PDP_05_Gaillard

PHOTOELECTREMICAL HYDROGEN PRODUCTION

Arun Madan
MVSystems, Inc.
May 19, 2009

DE-FC36-07GO17105

Overview

Timeline

- Project start date: 9/1/2007
- Project end date: 8/31/2009
- Percent complete: ~65%

Budget

- Total project funding*
  - DOE share: **$1,358,827**
  - Contractor share: **$339,707**
- Funding received in FY08
- Funding for FY09 (tbd)

** funds cover work reported in posters PDP04, PDP05, and PDP06*

Barriers

- Barriers for photoelectrochemical hydrogen production technologies:

  – Y: Materials Efficiency
  – Z: Materials Durability
  – AB: Bulk Materials Synthesis
  – AC: Device Configuration Designs

Partners

- Collaborations: National Renewable Energy Laboratory (NREL), University of Nevada at Las Vegas (UNLV), University of California at Santa Barbara (UCSB)
- Project lead: MVSystems, Inc.

Overview

poster PDP04:
Progress in the Study of ***Amorphous Silicon Carbide*** as a Photoelectrode in Photoelectrochemical Cells

poster PDP05:
Progress in the Study of ***Tungsten Oxide Compounds*** as Photoelectrodes in Photoelectrochemical Cells

poster PDP06:
Progress in the Study of ***Copper Chalcopyrites*** as Photoelectrodes in Photoelectrochemical Cells

poster PDP05

Progress in the Study of ***Tungsten Oxide Compounds*** as Photoelectrodes in Photoelectrochemical Cells

Nicolas Gaillard
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May 19, 2009

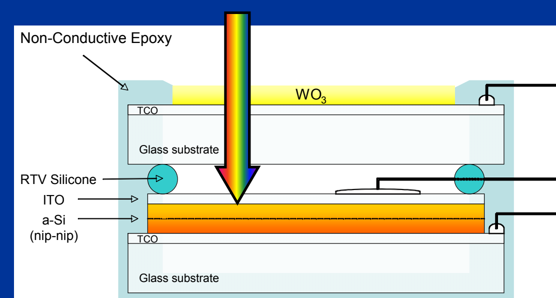
Relevance - Objectives

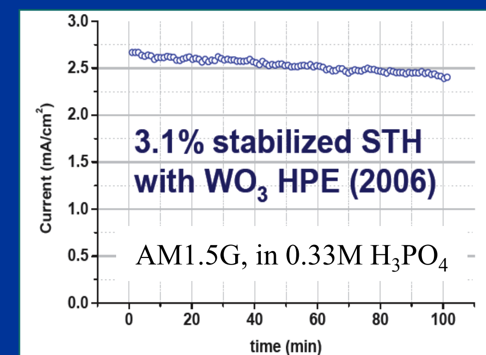
Advantages of tungsten oxide:

1) Good performances demonstrated in several applications
2) Film can be deposited using low-cost processes
3) WO_3 satisfies main criteria for water splitting

WO_3 PEC champion device:

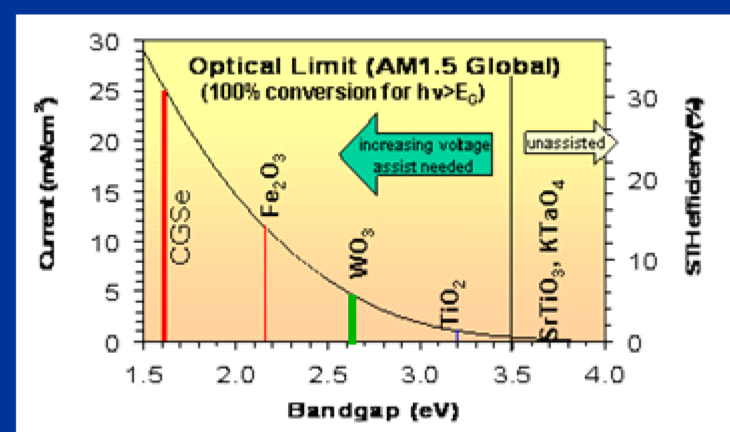
→3.1% STH efficiency in a standalone config. (MVS bottom PV cell).





…but this material suffers from :

1) its bandgap value (2.6 eV) that limits light absorption
2) the position of the valence band (E_V) vs. oxygen half-reaction potential: external bias needed.



Relevance-milestones

Program targets		WO_3 progress status
Year 1: 10/2007----9/2008		
✓ Material Photocurrent ≥ 3 mA/cm²	100% @ 12/2007	**2.8 to 3 mA/cm² demonstrated with pure WO_3-based PEC electrode**
✓ Durability 100 hrs	100% @ 1/2008	**100 hr durability achieved in 0.33M H_3PO_4 solution**
✓ Device STH efficiency ≥ 3.7%	85% @ 12/2007	3.1% achieved with mechanical stack using underlaying PV cell
Year 2: 10/2008----10/2009		
✓ Material Photocurrent ≥ 4 mA/cm²	90% @ 3/2008	**3.6 mA/cm² demonstrated with WO_3-based bilayer PEC electrode**
✓ Durability 200 hrs	50% @ 1/2008	100 hr durability achieved in 0.33M H_3PO_4 solution
✓ Device STH efficiency ≥ 5%	65% @ 3/2008	3.2% expected from current matching of both bilayer PEC electrode and PV cell J-V curve

(Towards the end of Year 2, a GO/NO-GO DECISION evaluation will be performed)

Relevance-barriers

Barrier	Challenges	Strengths
Y. Materials Efficiency	- **The bandgap of 2.6 eV for pure WO_3 limits PEC photocurrent levels to a maximum achievable STH of ~5%.** - The position of the conduction band minimum for pure WO_3 in standard acidic media is low, requiring additional biasing.	- Has "direct-like" bandgap and good carrier transport properties resulting in a high PEC photocurrent collection efficiency. - **Alloying of the material can theoretically lead to a reduction of bandgap** by raising the valence band while potentially increasing the conduction band at the same time, thereby reducing bias requirements.
Z. Materials Durability	The photostability over extended time periods for new tungsten-alloy compositions requires validation.	**Stability of pure tungsten oxide in acidic media is well documented and verified in various combinations of time and operating conditions.**
AB. Bulk Materials Synthesis	**Materials need to be fabricated using low temperature** deposition processes to be compatible with process scalable manufacturing.	**Low temperature deposition (bellow 300C) has been demonstrated** using sputtering techniques.
A.C. Device Configuration Designs	**Optimized tandem/multijunction device** configurations need to be developed to match the photocurrent and photovoltage characteristics of newly-developed tungsten-based compounds.	Thin films in general are compatible with the concept of multijunction devices, such as the hybrid photoelectrode. Sputtering, for example, of PEC top layer is compatible with an underlying solar cell. **STH efficiency of 3.1% demonstrated with underlaying PV cell.**

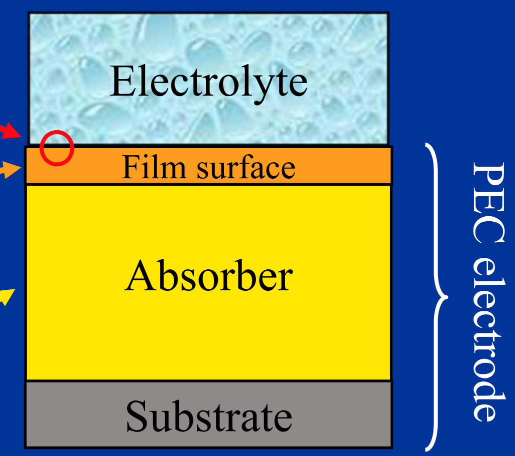
Approach

Improvements can be obtained from every component of the PEC electrode to achieve more than 4 $mA.cm^{-2}$ by 2009 (*)

Interface: **catalyst nano-particle** deposition to enhance charge transfer at the interface.
(under investigation since 2009)

Surface: band-edge position tuning **with bilayer** to reduce external bias
(under investigation since 2008)

Absorber (bulk): bandgap decrease **with ion incorporation** to enhance light absorption
(under investigation since 2006)



(*) Theory predicts a maximum photocurrent of 5 $mA.cm^{-2}$

Approach

THEORY

Effect of ions incorporation on material E_G and band-edges position.

CHARACTERIZATIONS

Photocurrent, Flat-band potential,

OER/HOR, efficiency, morphology,

advanced spectroscopy

SYNTHESIS

Bulk materials, bilayers,

catalyst nano-particles

Progress: Work Performed since 2008 Annual Merit Review and Peer Evaluation Report

- Continuing WO_3 bulk modification using ion incorporation:
  - *- Synthesis of new alloys (UH)*
  - *- Theoretical analysis on band-gap reduction (NREL)*

- Investigations on WO_3-based bilayer concept:
  - *- Fabrication of new devices (UH)*
  - *- Surface electronic properties analysis (UNLV)*
  - *- Crystallographic and structural analysis (NREL)*

- Evaluation of RuO_2 nano-particle deposition for catalytic treatment
  - *- Deposition of thick (1 micron) films (UH)*
  - *- Characterization of RuO_2 film's oxygen evolution rate vs. that of Pt foil (UH)*
  - *- First evaluation of RuO_2 nano-particle onto WO_3 film (UH and UCSB)*

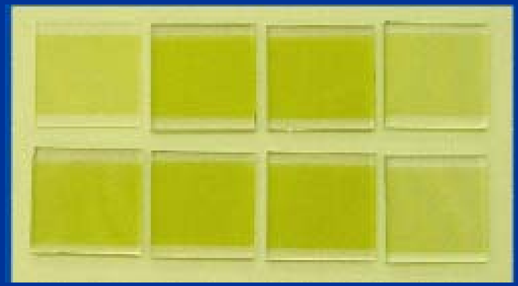
Progress: deposition and performance of WO_3

Perkin-Elmer 2400 three-gun Sputtering system

Reactive sputtering deposition:

- RF mode (13.56 Mhz)
- material target: pure W
- gas: argon (7 sccm) + oxygen (2.2 sccm)
- deposition temperature: 270°C

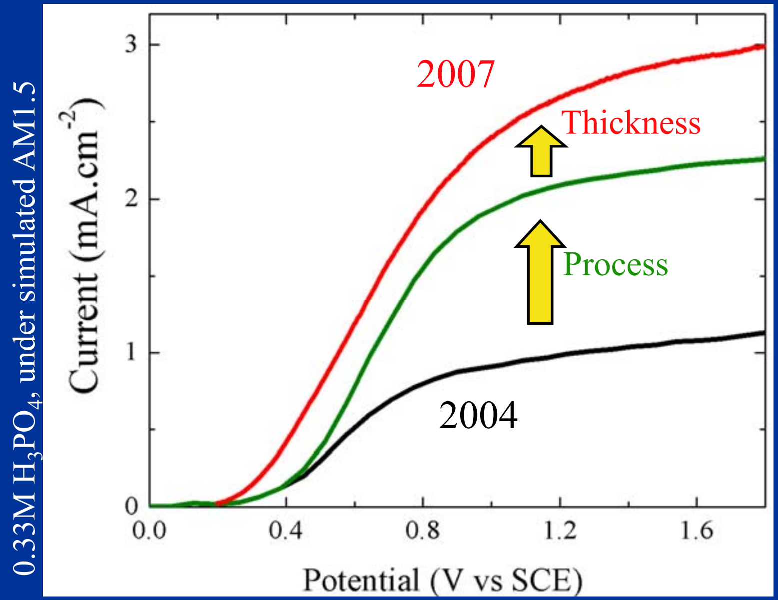
Low temperature process solves barrier AB



Pure WO_3 films

WO_3 E_G (2.6 eV) solves barrier AC

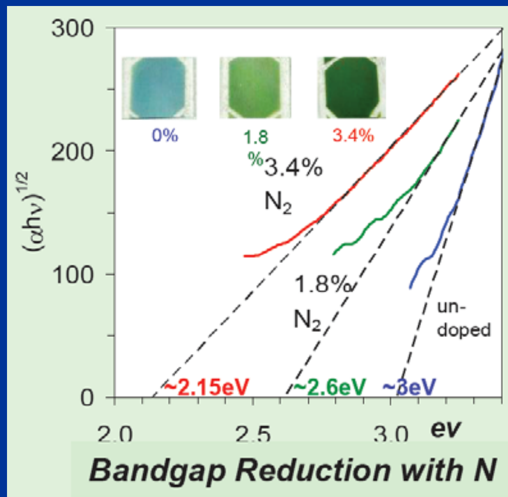
Electrical performances



Continuous improvement since 2004

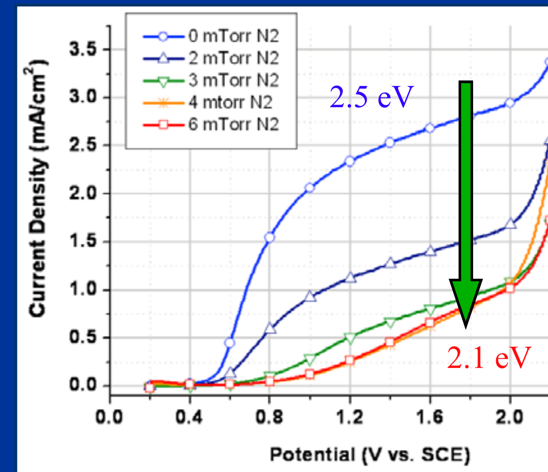
Progress: Absorber E_G modification

- Example: nitrogen incorporation using N_2 gas to reduce WO_3 bandgap (reported in 2008)



Effective band gap reduction

…but

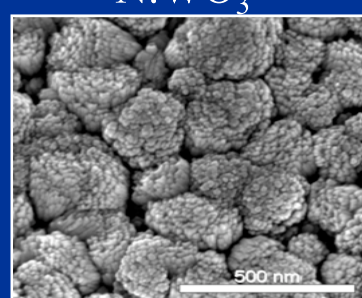


0.33M H_3PO_4 @AM1.5

Diminution of electrical performances

Pure WO_3

$N:WO_3$



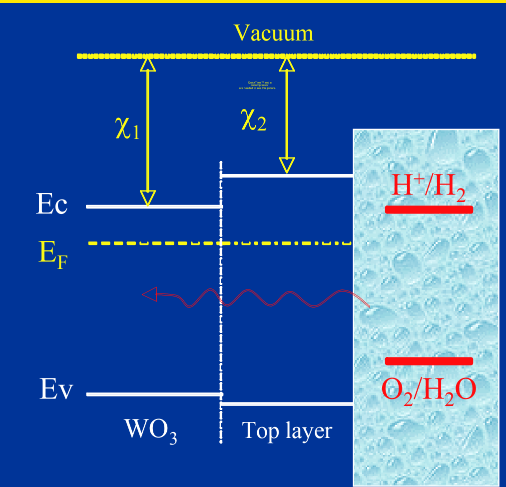
→ Ion incorporation strongly alters grain crystallographic properties & film performances

New avenue required to improve WO_3-based PEC electrode

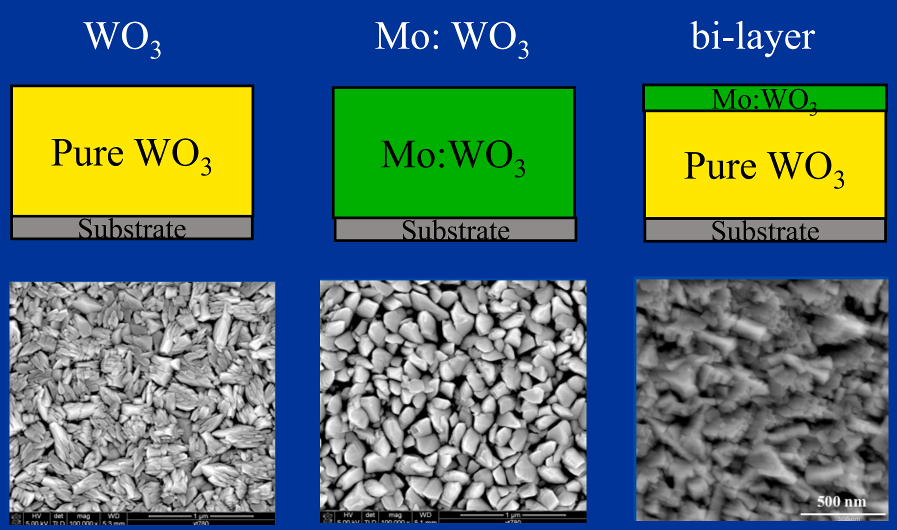
Addressing barrier Y

Progress: WO_3-based bilayer PEC electrode

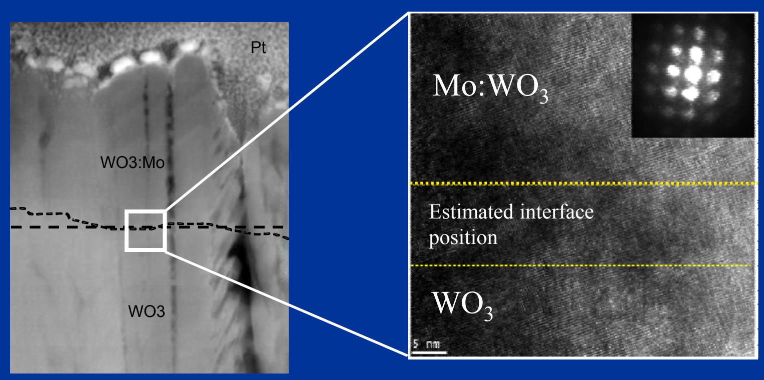
→Ion incorporation in WO_3 surface can shift both E_C & E_V, while keeping pure WO_3 optical and conduction properties



- Example: molybdenum incorporation into WO_3 surface



Top view of film morphology (scanning electron microscopy)



Scanning electron microscopy

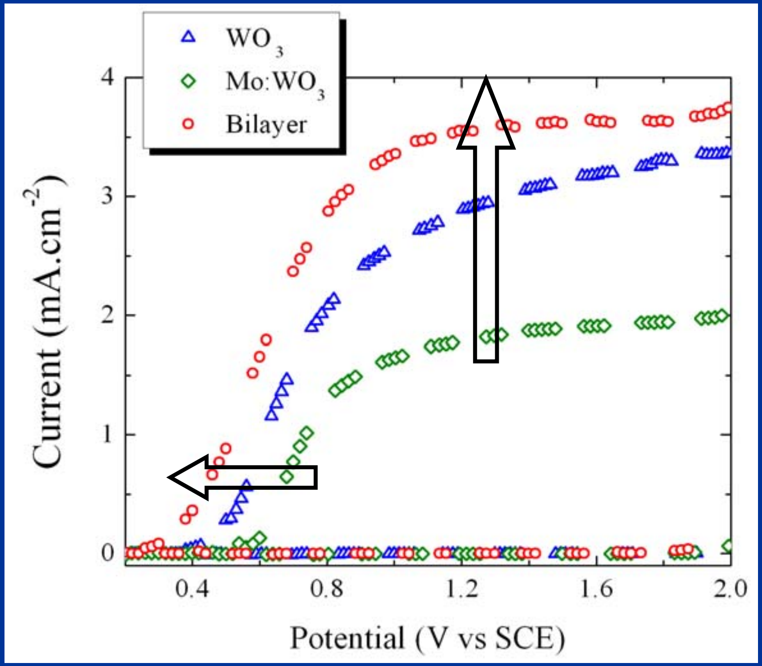
Transmission electron microscopy

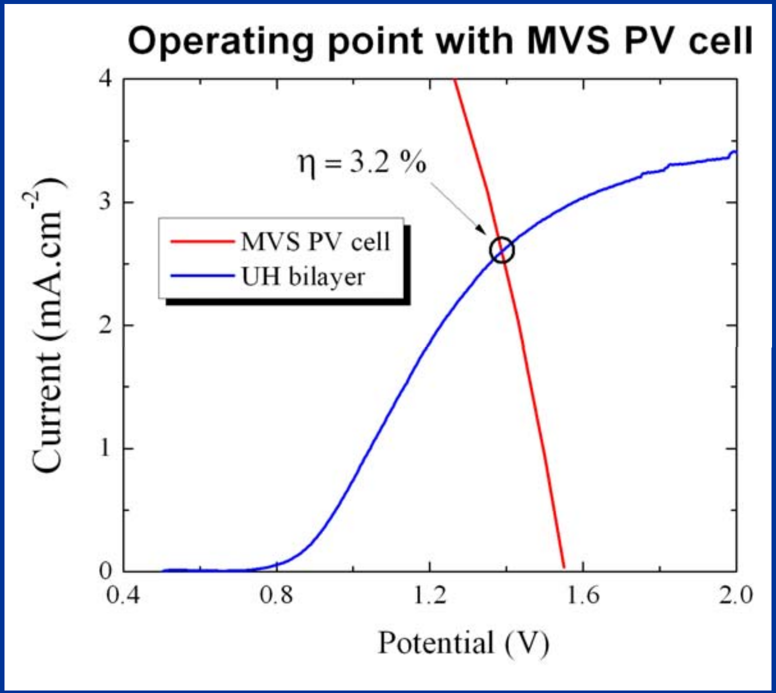
Top layer follows bottom film pattern: WO_3 bottom layer improve Mo:WO3 cristallinity

Addressing barrier Y

Progress: WO_3-based bilayer PEC electrode

- Example: molybdenum incorporation into WO_3 surface





Current matching simulation using both PEC & PV J-V curves

1) Bilayer vs. Mo:WO_3: +100% photocurrent, from 1.8 $mA.cm^{-2}$ to 3.6 $mA.cm^{-2}$

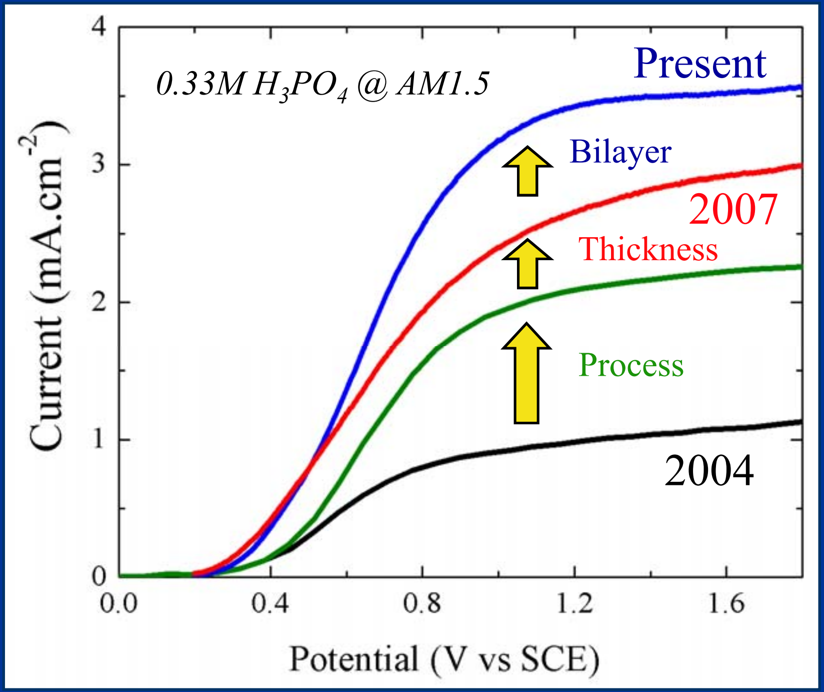
2) Bilayer vs. WO_3 : +15% photocurrent, From 3 $mA.cm^{-2}$ to 3.6 $mA.cm^{-2}$ (new champion device, 2008)

3.2% STH efficiency can be achieved with WO_3-based bilayer PEC electrodes

Addressing barrier Y

Progress: WO_3-based bilayer PEC electrode

- Example: molybdenum incorporation into WO_3 surface



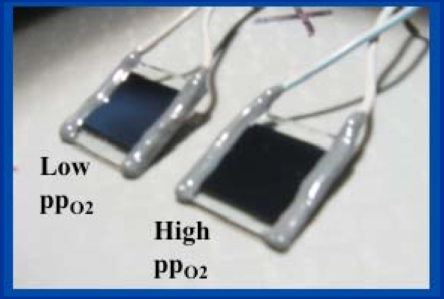
Continuing WO_3-based PEC electrodes performances improvement with bilayer

Addressing barrier Y

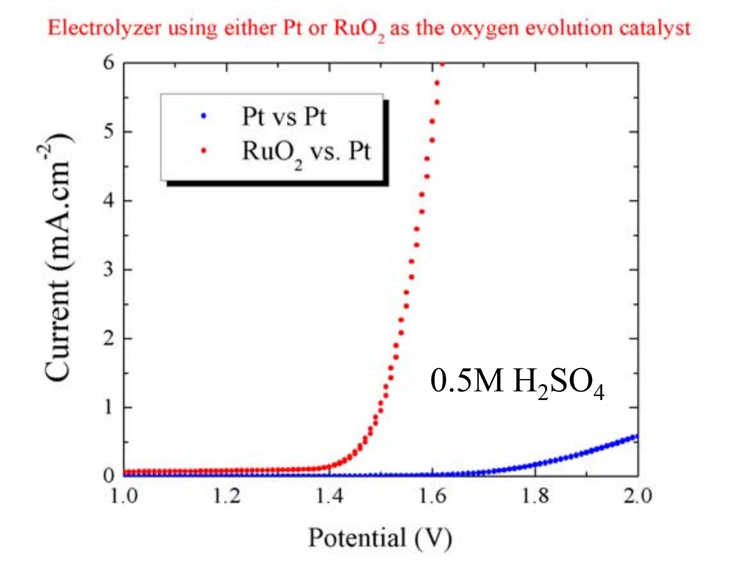
Progress: Catalyst nano-particle deposition

Step 1: thick film deposition

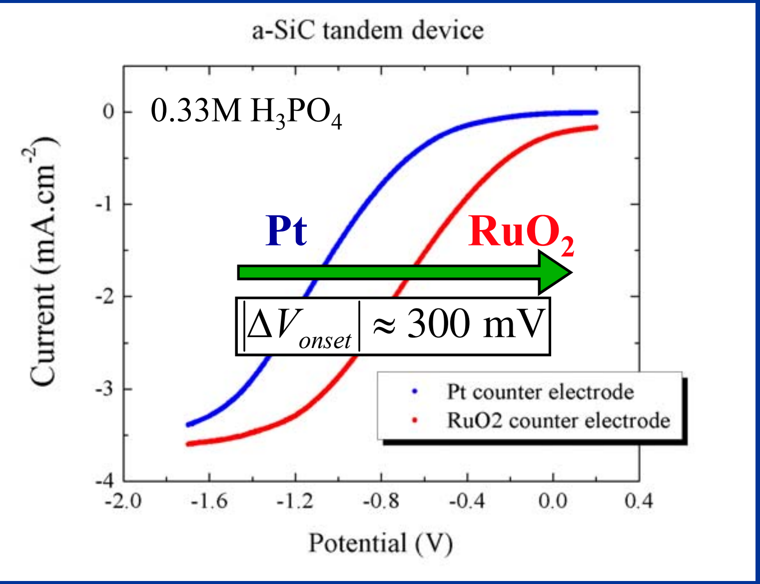
- Pure Ru target @ 200W
- Substrate (glass) temperature : 250^{o}C
- Various oxygen partial pressures



→ **Electrical characterization: electrolyzer**



→ **Electrical characterization: tandem a-SiC**

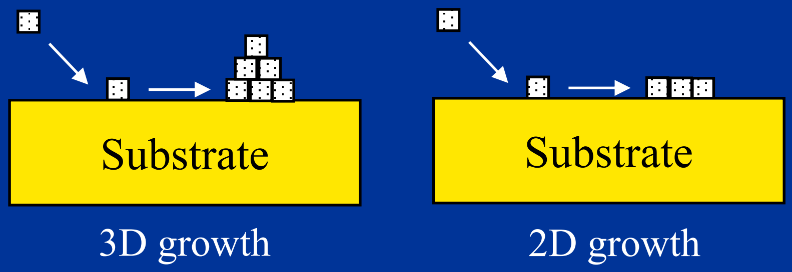


RuO_2 is a far better counter electrode for oxygen production than Pt

Addressing barrier AC

Progress: Catalyst nano-particle deposition

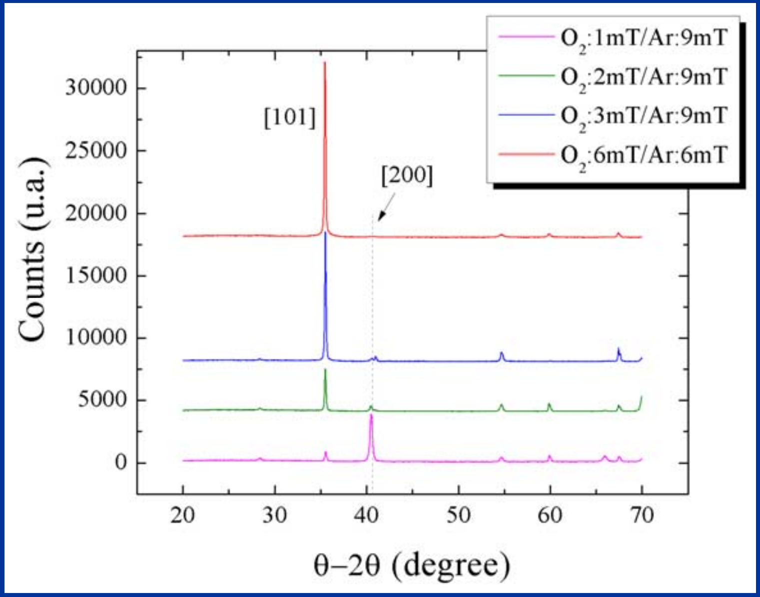
Step 2: catalyst nano-particle deposition



Particle formation requires 3D film growth

→ **Effect on oxygen partial pressure (p.p.) on bulk RuO_2 crystallographic properties**

XRD patterns of thick RuO_2 films



Low O_2 p.p.: grains oriented along [200], **i.e. 2D**

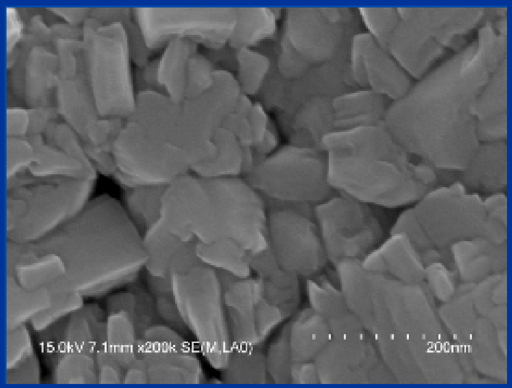
High O_2 p.p.: grains oriented along [101], **i. e. 3D**

Addressing barrier Y

Progress: Catalyst nano-particle deposition

Step 3: catalyst nano-particle characterization

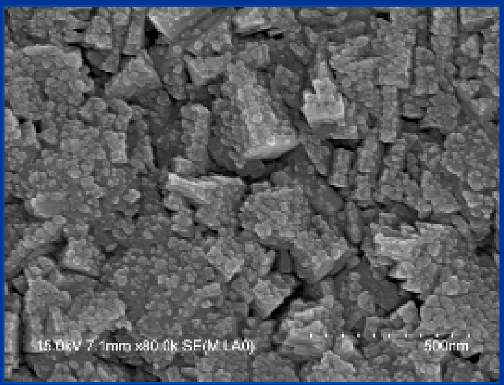
WO_3
(no nano-particles)

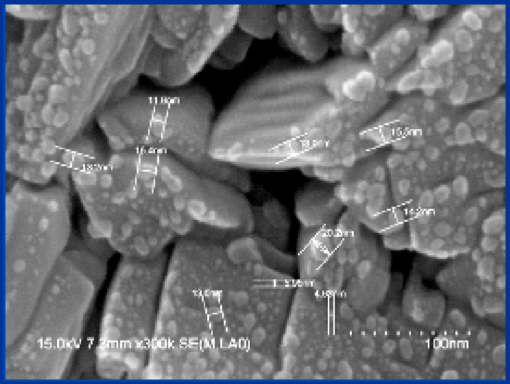


Catalyst nano-particles have been successfully deposited using 2 minute process after WO_3 synthesis

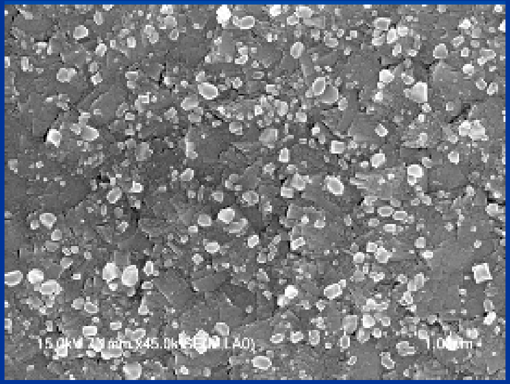
(electrical characterization ongoing)

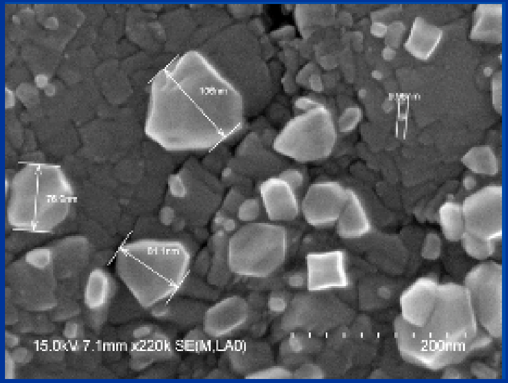
$WO_3 + RuO_2$
(low O_2 p.p.; 2D growth)





$WO_3 + RuO_2$
(high O_2 p.p.; 3D growth)





Addressing barrier Y

Collaborations

– US Department of Energy PEC working group: Leading task force on WO_3 and active participation to the Working Group on PEC measurement standardization.

– National Renewable Energy Laboratory: collaboration to perform theoretical research and advanced morphological analysis of new WO_3-based materials.

– University of Nevada at Las Vegas: collaboration to analyze the surface energy band structure of new photoelectrode materials.

– University of California in Santa Barbara: collaboration on surface treatment for catalytic purposes.

– MVSystems Incorporated: development of PV cell to demonstrate hydrogen production in a standalone configuration.

– International Energy Agency/HIA/Annex 26: collaboration with international institutes and universities including EMPA (Swiss) and University of Warsaw (Poland).

Future Work

1) New approaches for ion incorporation into WO_3 bulk to modify E_G

– Close collaboration with NREL theory team to define new ions: Al, Si and Se

– New processes development:

- use of seed layers to enhance crystallinity
- higher process temperatures
- post-deposition thermal annealing

2) Development of new surface modification techniques

– Deposition of catalysts nano-particle (RuO_2) to enhance charge transfer

– Discovery of new bilayer systems to optimize band-edge alignment

3) New techniques will be used to evaluate PEC films interface @ UNLV

– In vacuum: effect of ion incorporation on surface E_G

– In liquid (in situ): electrical environment of newly incorporated atoms

Tungsten Oxide Summary

- Relevance
  - 3.1% STH efficiency demonstrated in a standalone configuration with underlaying PV cell.
  - WO_3-based materials corrosion resistant in acidic solutions demonstrated worldwide.
- Approach
  - Synthesis: improvements can be performed on each component of the PEC electrode: absorber (light absorption), surface (band-edge position), interface (catalyst).
  - Characterization: large tool chest of specific techniques available form DOE working group.
- Progress
  - Increased photocurrent by +15% using bilayer # Better comprehension of crystallographic impact of films on WO_3-based PEC # Development of new RuO_2 material for oxygen evolution # First time evaluation of physical vapor deposition RuO_2 catalyst nano-particle in PEC world with controlled growth.
- Collaborations
  - Intense collaborations with DOE working groups (“WO_3 task force” + “Measurement standardization WG”) and international teams to effectively address key issues.
- Future Work
  - Continuing investigation of WO_3-based alloys with new ions (absorber) # evaluate the concept of bilayer with other materials (band-edge position) # maintaining efforts of catalyst nano-particle research (interface) # better understanding of the material/electrolyte interface properties.

Project Summary

➢Relevancy

The MVSystems/UH project is accelerating the development of **three important PEC thin-film materials classes** (a-SiC, WO3 and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting.

➢Approach

Use existing knowledge of the three PEC thin-film materials and their PV performances to apply them to a PEC system for hydrogen production.

➢Progress

Items	Thin-film materials	2008			2009			Note
		Target	**Achieved**	**Status**	**Target**	**Achieved**	**Status**	
Material photocurrent	a-SiC	$\geq$ 3 mA/cm^2	7-8 mA/cm^2	100%	$\geq$ 4 mA/cm^2	7-8 mA/cm^2	100%	
	WO_3		2.8-3 mA/cm^2	100%		3.6 mA/cm^2	90%	
	CGSe		20 mA/cm^2	100%		20 mA/cm^2	100%	
Material/Device durability	a-SiC	$\geq$ 100 hrs	100 hrs	100%	$\geq$ 200 hrs	150 hrs	75%	
	WO_3		100 hrs	100%		100 hrs	50%	
	CGSe		10 hrs	10%		10 hrs	5%	
Device STH efficiency	a-Si/a-SiC				$\geq$ 5%	1%	25%	H_2 production observed
	WO_3					3.2%	65%	expected from current matching
	CGSe							

Project Summary

➢ Collaboration

In order to promote the needed scientific breakthroughs in PEC R&D, collaborations have been developed within the US DOE PEC Working Group and with the IEA-HIA PEC Annex-26.

➢ Future work

(1) Further improve the properties of thin-film materials.
(2) Develop new surface modification techniques.
(3) Establish band diagrams for the thin-film photoelectrode/electrolyte system.
(4) New techniques will be used to evaluate PEC films interface @ UNLV and use new information to focus fabrication and device matching efforts effectively.
(5) Improve the PV performance of the thin-film solar cell used in the hybrid PEC device.