Midwest Optoelectronics

Project ID # PD056

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: 04/01/2005*
- *Project end date: 07/31/2014*
- *Percent complete: 92%*

Budget

- *Total project funding*
  - *DOE share: $2,113,888*
  - *Contractor share: $760,492*
- *FY12 DOE funding: $87,887*
- *FY13 DOE funding: $212,388*
- *Planned FY14 DOE funding: 0*
- *Total funding spent by 3/31/14: $1,998,805 plus $845,000 cost share*

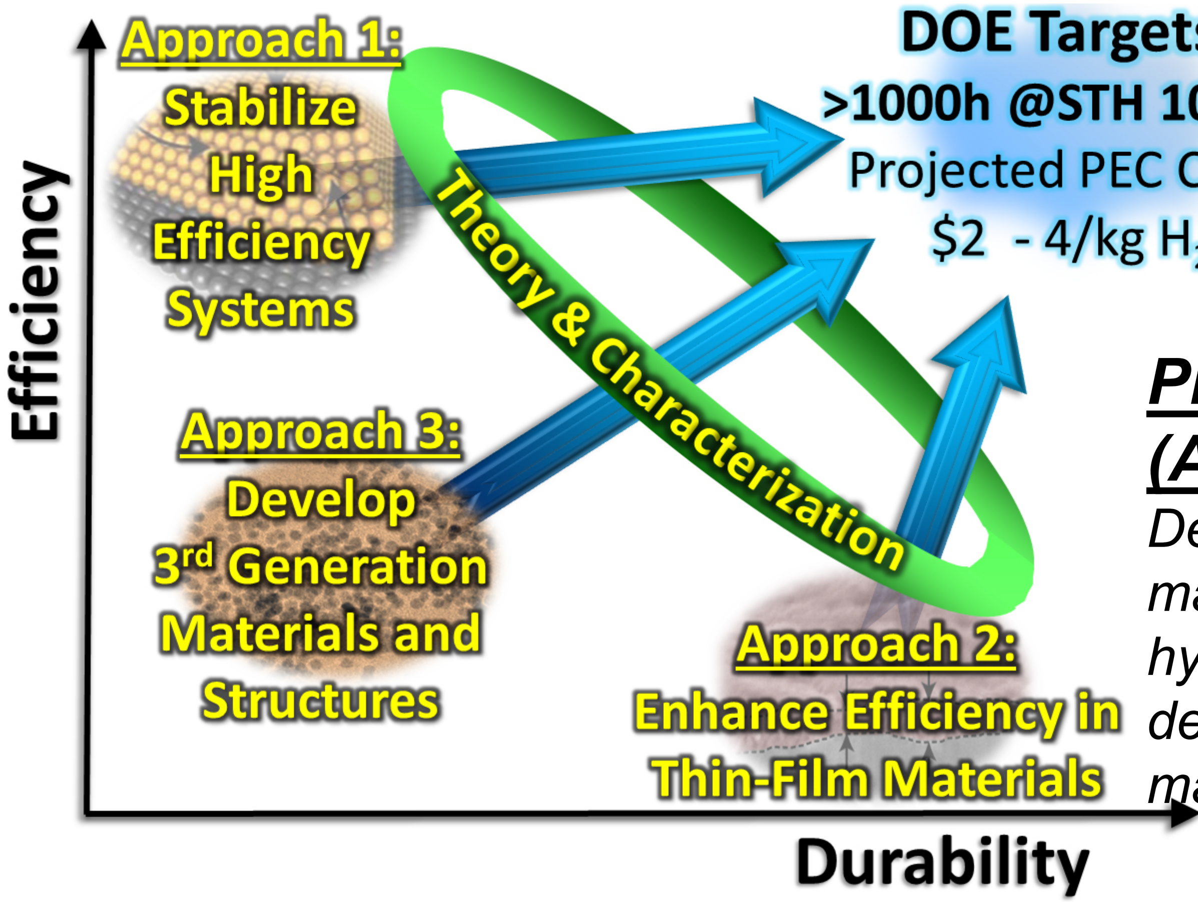
Partners

- *Xunlight Corporation (Xunlight)*
- *University of Toledo (UT)*
- *National Renewable Energy Lab. (NREL)*
- *South Dakota State University (SDSU)*

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



Project Focus (Approach 2)

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

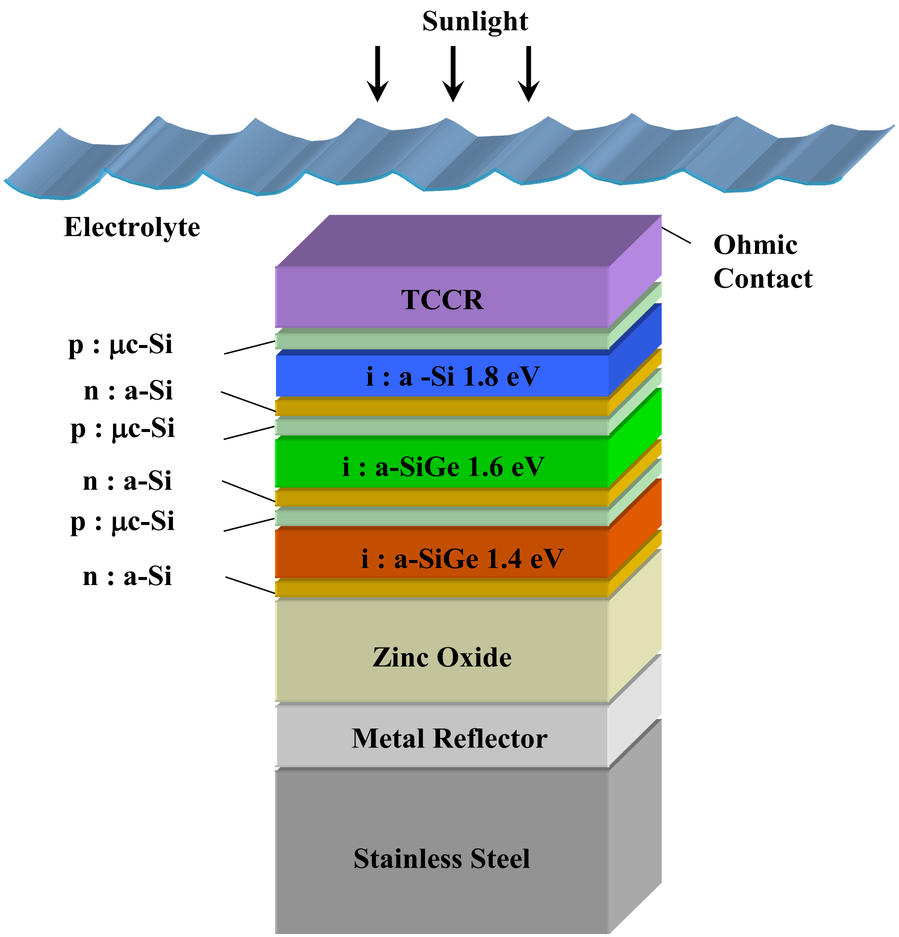
Relevance

Most critical goal: Cost, Cost and Cost! <$2-4/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 (for PV)*
- *8.3% stable solar cell efficiency and 7% stable module efficiency in production today (for PV)*
- *12% small area initial efficiency in R&D scale (for PV)*
- *Var. Mfg Cost: <$25/$m^2$*

Triple-junction structure: SS/Metal/ZnO/n-i(a-SiGe:H)-p/n-i(a-SiGe:H)-p/n-i(a-Si:H)-p/ITO, which could be used for both photovoltaic cells or PEC photoelectrodes.

STH efficiency is expected to be around 75% to 80% of solar photovoltaic efficiency, depending on overpotentials of catalysts used.

H2A Analysis ➔ 10% Triple-Junction Thin Film Si PEC system could be used to achieve \$2/gge

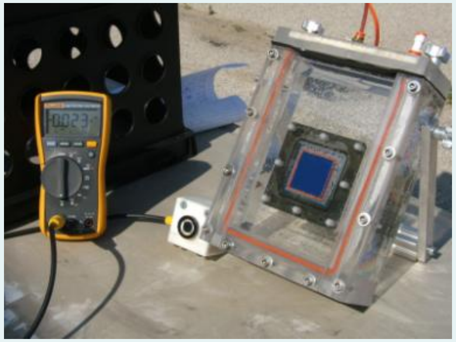
- *Our assumptions for the H2A model:*
  - *PEC electrode with catalyst: \$30/m^2*
  - *PEC Housing: \$10/m^2*
  - *Replacement cost: \$6/m^2 (every 2 years, at 20% of electrode cost)*
  - *Solar to Hydrogen (STH) efficiency =10%.*
  - *Tilted structures with 50% land coverage; land cost: \$500/acre*
  - *1825 hours of sunlight per year.*
  - *The plant is designed for 1 ton per day (TPD) (with the values described above)*
  - *and costs have been scaled to 50 TPD using a "learning factor" of 0.78.*

- *Results: Projected hydrogen generation cost at \$1.95/gge is achievable at 50 TPD scale.*

It is challenging, but achievable.
It requires investment and effort to achieve \$1.95/gge. .

Approaches

Two Main Approaches:

Types	PEC Panels	Electrode in Contact with electrolyte	STH Efficiency Achieved
Immersion-type PEC cell		The electrode is immersed in the electrolyte	5.7%
Substrate-type PEC cell		Only back-side	5.0%

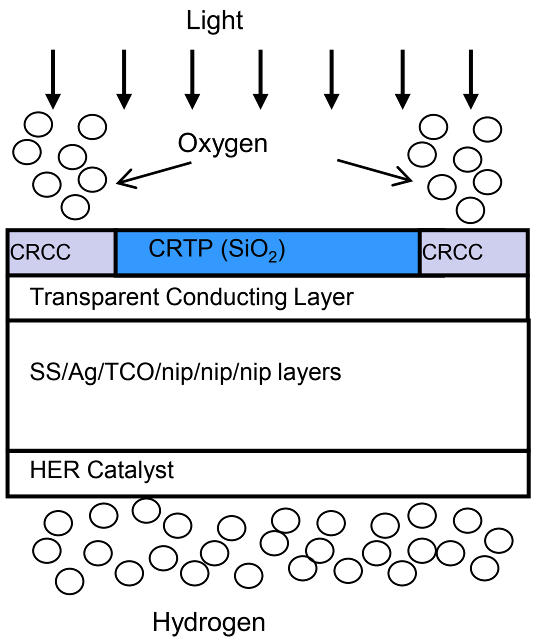
Research Tasks (Approaches)

The objective 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
1	Transparent, conducting and corrosion resistant (TCCR) coating for triple-junction tf-Si based photo-electrode.
3	Understanding and characterization of photo-electrochemistry.
4	Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems.
2	Hybrid multi-junction PEC electrode having semiconductor- electrolyte junction (down selected).
5	Development of device designs for large-area, substrate-type PEC panels (down selected)

Novel CRTP/CRCC Design

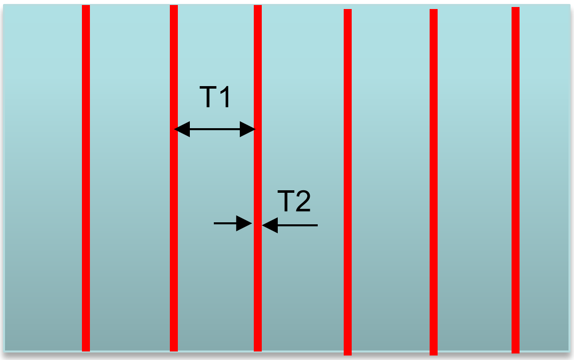
- *The traditional design's requirements for TCCR layer is not easy to meet, it needs to be **t**ransparent, **c**onducting and **c**orrosion **r**esistant, all at the same time.*
- *To overcome this problem, we have developed a novel design which separate the light absorption region which is **c**orrosion-**r**esistant **t**ransparent **p**rotective(CRTP) region; and the water-splitting, gas-generating region which is **c**orrosion-**r**esistant **c**onducting **c**atalytic (CRCC) region.*
- *For the CRTP coating, it needs to be transparent and corrosion resistive, but does not need to be conductive. Clear coat, SiO_2 would be good candidates*
- *For the CRCC coating, it needs to be conductive and corrosion resistive and a good catalyst, but does not need to be transparent. Co_3O_4 would be a good candidates, we can now afford to make it thicker to provide good corrosion resistive protection since it no longer needs to be transparent as when it was used as TCCR layer.*
- *With this novel design, we can avoid the simultaneous requirements for a highly transparent and highly conducting catalyst material.*
- *Two provisional patents have been filed.*



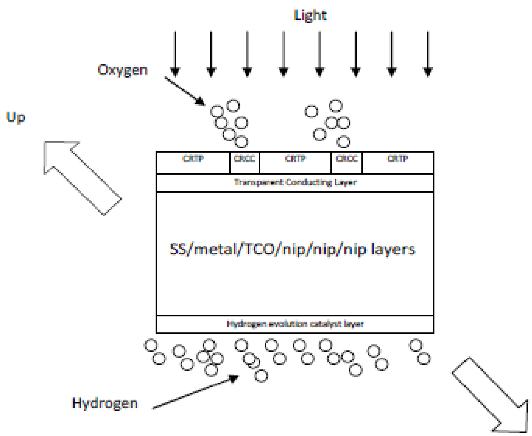
A novel photoelectrode structure that decouples CRCC and CRTP coatings

Technical Accomplishments and Progress

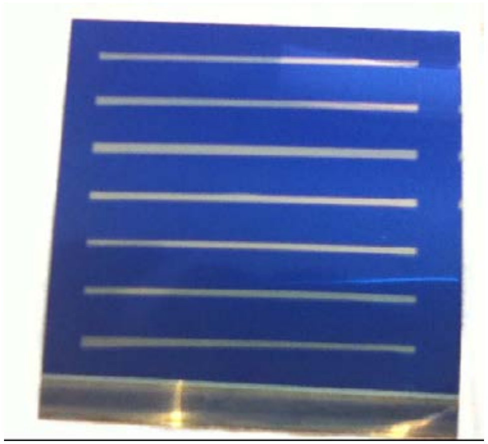
SiO_2 as CRTP coating and sputtered Co_3O_4 as CRCC coating



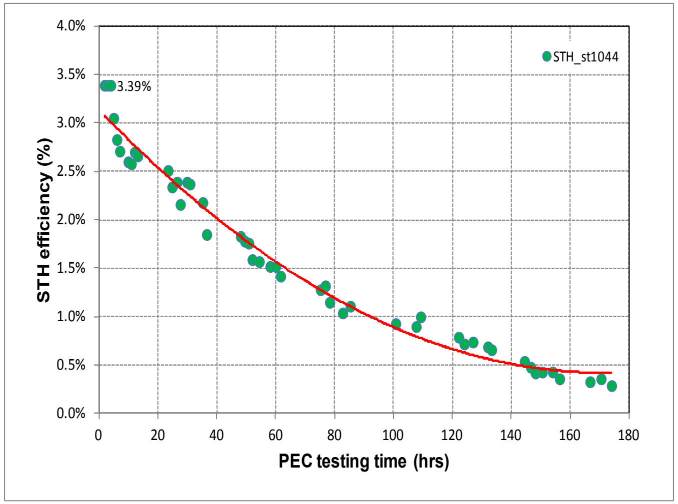
(a) Schematic of the design (T1 for CRTP & T2 for CRCC)



(b) Schematic of the photo-electrode in the novel design



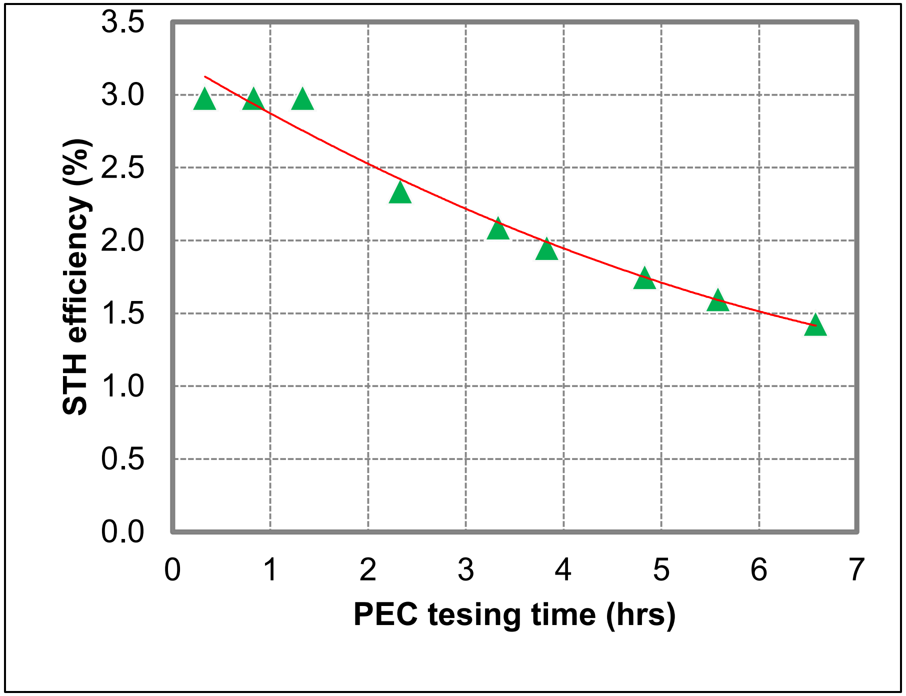
(c) A PEC electrode with SiO_2 as CRTP coating and sputtered Co_3O_4 as CRCC coating



(d) Solar to Hydrogen Efficiency

Clear coat as CRTP coating and electroplated Platinium as CRCC coating

(a) A PEC electrode with clear coat as CRTP and electro-plated Pt as CRCC

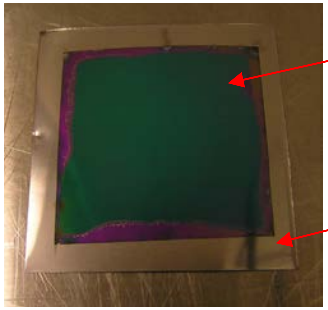


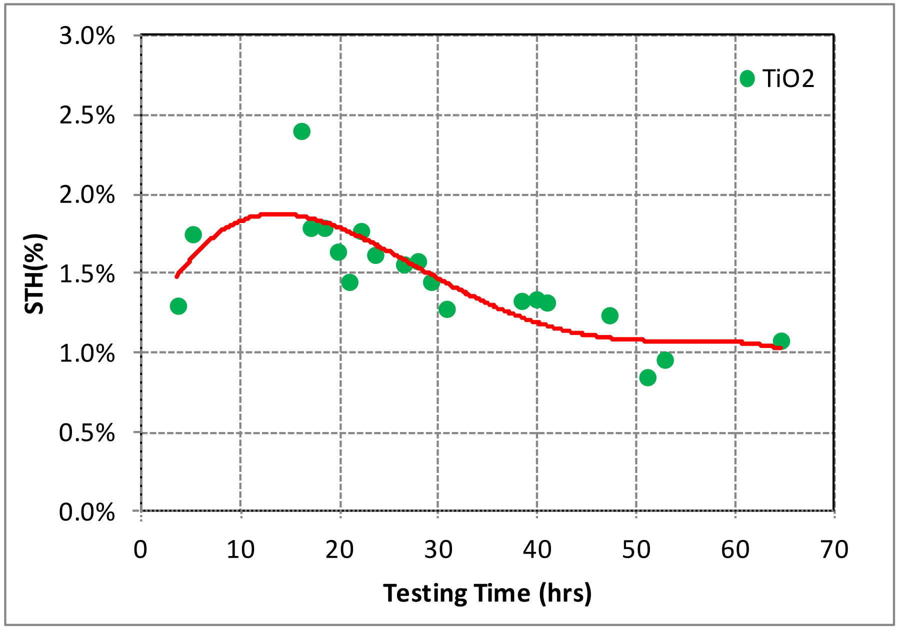
(b) Solar-to-Hydrogen efficiency over time

We developed two processes for coating CRCC and CRTP on solar cells: sputtering and electroplating technologies. These two processes are being further studied.

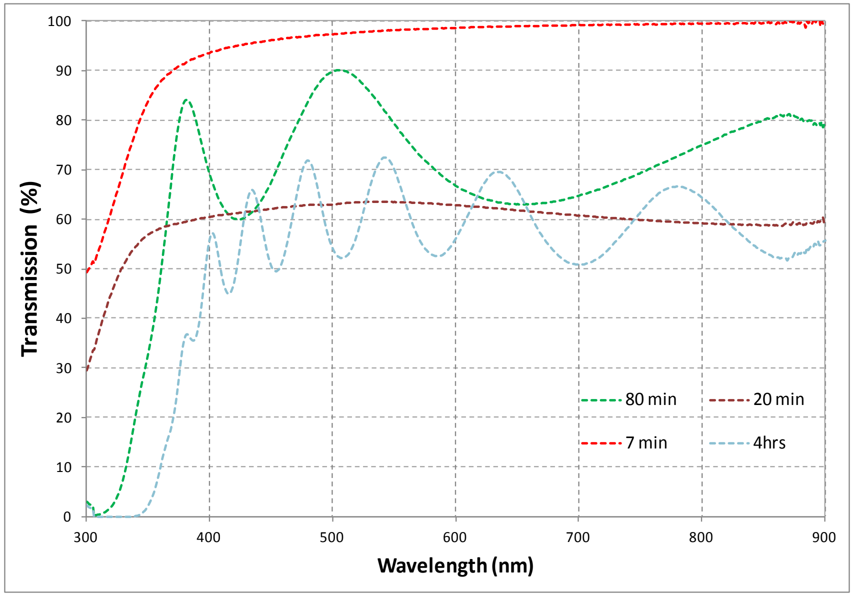
Titanium Oxide as a TCCR and Oxygen Evolution Catalyst

(a) An PEC electrode with TiO_2 TCCR coating





(c) Solar–to-Hydrogen efficiency over operation time for the photoelectrode with TiO_2 (deposition time of 20min)

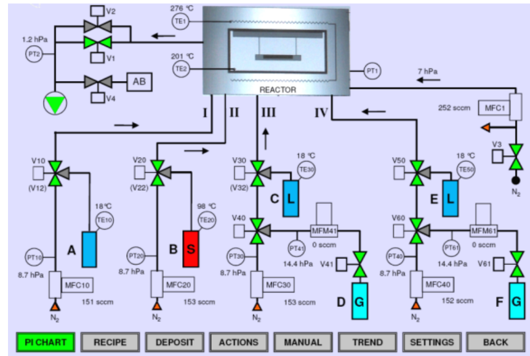


(b) Transmission spectra of TiO_2 films with various deposition times

Preliminary study has shown promising performance, e.g. 2.5% initial STH efficiency and durability of 65 hrs (STH>1.0%). Further study is under way.

Technical Accomplishments and Progress

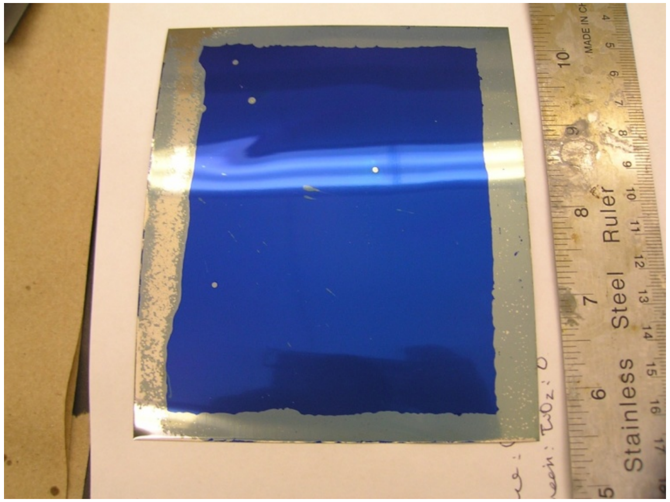
Atomic Layer Deposition (ALD) for Durable PEC Electrode



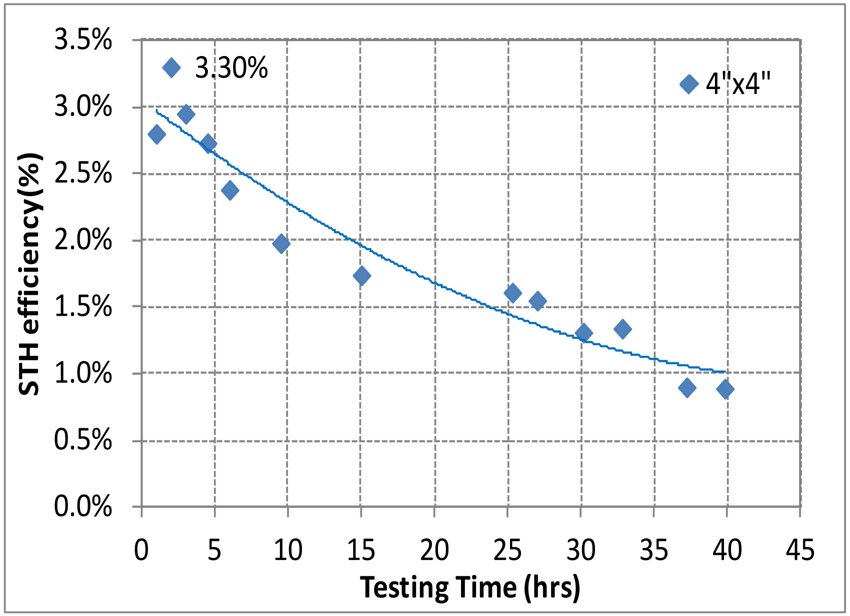
- *Left top: an ALD system under installation at SDSU*
- *Left bottom: Source gas control allows easy change of process gases upon applications*
- *Center: ALD gas control system provides programmable processes and convenient user interface*
- *Right: Process gas pulses*

- *PEC electrodes most often fail when the protective layer deteriorates due to pin-holes and defects.*
- *ALD has the unique advantage of producing conformal, uniform and compact coatings.*
- *We expect to demonstrate greatly enhanced durability of PEC electrodes based on ALD coatings.*

Increase the size of working immersion-type PEC device from 2"x2" to 4"x4"



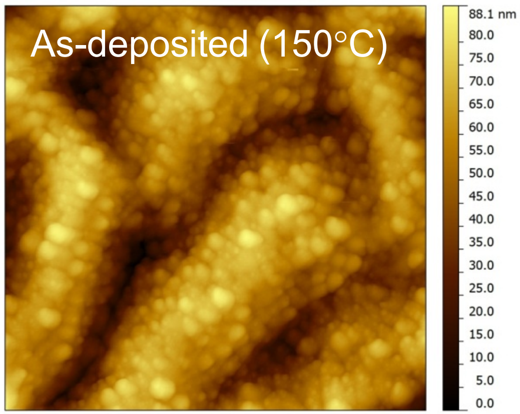
A 4" x 4" PEC electrode

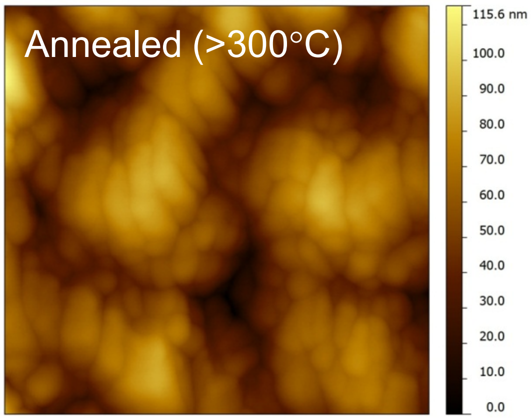


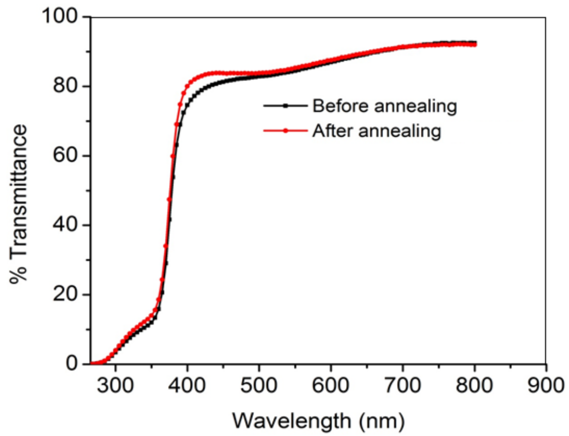
Solar-to-Hydrogen efficiency over time

The 4"x4" sample shows an initial efficiency of 3.3%, and a durability of about 40hrs. Further optimizations are underway.

Solution-based Transparent Conductive Coatings





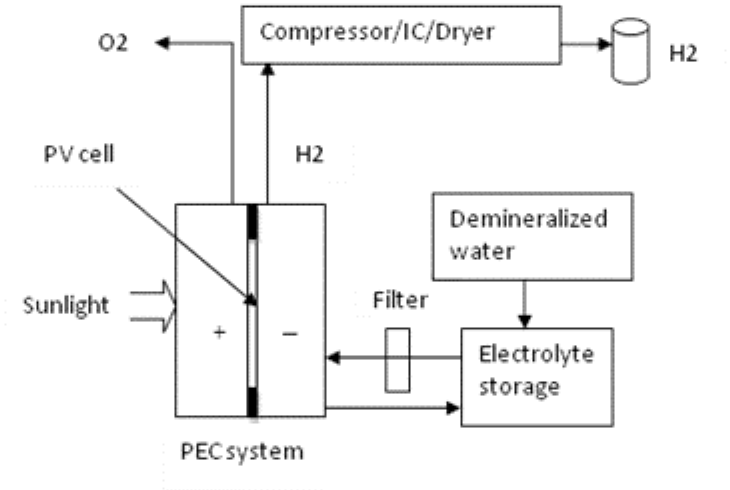


- *Solution process is potentially cost effective to replace vacuum deposition.*
- *Our initial efforts started with Zinc Oxide (ZnO) films.*
  - *ZnO films were prepared using sol-gel solution*
  - *Zinc Acetate, Ethanolamine and Methoxyethanol solution was mixed in definite proportion*
  - *Films were spin coated followed by 150℃ baking on hotplate for 20 minutes*
- *AFM images depict obvious crystallization after annealing (>300℃).*
- *Transmittance in visible range (>400 nm) to IR is over 85%.*
- *Further study on the electric conductivity is under way.*

Techno-economic Analysis

- *Our assumptions for the H2A model:*
  - *PEC electrode with catalyst: $30/m²*
  - *PEC Housing: $10/m²*
  - *Replacement cost: $6/m² (every 2 years, at 20% of electrode cost)*
  - *STH efficiency =10%.*
  - *Tilted structures with 50% land coverage; land cost: $500/acre*
  - *1825 hours of sunlight per year.*
  - *The plant is designed for 1 ton per day (TPD) and costs have been scaled to 50 TPD using a "learning factor" of 0.78.*
  - *Balance of system costs based on examples in Type 3 PEC system in a report from Directed Technologies with a projected reduction in installation costs due to modular design*

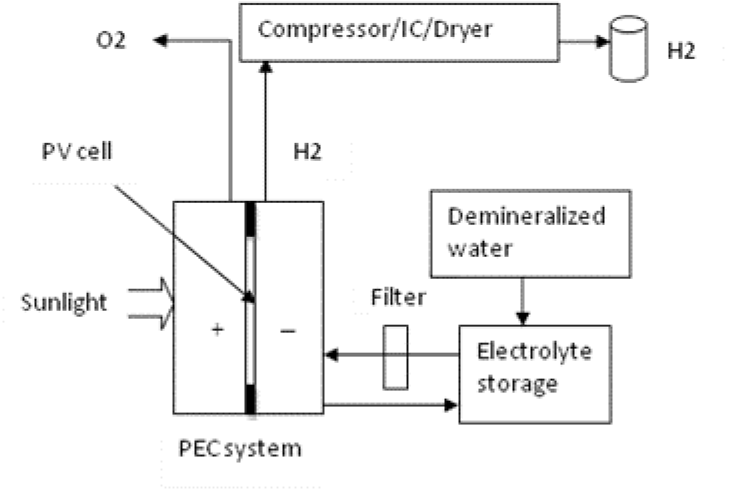
- *Results: Projected hydrogen generation cost is* ***$1.95/gge*** *at 50 TPD scale.*



Techno-economic Analysis – a more conservative case

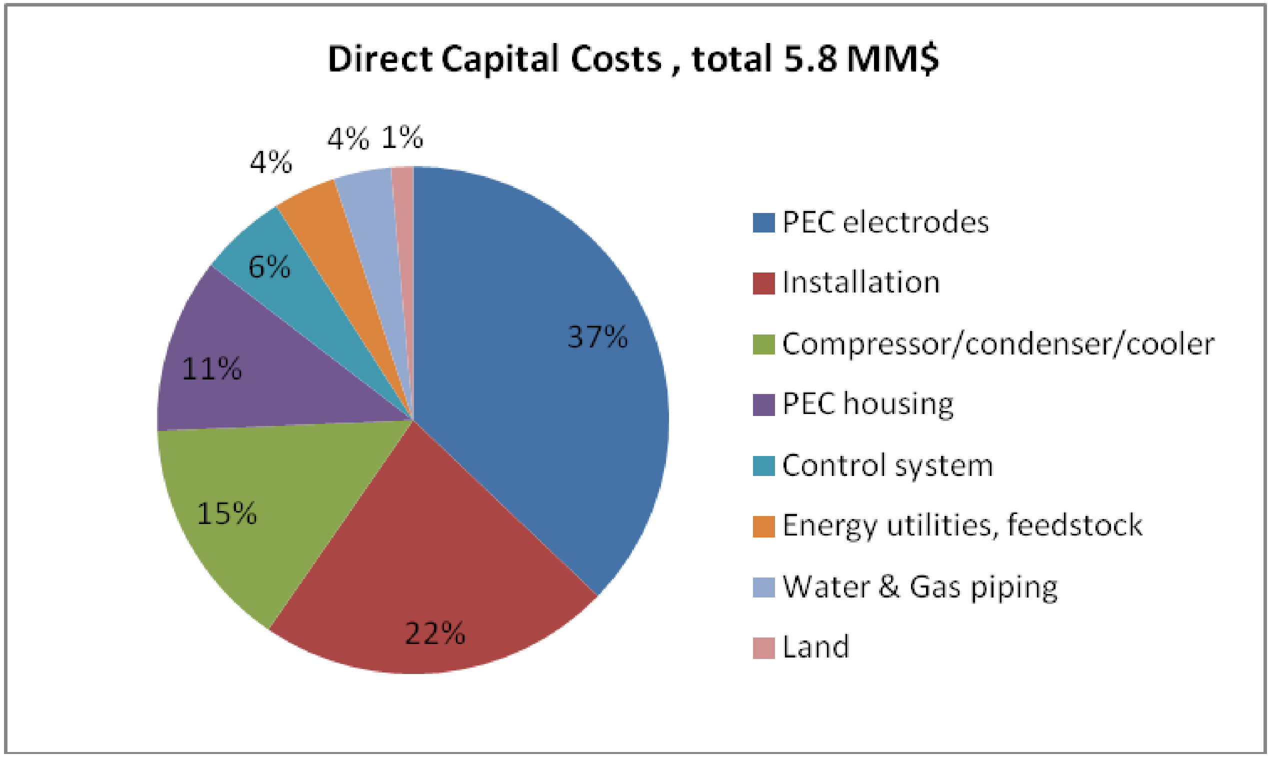
- *Our assumptions for the H2A model:*
  - *PEC electrode with catalyst: $40/m^2*
  - *PEC Housing: $12/m^2*
  - *Replacement cost: $8/m^2 (every 2 years, at 20% of electrode cost)*
  - *STH efficiency =10%.*
  - *Tilted structures with 50% land coverage; land cost: $3000/acre*
  - *1825 hours of sunlight per year.*
  - *The plant is designed for 1 ton per day (TPD) and costs have been scaled to 50 TPD using a "learning factor" of 0.78.*
  - *Balance of system costs based on examples in Type 3 PEC system in a report from Directed Technologies with a projected reduction in installation costs due to modular design*

- *Results: Hydrogen generation cost is $2.33/gge at 50 TPD scale.*
- *About 70% of the cost is from the capital cost, and 30% from Operation and Management.*



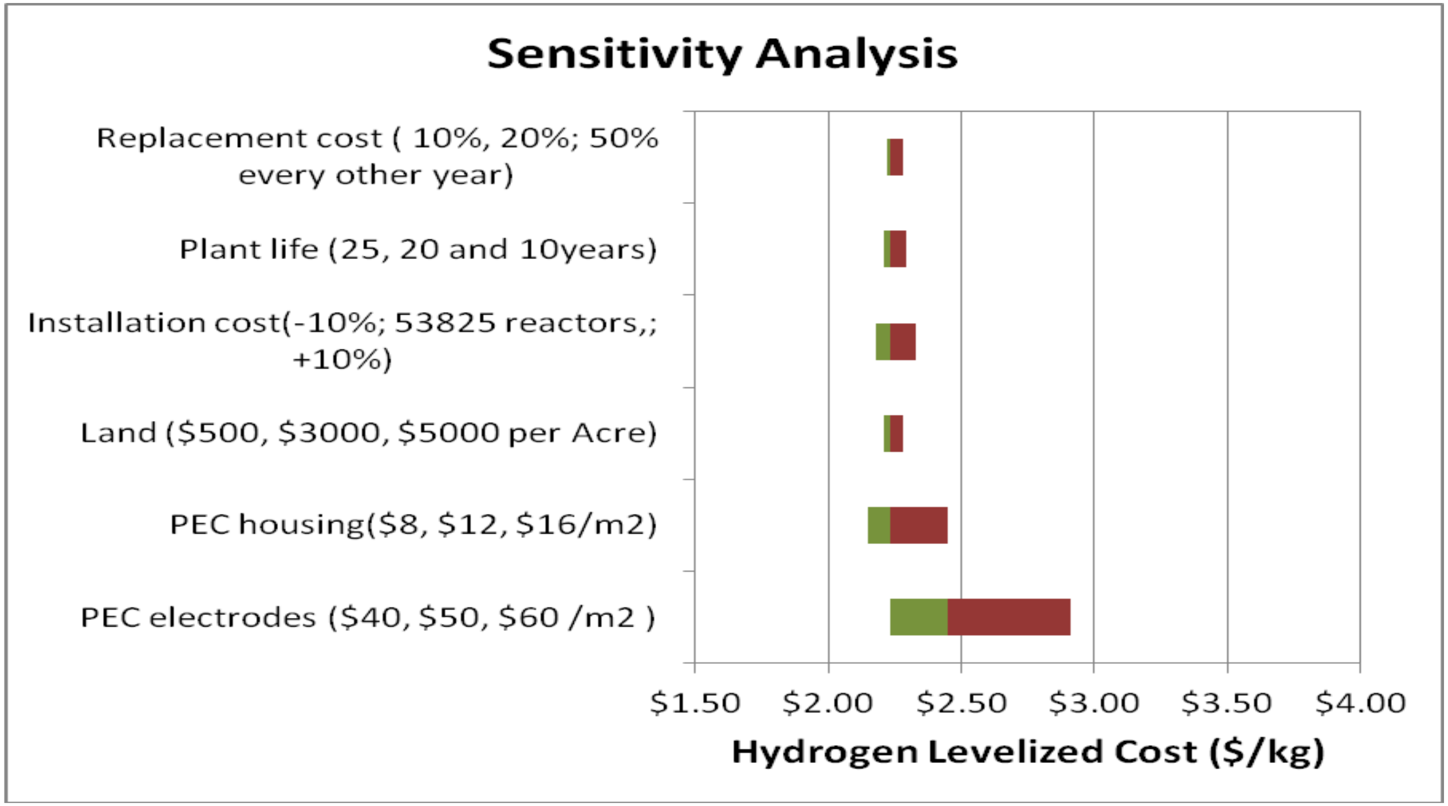
Relevance

Techno-economic Analysis: Capital Cost



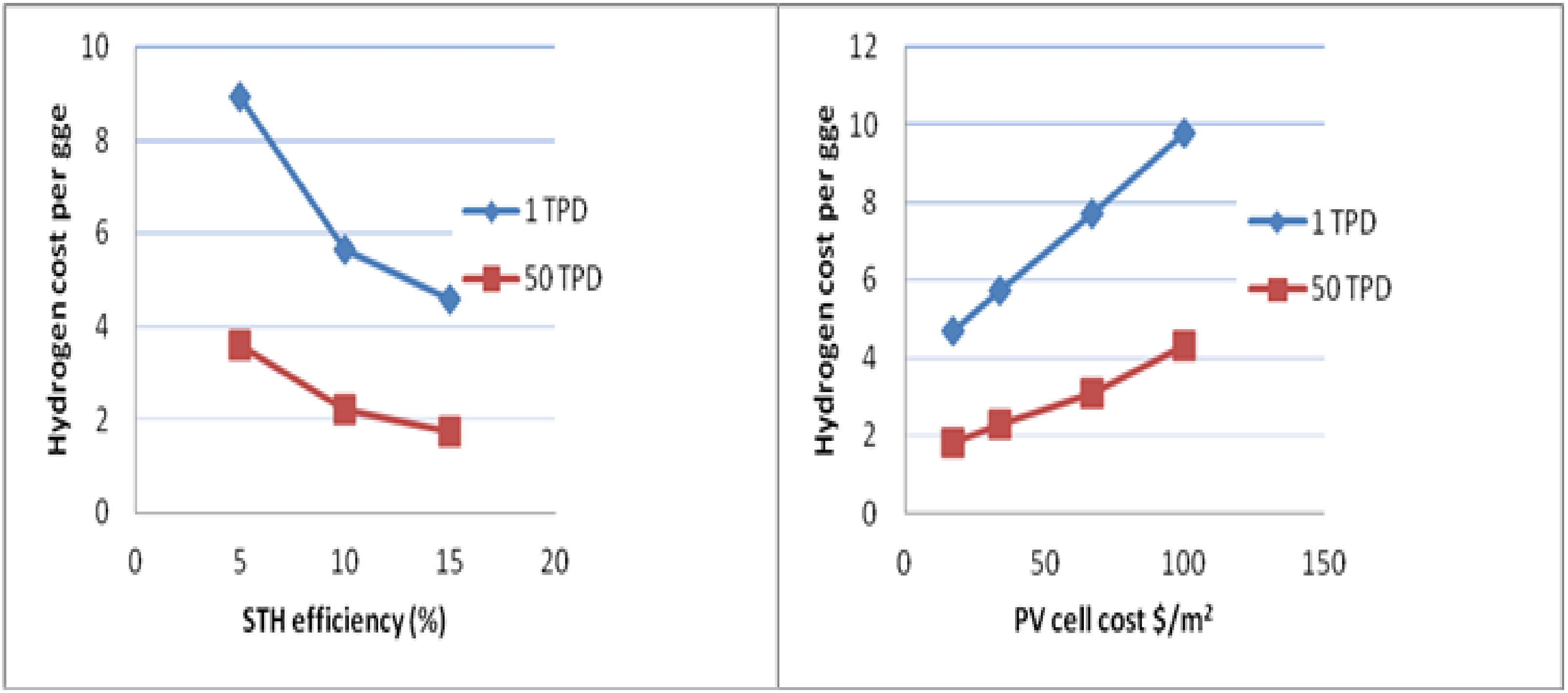
Capital cost allocation of a 1 TPD PEC hydrogen generation plant
In this model, PEC electrodes contribute 37% of the total capital cost. When the STH efficiency increases, the less PEC electrodes will be needed to achieve the same capacity, thus reducing the PEC electrode cost.

Techno-economic Analysis –Sensitivity Analysis



The cost of the PEC electrode and housing have larger impact on the hydrogen generation cost than the other components (a 10% baseline STH efficiency is assumed here.)

Techno-economic Analysis –Sensitivity Analysis



The hydrogen generation cost vs the STH efficiency with the PV cell cost kept at $40/M², for a 1 TPD plant and a 50 TPD plant.

The hydrogen generation cost vs the PV cell cost with the STH efficiency kept at 10%, for a 1 TPD plant and a 50 TPD plant.

Collaborations

Partners and Collaborators:

- ***University of Toledo (Academic): Prof. X. Deng, Prof. Y. Yan, Dr. C. Chen***
  - *UT helps with sputtering and characterization of TCCR material. (Tasks 1 and 4)*
- ***Xunlight Corporation (Industry):***
  - *Xunlight provided the triple junction solar cells and helped with depositing Co_3O_4 in the large area roll-to-roll machine for PEC electrodes (Tasks 4).*
- ***NREL (National Lab): Dr. John Turner, Dr. Art Nozik***
  - *NREL is working on improving the understanding of PEC process for a-Si based photo-electrodes. (Task 3)*
- ***South Dakota State University (Academic): Prof. Qi Hua Fan***
  - *SDSU helps develop a novel solution-based transparent conductive films for PEC electrodes and making protective coatings using Atomic Layer Deposition method. (Task 1)*
- ***California Institute of Technology (Academic): Prof. Nathan Lewis***
  - *Using Caltech's "leaky" catalyst layer for MWOE's triple-junction solar cells*
  - *Already shipped triple-junction devices to Caltech*
  - *Caltech sent special substrates to MWOE for fabrication of n-i-p type triple-junction PEC electrode with oxygen evolution from the front surface and p-i-n type triple-junction PEC electrode with hydrogen evolution from the front surface*

– ***Stanford University (Academic): Prof. Tom Jaramillo***
  - *Prepared samples for sending to Standard for PEC collaboration*

– ***Lawrence Berkeley National Lab (National Lab): Dr. Joel Ager***
  - *Prepared samples for sending to LBNL for PEC collaboration*

Partners and Collaborators:

-- Participation in PEC Working Group

- *PEC Hydrogen Working Group has discussed and preliminary accepted to use MWOE supplied triple-junction PEC electrode as a new standard for calibration of solar-to-hydrogen efficiency measurement to cross check STH measurement among different groups.*
- *Proposed to several working group members to lead a discussion on H2A analysis of thin-film PEC hydrogen production.*
- *PEC Hydrogen Working Group recognized that MWOE/UT/Xunlight supplied triple-junction PEC electrodes were used by various groups (U. Hawaii, NREL, GM, and MIT/SunCatalyst) in the past to produce record STH efficiencies for thin film PEC systems.*

University of Toledo (UT):

- *UT has provided a world-wide exclusive license to MWOE for its PEC technology portfolio.*

Proposed current and future work

- *Continue optimizing the novel CRTP/CRCC design, explore more material combinations for this design with the objectives of increase the STH conversion efficiency and the durability of the PEC system.*
- *Continue developing new TCCR materials, such as TiO_2 and other material for better durability and STH efficiency. .*
- *Develop new TCCR-deposition process and material with Atomic Layer Deposition technology.*
- *Further improve the performance of the large-size PEC system, and carry out outdoor testing. Experiment with new material for the PEC housing and the balance of system components with the objective of lowering the cost of the system.*
- *Continue collaborations with various groups - UT, Xunlight, NREL, SDSU, Caltech, Stanford, LBNL, and others -- for PEC development.*

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 triple-junction solar cell device with TCCR layer or CRTP/CRCC design 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 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 durability results both in the lab and real life outdoor conditions. Carried out the techno-economic analysis of our immersion type PEC system using H2A model .
- ***Technology Transfer/Collaborations:***

  Active collaboration with multiple PEC hydrogen groups around the World.

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

  Focus on the novel CRTP/CRCC design to further improve the STH efficiency and durability of the PEC system by exploring 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.