0.058
gd3009-2.33	0.574	0.515	0.059
gd3009-2.41	0.226	0.132	0.094
gd3009-2.45	0.572	0.521	0.051
gd3009-2.51	0.428	0.344	0.084
gd3009-2.54	0.565	0.379	0.186
gd3009-2.55	0.564	0.534	0.03
Average	**0.509**	**0.44**	**0.069**
stddev	**0.104**	**0.118**	**0.035**

- *The measurements indicate a voltage drop of ~0.07V (average) across the Co_3O_4 TCCR layer for Co_3O_4/ITO/PV-cell layer stacks, which is lower than the Go/no-go target (2010) of 0.35V for TCCR/PV-layer stack and satisfies the go/no-go criteria.*

2.3A Making Co_3O_4 on Large Scale System

- *The 2 MW roll-to-roll machine at Xunlight allows the fabrication of PEC electrodes and TCCR layer using steel substrates.*
- *Xunlight obtained a Co_3O_4 sputtering target (99%), which is used for fabricating TCCR layers on large areas. First sputtering trials for process development of obtaining stoichiometric Co_3O_4 layer are completed.*

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



Co_3O_4 layer were sputtered onto the SS web using 3kW pulsed DC power at a line speed of ~ 1"/min;

The O_2 flow was varied between 0-120 sccm;

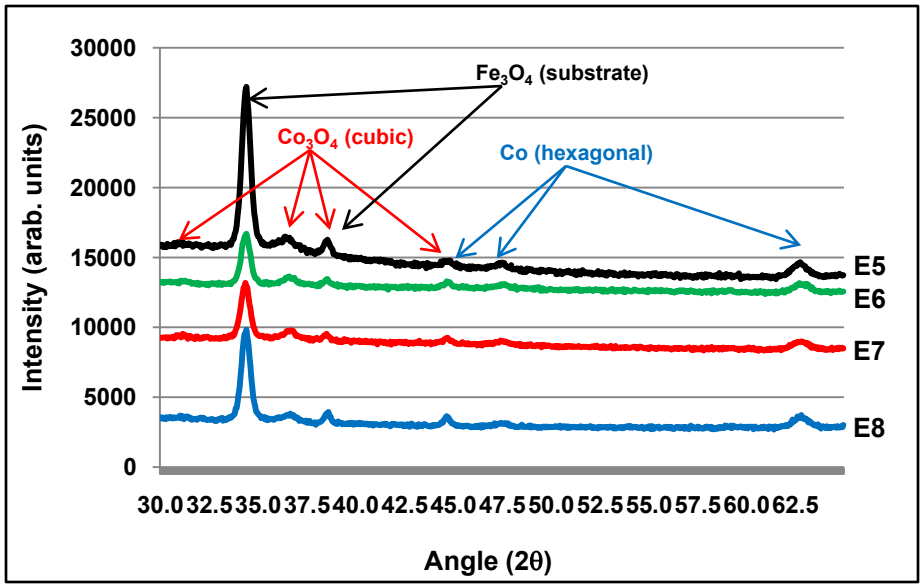
The substrate temperature was kept at ~200 C for all trials;

Run, experiment #	***Ar/Ar-O_2 flow***
Run 1, exp. 1	*120 sccm / 0 sccm*
Run 1, exp. 2	*110 sccm / 15 sccm*
Run 1, exp. 3	*100 sccm / 30 sccm*
Run 1, exp. 4	*80 sccm / 60 sccm*
Run 2, exp. 5	*80 sccm / 60 sccm*
Run 2, exp. 6	*60 sccm / 80 sccm*
Run 2, exp. 7	*40 sccm / 100 sccm*
Run 2, exp. 8	*20 sccm / 120 sccm*

2.3B Cobalt Oxide as a Material Class

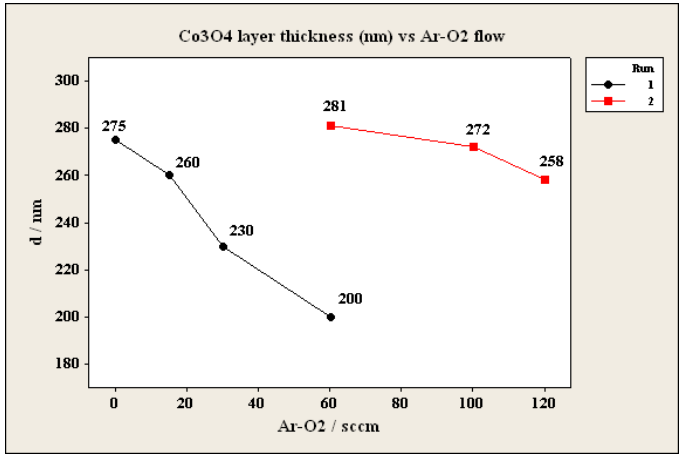
- *XRD measurements show that stoichiometric Co_3O_4 layers with a small Co content are obtained;*
- *Further process optimization will be done in order to obtain the required thickness (~ 30nm), transparency and uniformity of the Co_3O_4 layer;*
- *Large area a-Si cells with Co_3O_4 TCCR coating will be fabricated; after depositing all layers of the PEC electrode, the Ni-catalyst for hydrogen evolution will be electroplated onto the back-side of the SS substrate.*
- *The PEC electrodes will be used for building immersion-type PEC systems with an active area of 1ft × 1ft.*
- *UT will support Xunlight with material characterization and support measurements; these data will be used for on-going process improvements for PEC cell fabrication;*

XRD measurements:



- *Prototype systems will be evaluated regarding their hydrogen production capabilities and their long-term reliability.*

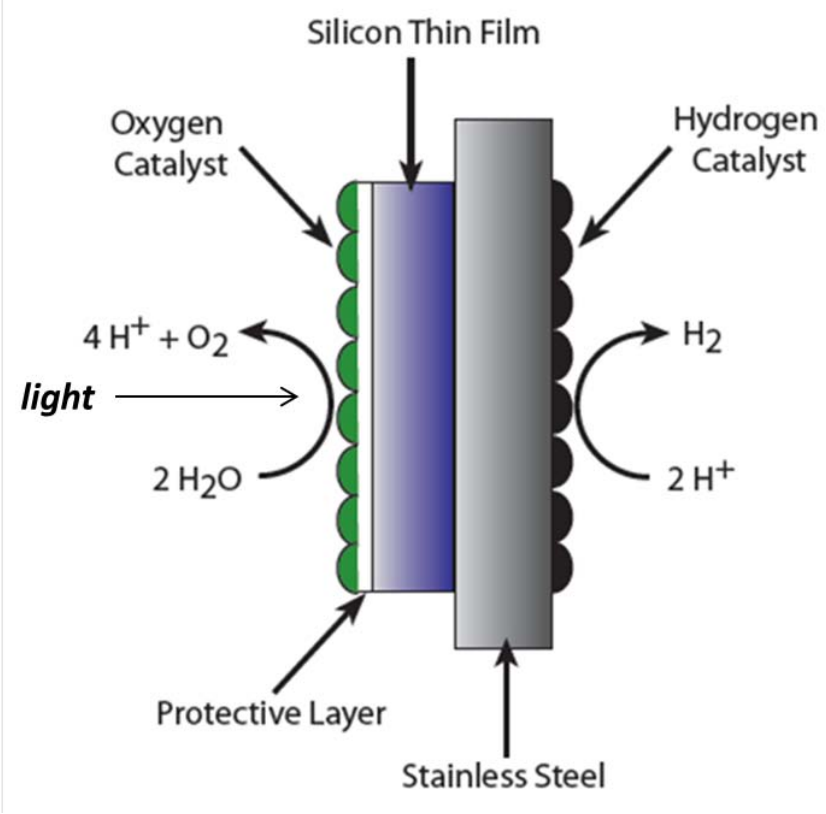
Co_3O_4 thickness vs. Ar-O_2 flow:



2.4A Sun Catalytix Update

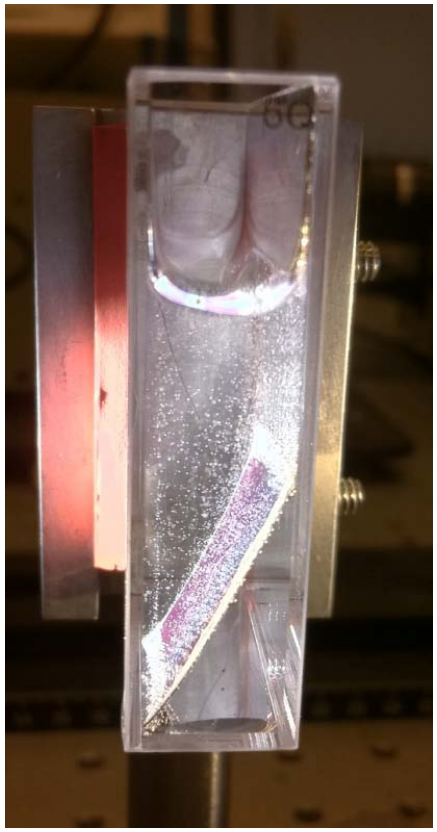
Xunlight PV with Sun Catalytix Catalysts

- *Triple junction a-Si PEC electrodes were coated using Sun Catalytix' oxygen and hydrogen evolution catalyst;*



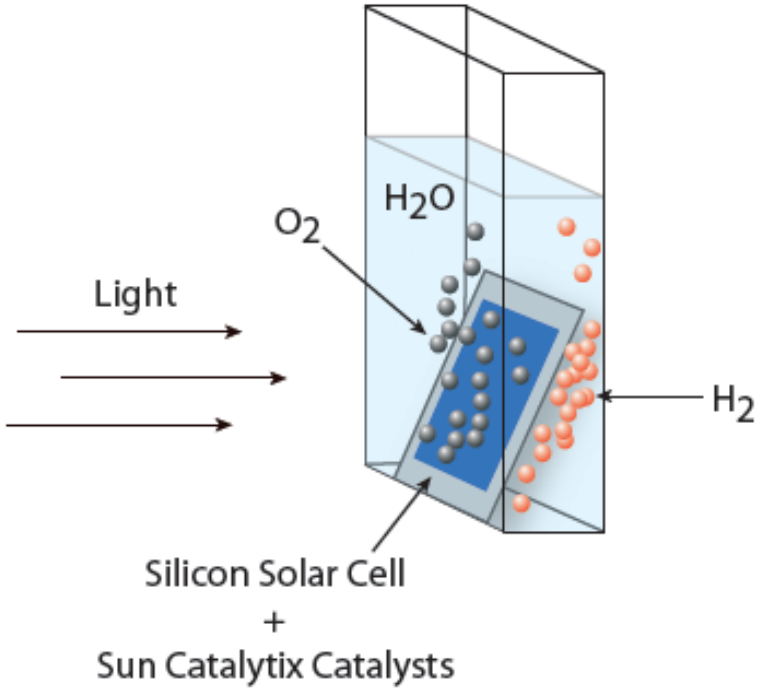
Geometry of the PEC cell containing Xunlight amorphous triple junction silicon photovoltaic with Sun Catalytix Co-OEC anode and earth-abundant cathode catalysts;

Image of PEC cell under illumination showing evolution of oxygen and hydrogen bubbles from water:



2.4B Sun Catalytix Update

Schematic of the PEC cell



Video:

Operation of the PEC cell made from Xunlight's triple junction PV and Sun Catalytix Catalysts

- *The PEC cell uses water as electrolyte;*

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

Performance Measure	Units	DOE 2012 Targets	2010 Go/No-Go	MWOE 2010 Status	References
Solar-to-Hydrogen efficiency	% Efficiency	8	N/A	TBD	PEC electrodes with TCCR layer will be made in Xunlight/MWOE's roll-to-roll machine and prototype PEC modules will be built and tested.
Durability	Hours	≥1000	≥700	606	Deng, X.; Abraham, M.; Coleman, M.; Collins, R.; Compaan, A.; Giolando, D.; Jayatissa, A. H.; Stuart, T.; Vonderembse, M.; Castellano, F., Ingler Jr., W. B. "Production of Hydrogen for Clean and Renewable Sources of Energy for Fuel Cell Vehicles", 2007 DOE Hydrogen Program Annual Merit Review and Peer Evaluation, Crystal Gateway Marriott, Arlington, VA., May 15, **2007**. (Poster)
Cost	gge	$2-3	N/A	TBD	
Deposition temperature	°C	≤250 (MWOE Target)	≤300	270	Same reference as above
Transparency of TCCR	% Trans-mission	≥90 (MWOE Target)	≥85	90	Same reference as above
Voltage drop across TCCR/PV-cell layer stack	V	≤0.15	≤0.35	0.07	See slide 17 and 18.

Technical Progress and Accp. --- Part 3

PAS Material Class for immersion-type PEC system

- ***Tested Materials:***
  - *Titanium dioxide – Not stable when deposited under 300°C which is the threshold for tf-Si films;*
  - *Iron oxide – Only fully stabilizes and increases in photoactivity after annealing;*
  - *Antimony Iron oxide – Same as Iron oxide;*
  - *In_2O_3-$InFe_2O_4$ – Extremely stable under initial trials, excellent conductivity, transmission needs improvement (or band gap lowered). It was shown to be photoactive only after annealing at higher than useful temperatures for tf-Si solar cells.*
  - *Due to the poor performance of the PAS materials, this line of study was down-selected in Dec 2010 in favor of the TCCR material research.*

Performance Metrics for PAS Material (Relevance)

Performance Measure	Units	DOE 2012 Targets	2010 Go/No-Go	MWOE 2010 Status	References
Solar-to-Hydrogen efficiency	% Efficiency	≥8		TBD No Module	
Durability	Hours	≥1000	≥700	24	Ingler Jr., W.B.; Sporar, D.; Deng, X. "Sputter Deposition of In-Fe_2O_3 Films for Photoelectrochemical Hydrogen Production" ECS Trans. Vol. 3 (State-of-the-Art Program on Compound Semiconductors 45 (SOTAPOCS 45) -and- Wide Bandgap Semiconductor Materials and Devices 7), **2006**, 253.
Cost	gge	$2-3		TBD	
Photocurrent of PAS	mA/cm^2	≥8 (MWOE Target)	≥5	0.0334	Same as above
Deposition temperature	°C	≤250 (MWOE Target)	≤300	200	Same as above

Overall Impact (Summary & Relevance)

- *The project is accelerating the development of systems for low-cost and high efficiency production of solar H_2, which supports achieving DOE program objectives of using PEC methods for successful water-splitting.*
- *The project has successfully demonstrated substrate-type PEC systems using tf-Si based photoelectrodes.*
- *The extensive research work on material classes for TCCR, PAS and H_2 evolution catalysts is addressing DOE MYPP Technology Barriers and supports the technical realization of large area PEC systems.*
- *Optimization of large area tf-Si photoelectrodes is an integral part of the development of low-cost systems for highly efficient production of solar H_2.*
- *The close collaboration between MWOE, Xunlight, UT and NREL is beneficial for accelerated success of this project.*

Proposed Current and Future work

Substrate-type PEC cell

- *Work on substrate-type PEC cell is completed;*

Immersion-type PEC cell

- *Research on improved TCCR layer based on oxide materials will be continued; most promising material classes and optimized processes are to be identified;*
- *Process development to fabricate large-area PEC electrodes will be continued; this work includes deposition of selected TCCR materials (Co_3O_4 etc.) onto a-Si devices using Xunlight's 2MW roll-to-roll deposition system;*
- *Development of high performance H_2 evolution catalyst materials will be continued;*
- *Prototype PEC systems will be designed, engineered and optimized.*

Proposed Current and Future work

Large area tf-Si photoelectrodes

- *2MW roll-to-roll machine for fabricating large area tf-Si triple junction photoelectrodes is completed and optimized;*
- *Next step is to transfer the promising results for TCCR material from small area development to this large area roll-to-roll machine, which can provide more uniform deposition and large electrodes for prototype PEC system.*
- *Deposition conditions will be optimized and the resulting TCCR material will be studied to achieve the best transparency, conductivity, and corrosion resistance properties.*
- *One foot by one foot PEC systems will be constructed, the hydrogen generation efficiency, life time, and cost will be studied.*

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.

  Have done extensive research with many different material classes for application as TCCR or PAS material. Identified several material classes which show promising results for TCCR application.

  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.
- **Technology Transfer/Collaborations:**

  Active collaboration with UT on material research and characterization. Transfer the lab research results to apply on large scale system.

  Collaborating with Sun Catalytix to deposit their catalyst on a-Si solar cells.
- **Proposed Future Research:**

  Will continue to explore TCCR material in the lab and apply the promising results to make large area PEC electrodes using the 2MW machine.

  Design and build commercial size, 1ft 1ft immersion-type PEC system and study the performance, efficiency, cost and durability.