Midwest Optoelectronics

Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

Liwei Xu (PI)
Midwest Optoelectronics, LLC, Toledo, Ohio
William B. Ingler Jr.
University of Toledo, Toledo, Ohio
Anke Abken
Xunlight Corporation, Toledo, Ohio

06/07/2010
6:30 to 8:30 PM - Atrium (lower level)

Project ID # PD056

THE UNIVERSITY OF TOLEDO 1872

Xunlight CORPORATION

Overview

Timeline

- Project start date: 10/13/2004
- Project end date: 12/31/2011
- Percent complete: 60%

Budget

- Total project funding
  - DOE share: $2,921,501
  - 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 projected for FY10: $413,613

Barriers

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

Partners

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

Project Objectives (Relevance)

- **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 photoelec-trode is not in direct contact with electrolyte.**

Performance Measure	Units	DOE 2012 Targets	MWOE 2010 Status
Solar-to-Hydrogen efficiency	% Efficiency	8	TBD
Durability	Hours	1000	500
Cost	gge	2-3	TBD
Current density of TCCR	mA/cm^2	8 (MWOE Target)	23.0
Photocurrent of PAS	mA/cm^2	8 (MWOE Target)	0.0334
Deposition temperature	°C	250 (MWOE Target)	250
Transparency of TCCR	% Transmission	90 (MWOE Target)	90
Voltage drop across TCCR/PV-cell layer stack	V	≤ 0.15	TBD

Milestones (Approach)

Year 1:

- Identify materials that meet the performance criteria for transparent, conducting, corrosion-resistant (TCCR) materials, including having stability for up to 300 hours. First round of materials to be produced at 350°C or lower with 70% or greater transparency and a voltage drop ≤0.7V across the TCCR layer for the TCCR/PV-cell layer stack under typical PEC device operating conditions.
- Identify materials that meet the performance criteria for photoactive semiconductor (PAS) materials, including having stability for up to 300 hours. First round of materials to be produced at 350°C or lower with 70% or greater transparency and demonstrate at least 3 mA/cm^2 photocurrent.

Year 2:

- Develop high quality TCCR and/or PAS materials with stability up to 700 hours. Second round of TCCR materials to be produced at 300°C or lower with 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. Second round of PAS materials to be produced at 300°C or lower and demonstrate at least 5 mA/cm^2 conductivity.
- **Go/No-Go Decision Point** (this decision point will occur at the end of "Year 2" and 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); and/or ≥700 hours of stability, capable of being fabricated at ≤300°C, and ≥5 mA/cm^2 photocurrent (PAS material).

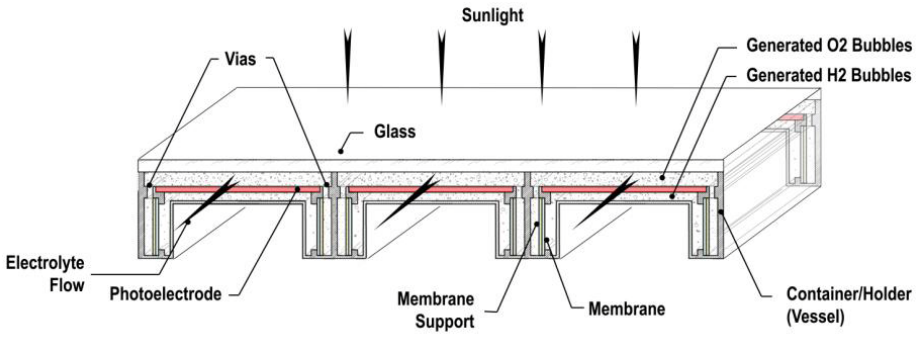
Year 3:

- Develop high quality TCCR and/or PAS 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. Third round of PAS materials to be produced at 250°C or lower and demonstrate at least 8 mA/cm^2 photocurrent.
- Complete techno-economic analysis and energy analysis for the PEC systems for hydrogen production.

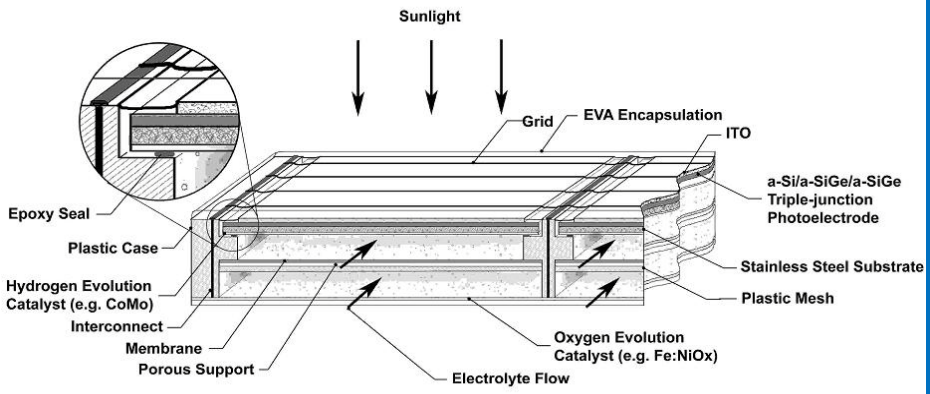
Approach

Two approaches are taken for the development of efficient and durable photoelectrochemical (PEC) cells.

An immersion-type PEC cell



A substrate-type PEC cell

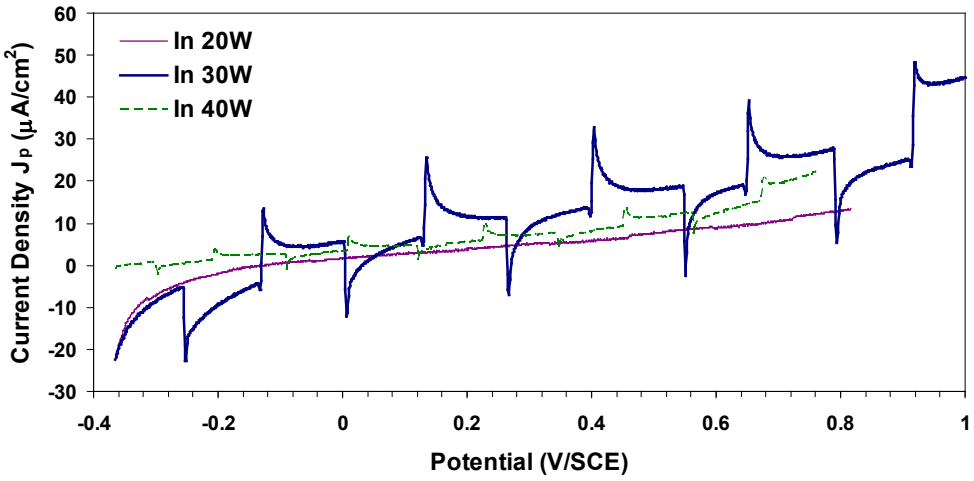


Research Tasks (Approach)

- **Task 1:** Transparent, conducting and corrosion resistant coating for triple-junction tf-Si based photoelectrode;
  [Year 1: 100%; Year 2: 50%; Total: 60%]
- **Task 2:** Hybrid multijunction PEC electrode having semiconductor-electrolyte junction;
  [Year 1: 100%; Year 2: 50%; Total: 60%]
- **Task 3:** Understanding and characterization of photoelectrochemistry;
  [Year 1: 100%; Year 2: 50%; Total: 60%]
- **Task 4:** Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems;
  [Year 1: 100%; Year 2: 50%; Total: 60%]
- **Task 5:** Development of device designs for large-area, substrate-type PEC panels;
  [Year 1: 100%; Year 2: 50%; Total: 60%]

Technical Accomplishments - Task 1 & 3

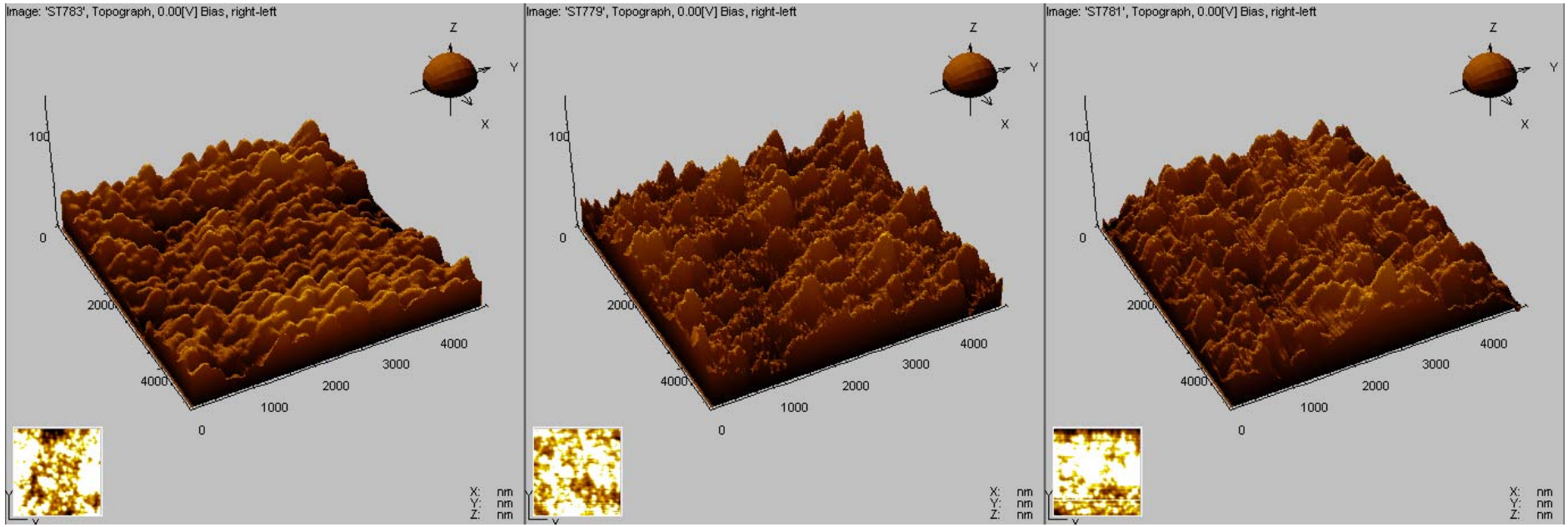
- Studied In_2O_3-Fe_2O_3 as a TCCR material.
- Work culminated with presentation at Spring 2009 MRS meeting and published in Journal of Materials Research – January 2010.
- From the work completed, the results indicate that samples made at 250 °C from indium and indium iron oxide targets powered at 30W and 100W, respectively, using a sputter deposition time of 90 minutes produced optimal results when deposited directly onto single junction amorphous silicon solar cells. At 0.65 V (vs. SCE), the best sample conditions display a maximum current density of 21.4 mA/cm^2.
- The effect of the power settings for indium during sputter deposition and the effect of the deposition time was studied.



- Photocurrent density vs. potential measured under chopped AM1.5G illumination on samples made by varying the indium sputtering power (20, 30, and 40 W): a current density maximum is obtained when using 30 W for indium & 100 W for $InFe_2O_4$ with a deposition time of 90 min.

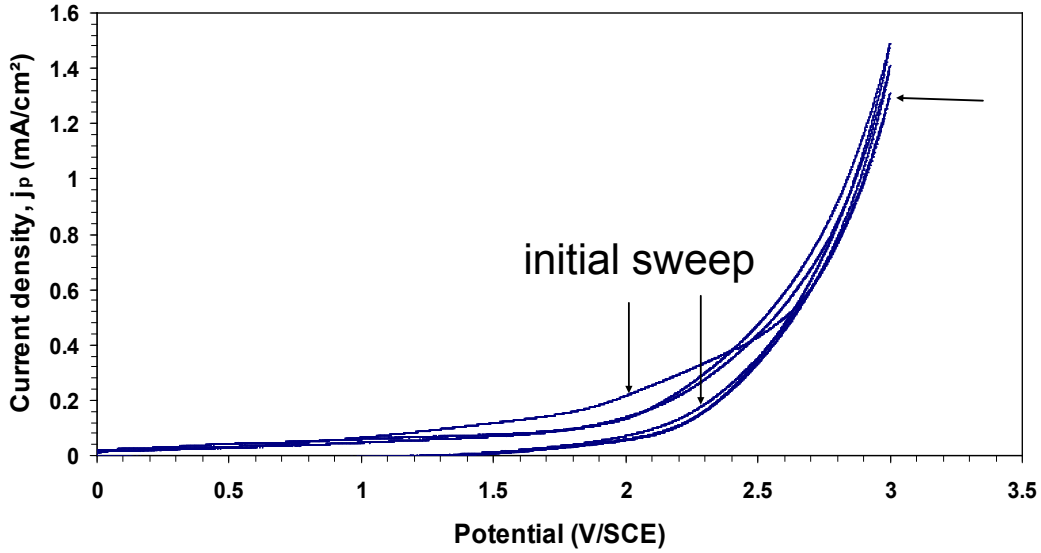
Technical Accomplishments - Task 1 & 3

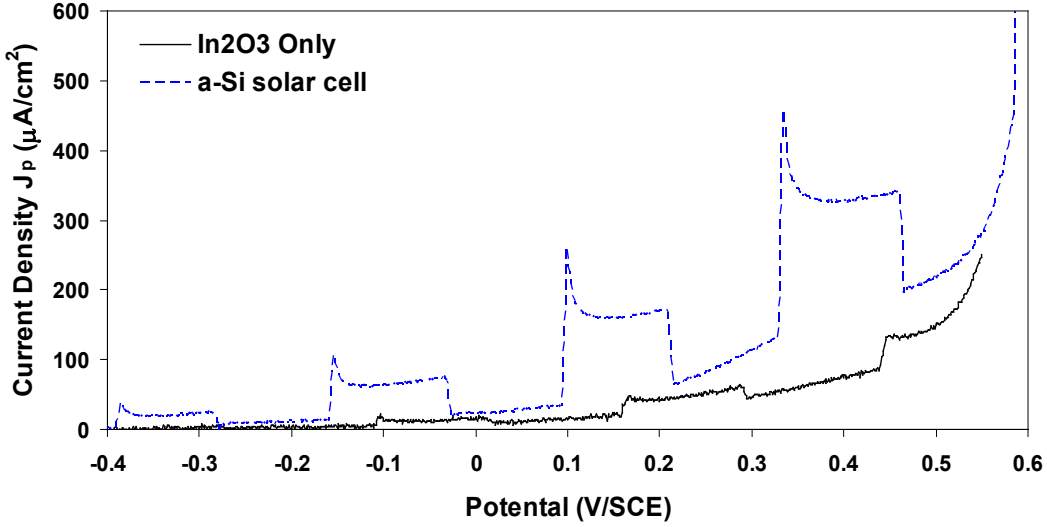
- AFM images for a coating deposited onto a-Si solar cells using 100 W for $InFe_2O_4$ and (a) 20 W for indium (b) 30 W for indium, and (c) 40 W for indium for a total deposition time of 90 min. For all three figures, the scale on x and y-axis are 5000 nm and on the z-axis, the scale is 150 nm.



(a) (b) (c)

Technical Accomplishments - Task 1 & 3





Stability plots for photocurrent density vs. potential measured under chopped AM1.5G illumination were run from -1 V to +3 V for 3 cycles: the sample was fabricated by using 30 W for indium and 100 W for $InFe_2O_4$ deposition with a deposition time of 90 min.

After the initial sweep the J-V curve stabilizes. The initial sweep (indicated with arrows) has the largest redox area corresponding to removal of particles from the surface of the oxide coating.

Photocurrent density vs. potential measured under chopped AM1.5G illumination on sample made at 30 W indium and with 90 min total deposition time and on an a-Si single junction solar cell.

Technical Accomplishments - Task 4

- 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

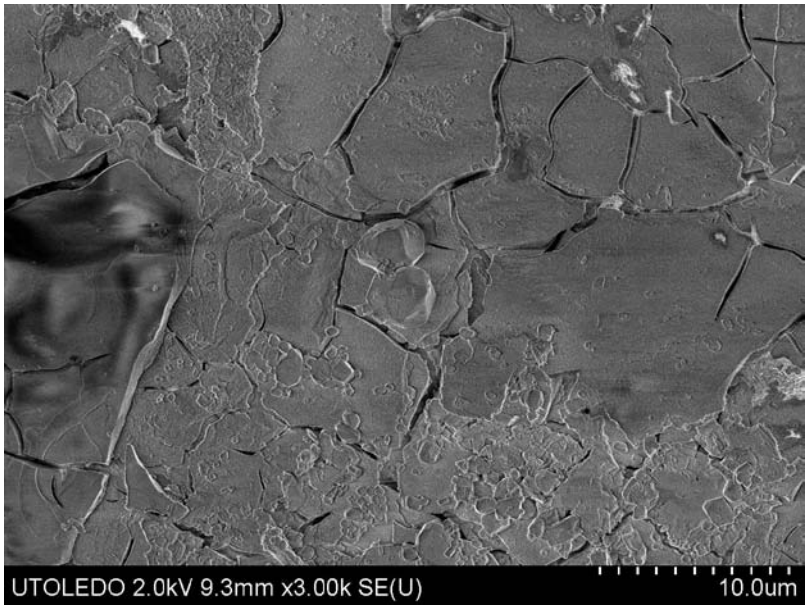
Zinc Chloride (5% $ZnCl_2$)
Copper Sulfate (5% $CuSO_4$)
Zinc Nitrate (5% $Zn(NO_3)_2$)

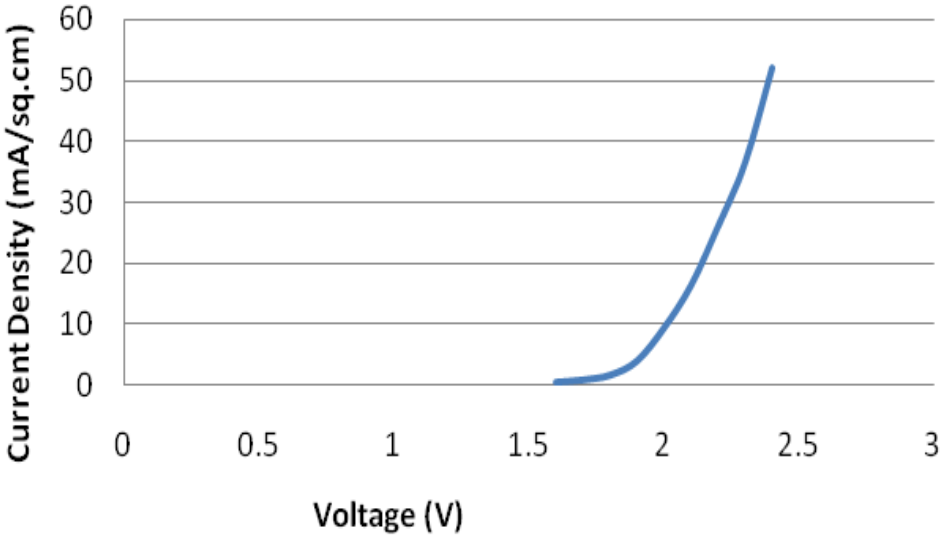
3 precursor salts were tested for their usefulness in obtaining the required micro-porosity for the catalytic Ni electrode; a precursor salt is added to the Ni-electrolyte and the material is embedded into the Ni-deposit during electrolysis; leaching of the electrode after Ni-deposition removes the precursor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

Note: All materials are tested as cathodes and anodes; the data for porous Ni-cathodes are shown.

Technical Accomplishments - Task 4

Zinc Chloride added to Nickel plating bath

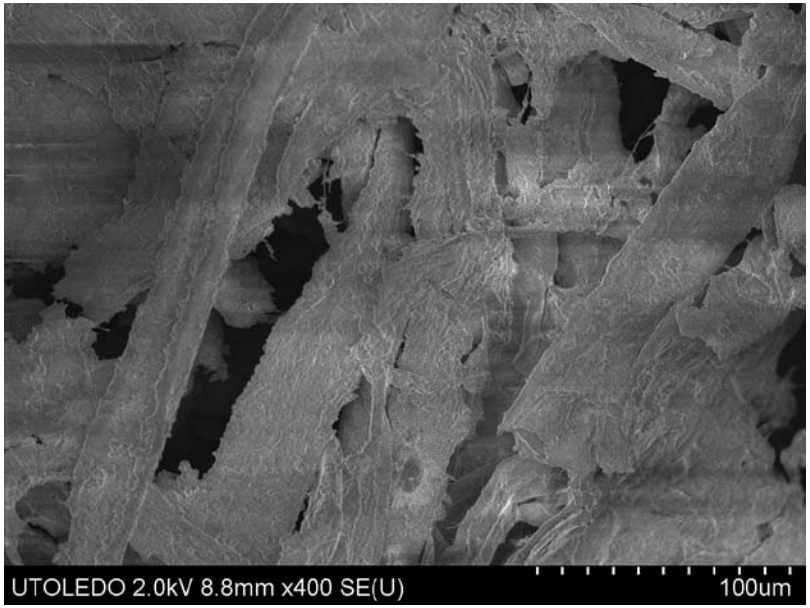


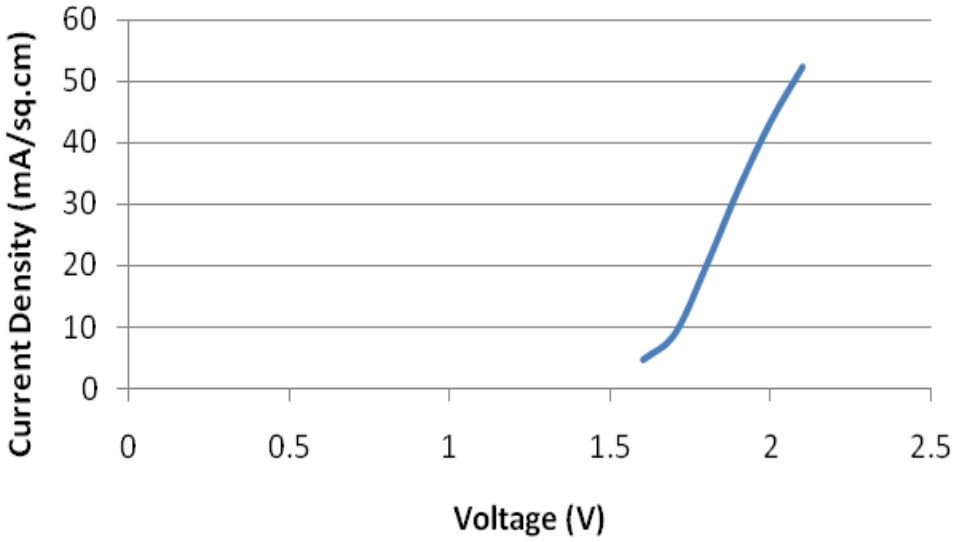


Voltage (V)	Current @ electrode spacing 1 cm	Current density (mA/cm^2)	Current @ electrode spacing 2 cm	Current density (mA/cm^2)	Current @ electrode spacing 3 cm	Current density (mA/cm^2)
1.6	0.01	0.388	0.01	0.388	0	0.000
1.7	0.02	0.775	0.02	0.775	0.01	0.388
1.8	0.04	1.550	0.05	1.938	0.03	1.163
1.9	0.10	3.875	0.09	3.488	0.07	2.713
2.0	0.24	9.300	0.18	6.975	0.15	5.813
2.1	0.42	16.275	0.31	12.013	0.29	11.238
2.2	0.67	25.963	0.53	20.538	0.52	20.150
2.3	0.94	36.425	0.85	32.938	0.80	31.000
2.4	1.34	51.925	1.24	48.050	1.12	43.400

Technical Accomplishments - Task 4

Copper Sulfate added to Nickel plating bath

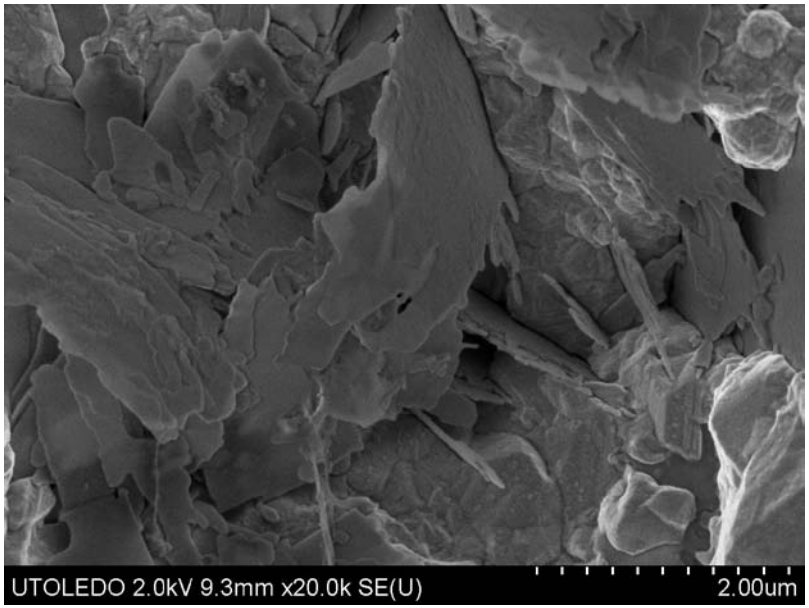


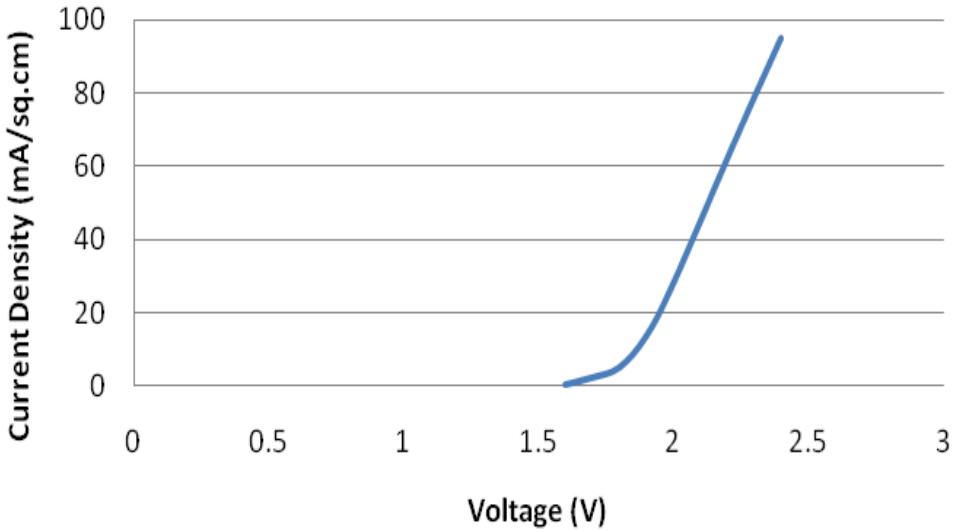


Voltage (V)	Current @ electrode spacing **1 cm**	Current density (mA/cm^2)	Current @ electrode spacing **2 cm**	Current density (mA/cm^2)	Current @ electrode spacing **3 cm**	Current density (mA/cm^2)
1.6	0.01	0.388	0.01	0.388	0.01	0.388
1.7	0.03	1.163	0.03	1.163	0.02	0.775
1.8	0.09	3.488	0.07	2.713	0.04	1.550
1.9	0.22	8.525	0.13	5.038	0.11	4.263
2.0	0.41	15.888	0.80	31.000	0.29	11.238
2.1	0.63	24.413	0.51	19.763	0.50	19.375
2.2	0.95	36.813	0.79	30.613	0.79	30.613
2.3	1.26	48.825	1.18	45.725	1.09	42.238
2.4	1.70	65.875	1.61	62.388	1.40	54.250

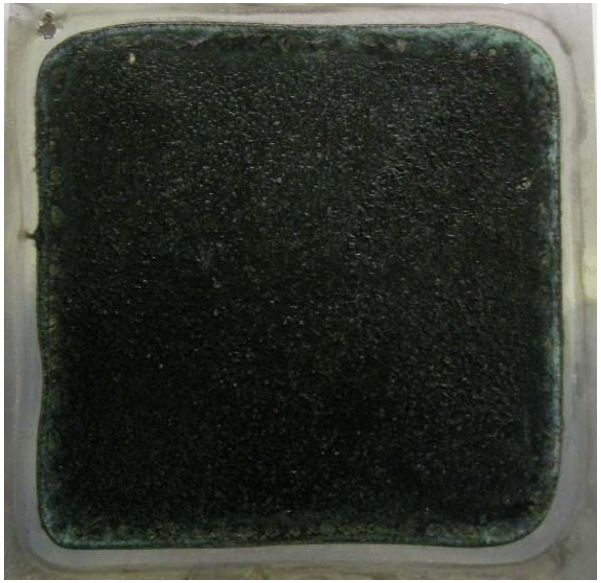
Technical Accomplishments - Task 4

Zinc Nitrate added to the Nickel plating bath



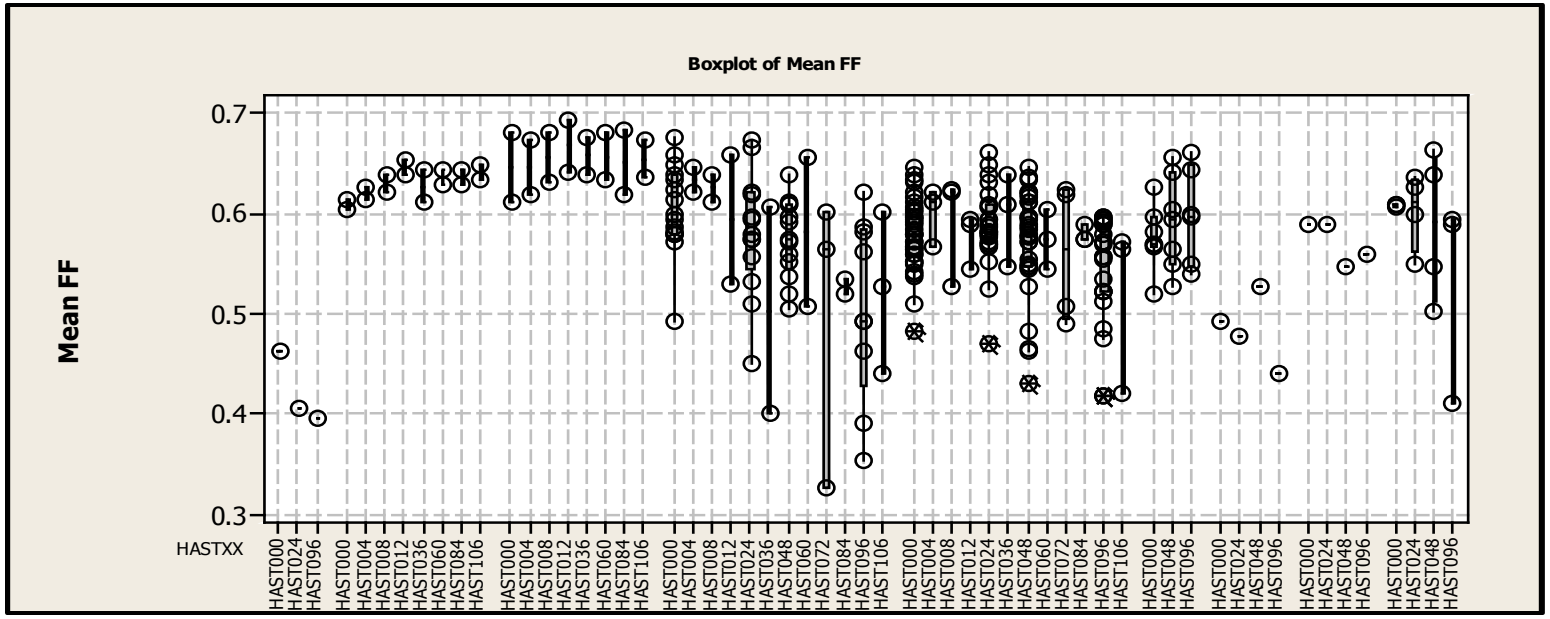


Voltage (V)	Current @ electrode spacing **1 cm**	Current density (mA/cm^2)	Current @ electrode spacing **2 cm**	Current density (mA/cm^2)	Current @ electrode spacing **3 cm**	Current density (mA/cm^2)
1.6	0.01	0.388	0.01	0.388	0.01	0.388
1.7	0.06	2.325	0.08	3.100	0.02	0.775
1.8	0.13	5.038	0.17	6.588	0.11	4.263
1.9	0.35	13.563	0.28	10.850	0.26	10.075
2.0	0.72	27.900	0.39	15.113	0.38	14.725
2.1	1.51	58.513	0.58	22.475	0.53	20.538
2.2	1.60	62.000	0.94	36.425	0.86	33.325
2.3	2.03	78.663	1.51	58.513	1.16	44.950
2.4	2.45	94.938	2.11	81.763	1.45	56.188



Technical Accomplishments - Task 5

- Identified reliability improvements of back-reflector used in PEC electrodes;
- Thin film Si-based PEC cells employ preferentially back reflectors for re-directing unabsorbed incident light back through the semiconductor layer enhancing the solar-to-hydrogen conversion efficiency of the device. A study was conducted addressing the long-term reliability of the back-reflector: Tests conducted in a high humidity environment were used for evaluating the device stability. The graph displays device Fill Factor (FF) after various hours of Highly Accelerated Stress Test (HAST) exposure. The experimental variable in this study is the composition of the back-reflector the tf-Si material is deposited onto. These results indicate that the best stability is obtained for BR1 under hot humid conditions, which refers to an expected improvement in long-term performance of the PEC electrode when using this back-reflector material.

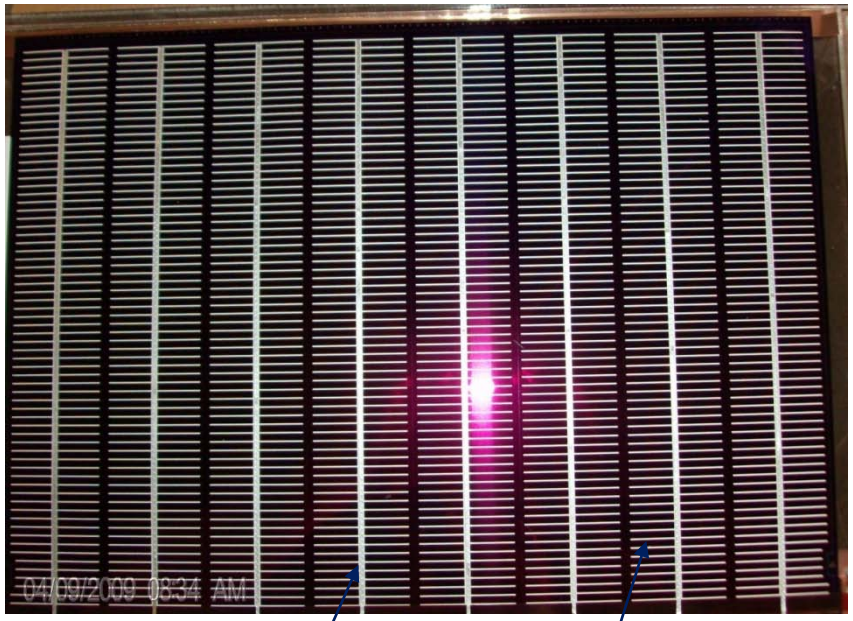


Technical Accomplishments - Task 5

- Developed Grid Isolation for PEC cells;
- The PEC cell design consists of two screen printed patterns directly overlaid on top of each other: a first layer of carbon conductive ink is printed directly onto the transparent conductive oxide surface of the tf-Si PEC cell.

The primary function of this layer is to form a protective barrier preventing silver ion migration into the PEC cell causing long-term reliability issues; the second layer is a printed silver ink pattern deposited directly onto the carbon pattern. A tin clad copper foil is applied along the central spine of the screen printed collector grid. The grid pattern consists of eight “fish bones”; each “fish bone” has a central bus and many small current collection fingers extending to either side along the length of the bus.

Grid for PEC cells

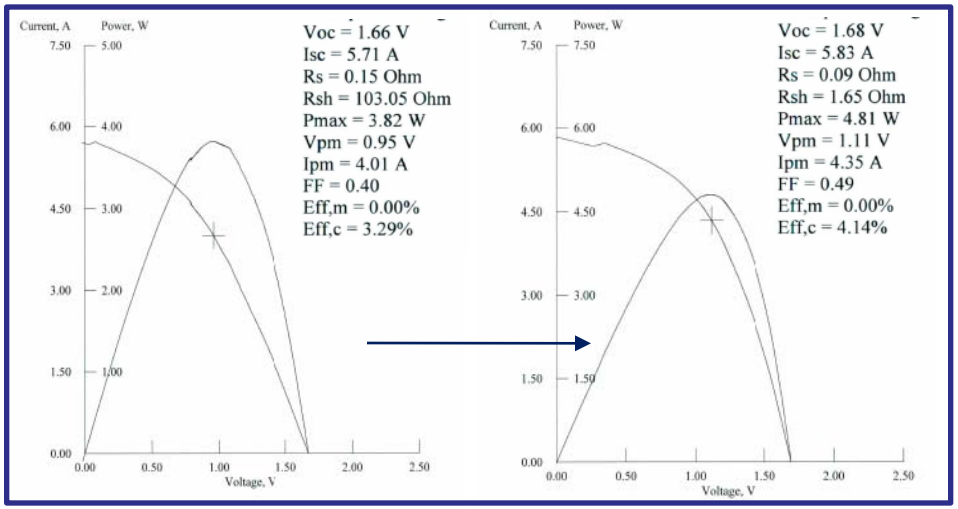


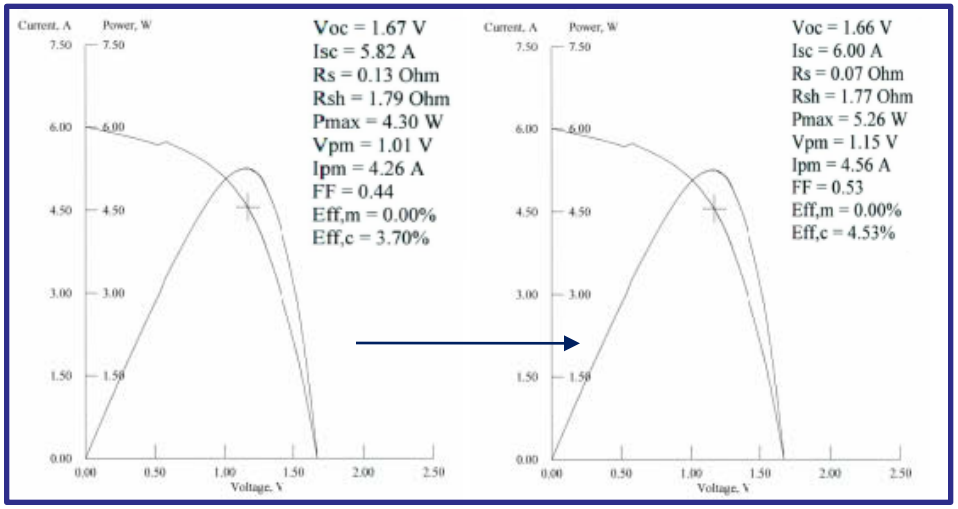
Technical Accomplishments - Task 5

- JV-curves of two tf-Si devices fabricated with a single tin-clad copper foil (a and c) and after the application of two more layers of tin-clad copper foil (b and d).
- The data show that the cell efficiencies of both cells improved significantly with the application of additional layers of tin-clad copper foil. This layer stack of tin-clad copper foil bussing material reduces the series resistance intrinsic in the cell design; thus the efficiency improves leading to improved electrolytic hydrogen production when used in a substrate-type PEC system.

	tin-clad foil	eff. / %	J_{SC} / mA cm^2	V_{OC} / V	FF	R_S / Ω	R_{sh} / Ω
a	single layer	3.29	5.71	1.66	0.40	0.15	103.05
b	triple layer	4.14	5.83	1.68	0.49	0.09	1.65
c	single layer	3.70	5.82	1.67	0.44	0.13	1.79
d	triple layer	4.53	6.00	1.66	0.53	0.07	1.77

a) single foil b) triple foil c) single foil d) triple foil





Collaborations

Partners:

- NREL (Federal):

  NREL is working on improved understanding of PEC process for a-Si based photoelectrodes (in collaboration with Dr. John Turner). (Task 3)

- University of Toledo (Academic):

  UT is developing TCCR coatings, H_2 catalysts for immersion- and substrate-type PEC cells. Developing prototype 1ft × 1ft PEC devices with UT. (Tasks 1,2, and 4)

Technology Transfer:

- NREL:

  NREL is supporting with device measurements on a-Si. a-SiGe, etc. (device characterization, stability testing etc.). (Task 3)

- University of Toledo:

  UT is integral as they finished another DOE H_2 grant that was on basic research transferred to this project. UT is continuing development of the material work they started on the previous grant. (Tasks 1, 2, and 4)

Proposed Future Work

- Task 1: Continue study and optimization of Co_2O_3 & In_2O_3-$InFe_2O_4$ TCCR coatings on solar cell surfaces.
- Task 2: Develop chemical plating for PAS & TCCR coating for immersion-type hybrid PEC cells.
- Task 4: Supported by University of Toledo immersion-type 4” × 4” PEC cells will be developed.
- Task 5: Supported by University of Toledo a 1ft × 1ft substrate-type PEC cell will be developed.
  - Long-term reliability studies and measurements on prototype will be done.
- Task 5: Work on improving the reliability of PEC cells will be continued.

Project Summary

- **Relevance:** Addresses DOE program objectives, specifically high-efficiency and low-cost production of hydrogen using photoelectrochemical methods.
- **Approach:** An immersion-type photoelectrochemical cell where the photo-electrode is immersed in electrolyte and a substrate-type photo-electrochemical cell where the photoelectrode is not in direct contact with electrolyte.
- **Technical Accomplishments and Progress:**
  Demonstrated a 4” × 12” substrate-type PEC cell with 12” × 12” model under development.
  Have secured external funding for development of roll-to-roll unit for a-Si solar cell deposition at Xunlight.
- **Technology Transfer/Collaborations:**
  Active collaboration with UT towards commercialization of research done at MWOE and Xunlight.
- **Proposed Future Research:**
  Will leverage research done at UT to develop substrate-type PEC. Computational components at UT and NREL will be used for improved identification of material classes for sputter deposition of PAS and TCCR layers.

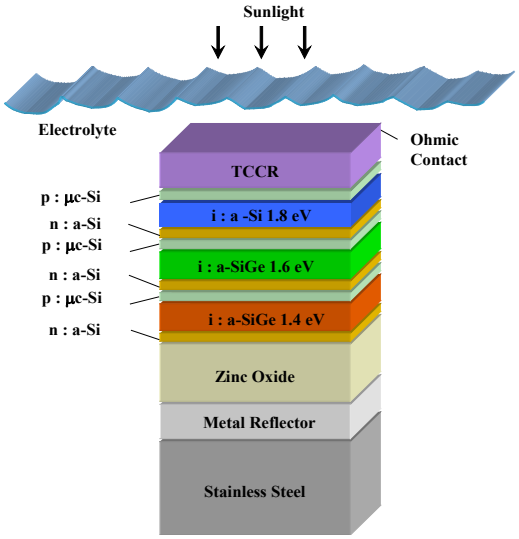
Supplemental Slides

Approaches for PEC electrodes

- Two separate approaches for the development of high-efficiency and stable PEC photoelectrode for the immersion-type PEC cells:

Approach 1A (Task 1):

- Develop triple junction tf-Si photoelectrodes covered with a transparent, conductive, and corrosion resistant (TCCR) protection layer;



Approach 1B (Task 2):

- Develop hybrid, triple junction photo-electrodes with a semi-conductor-electrolyte junction as the top junction and tf-Si alloys as the middle and bottom junctions;