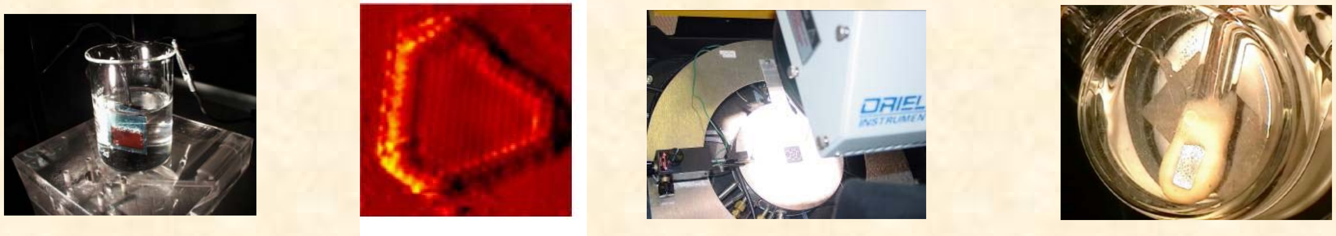


PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION:
DOE PEC Working Group Overview

Eric L. Miller
Hawaii Natural Energy Institute
University of Hawaii at Manoa

20 May 2009
D.O.E Hydrogen Program Review
Arlington, VA

 # PD_22_Miller

This presentation does not contain any proprietary or confidential information

OVERVIEW

The US DOE WORKING GROUP ON PHOTOELECTROCHEMICAL (PEC) HYDROGEN PRODUCTION

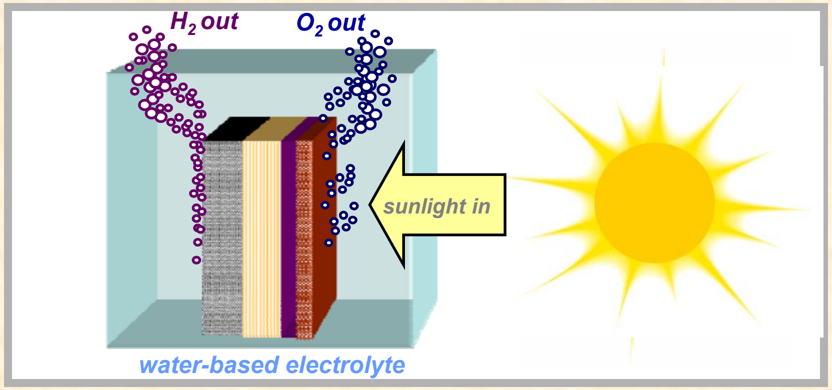
Roxanne Garland: Group Chair
U.S. Department of Energy

Eric Lars Miller: Group Co-Chair
University of Hawaii at Manoa

OVERVIEW PEC WORKING GROUP

The US DOE Photoelectrochemical (PEC) Working Group brings together Academic, Industry and National Laboratory leaders in the research and development of practical PEC semiconductor systems to produce hydrogen via solar water-splitting

photoelectrode-based PEC solar-H_2 production:



MULTIPLE PEC PROJECTS ARE FUNDED BY DOE: BUDGETS AND TIME-LINES VARY

WORKING GROUP ADDRESSES ALL PEC BARRIERS, INCLUDING:

Y: Materials Efficiency, Z: Materials Durability,

AB: Bulk Materials Synthesis, AC: Device Configuration Designs

OVERVIEW

Working Group Partners

Working Group Members with current DOE financial support include:

oral poster

University of Hawaii at Manoa	PDP05	PDP06
University of Nevada Las Vegas		PD24
University of California, Santa Barbara		PDP01
University of Nevada Reno		PDP09
Stanford University		PD25
National Renewable Energy Lab	PDP02	PDP03
MVSystems Incorporated		PDP04
Midwest Optoelectronics		PDP07
Directed Technologies Incorporated		PD23
University of Arkansas, Little Rock		PDP08

RELEVANCE

WORKING GROUP GOALS

The DOE PEC Working Group's primary objective is to develop practical solar hydrogen-production technology, using innovative semiconductor materials & devices R&D to foster the needed scientific breakthroughs for meeting DOE Hydrogen Program goals

DOE PEC "Multi-Year Program Plan" Targets

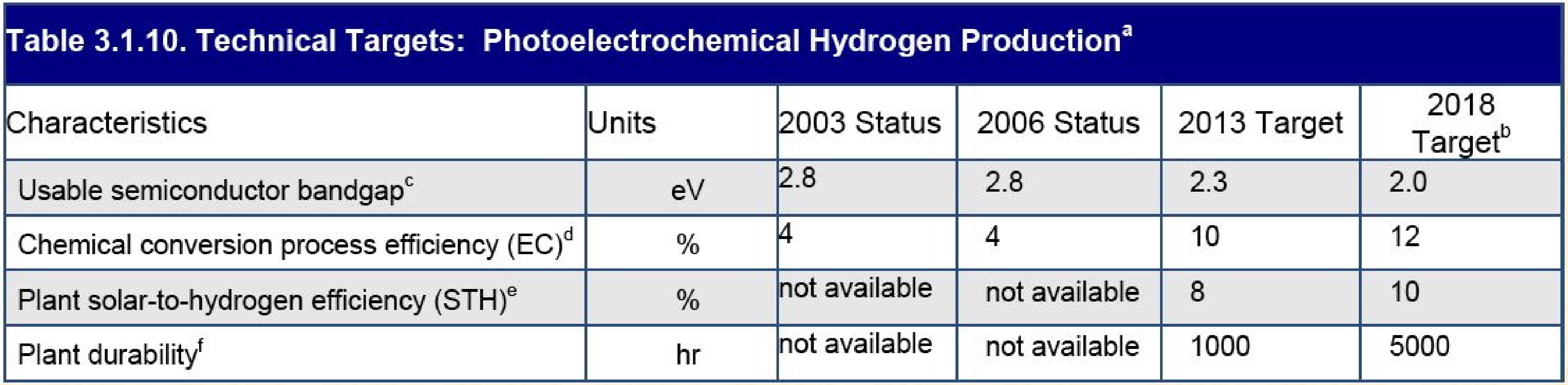
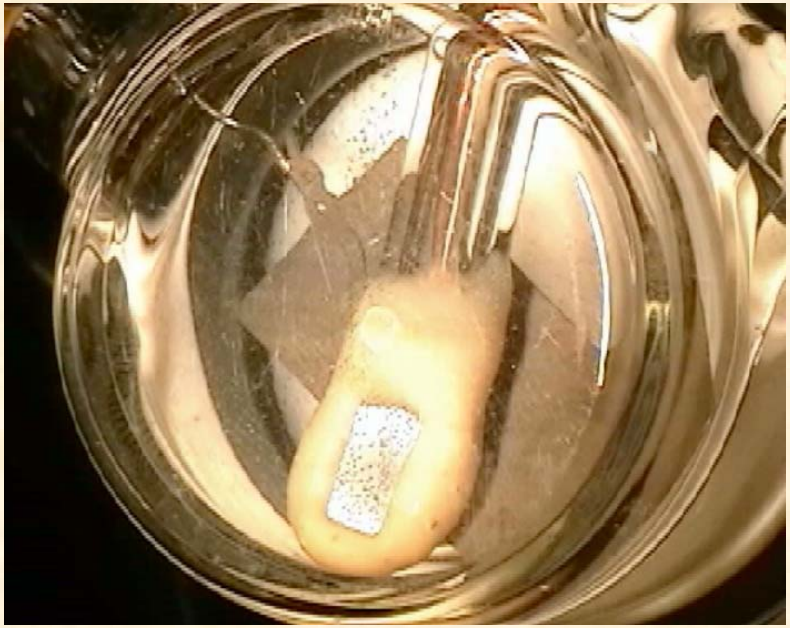


Table 3.1.10. Technical Targets: Photoelectrochemical Hydrogen Production[a]

Characteristics	Units	2003 Status	2006 Status	2013 Target	2018 Target[b]
Usable semiconductor bandgap[c]	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency (EC)[d]	%	4	4	10	12
Plant solar-to-hydrogen efficiency (STH)[e]	%	not available	not available	8	10
Plant durability[f]	hr	not available	not available	1000	5000

RELEVANCE THE PEC PROMISE

IMPORTANT LABORATORY BENCHMARK



- *NREL High-performance (16%) GaInP/GaAs tandem PEC cell demonstrates technological feasibility of PEC H_2 production*
- *Durability has been limited, and cost prohibitive with the III-V materials*

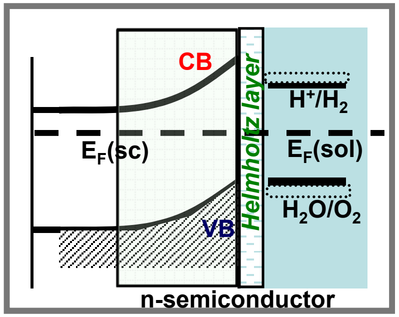
- ***PRACTICAL PEC*** **hydrogen production requires materials systems with high-efficiency, long-life & low cost.**
- **The development of new semiconductor materials meeting *ALL* criteria is the key objective of the PEC working group efforts**

RELEVANCE

THE PEC CHALLENGE

NO **Material System satisfies** ***ALL*** **requirements to practically split H_2O:**
Many have potential... ***Thus the PROMISE & CHALLENGE of PEC***

- **ABSORBER MATERIAL**
  - *Sunlight conversion depends on bulk optical bandgap*
  - *Nature of optical transitions (‘direct’ vs. ‘indirect’) is important*
  - *Good bulk transport properties key to harnessing photo-carriers*
- **INTERFACE DESIGN**
  - *Band-edge alignment important to reaction energetics*
  - *Surface bandgap plays an important role at interface*
  - *Interface kinetics critical in harnessing photo-carriers*



- **INTEGRATED DEVICE DEVELOPMENT**
  - *Multi-junction configurations important for maximum solar utilization*
  - *Auxiliary components and proper integration key to efficiency*
- **HYDROGEN PRODUCTION SYSTEM DEVELOPMENT**
  - *Balance of plant considerations could limit practicality*
- **COST OF LARGE-SCALE FABRICATION**

WORKING GROUP APPROACH

The main approach of our collaborative network of world-leaders in materials R&D focuses on integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost.

PEC R&D
"Tool Chest"

- **THEORY: Materials & Interface Modeling**
  - *Theoretical Calculations of Semiconductor Band Structures*
- **SYNTHESIS: Materials Discovery / Development**
  - *Physical and Chemical Vapor Deposition*
  - *Combinatorial & Manufacture-Scale Synthesis Techniques*
- **ANALYSIS: Materials & Device Characterization**
  - *Physical/Solid-State Electronic/Optoelectronic Properties*
  - *Solid-Solid & Solid-Liquid Interface Characteristics*
  - *Photoelectrochemical Behavior Analysis*
  - *Techno-Economics Systems Analysis*

USING THE PEC “TOOL-CHEST”

- **The PEC Tool-Chest of theory, synthesis, characterization and analytical techniques is being utilized in the development of new promising materials systems using the following strategies:**
  - ***Further development of the “standard” PEC semiconductor thin-films and nano-structures for higher efficiencies (e.g., iron-oxide and tungsten trioxide)***
  - ***Development of efficient PV semiconductor thin-films and nano-structures for effective use in PEC (e.g., copper chalcopyrites and amorphous silicon compounds)***
  - ***Development of new processes and technologies to reduce the cost and enhance the stability of high-performance (e.g., III-V nitrides)***
  - ***Discovery and development of “new” materials classes based on the accumulated knowledge-base from PEC research efforts to date (e.g., WS_2 and MoS_2 nanoparticle systems).***

PEC MATERIALS "WHITE PAPERS"

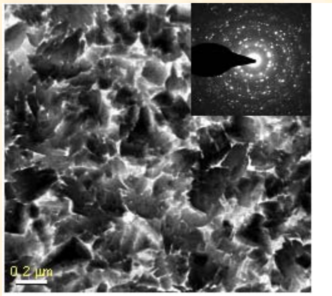
- ***White Paper*** approach implemented by the PEC Working Group to organize / coordinate research and development of the most promising PEC materials classes

- ***White Papers*** are concise *living documents* summarizing the research status of the active PEC materials classes under investigation and outlining a research roadmap for each

- ***White Papers*** for active materials classes are assigned coordinating Task Leaders from the DOE PEC WG, who organize collaborative activities among group members

- ***White Papers*** have been structured according to the vision outlined by the *US DOE Multi-Year Program Plan*, to promote progress in meeting DOE goals via identification of technical barriers and development of approaches to solve them

MATERIALS PROGRESS

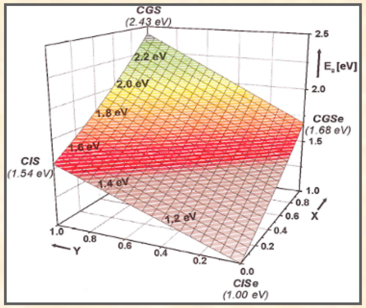


Highly crystalline WO_3

- **Tungsten-Oxide-Based Materials**
  - *Task Force Leader: Nicolas Gaillard (HNEI)*

a stable & inexpensive material used in PEC applications, but band-gap and interface need to be optimized

PDP05



- **Copper-Chalcopyrite-Based Materials**
  - *Task Force Leader: Jess Kaneshiro (HNEI)*

efficient photon absorbers with alloy-tunable bandgap, but interface needs to be improved and stabilized

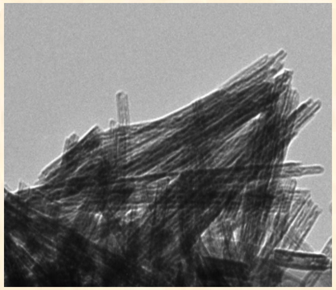
PDP06

- **Amorphous-Silicon-Based Materials**
  - *Task Force Leader: Arun Madan (MVS)*

PDP04

inexpensive & well-understood thin-films of variable bandgap, but interface needs to be improved and stabilized

MATERIALS PROGRESS



- **Iron-Oxide-Based Materials**
  - *Task Force Leader: Eric McFarland (UCSB)*

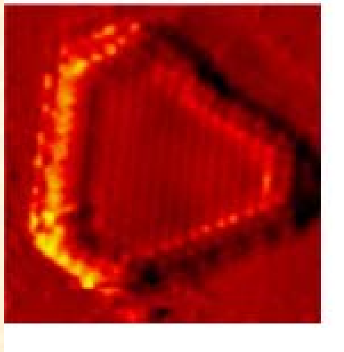
PDP01

inexpensive material of near-ideal bandgap, but extremely poor optoelectronic properties have limited its application

- **Crystalline III-V-Based Materials**
  - *Task Force Leader: Todd Deutsch (NREL)*

PDP02

high quality semiconductor class with tunable bandgap, but interface stability and cost remain the primary barriers

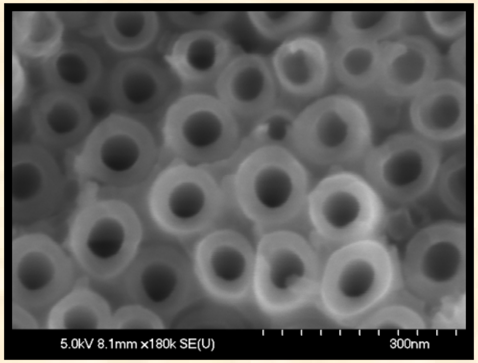


PD25

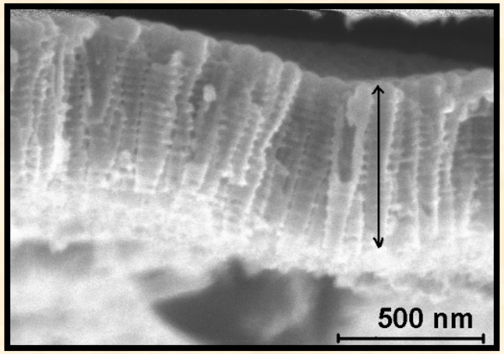
- **MoS_2 / WS_2-Based Materials**
  - *Task Force Leader: Tom Jaramillo (Stanford)*

good hydrogen catalysts, but quantum-confinement is needed to raise bandgap for PEC, and stable configurations are needed

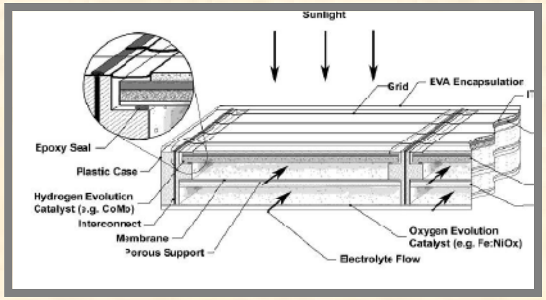
OTHER PEC PROGRESS



- **Nanotubular Based Coupled Semiconductors** **PDP09**
  - *Mano Misra (UNR)*

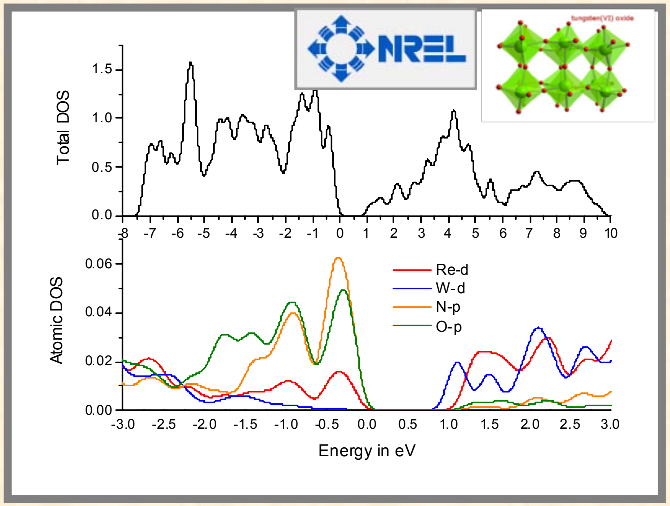


- **PEC H_2 Production: Interfaces** **PDP08**
  - *Malay Mazumder (UALR)*



- **Integrated Solar-Electrolysis Systems** **PDP07**
  - *William Ingler (MWOE)*

BUILDING UP THE TOOL-CHEST

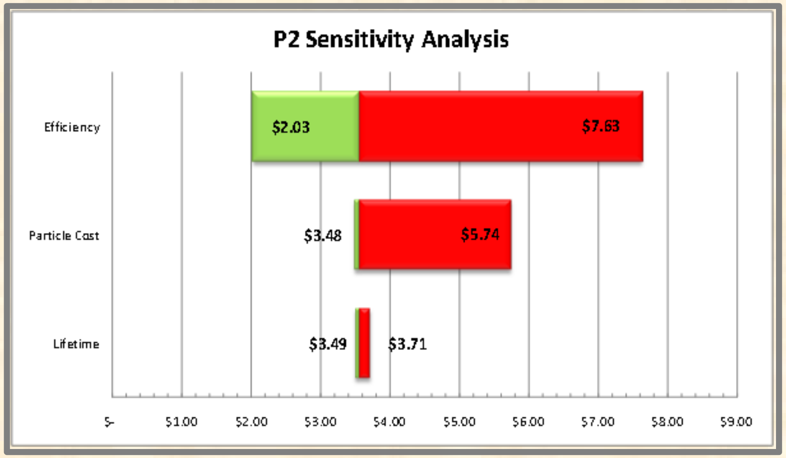


- ***Advances in PEC Materials Theory***

  –Yanfa Yan (NREL)

  PDP03

  sophisticated theoretical models of band states and bandgap, including effects of surface, interfaces and grain-boundaries, are vital to breakthroughs in PEC materials



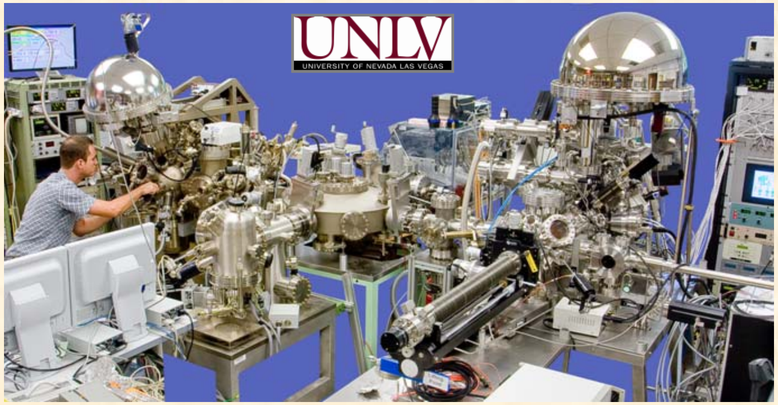
- ***Techno-Economics Analysis Progress***

  –Brian James (DTI)

  PD23

  a basis for evaluating the long-term feasibility of large-scale PEC production technologies in comparison with other renewable approaches

BUILDING UP THE TOOL-CHEST

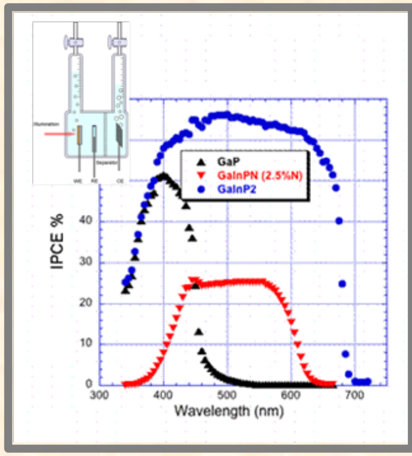


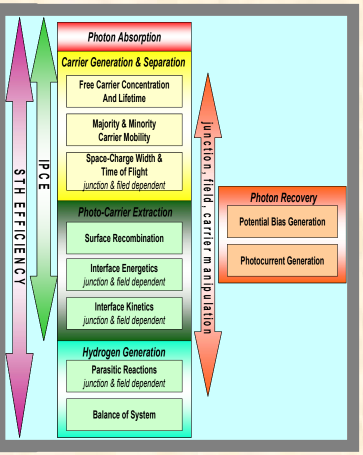
solid-state / surface characterization tool

- ***PEC Characterizations Advances***

  –***Clemens Heske (UNLV)*** **PD24**

  state-of-the-art techniques in materials & surface characterizations, in-situ and ex-situ, are providing keys to understanding the complex PEC interface





STH EFFICIENCY

IPCE

Photon Absorption

Carrier Generation & Separation

Free Carrier Concentration And Lifetime

Majority & Minority Carrier Mobility

Space-Charge Width & Time of Flight *junction & filed dependent*

Photo-Carrier Extraction

Surface Recombination

Interface Energetics *junction & field dependent*

Interface Kinetics *junction & field dependent*

Hydrogen Generation

Parasitic Reactions *junction & field dependent*

Balance of System

junction, field, carrier manipulation

Photon Recovery

Potential Bias Generation

Photocurrent Generation

- ***Standardized Testing & Screening***

  –***Huyen Dinh (NREL)***

  lack of standardized conditions and procedures for reporting PEC results has greatly hampered PEC research progress in the past

ROLE OF COLLABORATION

- **The DOE PEC Working Group encourages collaboration among its members, and with the broader research community (e.g., through the IEA-HIA Annex-26 activities)**
- **Collaboration enables effective pooling of Working Group resources in theory, synthesis, characterization and analysis**
- **Collaboration among different materials class Task Forces facilitates progress in all, stemming from common research synergies in materials and interface science**

National Renewable Energy Laboratory
Innovation for Our Energy Future

Successful Working Group Collaboration:

Standard PEC Characterization

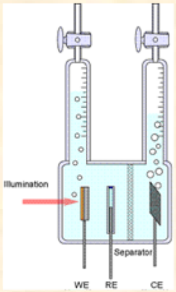
Task Leader:
Huyen Dinh

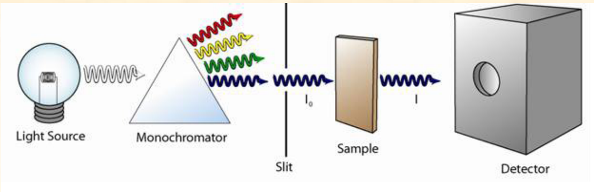
Standardized Testing Overview

- **Goals:**
  - Develop standardized testing and reporting protocols for PEC material/interfaces evaluation
  - Publish the standardized PEC characterization techniques in a peer-reviewed journal to reach the maximum number of people
- **Purpose & Scope:**
  - Properly define the efficiencies (STH) that should be used for wide-scale reporting vs. efficiencies (IPCE) that are useful for scientific, diagnostic purposes only
  - Describe proper PEC procedures for characterizing planar photoelectrode materials
  - Focus on single band gap absorber material only
  - Describe the techniques, the knowledge gained, the experimental set-up and procedure, the data analysis, and the potential pitfalls/limitations

Relevance of Standardized Testing

- Help researchers from different groups characterize PEC materials and report results in a way which allows direct comparison
- Promote credibility through published work
- Help funding organizations and researchers better compare various materials by providing a common understanding of the materials along with the ability to screen materials quickly
- Guide research toward the most promising materials that meet all PEC requirements





An International Joint Effort

- **Common US-DOE / IEA-HIA Goals :**
  - Develop standardized testing and reporting protocols for PEC material/interfaces evaluation
  - Publish the standardized PEC characterization techniques in a peer-reviewed journal to reach the maximum number of people

Department of Energy

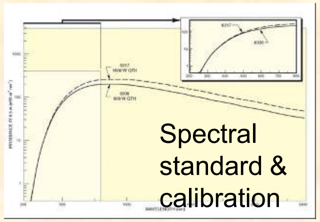
Zhebo Chen (SU), US
Todd Deutsch (NREL), US
Huyen Dinh (NREL), US
Kazunari Domen (UofTokyo), Japan
Arnold Forman (UCSB), US
Nicolas Gaillard (HNEI), US
Roxanne Garland (DOE), US
Thomas Jaramillo (SU), US
Alan Kleiman (UCSB), US
Grant Mathieson (Ansto), Australia
Mahendra Sunkara (UofL), US
Kazuhiro Takanabe (UofTokyo), Japan

International Energy Agency

Initial Document Outline

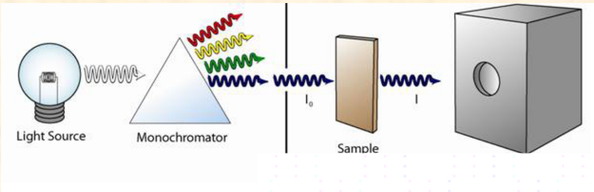
- A. Introduction – purpose & scope
- B. Efficiency Definitions
- C. Experimental Set-up
  1. Electrode preparation
  2. Surface area determination
  3. 3- and 2-electrode cell set up & connections
  4. Catalyst surface treatments
  5. Spectral standard & calibration
- D. PEC characterization flow chart
- E. PEC techniques
  1. UV-Vis (Band gap)
  2. Illuminated Open Circuit Potential (OCP)
  3. Mott-Schottky (Vfb)
  4. Dark, Light, & Chopped I-V
  5. Photocurrent Onset
  6. Incident Photon Conversion Efficiency (IPCE)
  7. Photocurrent spectroscopy
  8. 2-electrode short current density and J-V (STH efficiency)
  9. Hydrogen Detection (STH efficiency)
  10. photocurrent density vs. time stability
- F. Glossary of terminology
- G. References

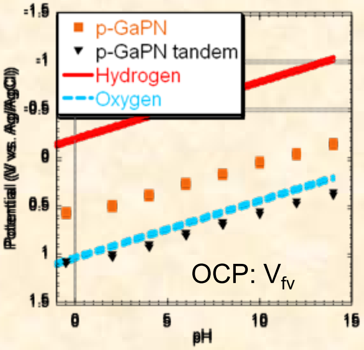
Electrode preparation



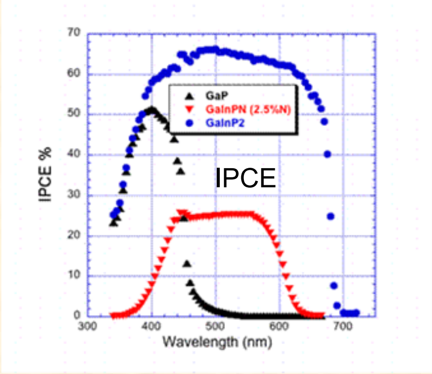
Spectral standard & calibration

UV-Vis

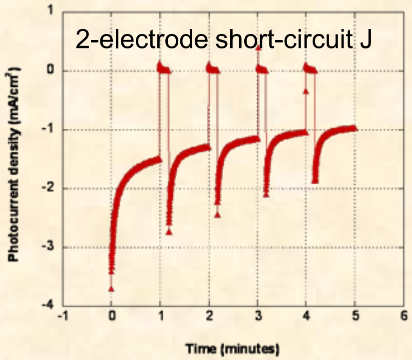




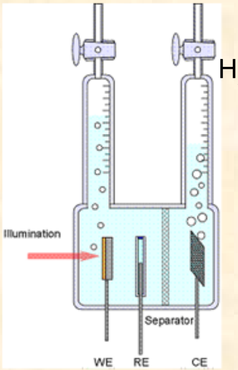
OCP: V_{fv}



IPCE

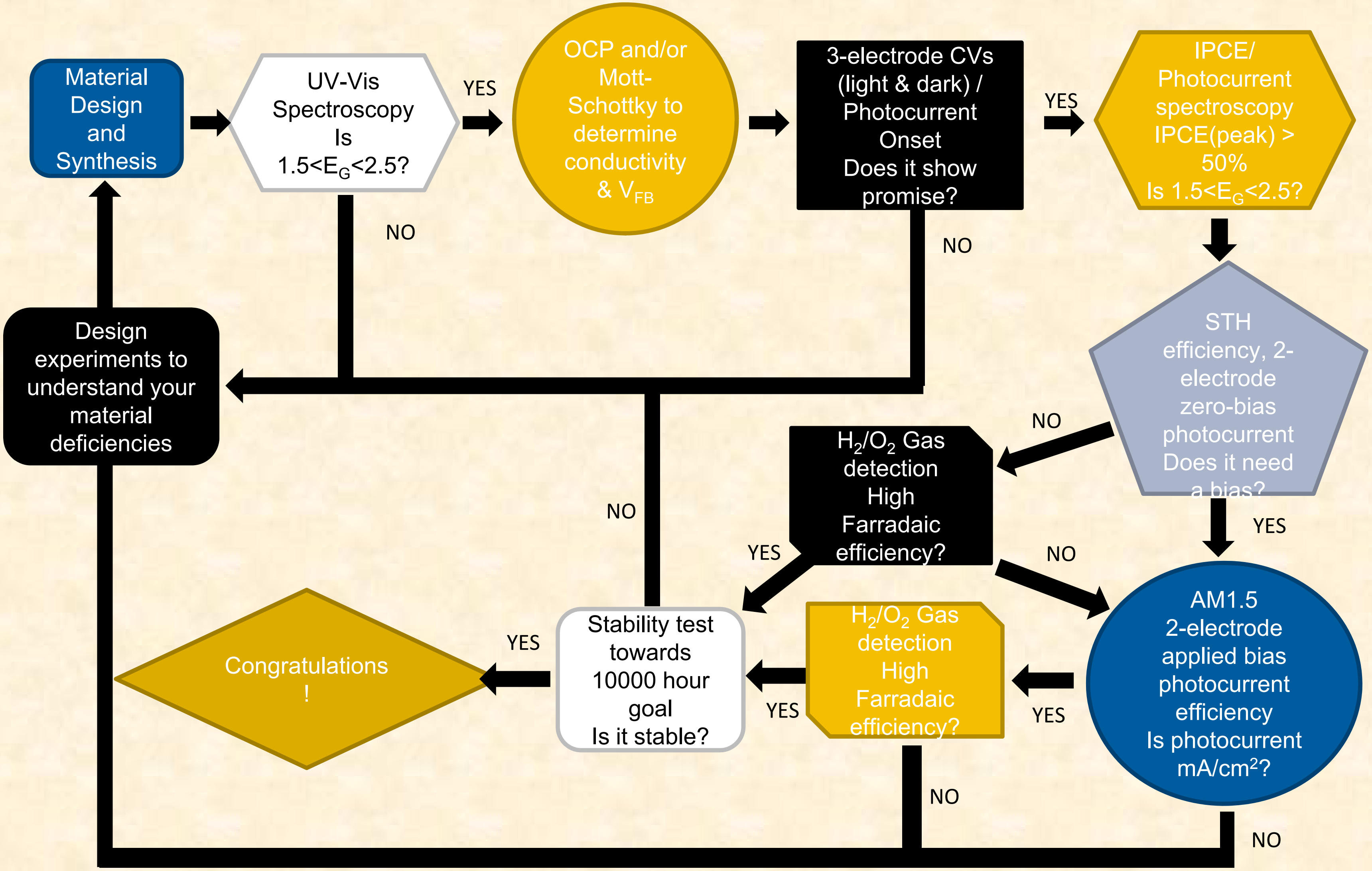


2-electrode short-circuit J



H_2 Detection

PEC Characterization Flow Chart



Material Design and Synthesis

UV-Vis Spectroscopy Is $1.5<E_G<2.5$?

YES

NO

OCP and/or Mott-Schottky to determine conductivity & V_{FB}

3-electrode CVs (light & dark) / Photocurrent Onset Does it show promise?

YES

NO

IPCE/ Photocurrent spectroscopy IPCE(peak) > 50% Is $1.5<E_G<2.5$?

Design experiments to understand your material deficiencies

STH efficiency, 2-electrode zero-bias photocurrent Does it need a bias?

NO

YES

H_2/O_2 Gas detection High Farradaic efficiency?

YES

NO

NO

AM1.5 2-electrode applied bias photocurrent efficiency Is photocurrent mA/cm^2?

YES

H_2/O_2 Gas detection High Farradaic efficiency?

YES

NO

Stability test towards 10000 hour goal Is it stable?

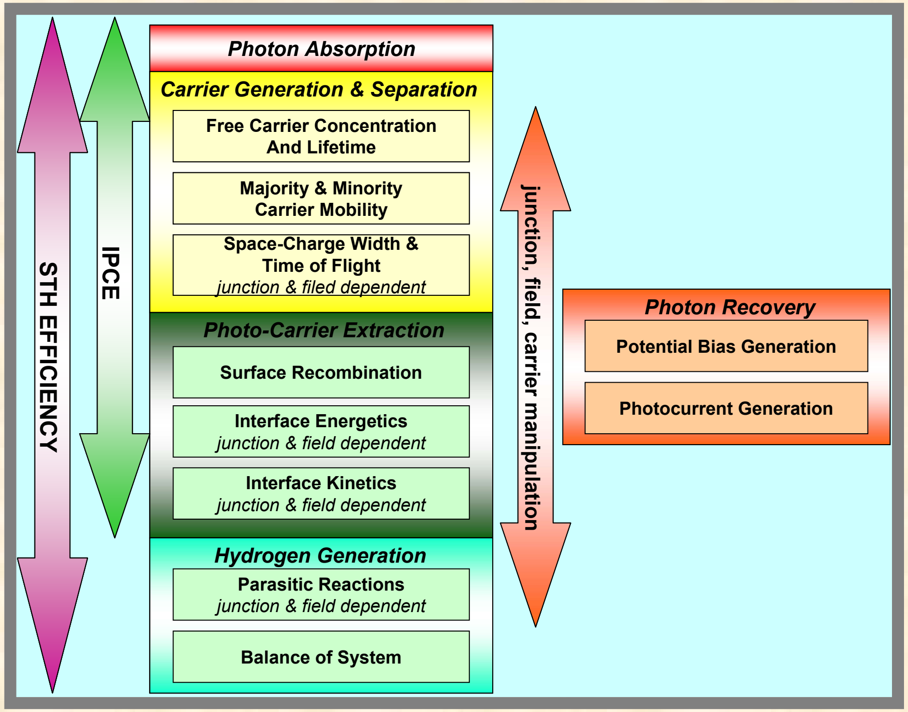
YES

Congratulations !

NO

- **Recommended application of standardized testing procedures**

PEC Materials Screening



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Interface Kinetics
junction & field dependent

Hydrogen Generation

Parasitic Reactions
junction & field dependent

Balance of System

junction, field, carrier manipulation

Photon Recovery

Potential Bias Generation

Photocurrent Generation

- **Standardized testing methods in addition to advanced characterization tools are being incorporated into screening protocols for up- and down-selecting PEC materials for DOE R&D**
- **Screening protocols ranging from top-level device performance, to detailed measurement of performance-limiting materials and interface properties are being developed**

Future Plans in Standardized Testing

- **Future Document Topics:**
  - Standard Documents for Particulate Colloidal Systems
  - Tandem / Multi-Junction Cell Systems
  - Strategies for Material Design & Synthesis

- **Expand collaborative effort internationally through coordination with IEA-HIA Annex-26**

DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA

Future Plans for PEC Working Group

- **Continued Development of the PEC Tool Chest:**
  - Improved theoretical models
  - Innovative synthesis improvements
  - Advanced ex-situ and in-situ materials characterizations
  - Continued Techno-Economics analyses
  - Continued refinement of standard testing & screening protocols
- **Continued Development of PEC Focus Class Materials:**
  - Ongoing implementation of White Paper approach
  - Research progress benefiting from Tool Chest advances
- **Deployment of Screening Protocols to Focus R&D:**
  - Up-selection of promising new materials classes
  - Down-selection of materials with unyielding barriers

PEC Working Group Summary

The PROMISE: PEC is a *Holy-Grail* of Solar-to-Hydrogen Conversion

- *Efficient STH conversion possible at low temperature operations*
- *Successful laboratory demos: 16% STH in high-cost, low durability systems, 3-4% in low-cost, high durability systems*

The CHALLENGE: Major Breakthroughs are Needed for Practical PEC

- *Materials and interfaces meeting ALL required criteria have been elusive*

US DOE PEC Working Group is Facing the Challenge, Collaboratively

- *Building a Tool Chest of the most advanced scientific techniques*
- *Applying Tool Chest in the R&D of the most promising materials classes*
- *Building an ever-growing international network of bright young scientists to break the barriers!*

PEC Working Group Invitation

Please Attend the AMR PEC Presentations

oral *poster*

University of Hawaii at Manoa	**PDP05**	**PDP06**
University of Nevada Las Vegas		**PD24**
University of California, Santa Barbara		**PDP01**
University of Nevada Reno		**PDP09**
Stanford University		**PD25**
National Renewable Energy Lab	**PDP02**	**PDP03**
MVSystems Incorporated		**PDP04**
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University of Arkansas, Little Rock		**PDP08**

Acknowledgements

- **The U.S. Department of Energy**
- **The International Energy Agency, and**
- **ALL the Talented, Enthusiastic and Hard-Working Working Group Members**

Mahalo Nui Loa