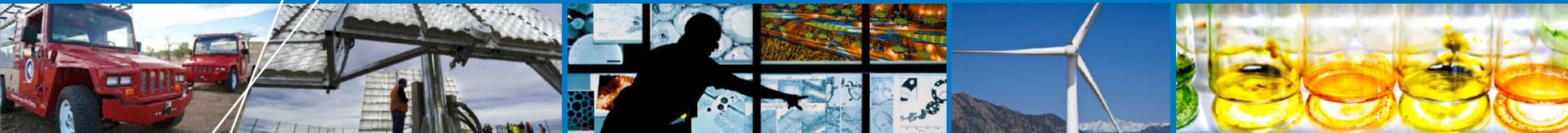


# Semiconductor Materials for Photoelectrolysis



**2014 U.S. DOE Hydrogen & Fuel Cells Program  
Review**

**Todd G. Deutsch, John A. Turner**

**June 18<sup>th</sup>, 2014**

**Project ID: PD035**

# Overview

## Timeline

- **Project start date: 2004**
- **Project end date: 9/2014\***
- **Percent complete: 90%**

## Budget

- **Total project funding**
  - DOE share: \$10.5M
- **Funding received in FY13: \$720k\*\***
- **Planned funding for FY14: \$750k**

\* Project continuation and direction determined annually by DOE

\*\* Includes UNLV support

## Barriers

### • Barriers addressed

- AE. Materials Efficiency –Bulk and interface.
- AF. Materials Durability – Bulk and interface
- AG. Integrated Device Configurations
- AI. Auxiliary Materials

## Partners

### • Interactions/collaborations

- Lawrence Livermore National Lab
- University of Nevada Las Vegas (UNLV)
- Los Alamos National Laboratory
- Colorado School of Mines
- University of Colorado-Boulder
- University of Louisville
- University of Hawaii
- Stanford University
- University of Texas-Arlington
- Program production solicitation
  - MVSsystems, Inc.

# Relevance

## Objectives

- Long-Term: Develop highly-efficient, durable material that can operate under 10-15x solar concentration and generate renewable hydrogen for <\$2/kg from photoelectrochemical (PEC) water splitting
- Current year:
  - Push boundaries on achievable semiconductor photoelectrochemical solar-to-hydrogen (STH) efficiencies
  - Continue development of stabilizing surface modifications viable at high current densities

Characteristics	Units	2011	2015	2020	Ultimate
		Status	Target	Target	Target
Photoelectrochemical Hydrogen Cost <sup>b</sup>	\$/kg	NA	17.30	5.70	2.10
Capital cost of Concentrator & PEC Receiver (non-installed, no electrode) <sup>c</sup>	\$/m <sup>2</sup>	NA	200	124	63
Annual Electrode Cost per TPD H <sub>2</sub> <sup>d</sup>	\$/yr-TPDH <sub>2</sub>	NA	2.0M	255K	14K
Solar to Hydrogen (STH) Energy Conversion Ratio <sup>e,1</sup>	%	4 to 12%	15	20	25
1-Sun Hydrogen Production Rate <sup>g</sup>	kg/s per m <sup>2</sup>	3.3E-7	1.2E-6	1.6E-6	2.0E-6

# Relevance

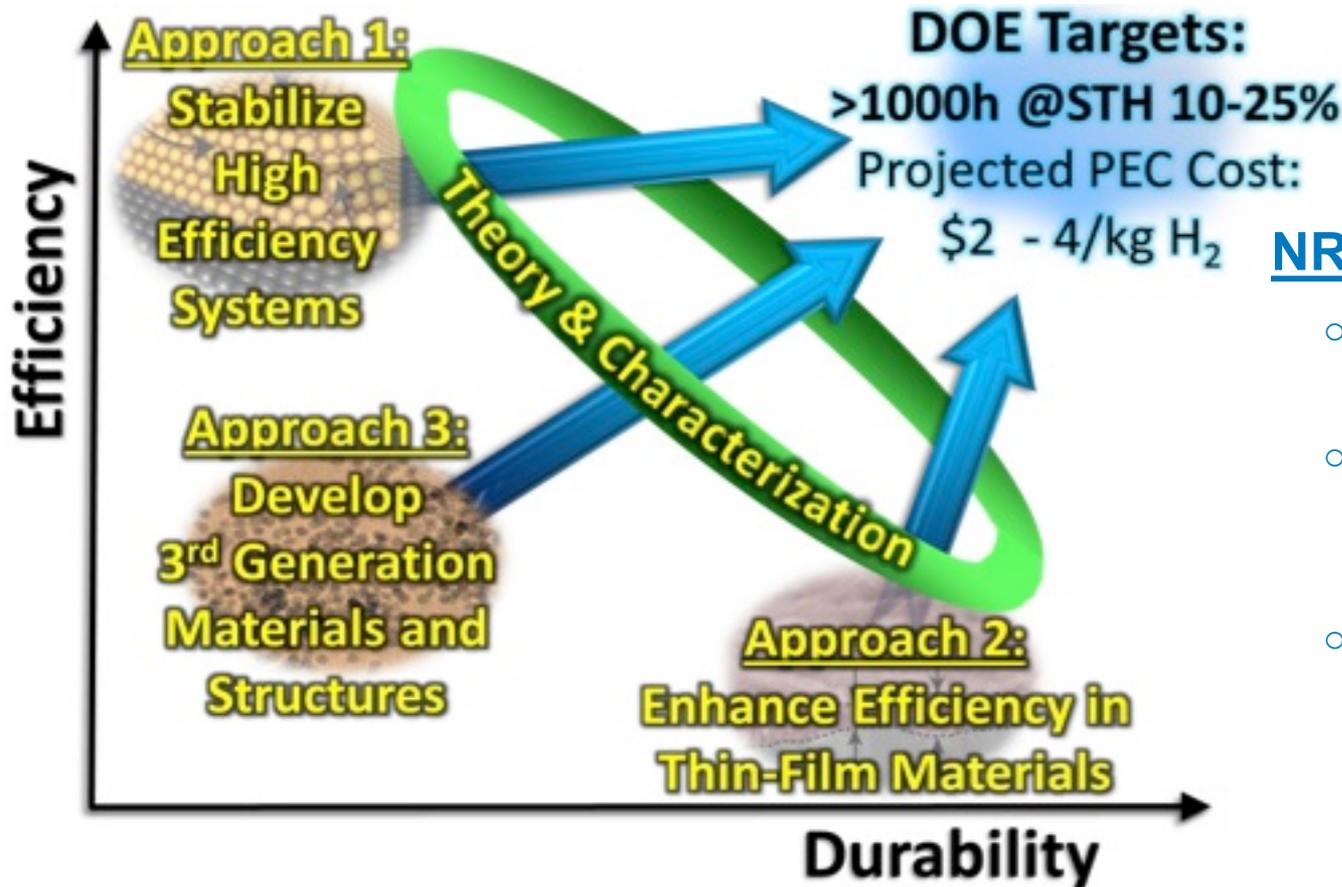
## Impact in the last year

- Materials Efficiency: Designed new tandem configurations
- Materials Durability: Extended lifetime and transferred passivating surface modification to other advanced III-V systems
- Integrated Device Configurations: Tested photoreactor on solar tracker, working on next generation design
- Auxiliary Materials: Discovered (negative) impact of surfactant composition and concentration on long-term testing

Table 3.1.8.A Example Parameter Values to Meet Cost Targets: Photoelectrochemical Hydrogen Production (Photoelectrode System)					
Characteristics	Units	2011 Status	2015	2020	Ultimate
Solar to Hydrogen (STH) Energy Conversion Ratio	%	NA	15	20	25
PEC Electrode cost <sup>a</sup>	\$/m <sup>2</sup>	NA	300	200	100
Electrode Cost per TPD H <sub>2</sub> <sup>b</sup>	\$/TPD	NA	1.0M	510K	135K
Electrode Replacement Lifetime <sup>c</sup>	Years	NA	0.5	2	10
Balance of Plant Cost per TPD H <sub>2</sub> <sup>d</sup>	\$/TPD	NA	420K	380K	310K

# Approach

The US DOE PEC Working Group approach towards efficient and durable solar H<sub>2</sub> production



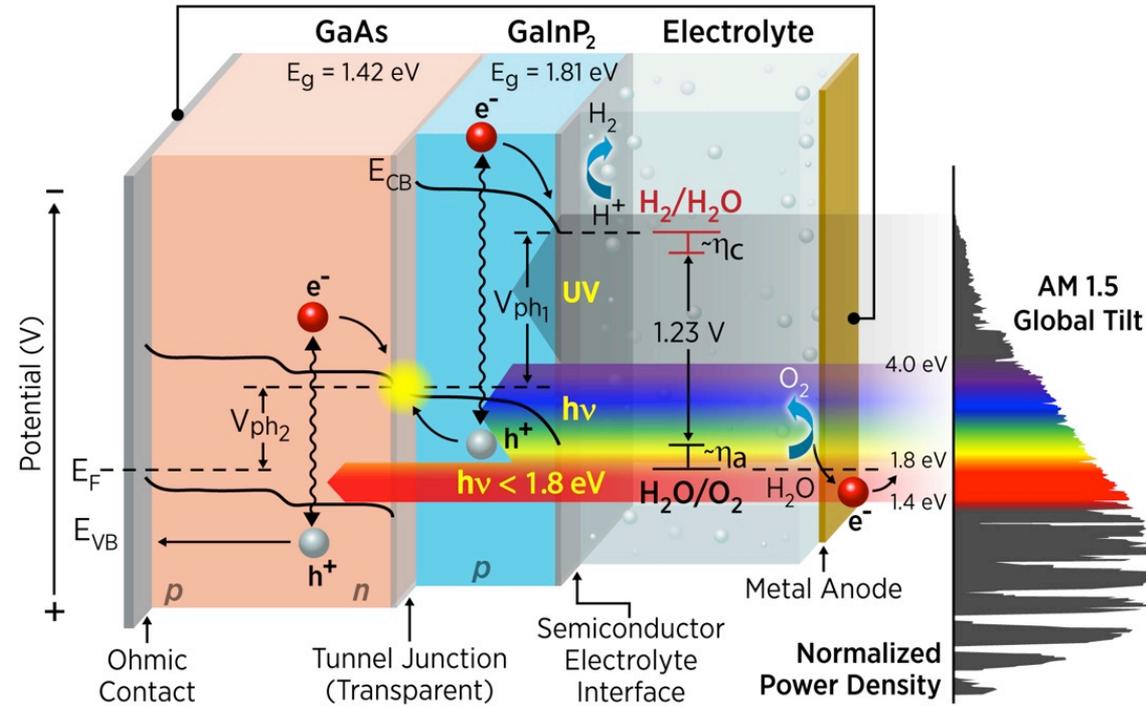
## NREL-led Project Focus:

- Extend durability of highly efficient materials
- Ensure efficiencies are not compromised by durability treatments
- Investigate new materials that can achieve ultra-high future efficiency goals

# Approach: Multijunction III-V Semiconductors

## Highest efficiency

- Our model material GaInP<sub>2</sub>/GaAs is the only PEC system that exceeds unbiased 10% STH efficiency
  - 12.4% with Pt-black counter electrode (CE), >16% with RuO<sub>2</sub> CE at moderate bias
- High efficiency is a result of spectral splitting through stacked tandem absorbers and high-quality material
- Metal organic chemical vapor deposition (MOCVD) synthesis by NREL's III-V group



## Focus: improve durability and efficiency

- Extend lifetimes under operating conditions from a few hours to several thousand hours in statistically significant sample sets
- Investigate other novel III-V materials and configurations with appropriate bandgaps for achieving higher STH efficiencies in tandem devices

## Lowered synthesis costs

- Outside current scope
- Several emerging technologies
  - Epitaxial lift-off
  - Spalling
  - Hydride vapor phase epitaxy
  - Close-spaced vapor transport

# Approach: Surface Validation Team

Understanding and remedying semiconductor photocorrosion at PEC interfaces is a complex task that has benefitted significantly from a collaborative approach which teams experts with unique capabilities and resources

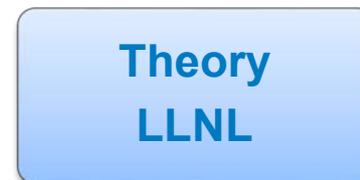
- **Heske group at UNLV**

- XPS, XAS, XES, IPES, UPS, AFM
  - Some measurements at Advanced Light Source (ALS)
- Snapshots of surface pre-, intermediate, post-exposure
- Identify common features of and conditions that lead to corrosion
- Characterize stabilized surfaces



- **Ogitsu group at LLNL**

- Develop theoretical tool chest for modeling PEC systems
- Simulate x-ray spectra to correlate UNLV experimental results with surface/near surface compositions
- Model III-V surfaces to uncover the key mechanisms of surface corrosion



# Approach – Milestones

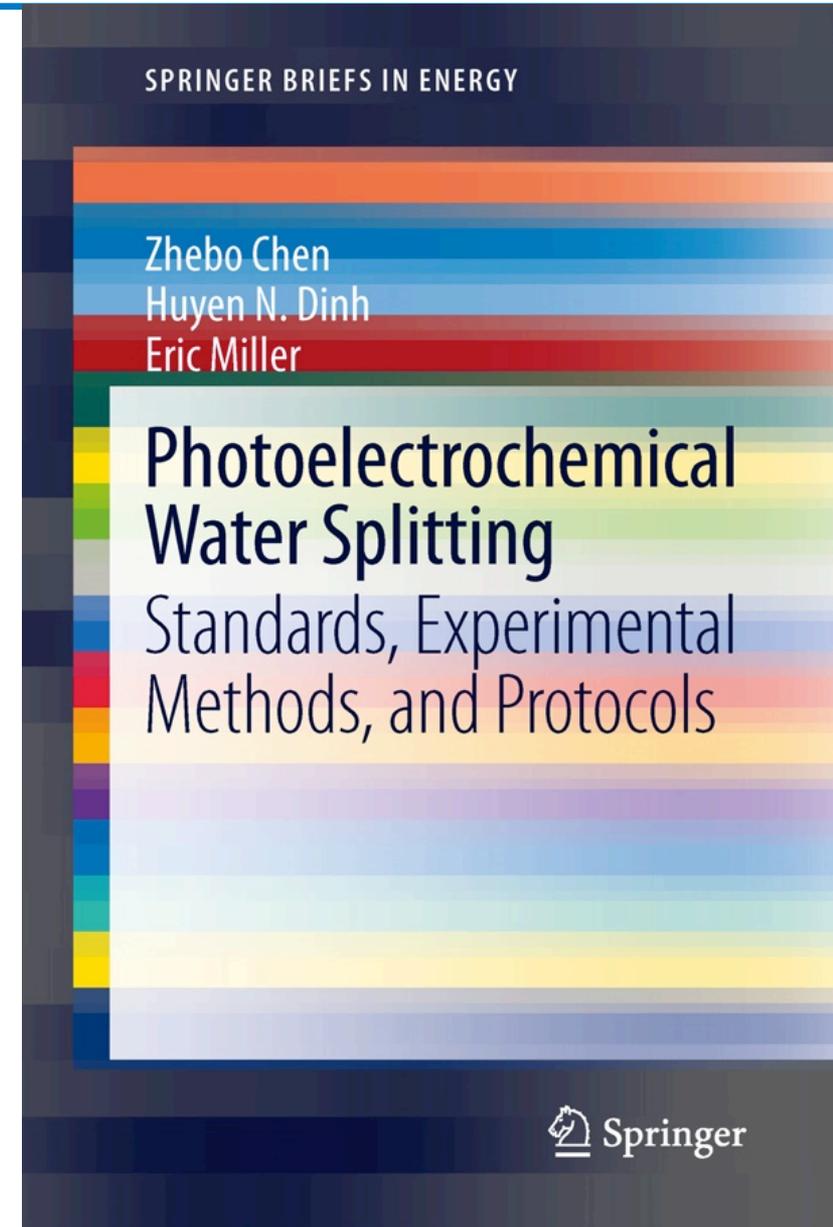
<b>FY 2013 Milestones (occurring after 2013 AMR)</b>	<b>Due Date</b>	<b>Status</b>
Complete 100 hours of short-circuit lifetime measurements on GaInP <sub>2</sub> /GaAs tandem cells, which have had the best available nitrogen ion implanted surface passivation treatments, operated at an initial STH conversion efficiency of at least 10% to characterize durability.	07/13	Complete
Evaluate stability of dilute bismide semiconductor material in a PEC environment against near-term goal of 100 hours at 10mA/cm <sup>2</sup> and make go/no-go decision on further studies.	07/13	No-go
Evaluate III-V material efficiency and durability using photoreactors with intrinsic solar concentration (≤10x) under on-sun conditions and report on material efficiency and durability. Compare results to near-term goal of ≥10% for 100 hours.	09/13	Complete
<b>FY 2014 Milestones</b>	<b>Due Date</b>	<b>Status</b>
Apply nitrogen ion implantation surface passivation treatment to p-InP with a bandgap of 1.33 eV that could enable STH efficiencies greater than 20% in tandem configuration, and evaluate its potential for corrosion mitigation under operating conditions ~25 mA/cm <sup>2</sup> .	12/13	Complete
Generate a waterfall chart for III-V PEC water splitting systems for presentation at the AMR.	03/14	Complete
Introduce inhibiting ions to electrolytes to protect epilayer p-GaInP <sub>2</sub> to achieve 300 hours durability at 10mA/cm <sup>2</sup> under AM1.5G illumination.	06/14	Complete
Optimize parameters of III-V protective surface treatments demonstrating durability in 80% of electrodes tested for 300 hours at a constant current under AM1.5G illumination. Compared with the original focus on GaInP <sub>2</sub> , the modified focus will be on developing the lower-bandgap binary forms of the III-V material system, motivated by their potential for higher STH efficiency. Two lower band gap binary materials will be evaluated: GaAs will be tested at 15mA/cm <sup>2</sup> and InP will be tested at 25mA/cm <sup>2</sup> . Failure is determined by >20% loss in the initial value of light-limited photocurrent density in three-electrode current-potential curves.	09/14	60%
Within a 3-inch tandem GaInP <sub>2</sub> /GaAs wafer, establish a 70% yield of individual electrodes that exceed 10% STH efficiency.	09/14	20%
With the goal of meeting the ultimate MYRD&D water splitting efficiency targets, design tandem configurations, in conjunction with III-V growth experts, with optimal bandgap combinations targeting 1.3 eV for the top cell and 1 eV for the bottom cell. Complete growth and PEC characterizations and verify current density greater than 20 mA/cm <sup>2</sup> under AM1.5G illumination.	09/14	40%

Major milestones remain on-track

# Technical Accomplishments – Standardized Methods for PEC

## Springer Short Book Published

- Huyen Dinh (NREL), Zhebo Chen (Stanford), Eric Miller (DOE) co-editors turned 160-page manuscript that we developed with the PEC working group into 125 pages for book publication on the topic of standardized methods for PEC characterizations
- Abbreviated manuscript published as a Journal of Materials Research paper has been cited 208 times since 2010
  - Deutsch and Turner from NREL as well as our collaborator Heske from UNLV were contributing authors (among several others)

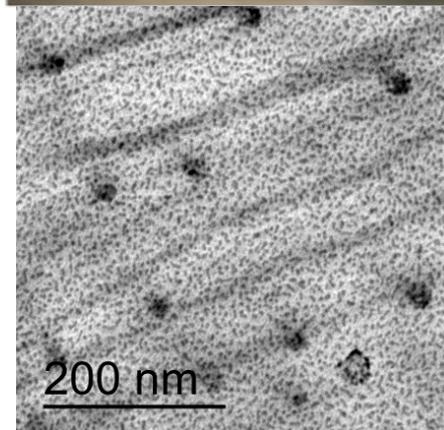
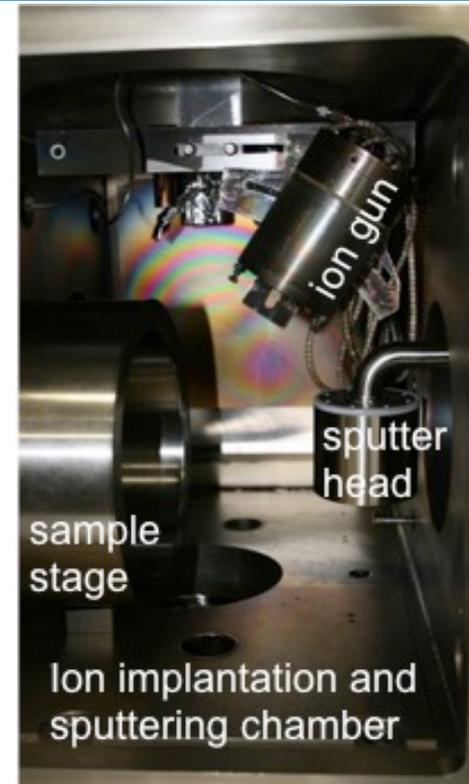


# Technical Accomplishments – Continued Optimization of Passivation Treatment Process on GaInP<sub>2</sub>

- Rotating sample stage – 15 rpm
- N<sub>2</sub><sup>+</sup> ion implantation first
  - Key parameters: Angle (55°), distance (20 cm), pressure (8x10<sup>-4</sup> N<sub>2</sub>), beam voltage (550 V), beam current (12 mA)
  - Rotated 9 min through ion source (exposed 30 s)
- PtRu alloy sputtering second
  - Two passes through sputter plume (exposed < 0.5 s)

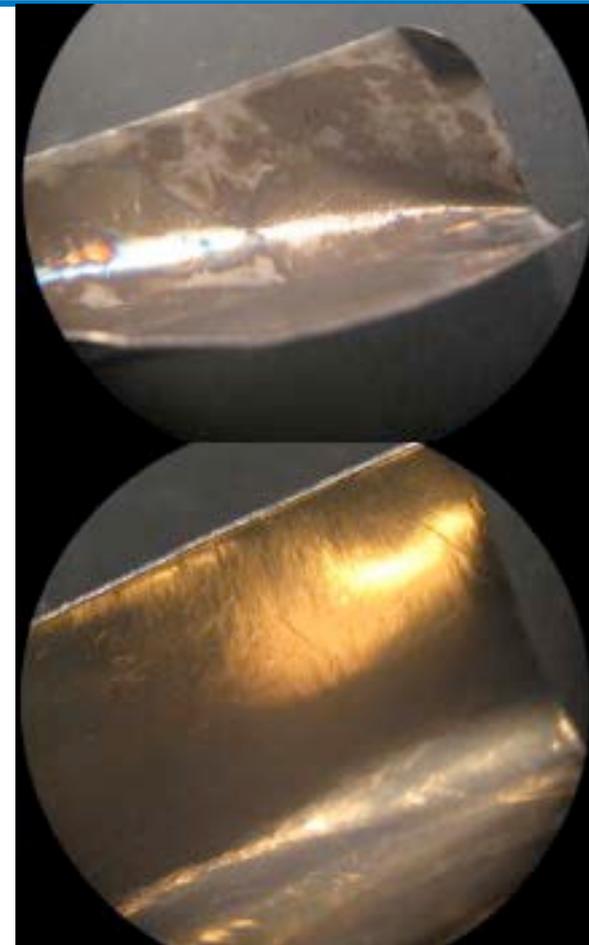
## PtRu morphology & loading

- Scanning transmission electron microscopy
  - ~ 5 nm particles with approximately 30% surface coverage
- Inductively coupled plasma mass spectrometry
  - Several samples digested in aqua regia, diluted solutions analyzed for PtRu
  - Equivalent coverage (assuming a continuous thin film) is between 1-2 nm
    - Adds \$2/m<sup>2</sup> to absorber costs
    - Requires 66 g of Pt for a 1000 kg/day type 4 reactor array using ultimate DOE targets (25% STH, 15x concentration)



# Technical Accomplishments- Stability Testing of Stand-Alone PEC Water-Splitting Tandem Devices

- **Milestone: Tested GaInP<sub>2</sub>/GaAs tandem electrodes for 100 hours at short-circuit (true zero bias)**
  - 3 M H<sub>2</sub>SO<sub>4</sub> with 2g/L Zonyl® FSN-100 Fluorosurfactant
  - AM 1.5G (tungsten source, GaInP<sub>2</sub> reference cell)
  - Zero V vs. Pt, Pt-black, RuO<sub>2</sub>, or IrO<sub>2</sub> anodes
  - 14 surface-modified electrodes tested
- **Results**
  - 15 mA/cm<sup>2</sup> – average starting current density
  - 61 hours – average time to failure (first anodic data point)
  - Three electrodes exceeded 100 hours (103, 103, 110)
    - 2015 MYRDD target is 875 hours (0.5 year replacement, 20% capacity factor)
  - Water oxidation overpotential increased by several hundred mV due to fouling of counter electrodes; this led to a drop in overall water splitting current to below 10% STH in several minutes to several hours.
  - Sonication in CCl<sub>4</sub> restored counter electrode appearance and performance
  - **Identified auxiliary component (surfactant, counter electrode) issues critical to device performance and durability and we are taking steps to address**

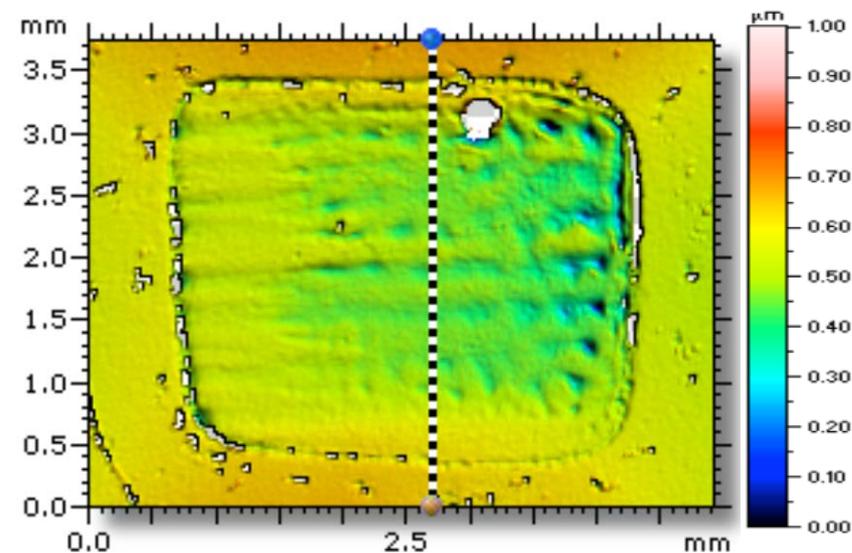
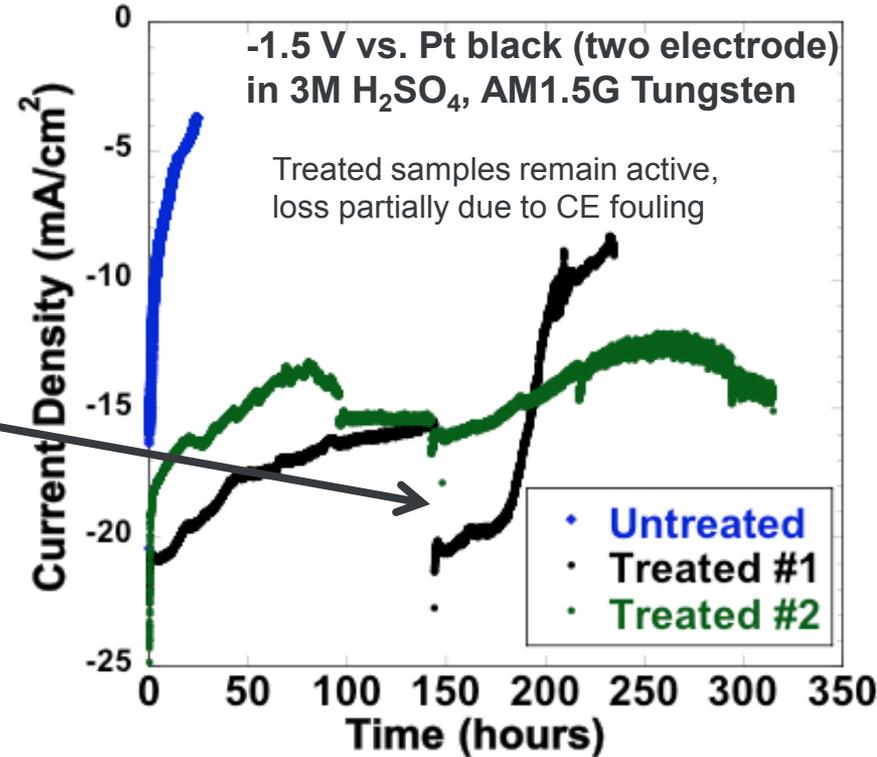


Platinum black counter electrodes used for durability testing. The film caused by operating as an anode in fluorosurfactant is apparent in the top photo, the bottom is after sonication in CCl<sub>4</sub>.

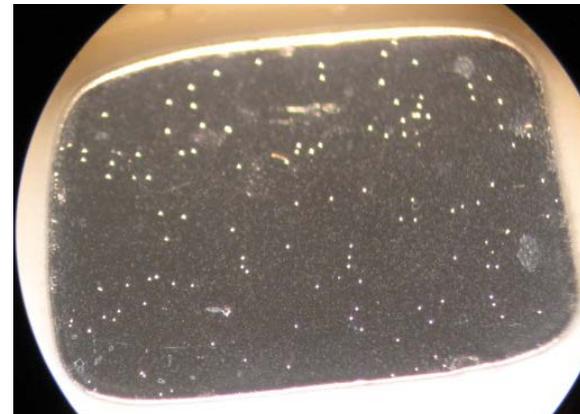
# Technical Accomplishments – Over 300 Hours of Durability on GaInP<sub>2</sub>

To maintain high currents in spite of electrode fouling, long-term durability testing performed under constant bias

- Untreated GaInP<sub>2</sub>:
  - Failed in 24 hours
- Treated GaInP<sub>2</sub> #1:
  - Stopped @ 144 h, CE cleaned, solution tested, restarted with fresh electrolyte
- Treated GaInP<sub>2</sub> #2:
  - Just restarted @ 148 h



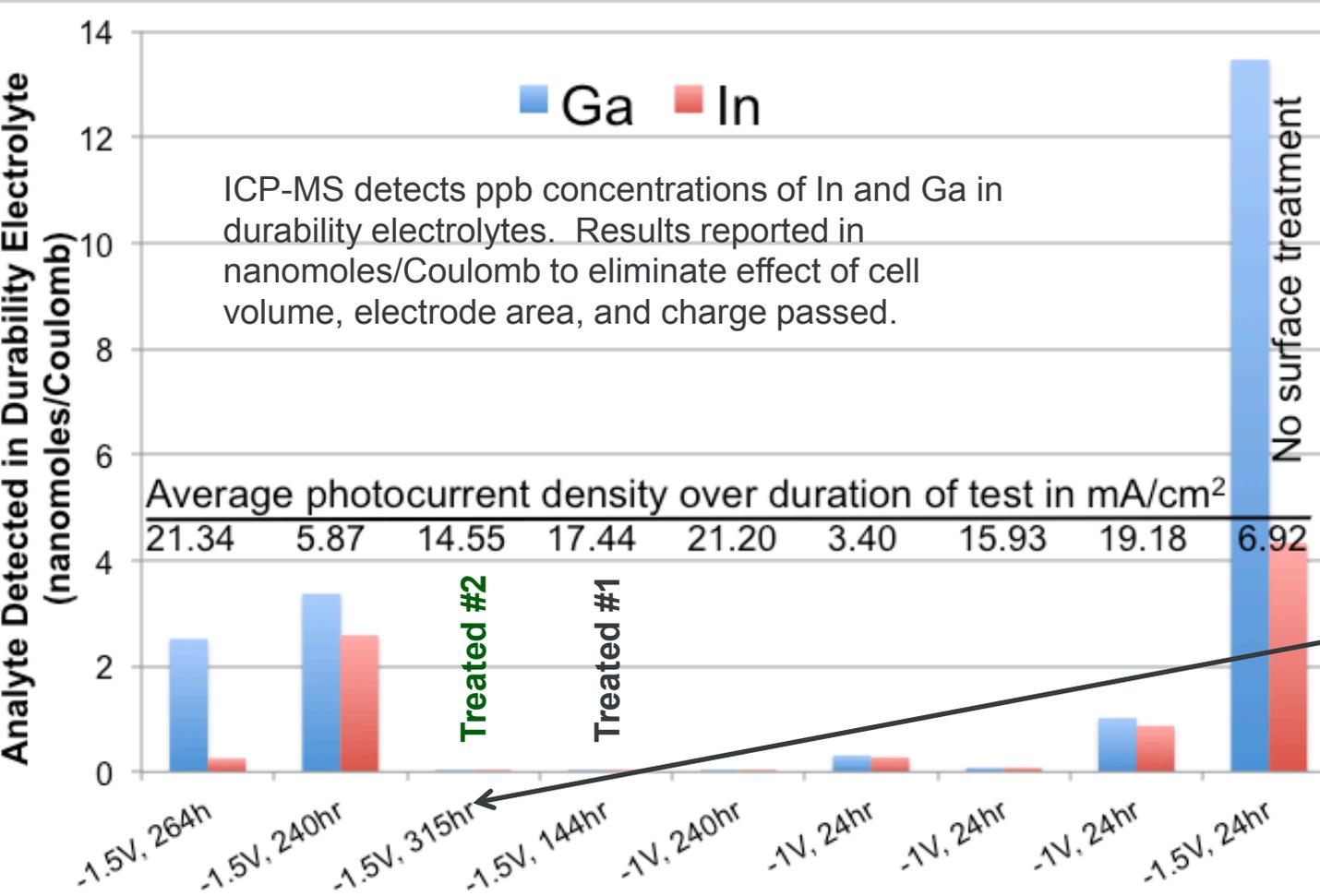
Optical profilometry of Treated #2 electrode surface after 315 hours of testing reveals very minor etching



Photograph of Treated #1 electrode surface after 144 hours. Similar to untested surface.

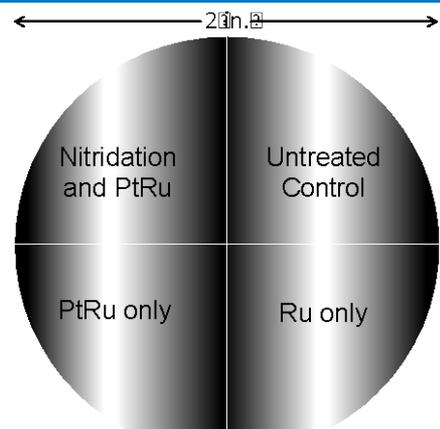
# Technical Accomplishments – Long-term Stability of Tandem Electrodes GaInP<sub>2</sub>/GaAs Confirmed with ICP-MS

- Resistance to corrosion assessed by measuring gallium and indium concentrations in durability electrolytes by inductively coupled plasma mass spectrometry (ICP-MS)
- Lower values are correlated with greater stability; Ga and In not stripped into solution as aqueous ions during operation



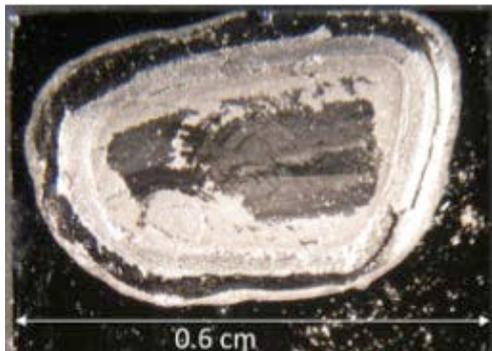
Very small quantities of Ga and In were detected in solution for Treated#2 after 315 hours averaging nearly 15 mA/cm<sup>2</sup>, showing viability of surface passivation to get to near-term 875 h durability target.

# Technical Accomplishments – Surface Passivation of Advanced III-Vs for Potential for Higher Efficiency



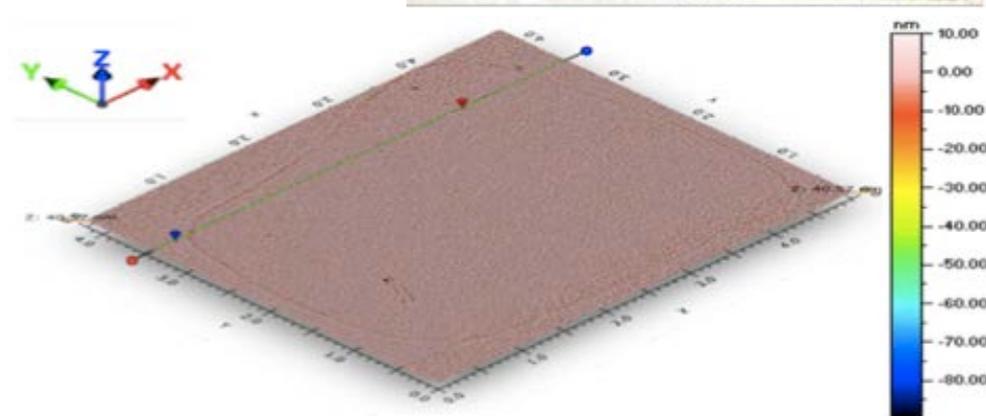
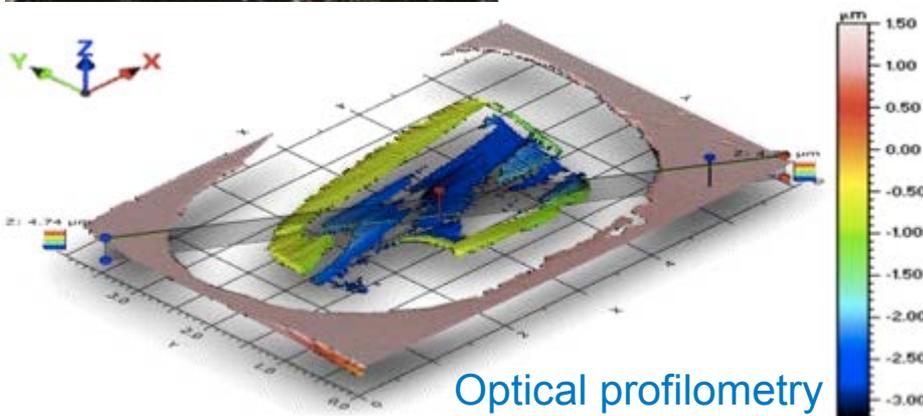
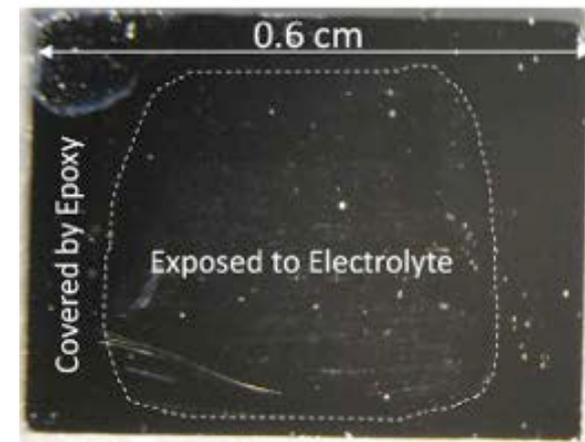
## Milestone

- 2-inch diameter, 4  $\mu\text{m}$  thick, p-InP grown by MOCVD on InP substrate
- Three of the four quarters had a different surface modification
- Durability testing:
  - 3 M  $\text{H}_2\text{SO}_4$  w/ Zonyl. 24 hours, 25  $\text{mA}/\text{cm}^2$
  - **1.7 times the photocurrent magnitude** of 315 h  $\text{GaInP}_2$



Typical untreated electrode: extensive damage and significant ( $\sim 4 \mu\text{m}$ ) etching in exposed area

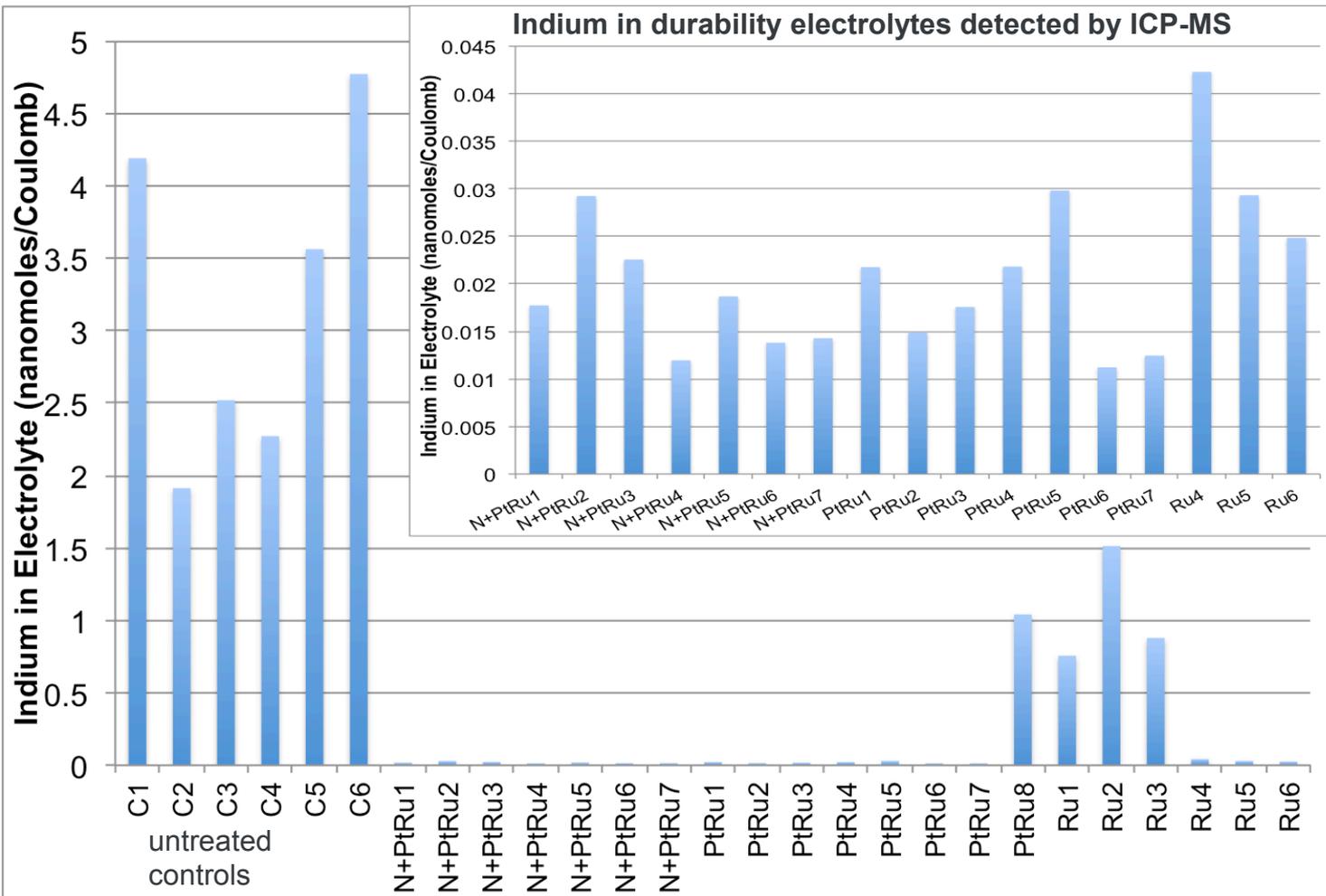
Typical treated electrode: This N-ion implanted & PtRu sputtered electrode had a pristine surface after durability testing



# Technical Accomplishments – Effectiveness of Surface Passivation of p-InP at High Current Confirmed with ICP-MS

## 21 treated and 6 untreated p-InP electrodes tested at 25 mA/cm<sup>2</sup> for 24 hours

- 17 of 21 had no obvious degradation and only trace quantities of indium (~25 ppb) in electrolyte
- 14 of 15 electrodes treated with PtRu were successfully protected from corrosion
- 6 of 6 untreated electrodes were severely damaged; ICP-MS found ~4 ppm indium in electrolyte



ICP-MS results show the surface passivation recipe designed for GaInP<sub>2</sub> protects InP from corrosion at very high current densities.

# Technical Accomplishments – Photoreactor Testing

- **Milestone: Tested GaInP<sub>2</sub>/GaAs tandem electrodes in photoreactor on solar tracker with optical concentration under on-sun conditions.**
  - Surface-modified electrodes; 3 M H<sub>2</sub>SO<sub>4</sub> w/ Zonyl<sup>®</sup> FSN-100; ~5x concentration; biased -1 V vs. Pt-black counter electrode; product gases collected over 4 hours

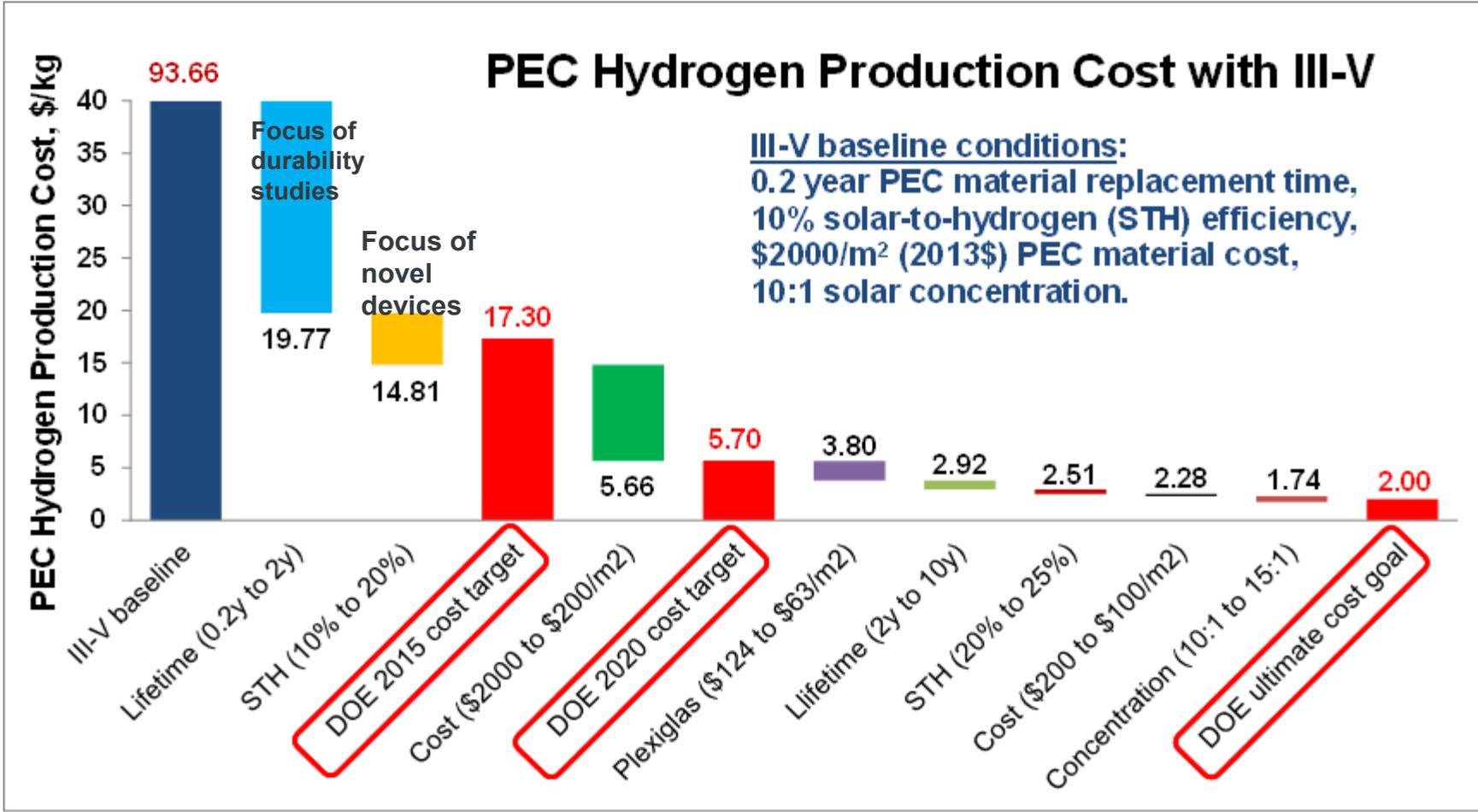


## Results (typical)

- Current declined 47 mA/cm<sup>2</sup> to 14 mA/cm<sup>2</sup> over 4 h
- 4.40 ml H<sub>2</sub>, 1.90 ml O<sub>2</sub>  
ratio H<sub>2</sub>/O<sub>2</sub> = 2.0:0.86
- Charge passed = 37.11C  
equates to 5.80 ml H<sub>2</sub> for  
100% current efficiency
- 76% Faradaic yield for H<sub>2</sub>
- Visibly damaged electrode  
surfaces
- Issues could be related to  
non-ideal (leaky), first-  
generation photoreactor



# Technical Accomplishments – Waterfall Chart



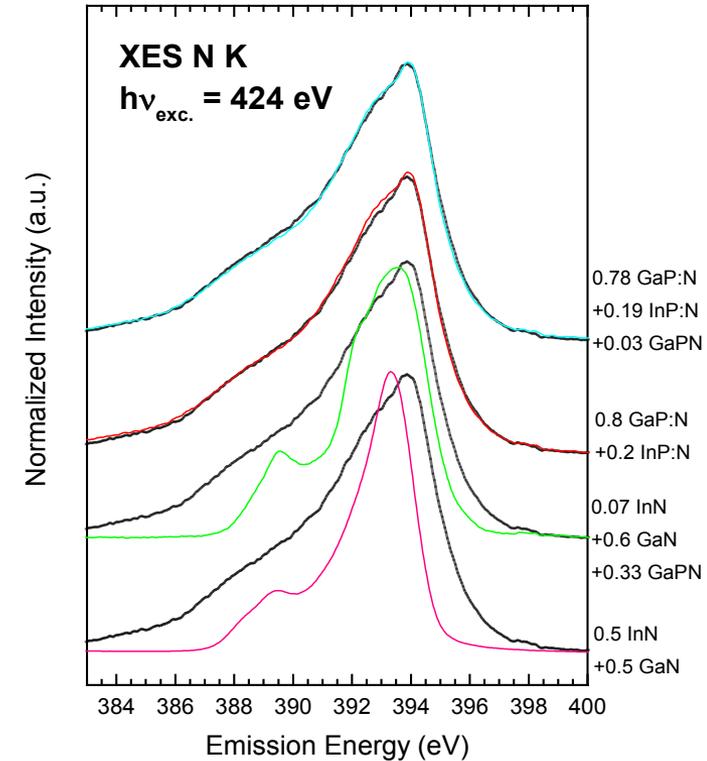
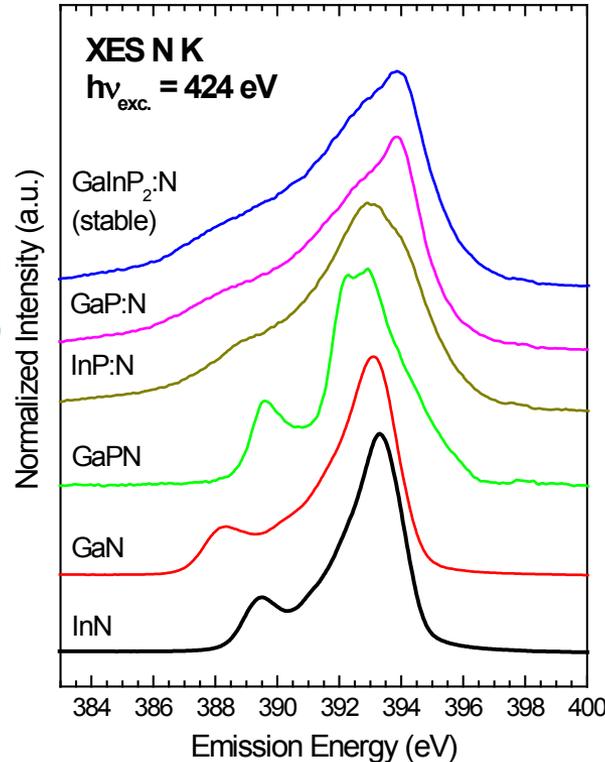
Waterfall chart projecting cost reductions in PEC hydrogen production by making serial iterations with the H2A Future Central Hydrogen Production from Photoelectrochemical Type 4 version 3.0 case study (scaled to 2000 kg/day, 98% plant capacity factor) with our anticipated progress towards technical targets.

# Technical Accomplishments – UNLV Spectroscopic Characterization at Berkeley Advanced Light Source

## X-ray Emission Spectroscopy (XES) taken by Heske group (UNLV)

Because N is a minor component in these materials, this study can only be carried out using high-brilliance synchrotron radiation and, in particular, the UNLV group's high-transmission soft x-ray spectrometer.

Co-investigators: M. Blum, S. Alexander, S. Rosenberg, M. Bär, L. Weinhardt, C. Heske



### Nitrogen K-edge XES: indicates a complex chemical environment of N

- Left plot – UNLV collected XES spectra on NREL N-treated GaP:N, InP:N, GaInP<sub>2</sub>:N, as well as GaP<sub>0.98</sub>N<sub>0.02</sub>, GaN, and InN reference samples
- Right plot – Multiple-spectrum weighted sum fits by UNLV show GaInP<sub>2</sub>:N can not be described by sum of GaN and InN; it closely resembles GaP:N but fit requires InP:N and a little GaPN
  - Describing the chemical environment of N in GaInP<sub>2</sub>:N requires considering P-N interactions
  - Critical clues for LLNL theoretical modeling of complete simulated GaInP<sub>2</sub>:N spectrum ([PD058](#))

# Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- **“This project needs to focus more on on-sun trials.”**
  - Response: That has been an emphasis in the last year. We had some success with our first-generation photoreactor and are incorporating improvements in to our next design for this outdoor season.
- **“The absence of Faradaic efficiency measurements is a notable weakness of this project, given that its primary objective is to investigate the stability of these materials.”**
  - Response: We completed Faradaic efficiency measurements this year and started a project using Hoffman apparatus to assess the influence of surfactant and segmented cells on Faradaic yields.
- **“This [surface modification] approach should be extended to other materials to view how universally useful the nitrogen ion treatment may be for III-V materials.”**
  - Response: We extended this approach to p-InP and p-GaAs. The treatment had a high success rate on InP and demonstrates it is a viable approach to protecting electrodes under high current densities. The preliminary results on GaAs are also promising.

# Collaborations

- Partners (extensive collaboration with all)
  - University of Nevada Las Vegas
    - Key partner in surface validation project
  - Lawrence Livermore National Laboratory
    - Key partner in surface validation project (PD058)
  - University of Hawaii
    - Gaillard group – cooperative PEC characterization; sample exchange and validation
  - Stanford University
    - Jaramillo group – Key partner in PEC standardization efforts
  - University of Texas-Arlington
    - Professor Muhammad Huda for PEC materials theory and modeling
  - Los Alamos National Laboratory
    - Todd Williamson – InGaN samples
  - Colorado School of Mines
    - Graduate, postdoc and assistant professor research associates; electron microscopy and XPS user facilities; sample exchange
  - University of Colorado-Boulder
    - Two NSF-graduate research fellow associates under Steve George and Art Nozik are part of our group
  - University of Louisville
    - Sunkara group – novel III-Vs ( $\text{GaAs}_x\text{Sb}_{1-x}$ )
    - Joint characterizations/publication
  - University of Oregon
    - Boettcher group – Joint InGaN PEC characterizations
  - We were identified as (unfunded) partners on six NSF proposals primarily for sample benchmarking
    - Oregon, Stanford, Colorado School of Mines, Toledo, Louisville, Nevada-Reno

# Remaining Challenges and Barriers

- **Efficiency:**
  - Push solar-to-hydrogen efficiency from 12% to beyond 20% for meeting ultimate DOE targets
- **Durability:**
  - Extend our 0.2 year durability to 2 years in the short-term and 10 years long-term
  - More realistic real-world durability assessments
  - Identification and control of non-obvious but stability-relevant process parameters
- **Semiconductor costs:**
  - Reduce synthesis costs by factor of 10 compared to current cost of small-batch III-V materials
- **System testing:**
  - Identify promising photoreactor designs and components
    - Window/body material, sealant/epoxy, membrane, counter electrode

# Future Work– Towards *Economical* Hydrogen

In order to achieve the EERE plant-gate, untaxed cost targets of \$1-2/kg H<sub>2</sub> (1kg H<sub>2</sub> = 1gge) requires a PEC system that has 25% solar-to-hydrogen (STH) efficiency, a semiconductor cost around \$150/m<sup>2</sup>, and 10 years of stability.

- **Efficiency**

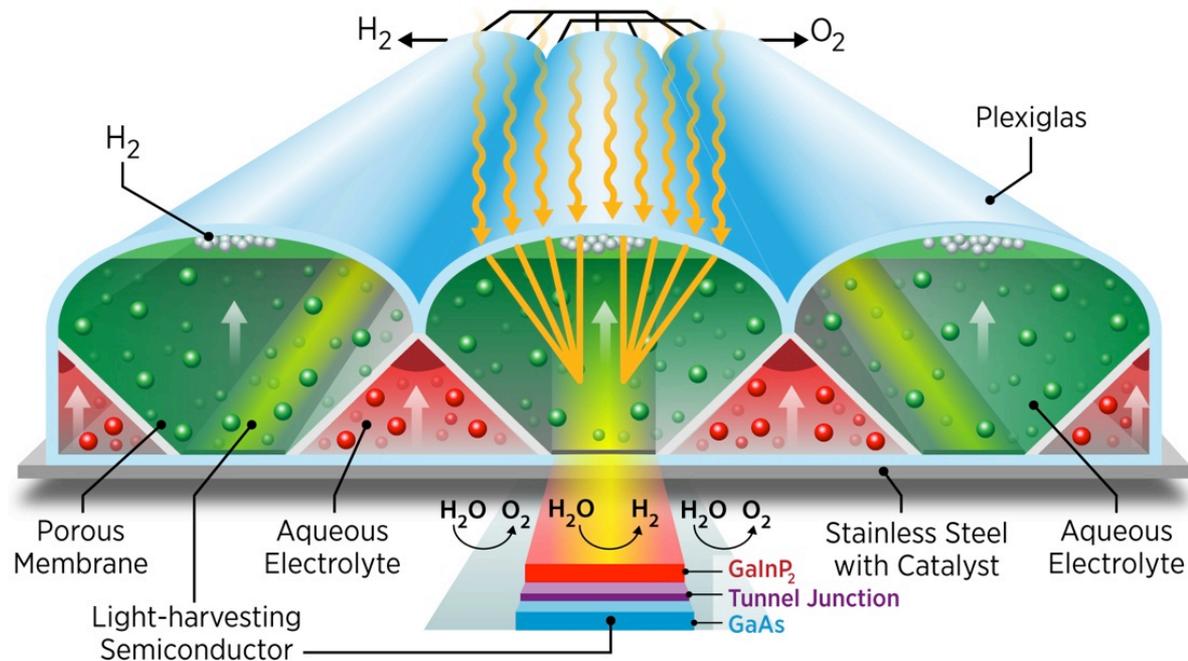
- Novel III-V tandem structures with more optimal bandgaps
  - 20% STH within 1-year
  - 25% STH within 3-years

- **Durability**

- Catalytic nitride, oxide, and sulfide surface modifications to achieve several thousand hours of durability

- **Semiconductor Cost**

- Modeling achievable cost reductions from innovative III-V synthesis routes being developed by other DOE programs (SunShot, arpa-e)
  - Epitaxial lift-off, spalling



**Photoreactor Prototyping:** Fabricate innovative reactor designs that utilize low optical concentration (10x) to minimize area of semiconductor required

# Project Summary

- Relevance:** Spearheading research in high-efficiency materials in order to meet DOE metrics and objectives for solar-hydrogen generation
- Approach:** Focus on high-efficiency III-V crystalline semiconductor systems, an NREL core competency: investigation of new materials and configurations as well as stabilization of GaInP<sub>2</sub> surface
- Technical Accomplishments:** Springer brief (book) on PEC standards published; continued optimization of surface treatment conditions and PtRu quantification; short-circuit treated tandem testing – exceeded 100 hours; biased tandem durability – 315 hours of stability @ ~15 mA/cm<sup>2</sup> (improvement on previous 115 hours @ 10 mA/cm<sup>2</sup>); demonstrated passivation on InP at high current densities; outdoor testing under concentrated sunlight with Faradaic yield measurements; waterfall chart and; along with UNLV & LLNL, made progress in understanding of N in GaInP<sub>2</sub>
- Collaborations:** Several ongoing, active collaborations with synthesis, modeling, and characterization groups
- Proposed Future Work:** Auxiliary components: identify suitable surfactant – segmented cells; new III-V configurations for higher efficiencies (20% and beyond); use understanding of surface passivation arising from surface validation collaboration to extend durability from 0.2 years to 0.5 years (near-term) and 2 years (mid-term); test passivation on additional III-V materials (arsenides); photoreactor for III-V efficiency and stability evaluation under concentrated on-sun conditions; III-V economics at scale

# Acknowledgements

---

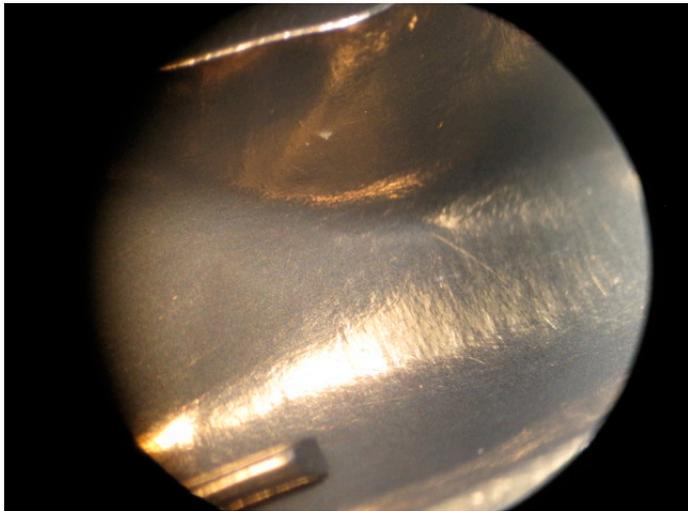
- Henning Döscher – NREL
- Heli Wang – NREL
- Clay Macomber – NREL
- Huyen Dinh – NREL
- Erin Brahm – (intern) Berkeley (GS)
- James Young – NREL/CU-Boulder (GS)
- Skye Rios – NREL/CU-Boulder (GS)
- Anna Duda– NREL
- Arrelaine Dameron – NREL
- Andrew Norman – NREL
- All of our amazing collaborators noted throughout this presentation

# Technical Back-Up Slides

# Platinum Counter Electrode Fouling



Platinum black counter electrode with shiny film due to durability testing

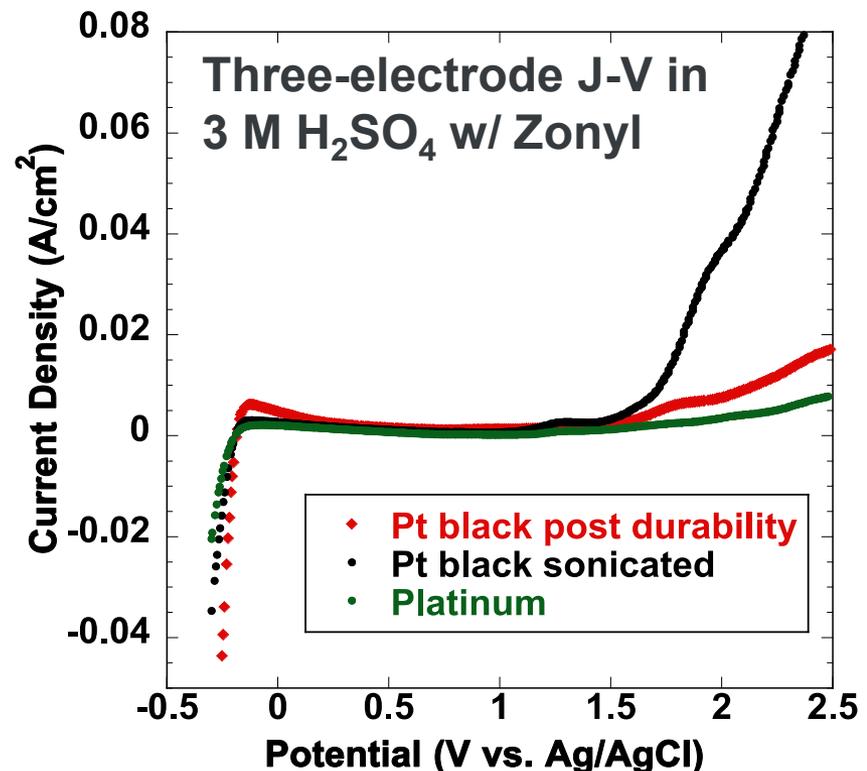


The same platinum black electrode after five minutes sonication in  $\text{CCl}_4$

- Zonyl non-ionic fluorosurfactant leaves visible film on counter electrode (anode) reducing water oxidation activity

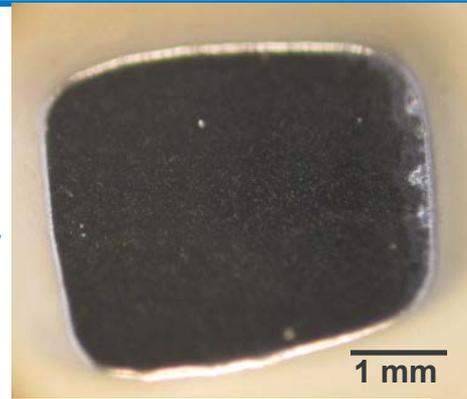
Trends in Analytical Chemistry 54 (2014) 45–55.

- Sonication in organic solvent restores anode appearance and performance

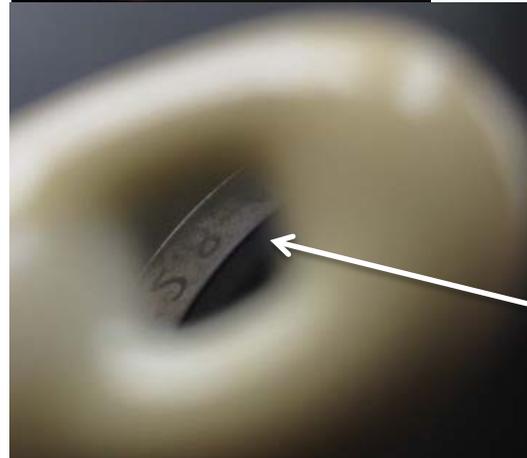
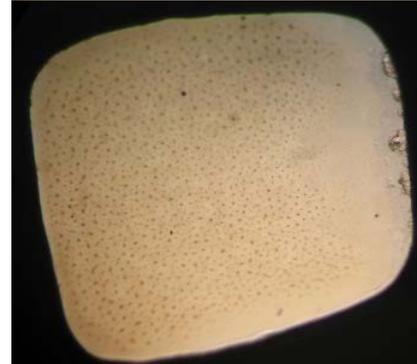


# Ten Continuous Days of Stability

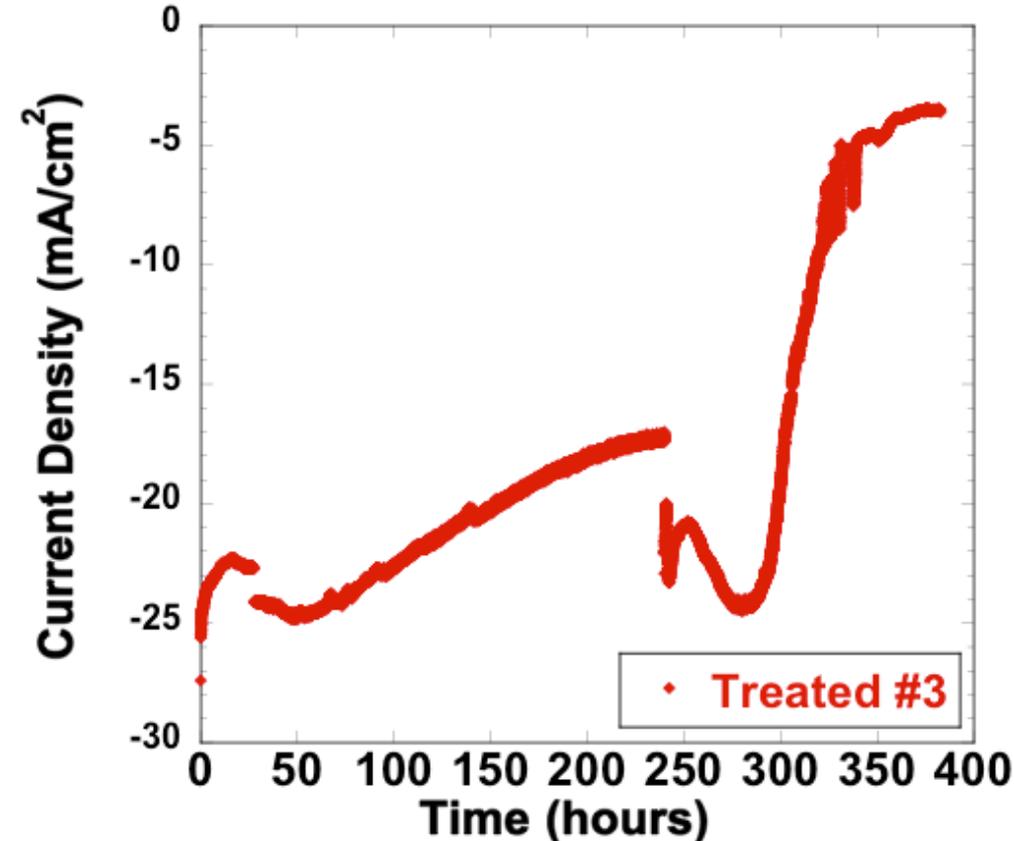
- Treated tandem electrode biased -1.5 V vs Pt black counter electrode
- Test stopped at 240 hours and the electrode was photographed (right), solution analyzed (slide 13).
- Restarted with fresh solution and cleaned counter electrode
- Failed around 300 cumulative hours



Photographs of the surface under varying lighting condition after 240 hours show damage along the right side (bottom of electrode during operation) and spots over the whole surface.



Despite these features the electrode exhibited specular reflection.



# Raw ICP-MS Data from Biased Tandem Durability Tests & Platinum Loading Cost Calculations

- 3 M H<sub>2</sub>SO<sub>4</sub> durability solutions were diluted 1:100 for ICP-MS testing
- Last two columns are data presented on slide 13
- Surfactant foam on top of electrolyte surface limits solution volume measurements to estimates within 0.5 mL

Test Conditions	Comments	Solution Volume (mL)	Electrode Area (cm <sup>2</sup> )	Total charge (C/cm <sup>2</sup> )	Solution Ga (ppb)	Solution In (ppb)	Moles Ga in Solution	Moles In in Solution	nano-moles/C Ga	nano-moles/C In
-1.5V, 264h	treated	19.5	0.109	20283.0	19884.01	3344.23	5.56E-06	5.68E-07	2.52	0.257
-1.5V, 240hr	treated	20.0	0.108	5070.8	6429.06	8120.65	1.84E-06	1.41E-06	3.37	2.583
-1.5V, 315hr	treated	25.0	0.105	16500.9	180.17	157.97	6.46E-08	3.44E-08	0.0373	0.0199
-1.5V, 144hr	treated	24.0	0.119	9039.9	47.84	62.02	1.65E-08	1.30E-08	0.0153	0.0121
-1V, 240hr	treated	22.5	0.0708	18313.0	51.94	61.83	1.68E-08	1.21E-08	0.0129	0.00934
-1V, 24hr	treated	24.0	0.086	294.2	22.84	33.24	7.86E-09	6.95E-09	0.311	0.275
-1V, 24hr	treated	20.5	0.114	1376.1	40.91	66.02	1.20E-08	1.18E-08	0.0767	0.0751
-1V, 24hr	treated	19.5	0.104	1656.9	627.79	883.93	1.76E-07	1.50E-07	1.02	0.871
-1.5V, 24hr	untreated	20.0	0.068	597.8	1907.94	1009.91	5.47E-07	1.76E-07	13.5	4.33

Assumptions used for calculating Pt costs and demand on slide 10:

Cost Pt/m<sup>2</sup>: 1 cm<sup>3</sup> = 2 nm thick film that is 500 m<sup>2</sup>; Density of Pt = 21.45 g/cm<sup>3</sup> so a 2 nm film is 23.31 m<sup>2</sup>/g; \$1433/Troy Oz = \$46.07/g; \$46.07/g ÷ 23.31 m<sup>2</sup>/g = **\$2/m<sup>2</sup>**

Amount needed: 25% capacity factor, 1540 m<sup>2</sup> of absorber required for 1000 kg/H<sub>2</sub> per day under 15x concentration. 1540 m<sup>2</sup> ÷ 23.31 m<sup>2</sup>/g = **66.07 g Pt per 1000 kg/day H<sub>2</sub> array**

# Technical Back-Up

## Logistical issues with surfactant



No surfactant



Surfactant



H<sub>2</sub> and O<sub>2</sub> sulfamic acid foam

Surfactant is necessary to facilitate bubble evolution but makes quantitative analysis of electrolysis products nontrivial

Semiconductor degradation is much more rapid under bubble evolution in electrolyte without surfactant

# Technical Back-Up

- IPCE of treated GaInP<sub>2</sub> electrode pre- and post-durability agrees with the observation of higher photocurrents after durability testing
- One possible explanation: hydrogen evolution could passivate surface damage caused by ion implantation leading to improved IPCE at higher energies.

IPCE conditions:  
3 M H<sub>2</sub>SO<sub>4</sub> with fluorosurfactant  
-0.75 V vs. Ag/AgCl  
300 W Xe lamp with 335 nm long-pass filter  
Light chopped at 0.2 Hz

