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DOE Hydrogen Program

Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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5:15 PM – Session A

Project ID # PD37

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Office of Energy Efficiency & Renewable Energy
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Overview

Timeline

- Project start date: 10/13/2004
- Project end date: 3/1/2009
- Percent complete: 33%

Budget

- Total project funding
  - DOE share: $2,921,501
  - Contractor share: $760,492
- Funding received in FY05: $100,000
- Funding received in FY06: $200,000
- Funding received in FY07: $400,000, $200,000 for NREL
- Funding for FY08: $500,000

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

- University of Toledo
  - Dr. Xunming Deng
- National Renewable Energy Lab.
  - Dr. John Turner

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Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film-Si based photoelectrodes.
- To develop and demonstrate, at the end of the 3-year program, tf-Si based PEC photoelectrodes and device designs with the potential to achieve systems with 10% solar-to-hydrogen efficiency with a durability of 5,000 hours by 2018.

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Milestones

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 at least 3 mA/cm2 photocurrent.***
- ***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 at least 3 mA/cm2 photocurrent.***

Year 2:

- ***Develop TCCR material with a stability up to 700 hours. Second round of materials to be produced at 300°C or lower with 85% or greater transparency and at least 5 mA/cm2 photocurrent.***
- ***Develop high-quality PAS material with a stability up to 700 hours. Second round of materials to be produced at 300°C or lower and at least 5 mA/cm2 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 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 ≥5 mA/cm2 photocurrent (TCCR material); ≥700 hours of stability, capable of being fabricated at ≤300°C, and ≥5 mA/cm2 photocurrent (TCCR material).***

Year 3:

- ***Develop TCCR material with stability up to 1,000 hours. Second round of materials to be produced at 250°C or lower with 90% or greater transparency and at least 8 mA/cm2 photocurrent.***
- ***Develop high-qualify PAS material with stability up to 1,000 hours. Second round of materials to be produced at 250°C or lower and at least 8 mA/cm2 photocurrent.***
- ***Complete techno-economic analysis and energy analysis for the PEC systems for hydrogen production.***

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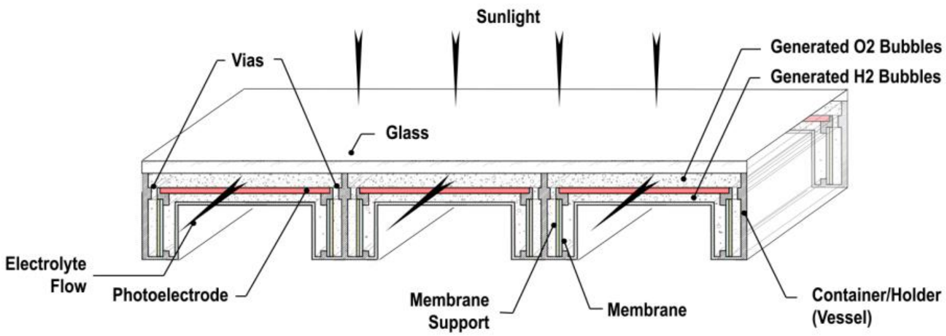
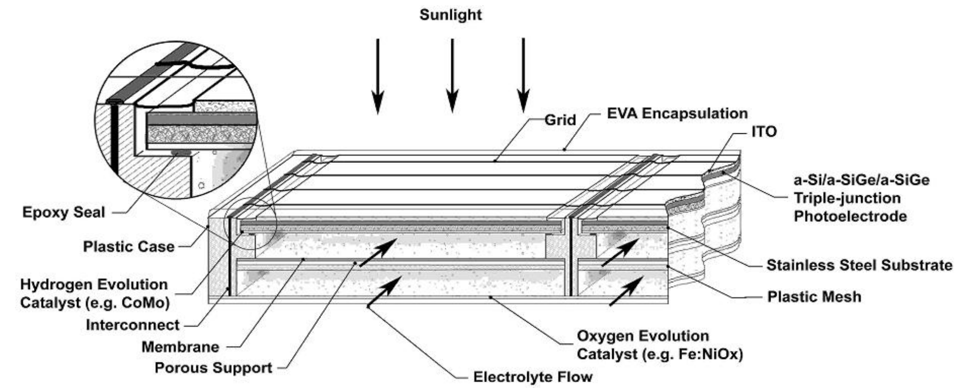
Approach

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

An immersion-type PEC cells



A substrate-type PEC cell



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Research Tasks

- Task 1: Transparent, conducting and corrosion resistant coating for triple-junction tf-Si based photoelectrode [Phase 1: 100%; Total: 33%]
- Task 2: Hybrid multijunction PEC electrode having semiconductor-electrolyte junction [Phase 1: 100%; Total: 33%]
- Task 3: Understanding and characterization of photoelectrochemistry [Phase 1: 100%; Total: 33%]
- Task 4: Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems [Phase 1: 100%; Total: 33%]
- Task 5: Development of device designs for large-area, substrate-type PEC panels [Phase 1: 100%; Total: 33%]

Approaches for PEC electrodes

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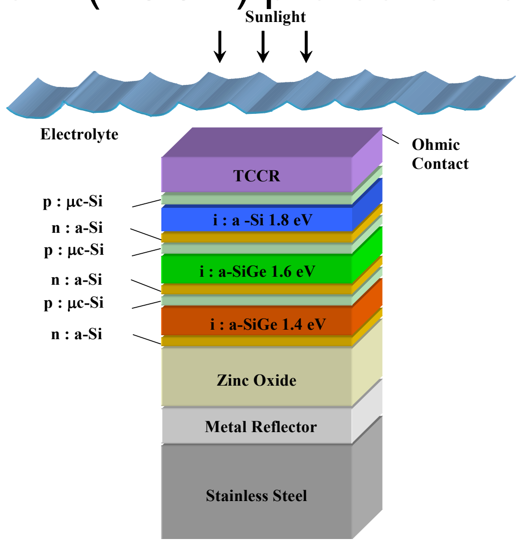
Two separate approaches for the development of high-efficiency and stable PEC photoelectrode for the immersion-type PEC cells:

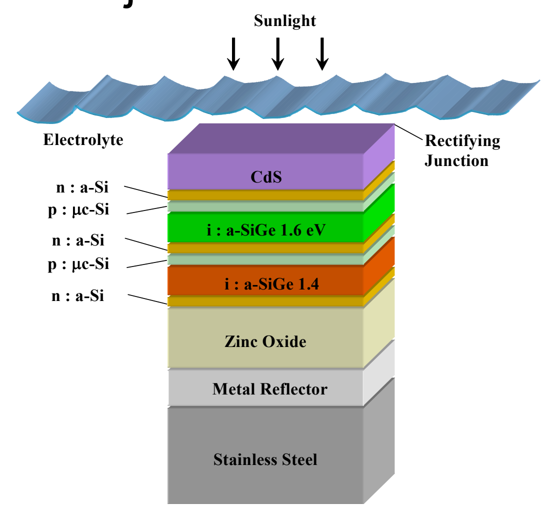
Approach 1A (Task 1):

- 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 photoelectrodes with a semiconductor-electrolyte junction as the top junction and tf-Si alloys as the middle and bottom junctions



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Major Activities under Task 1 and 2

- Fabrication of triple-junction a-Si/a-SiGe/a-SiGe solar cells (Photoelectrodes)
- Fabrication of triple-junction a-Si/a-SiGe/nc-Si solar cells (Photoelectrodes)
- Construction and operation of a 3 ft × 3 ft chamber for fabrication of thin film silicon solar cells on stainless steel substrate
- Deposition of transparent, conducting and corrosion-resistant coating using sputtering
- Optimization of a sputter system with four linear targets (4”x15”), capable of making TCCR films on 1ft × 4ft substrates.

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Large area tf-Si solar cell are readily available for immersion-type PECs

1ft x 3ft a-Si Photoelectrodes from new PECVD system

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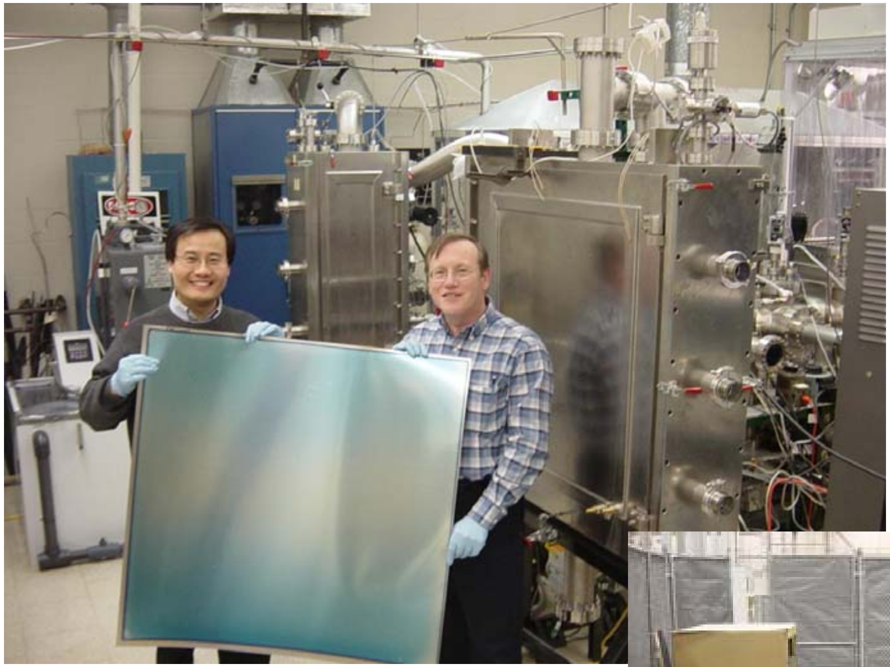
tf-Si Deposition Chambers

A second new PECVD system, capable of making 3 ft x 3ft photoelectrodes have been designed and constructed. Amorphous Si photoelectrodes (solar cells) have been fabricated in this new system.



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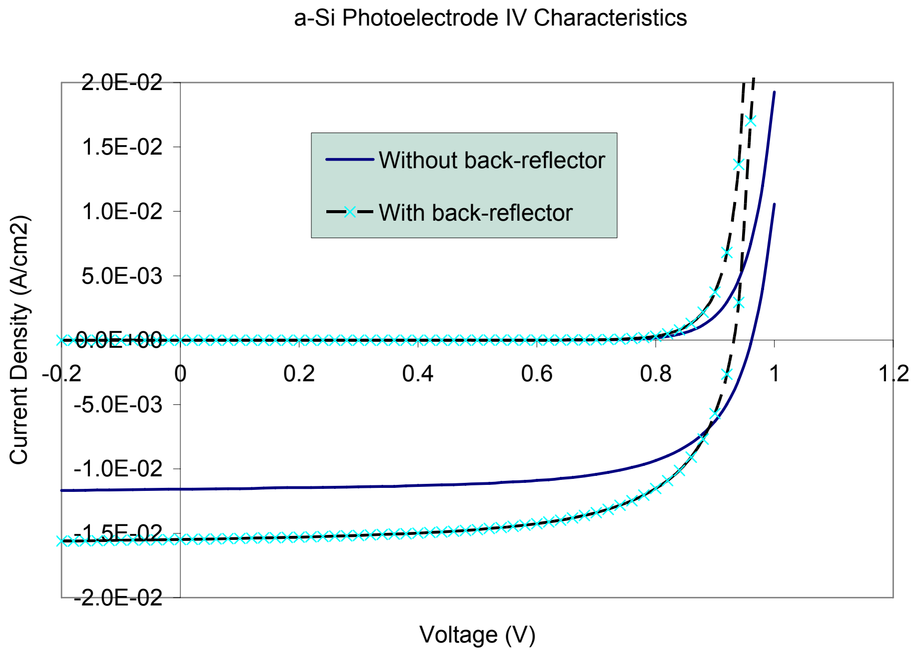
Large area a-Si/nc-Si tandem-junction solar cell



1' x 3' single junction amorphous silicon based photo cells were fabricated. I-V characteristics of 0.25 cm^2 single-junction amorphous silicon based photo cells taken from these larger samples, measured with AM1.5 illumination. One of the cells incorporates back-reflecting layers. The cells show good photoelectric conversion efficiency and fill factor. Although these cells are single junction, this is an important step towards fabricating multijunction, semiconductor-electrolyte junction photoelectrodes.

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Task 3: Understanding and Characterizing PEC

- Several efforts are on going under this task.
  - NREL team is currently developing improved understanding of PEC process for a-Si based photoelectrodes in collaboration with John Turner.
  - An outdoor solar testing facility has been utilized and used for outdoor testing of PEC panels for long-term stability and output.

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Task 4: Immersion-type PEC cell

- Focus on Task 4 is on the construction and optimization of deposition system that will be used for making large-area photoelectrode for immersion-type PEC cells
- Designed and constructed a system capable of making 3ft × 3ft photoelectrodes
- Improved deposition uniformity over large area
- Focused on electrodeposited ZnO that will be used for BR optimization
- Continued the design and optimization of immersion-type PEC cells

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Electrodeposited ZnO Films

- **Film quality improvement of electrodeposited ZnO**
  - One of the main drawbacks with tank electrodeposition of ZnO is the non-uniform deposition. For optoelectronic applications such as photovoltaic back reflectors and TCCRs a higher film quality is expected. This problem has been addressed by two different approaches.
- **Modifications to Bath**
  - The objective of this approach was to control the ionic reactions. Two main processes that were run,
    - Increase ionic conductivity by adding KCl
      - No significant improvement
    - Change pH by using HNO_3 or KOH
      - pH 5.4 to 5.7 showed improvement in uniformity but the solution becomes unstable
  - X-ray diffraction measurements verify that for all these bath conditions we get uncontaminated ZnO films.

XRD spectra for various bath conditions to produce electrodeposited ZnO films

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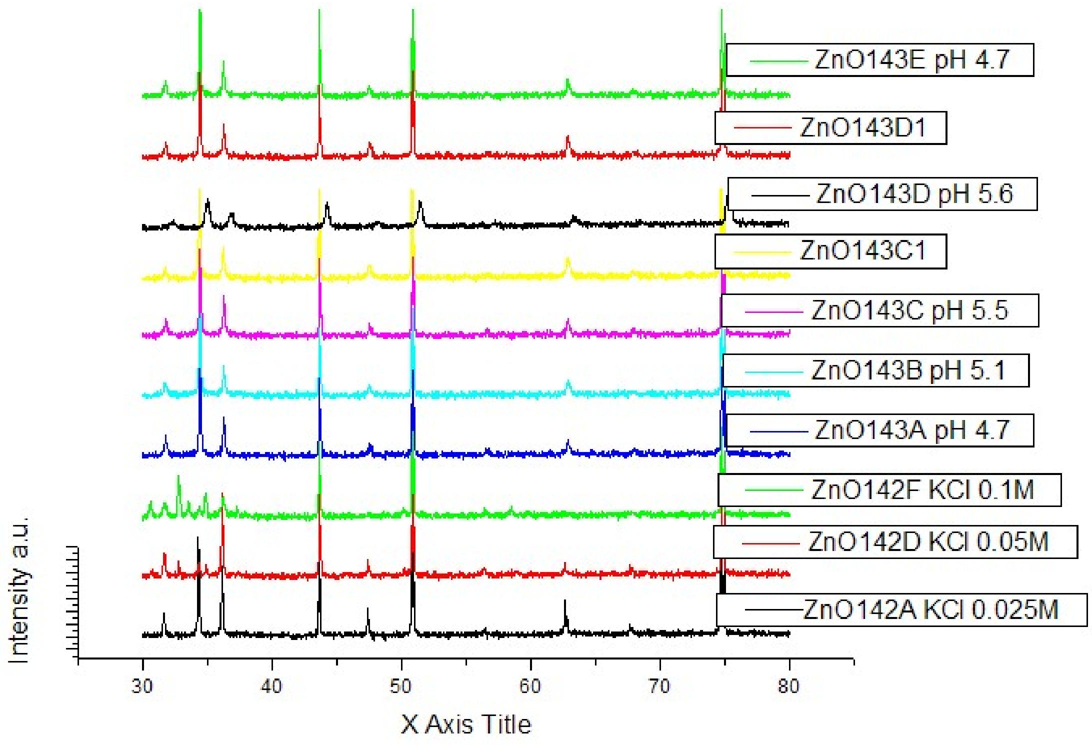
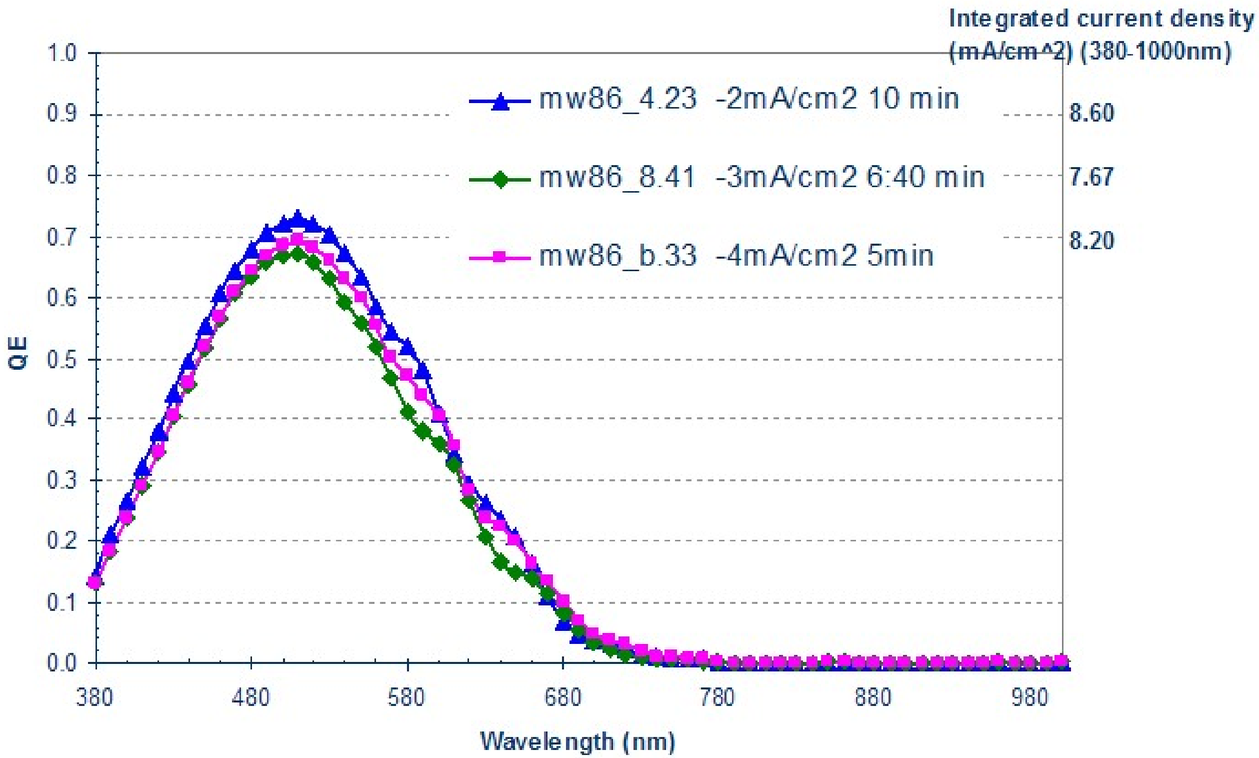


The advantages of this new method:

- Uniform plating
- Edge effect is minimum
- Uniform temperature distribution
- Possibility to be done at higher temperatures
    - $Zn(OH)_2$ to ZnO is favorable at higher temperatures
- Need less solution to run experimental run

Quantum Efficiency with Electro-deposited ZnO used in the Back Reflector



- Quantum efficiency plots for three solar cells with ZnO electrodeposited at 2, 3, and 4 mA/cm^2

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Task 5: Fabrication of Substrate-Type PEC cells

- Focus under this task has been on establishing facilities to make substrate-type PEC cells in large area.
- Improved screen-printing techniques.
- Designed and built a fabrication facility for making substrate-type PEC electrodes.
- Designed, developed and constructed a photo-assisted electrochemical shunt passivation system to remove shunts and shorts in the photoelectrodes.
- Long-term testing of substrate-type modules.

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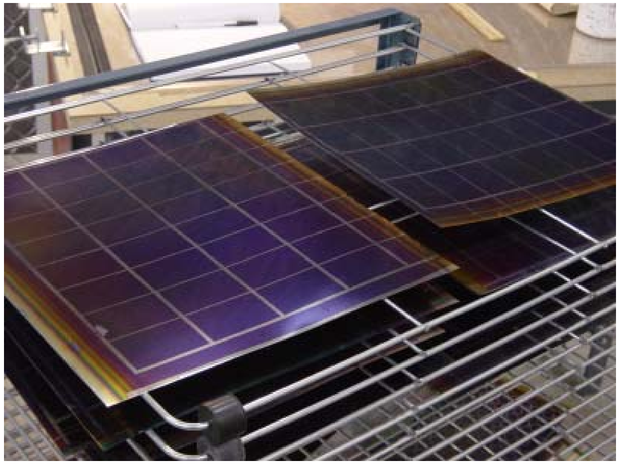
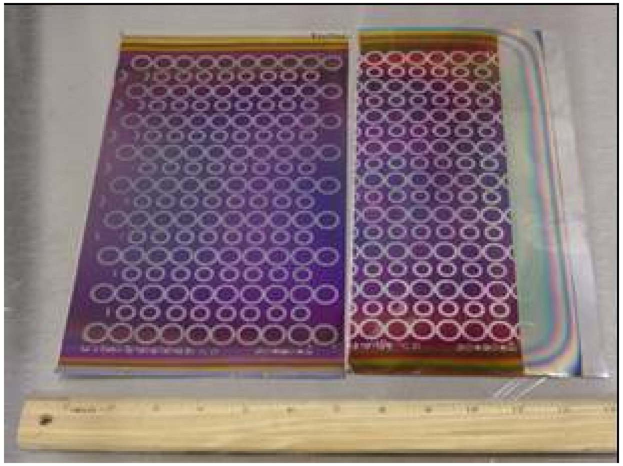
Improved Equipment for Screen-Printing Techniques



Grids are 1 mil thickness for adequate conductivity



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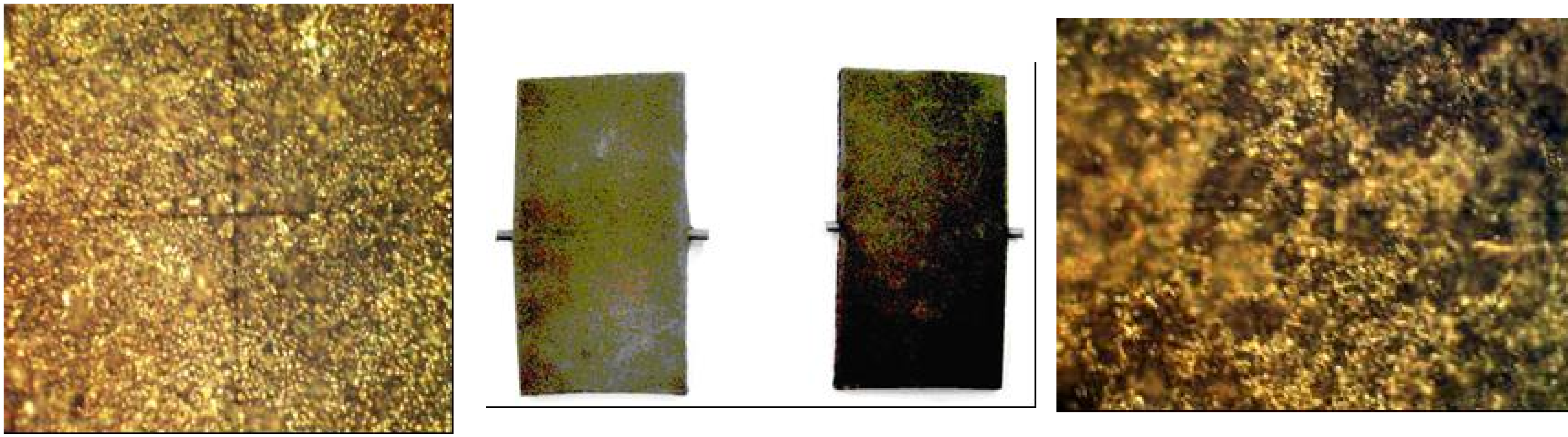
Investigation into cheaper electrocatalyst materials



- The sintered nickel-cobalt oxide catalyst. The left and right side photos are 20× magnification of the porous structure of the catalytic surface.

- Fabrication of 12’’ × 12’’ substrate-type solar cells is in progress. Optimization of triple junction amorphous silicon cell for use in the substrate PEC cell is also under progress.

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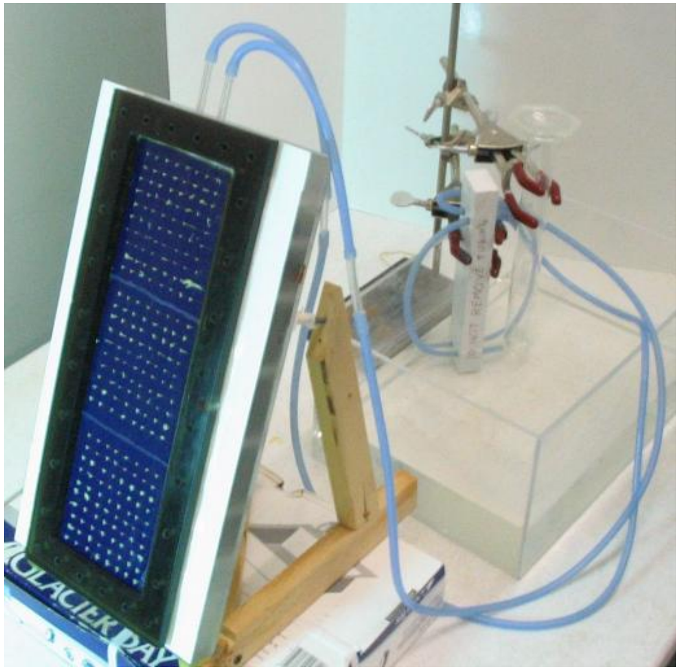
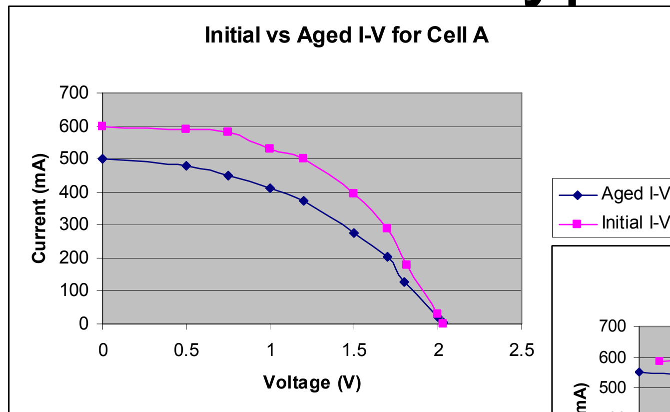
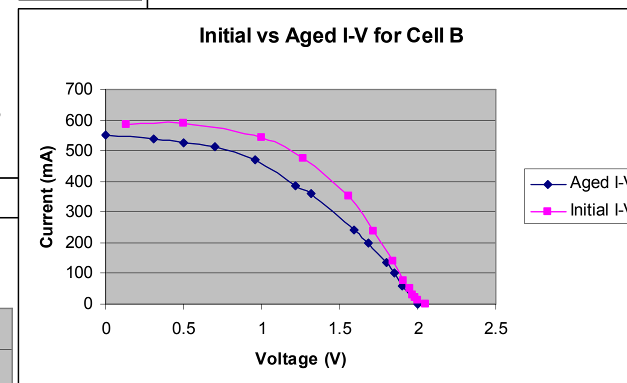
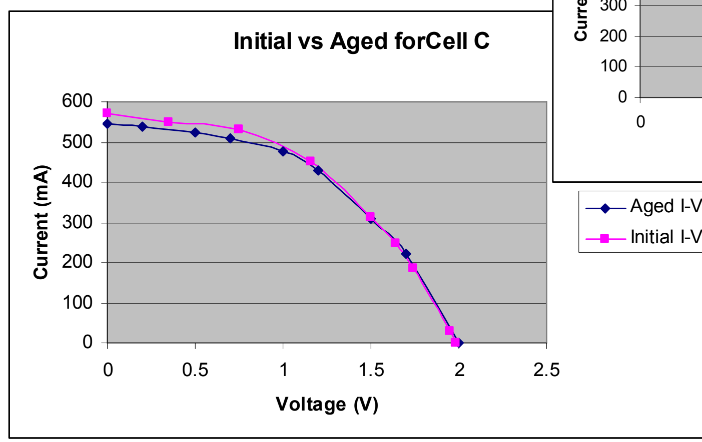
Degradation Testing of Substrate-type Cell









Degradation in photoelectrochemical cell was observed after 140 days. The measurements were made at 88 to 95 mW/cm^2 solar radiation.

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Future Work

- Continued study into optimization of present oxide materials – Identify classes of materials most promising to phase 2 goals.
  - Material classes are focusing on iron oxide and titanium dioxide material classes with various dopants such as antimony and indium for iron oxide and nitrogen and carbon for titanium dioxide.
  - Deposition of oxides under higher power and with metallic targets to improve stability and oxide structure study new materials beyond present set.
- Leveraging our resources on a substrate-type PEC as all the materials required to build one on site are now available – large area solar cell, electrolyzers.
  - Production of final module design (substrate-type PEC) with electroplated nickel on back of stainless steel with triple junction a-Si on front.
- Improvement in voltage and efficiency of large area solar cells.

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Project Summary

- Relevance: Addresses DOE program objectives, specifically high-efficiency and low-cost production of hydrogen using photoelectrochemical methods.
- Approach: An immersion–type photoelectrochemical cells where the photoelectrode is immersed in electrolyte and a substrate-type photoelectrochemical cell where the photoelectrode is not in direct contact with electrolyte.
- Technical Accomplishments and Progress: Demonstrated a 4” × 12” substrate-type PEC 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 integrate computational components at UT and NREL to better identify classes of materials to sputter for PAS and TCCR layers.

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