Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

RU-EMN – Best-in-class Platinum Group Metal-free Catalyst Integrated Tandem Junction PEC Water Splitting Devices

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Presenter: G. Charles Dismukes
Rutgers, the State of University of New Jersey
6/13/2018

RUTGERS 1766-2016 250

Project ID # pd160

NREL BERKELEY LAB Sandia National Laboratories INL Idaho National Laboratory Lawrence Livermore National Laboratory SRNL

Project Overview

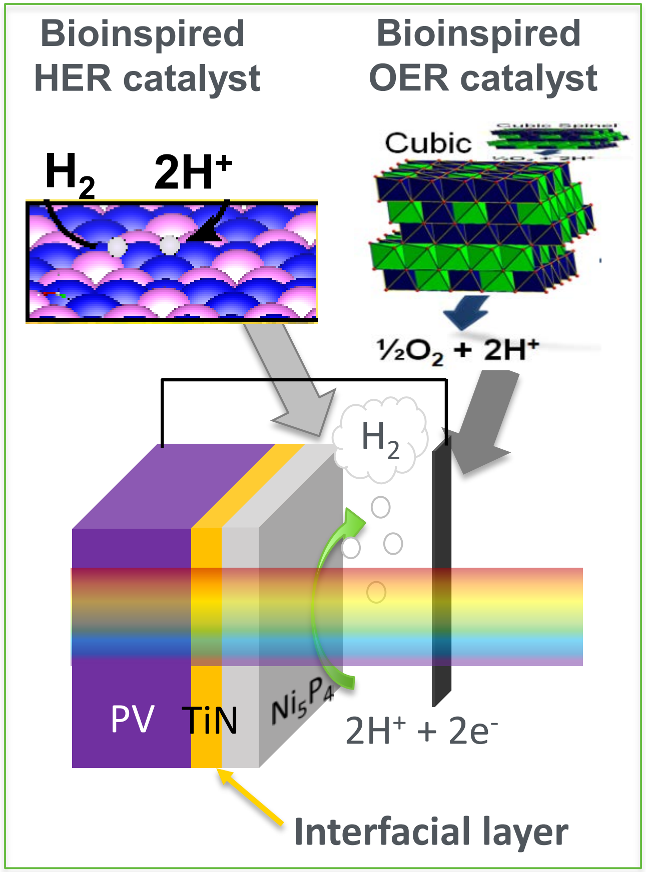
Partners

Rutgers PIs: E. Garfunkel & G. C. Dismukes,
coPI: M. Greenblatt
NREL: T. Deutsch, D. Friedman & A. Zakutayev

Award #	EE0008083
Start Date Yr 1 End Date Project End Date	09/01/17 08/31/18 TBD
Total DOE Share Total Cost Share Year 1 DOE Funding*	$750,000 $83,334 $250,000

Vision

Identify the best technical approaches to fabricate both High Performance (HP) & High Value (HV) PGM-free PECs:
-Using HP PEC NREL-proprietary tandem III-V photovoltaic
-Using HV PEC NREL nitrides & Rutgers oxynitrides in tandem
-Using Rutgers-proprietary electro-catalysts for O_2 - and H_2 - evolution



Impact

- Reveal performance limits of two limiting PV configurations (HP vs HV) using best PGM-free Cats.
- Identify & solve interfacing problems.

- *this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach- Summary

Project Motivation

High-performance Photovoltaics: State of the art material competing with NREL HP III-V tandems (STH 16.7%) is: Multi-junction Silicon (STH 3.9%).

High-value (HV) – emerging photoabsorbers (level 3 readiness): NREL-developed $ZnSnN_2$, coupled with $SrNbO_2N$ are potential efficient and low-cost with high potential impact on global energy economy. Early development hurdles.

TiN vs TiO_2 - Rutgers developed thin-film passivation and protection layer.

$LiCoO_2$ OER catalyst – Rutgers developed alkali cat. w. performance on par with PGM-catalysts.

Ni_5P_4 HER catalyst - Rutgers developed acid & alkali cat. w. performance on par with Pt.

Barriers

Replace PGMs catalysts with non-noble metal catalysts without compromising efficiency

➔ Apply active thin-film of RU-eCats which are on par with PGMs catalysts.

Reduce light losses in Cat/Absorber interface (5 nm MoS_2/MoO_x ~ 25% current loss)

➔ Uses optimum thickness of catalyst with protection/anti-reflective layers (6.8 nm NiP_2/4 nm TiN ~ no current loss).

Photoelectrodes corrosion in alkaline electrolyte

➔ Use proper protection layer with alkaline stable RU-eCats.

➔ Use compatible alkaline buffers.

Key Impact – year 1

Metric	State of the Art	Expected Advance
HP - STH	Non-PGM STH 10%	*Match or beat using non-PGM RU-eCats.*
HV - Parameter 1 *($BiVO_4$ benchmark)*	$J_{ph}\|_{E=1.23V\ RHE}$ = 1.5mA/cm^2, Stable >90% for 1h, material-cost	Improve two or more metrics.

Partnerships

<u>HydroGEN partners:</u>

Daniel Friedman (NREL)
III-V Semiconductor Epi-Structure Device Design and Fab
MOCVD GaInP/GaAs growth & engineering capabilities

Todd Deutsch (NREL)

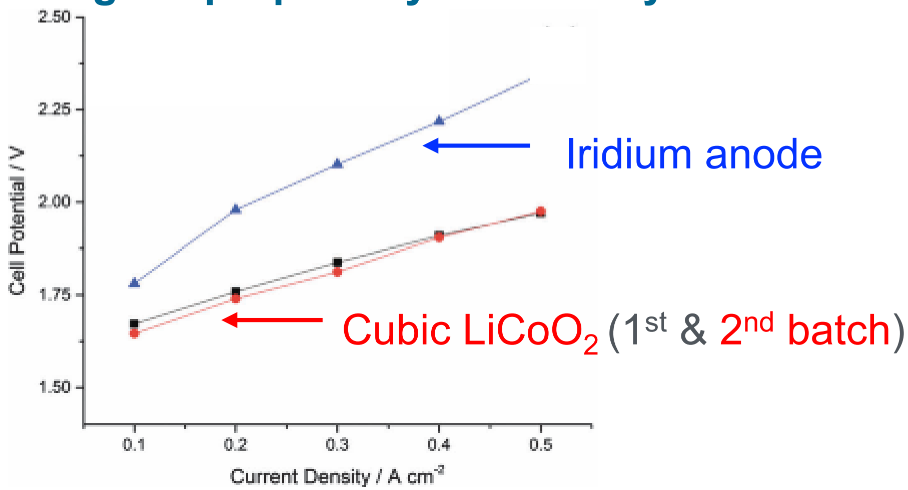
On Sun Characterization of Bulk and Interfaces
Solar testing and benchmarking capabilities

Andriy Zakutayev (NREL)
High-Throughput Thin-film Combinatorial Capabilities
Multi-source and reactive sputtering capabilities

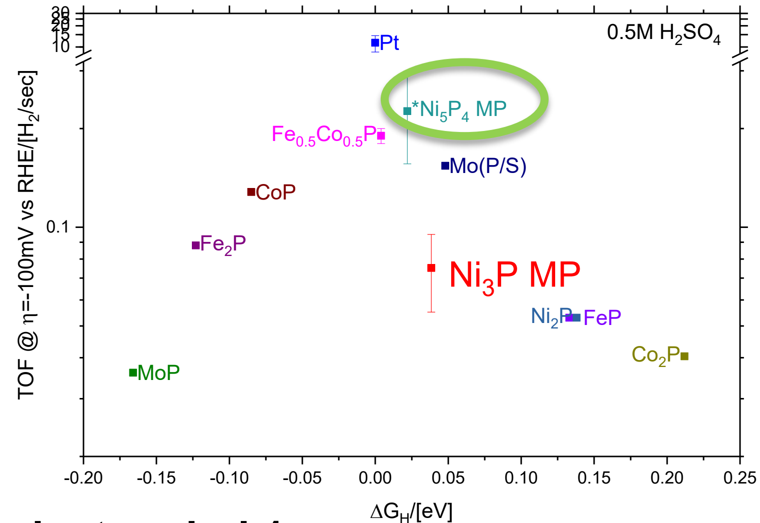
Approach- Innovation year-1 Thrust

Design of catalyst/photoabsorber interfaces using PGM-free RU-eCats with state-of-the-art performance to NREL proprietary photoabsorbers.

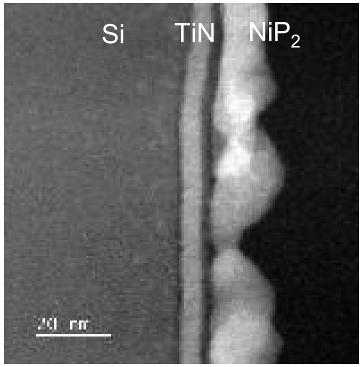
Rutgers' proprietary OER catalyst

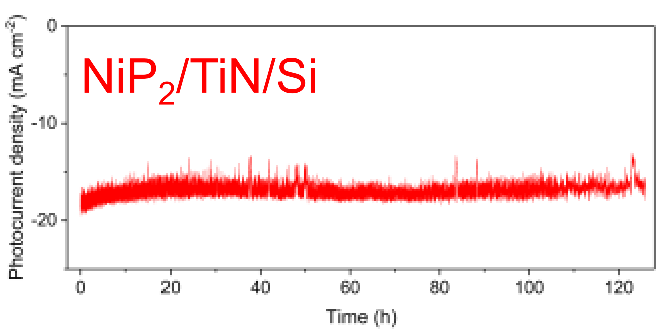


Rutgers' proprietary HER catalyst



Designing RU-protection layer to stabilize photoabsorber interface and RU-eCat adhesion.





Budget period 1 summary:

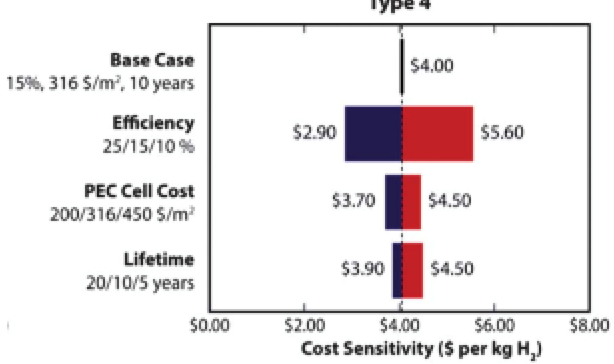
Design, fabricate, characterize, and test first example of Rutgers protection (TiN) and eCat (Ni_5P_4, and $LiCoO_2$)layers on NREL HP (np-GaInP/n^+-GaAs) and NREL HV ($ZnSnN_2$).

Relevance & Impact

Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration[a]

Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Solar to Hydrogen (STH) Energy Conversion Ratio[e, f]	%	4 to 12%	15	20	25

TEA of Type 4, tracking concentrator array PEC



Pinaud *et al. Energy Environ. Sci*. **6**, 1983 (2013)

- This project supports the development of non-PGM and scalable electrocatalysts for PEC water splitting. It will lower H2 costs by increasing STH efficiency, decreasing production costs using lower cost materials, and increase lifetime. These are critical to achieving the DOE target of hydrogen for <$2/kg.

HydroGEN consortium

Rutgers utilizes photoabsorbers and characterization facilities from three NREL nodes: 1) MOCVD GainP/GaAs growth & engineering capabilities (Friedman)[2) Solar testing and benchmarking capabilities (Deutsch); 3) Multi-source and reactive sputtering capabilities (Zakutayev).

This team develops innovative approaches to making interfaces with combined protection/anti-reflective layers. Bi- and tri-weekly meetings coordinating efforts have been undertaken.

Rutgers offers unique Nion STEM with ultra-high resolution EELS vibrational spectroscopy, Rutherford (and medium ion) backscattering spectroscopy and high resolution He-ion microscopy capabilities through collaboration.

Approach- Milestones

Milestones	Anticipated Qtr	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Status
#1	Q1	Determine which substrate has the best performance/cost while optimizing the loading of the $LiCoO_2$ catalyst	E vs OER < 500mV, stable for 24h, loadings ≥ RDE pellets, Electrochemical test in flooded cells, Rutgers	**complete**
#2	Q2	Device test under illumination showing: V_{OC} > 1.85 V, J_{SC} > 10 mA/cm^2, and η_{eff} > 25%	Photoeletrochemical benchmarking, NREL	**complete**
Go/No-Go Crtieria for Thrust 1	Q4	Evaluation of high performance PEC device with renewable catalysts	STH> 10%, stability > 24h, and/or J_{ph} (at 0 V vs. RHE) > 10mA/cm^2, Photoelectrochemical benchmarking, Rutgers and NREL	**50%**
#3	Q3	Fabricate and report optimized $ZnSnN_2$ device	Optimize reflector - max reflectivity, Balancing the highest possible carrier mobility with closeness to 1.1eV bandgap, Rutgers	**25%**
Go/No-go Criteria for Thrust 2	Q4	$LiCoO_2$/$ZnSnN_2$ photoanode fabricated and benchmarked against $BiVO_4$	Must outcompete on (at least 2): J_{ph} (1.5mA/cm^2 at 1.23 V vs. RHE), stability >90% after 1h, and material cost, Rutgers, NREL	**2%, started**

All milestones are completed or on-track for on-time completion

Accomplishments – Overview

Q1 (end of 2017) | Q2 | now | Q3 | Q4 Go/No-Go decision

Milestone #1 ✓
(HP anode)

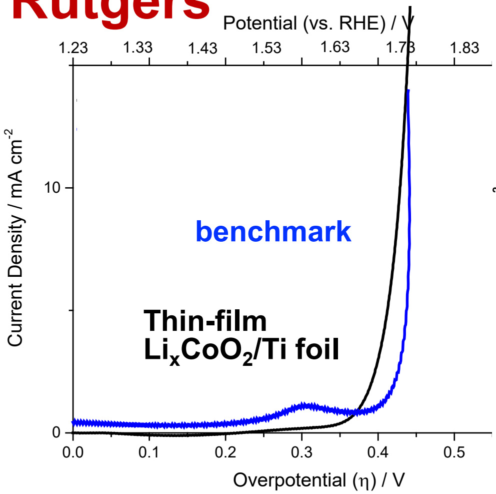
Milestone #2 ✓
(HP photoabsorber)

Milestone #3 On-track
(HV synthesis photoabsorber)

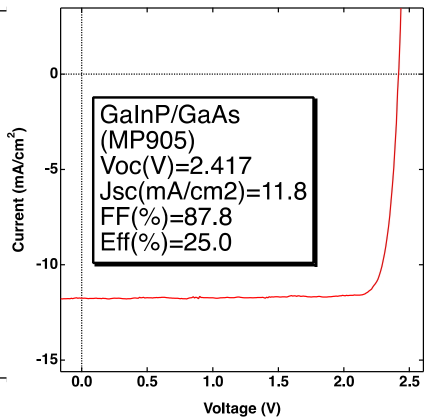
HP device:
STH >10% using PGM-free with III-V tandem device

HV photoanode:
J_{ph} (1.5 mA/cm^2 at 1.23 V vs. RHE), stability

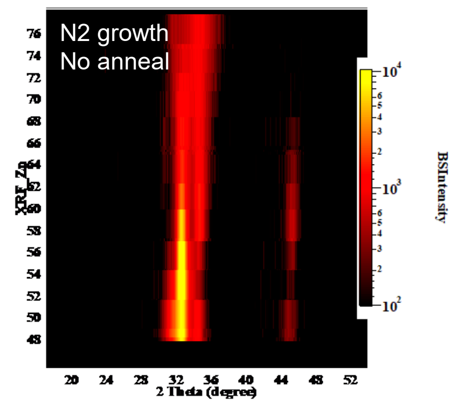
Rutgers



NREL



NREL

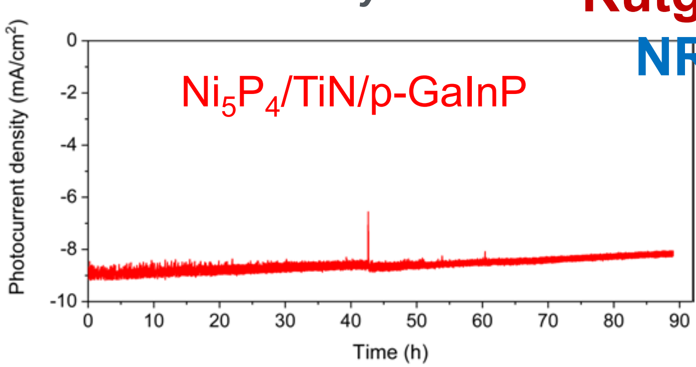


Promising data from Task #2 (HP catalyst/protection layer) ✓

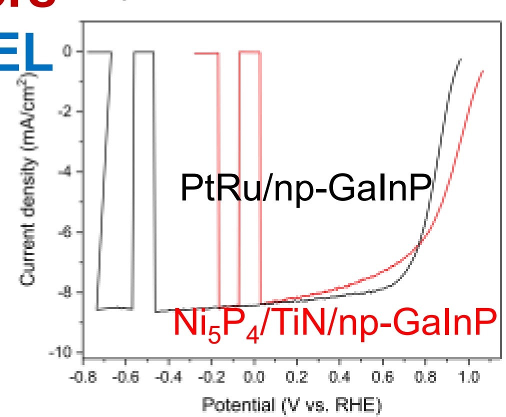
Durability test

Rutgers

NREL



Ni_5P_4 is on par with PtRu



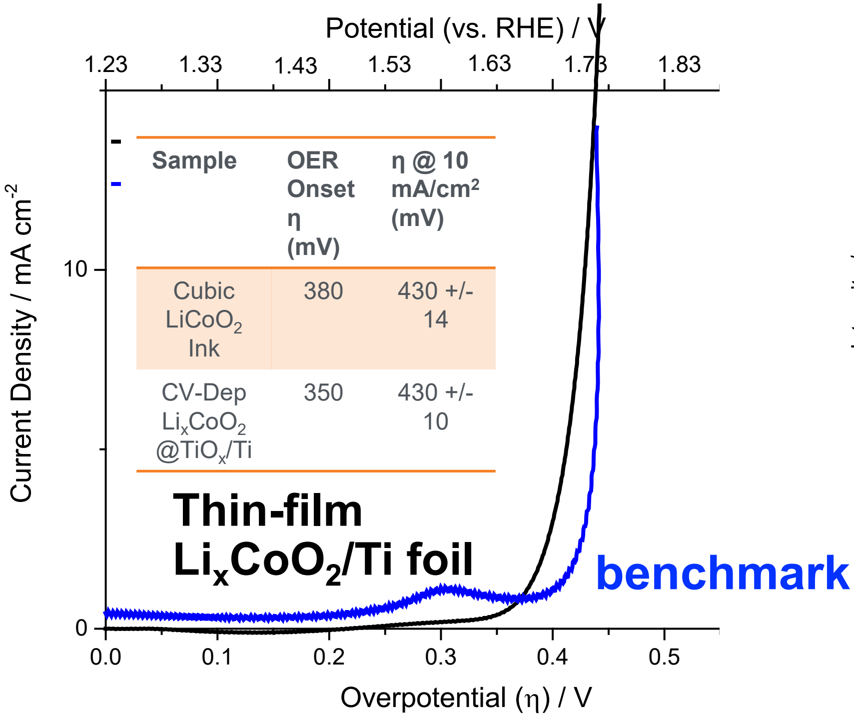
NREL: III-V semiconductor node & semiconductor characterization nodes

NREL: High throughput experimental thin-film node

Accomplishments: Electrochemical (dark) anode

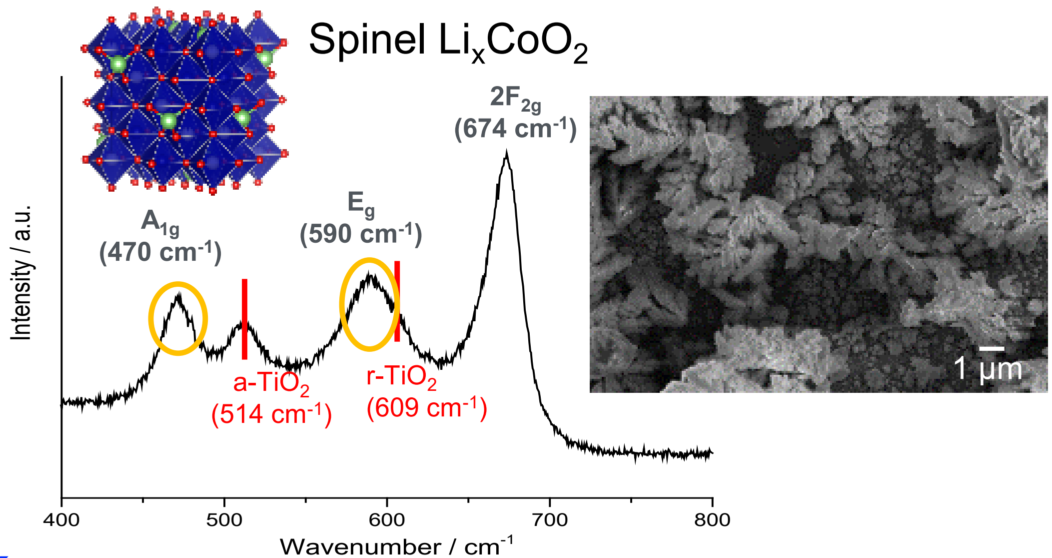
- Milestone 1 (**achieved Q1**) realize a stable non-PGM alkali $LiCoO_2$ electroanode (on par with published cubic-$LiCoO_2$ benchmark) with at least long-term stability (>1 day) required in milestone #1.

Overpotential achieved Milestone #1



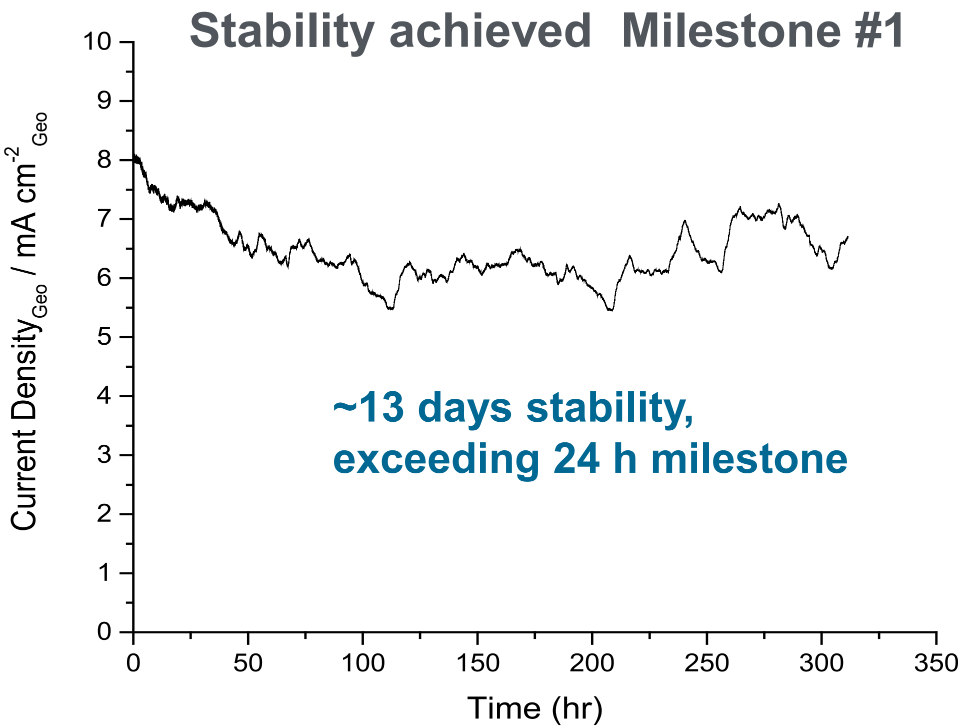
Sample	OER Onset η (mV)	η @ 10 mA/cm² (mV)
Cubic $LiCoO_2$ Ink	380	430 +/- 14
CV-Dep Li_xCoO_2 @TiO_x/Ti	350	430 +/- 10

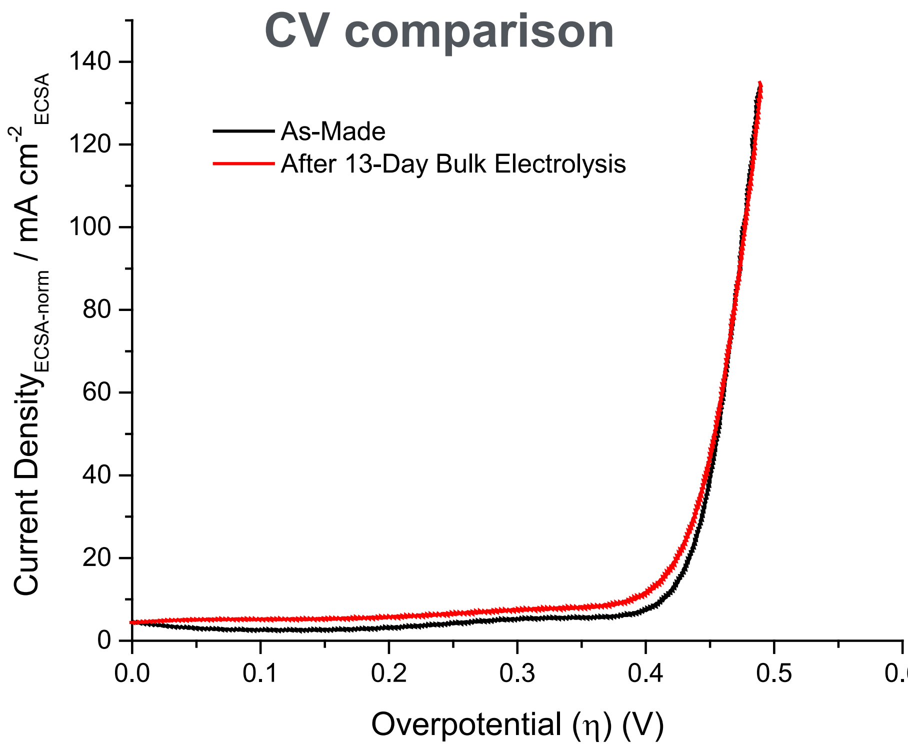
Characterizations (Raman/SEM)



- Technical target: Overpotential, η ≤ 430 mV at 10 mA/cm2geo in pH 14 electrolyte
- Raman spectroscopy signals indicates localized spinel structure. XPS confirm only Co^{3+} precluding unstable Co_3O_4 formation (Data not shown).

Accomplishments: Electrochemical (dark) anode

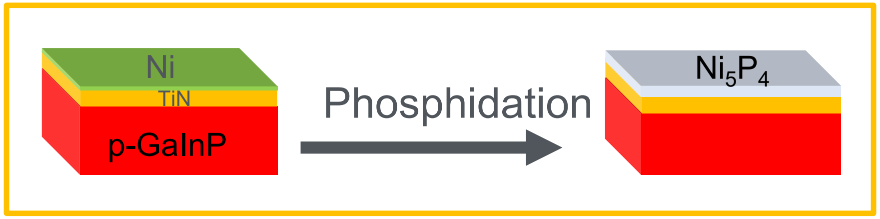




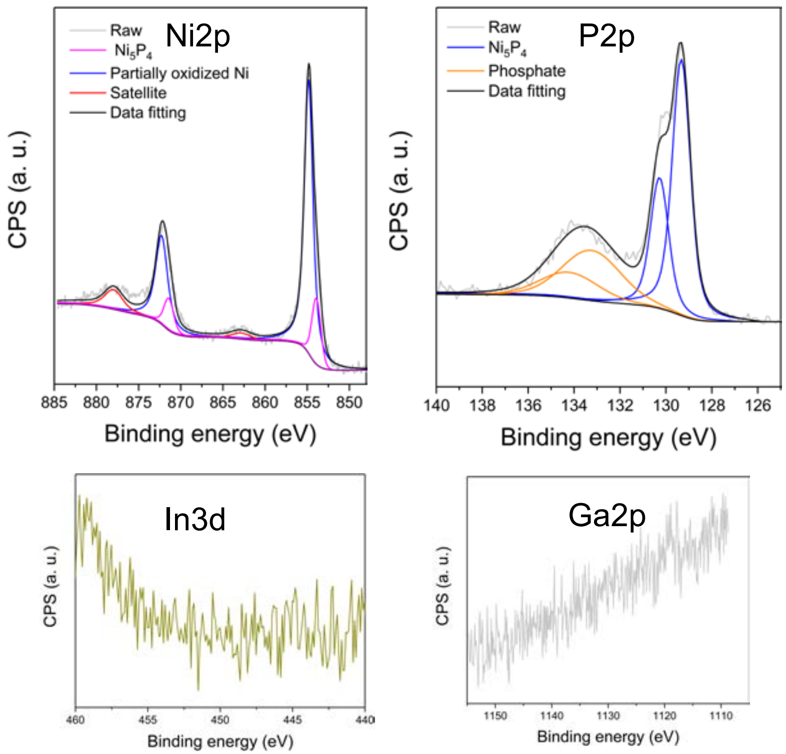
- Chronoamperometric analysis for OER confirms >12 days of stability.
- Surface area normalized CVs shows same intrinsic activity. Minor decreased activity (during durability test) is due to loss of surface area attributed to particle detachment.
- **Achieved Task 3 "Optimize $LiCoO_2$ electrode loading" and milestone 1.**

Accomplishments:
Successful integration of Ni_5P_4/TiN on p-type GaInP

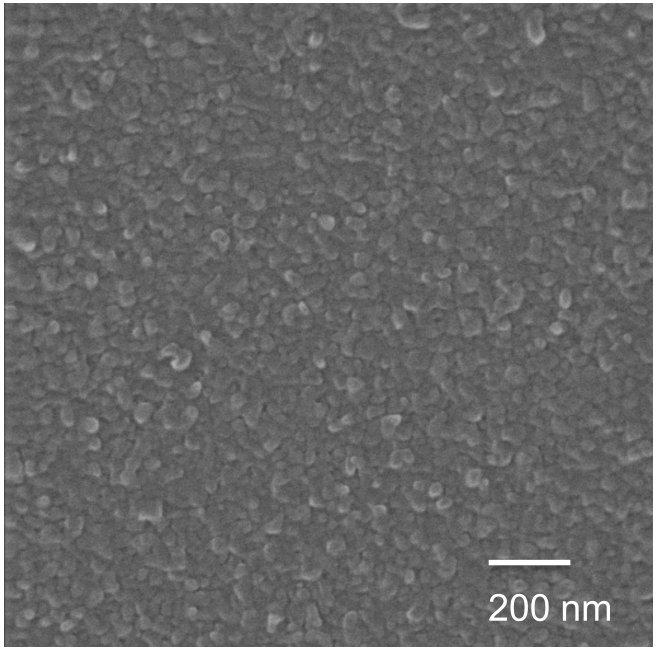
Transferring optimized synthesis condition for proprietary NREL PV
- Synthesis development of catalyst/protection layers, Tech slide 1, 2



Top layer XPS



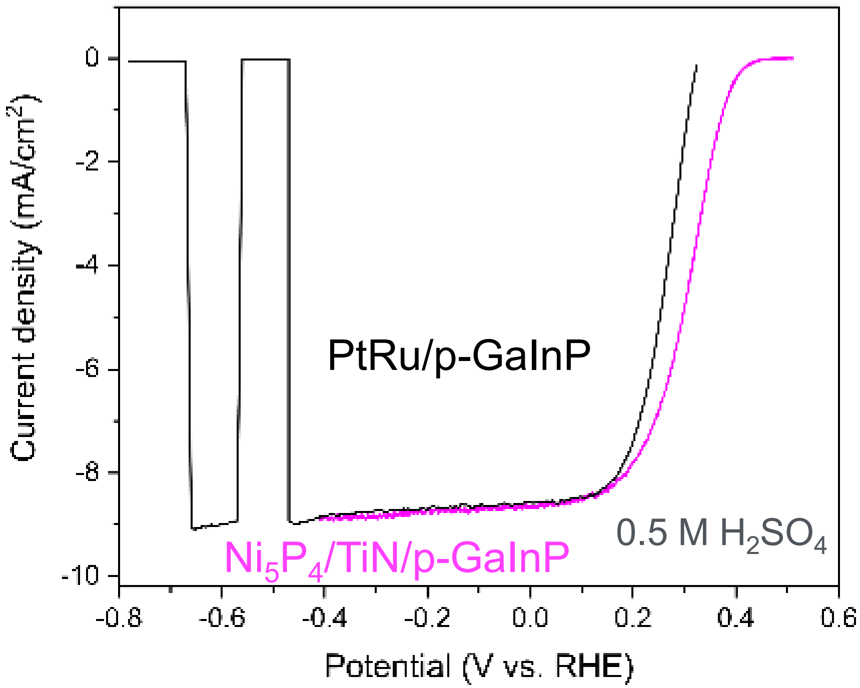
Helium Ion Microscope (HIM) image shows uniform catalyst coverage



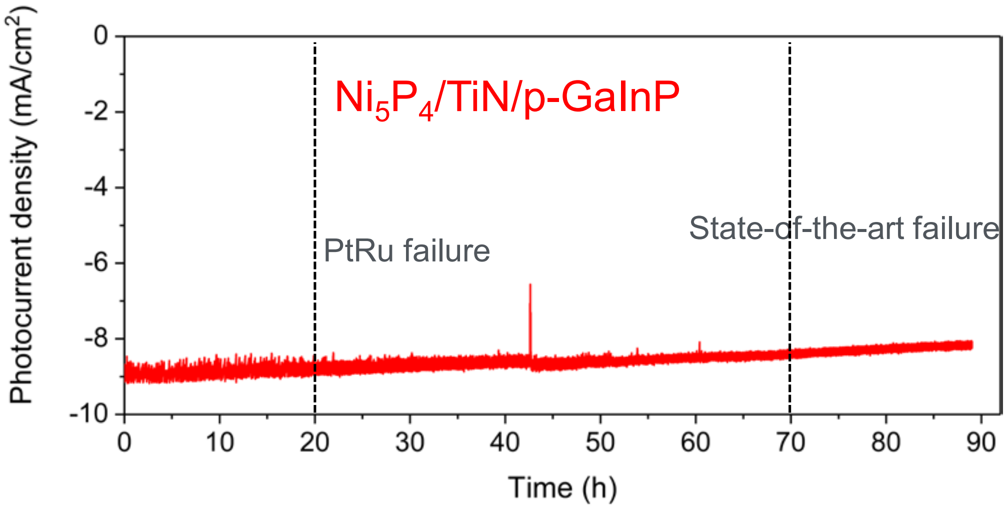
- Top layer XPS confirms successful formation of nickel phosphide catalyst without atomic diffusion of In and Ga

Accomplishments:
Successful integration of Ni_5P_4/TiN on p-type GaInP

J-V Performance
On par with PGM benchmark

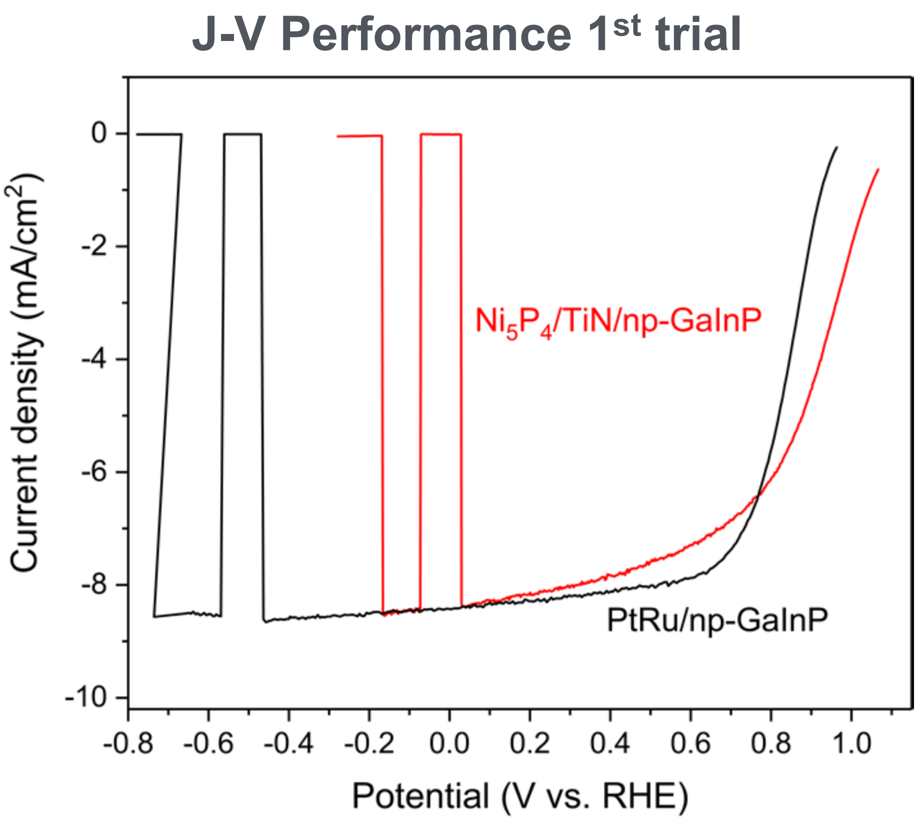


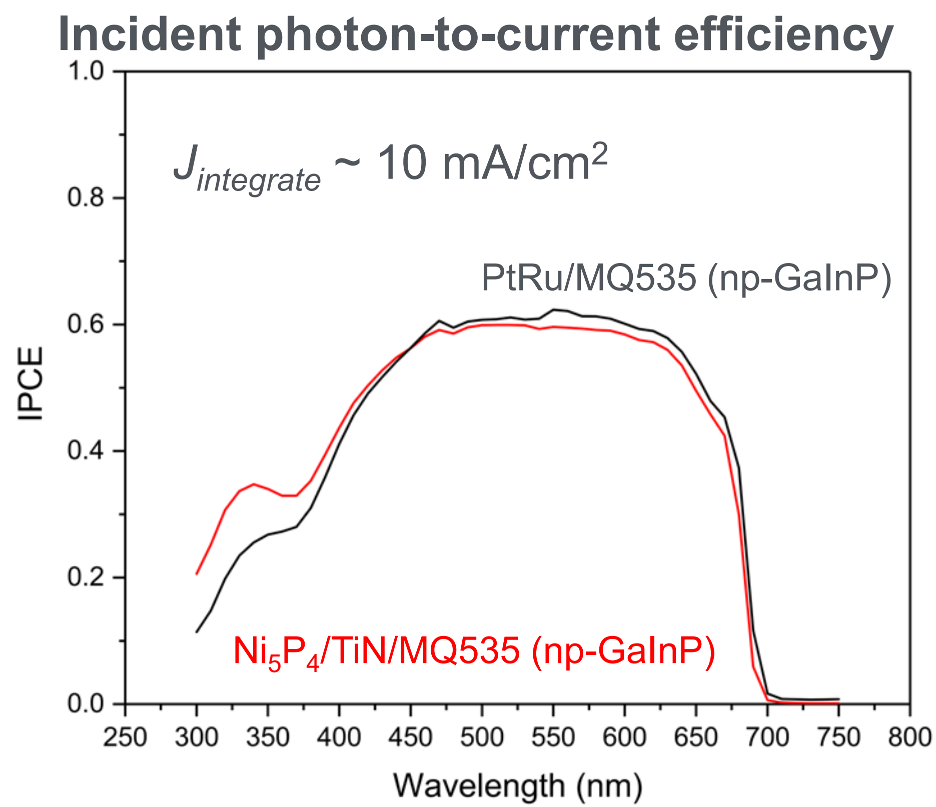
Durability test



- Ni_5P_4/TiN layers on p-GaInP are on par with PtRu/p-GaInP. (V_{onset} ,and J_{sat})
- Durability test demonstrates 89 h stability of Ni_5P_4/TiN/p-GaInP device in acid
- **Achieved Task 2 "Optimize catalyst/photoabsorber (Nickel Phosphide/GaInP) interface"**

Accomplishments:
Benchmarking Ni_5P_4/TiN/np-GaInP at NREL_Deutsch



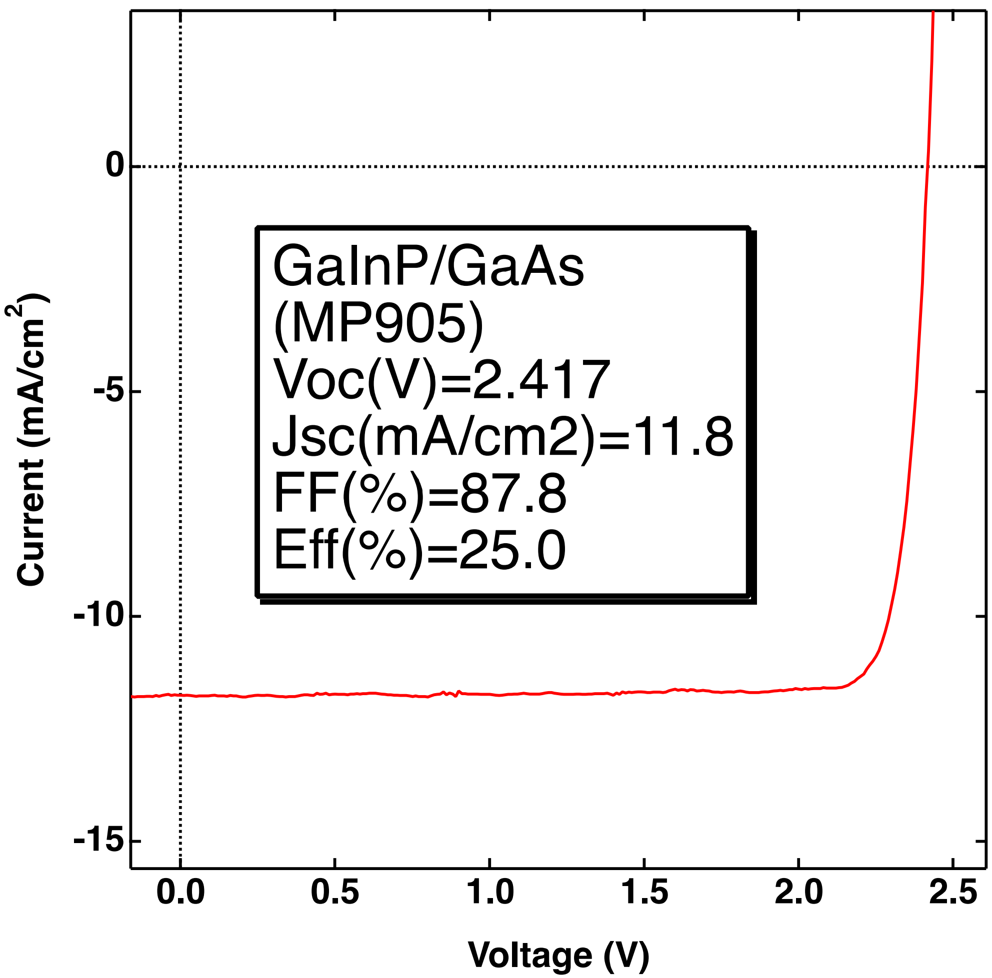


- PEC measurement were verified at the **NREL node**.
- Introducing buried junction np-GaInP increases V_{onset} (from 0.4 V to 1.0 V vs. RHE).
- Test proves the performance of Ni_5P_4/TiN/np-GaInP is on par with benchmark PtRu/TiN/np-GaInP.

Accomplishments:
NREL fabrication of GaInP/GaAs high-efficiency PV

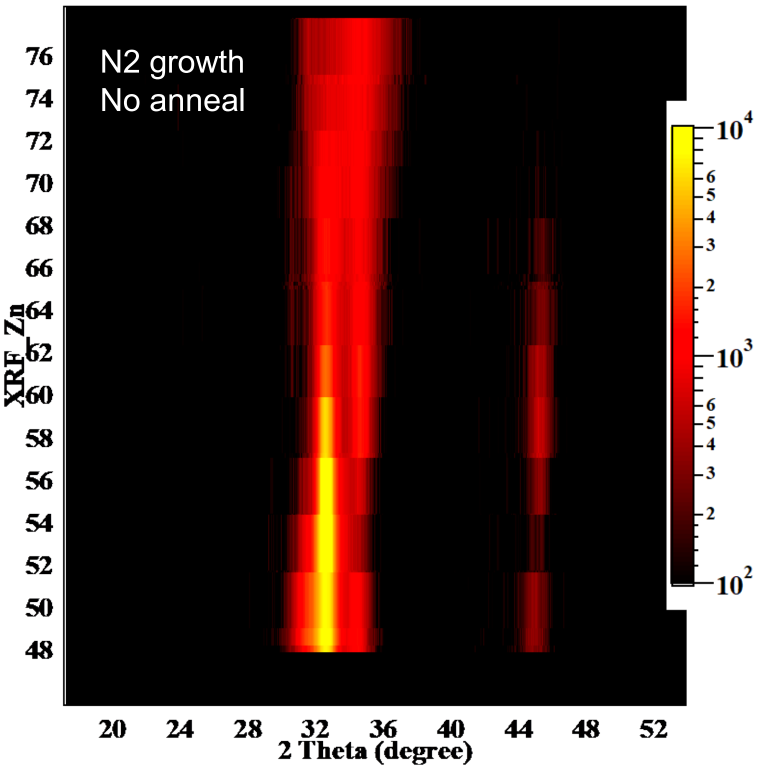
Milestone #2 (**achieved Q2**) fabricate a high-efficiency PV cell for photoabsorbers: V_{OC} > 1.85 V, J_{sc} > 10 mA/cm^2, and η_{eff} > 25%

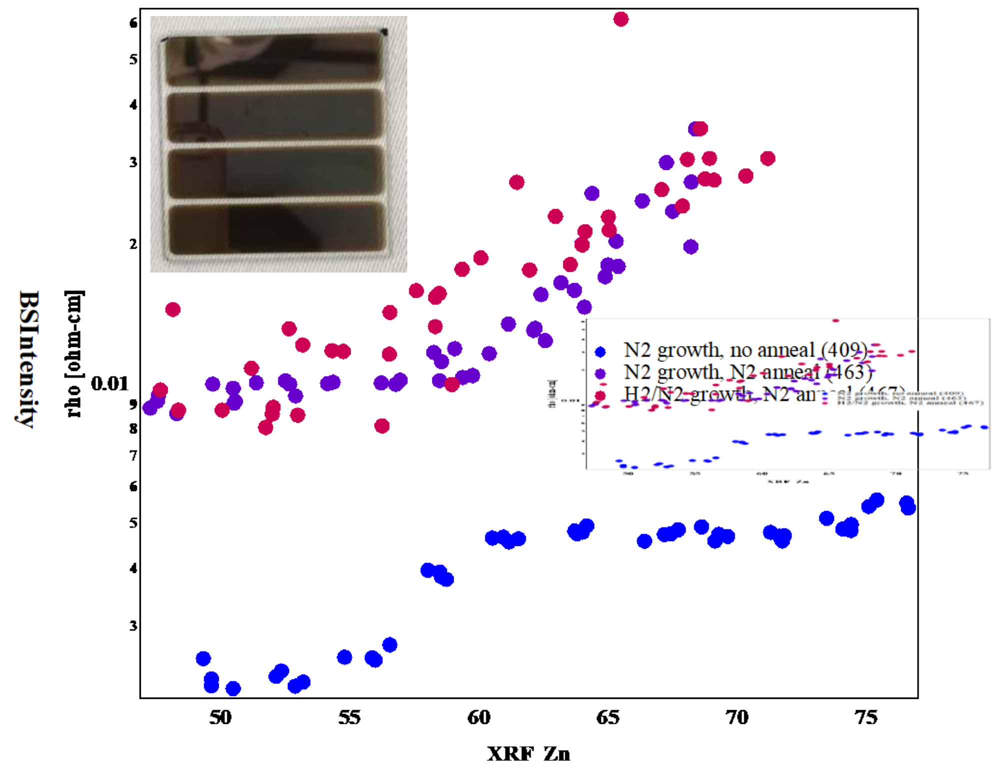
- NREL_Friedman node provided an upright tandem photoabsorber (GaInP/GaAs) that exceeds required properties. This photoabsorber will be coupled with RU-eCat and protection layer for unassisted water splitting.
- **Achieved Milestone #2**



Accomplishments:
NREL fabrication of thin-film $ZnSnN_2$

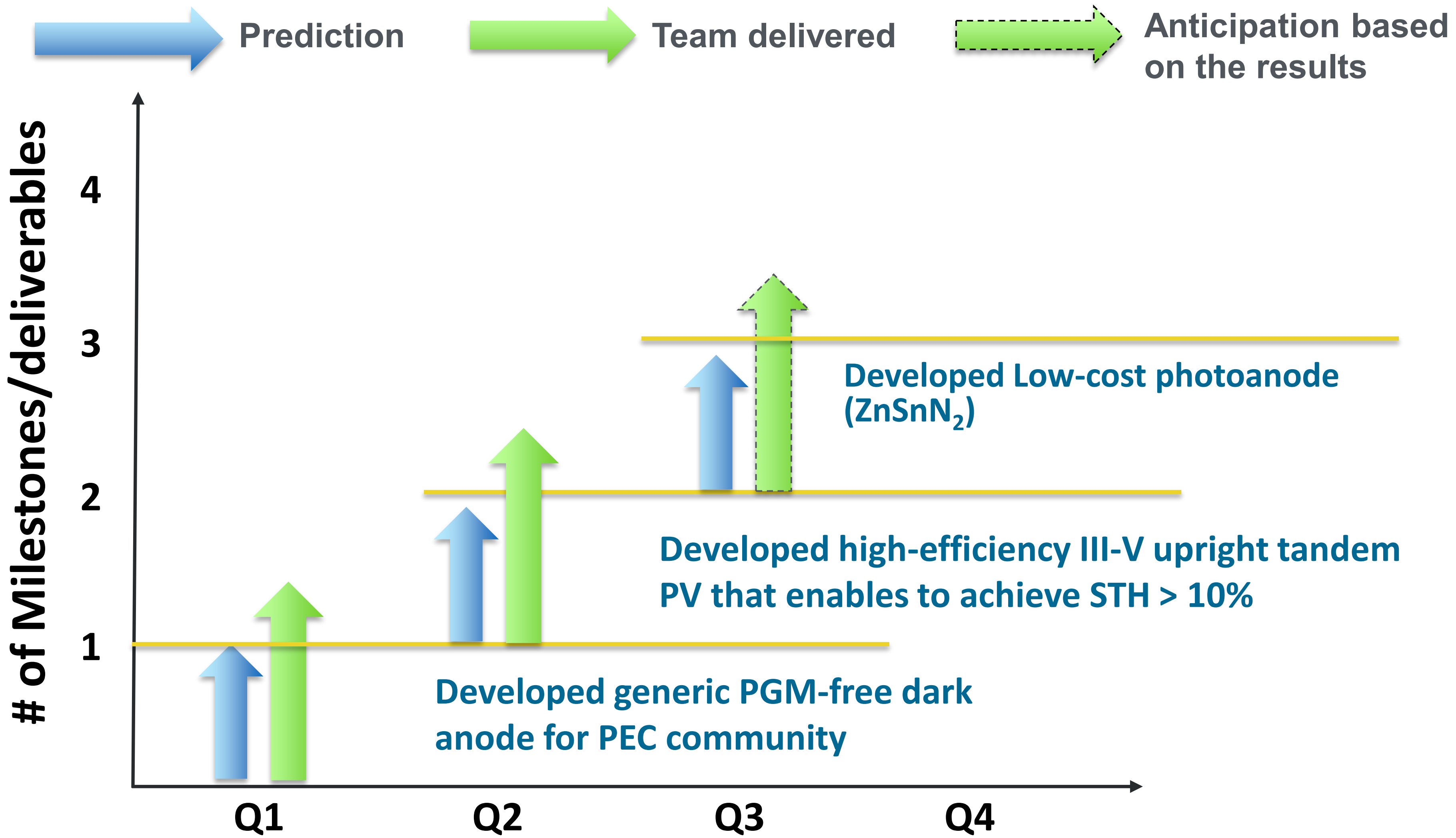
Milestone #3: Fabricate $ZnSnN_2$thin film:





- NREL_Zakutayev node provided synthesis (confirmed by XRD, XRF) and investigated post-annealing conditions for $ZnSnN_2$ that can generate proper conductivity for photoanode applications.
- **Task9 On-track to achieve milestone #3,** "Fabricate $ZnSnN_2$ photoabsorber "

Accomplishments - Outlook



Collaboration: Multiple interactions with HydroGEN nodes

NREL: III-V semiconductor & semiconductor characterization nodes

NREL: High throughput experimental thin-film node

Date	Meetings w/	Presenter	Outcomes
11/13/17	NREL NREL	N/A	HydroGEN kick-off meeting – project initiation
1/26/18	NREL	Rutgers	Understanding native oxides on GaInP for improving TiN adhesion **(Task 2)**
2/23/18	NREL	Rutgers	Optimize fabrication conditions for Ni_5P_4 thin-film Successful fabrication of Ni_5P_4/TiN on p-GaInP **(Task 2)**
3/16/18	NREL	Rutgers	Characterization of Ni_5P_4/TiN/p-GaInP and npGaInP Discussion for benchmarking test (IPCE) **(Task 2,4, and Go-No/Go1)**
3/22/18	NREL	NREL	Optimization of fabrication condition for $ZnSnN_2$ **(Task 9, Milestone 3)**
4/13/18	NREL	Rutgers NREL	Prove Ni_5P_4 is on par with PtRu on GaInP (Task 2, Go-No/Go1) Fabrication of np-GaInP/np-GaAs tandem PV **(Task 1, Milestone 2)**

Collaboration: Data sharing within HydroGEN

Data sharing:

Verified data uploaded to HydroGEN site and Datahub. Quarterly reports with input from both RU and nodes shared in HydroGEN site and Datahub. This has allowed the continues sharing of progress, samples needed, problems encountered, verification of experimental test procedures. The continuous sharing of results have been critical to the fast paced progress on this project. Sharing to the water splitting R&D community will be realized through publication as well as opening access to the verified raw data in the datahub after the project period. Data shared in publications will be opened for sharing at the time of publication.

HydroGEN community interaction:

Pre-proposal submission	**Means of communication**	**Node/point of Contact(s)**
	In-person (ECS conference)	James Young NREL
	Telecon	Todd Deutsch NREL
Post-award	**Means of communication**	**Node/point of Contact(s)**
	Telecon	Todd Deutsch NREL
	Telecon	Michael Ulsch NREL
	In-person (Kick-off meeting)	Todd Deutsch NREL, Michael Ulsch NREL, Daniel Friedman NREL, Aditya Mohite LANL, PEC workgroup
	Biweekly Telecon for progress reports	Todd Deutsch NREL, Daniel Friedman NREL
	Telecon for progress report	Andriy Zakutayev NREL
	In-person (Seattle ECS meeting)	PEC working group

Proposed Future Work Y2 & Y3

Thrust #1, High Performance PEC

Scope: Build complete PEC device based on NREL's incrementally advanced III/V-photoabsorbers & next generation RU-eCats.

- State-of-the-art PECs operate in acid electrolyte, where PGM-free anodes are not stable. Extending operation to alkali presents the first attempt to achieve this key-property for fully PGM-free operation.

Y2: Fabricate protection/catalyst layers for alkali operation. Improve performance under diurnal cycle (low current regime) where recombination & photocorrosion may increase. ***Outcome: stable operation for > 24h in alkali, stable performance under diurnal cycle.***

- Evaluating the long-term stability of the optimized device is crucial for an accurate H2A and LCA analysis. Cost-benefit analysis will quantify the impact of the achieved improvements over state-of-the-art PEC devices to achieve target of <$2/kg H_2.

Y3: Extended stability tests under solar concentration. Perform H2A and LCA modelling employing HydroGEN node. ***Outcome: Long-term stability, effect of electrolyte, effects of PGM-free catalysts on H_2 costs.***

Thrust #2, High Value PEC

- State-of-the-art HV PECs show limited performance and stability. Thin-film fabrication of oxynitride and double inorganic perovskite salt (DIPS) based electrode represent level 3 (early stage development) photoabsorbers with low-cost potential.

Y2-Y3: Development of level 3 photoabsorbers with HydroGEN nodes. Build complete PEC device based on $ZnSnN_2$ photoabsorber/RU-eCat electrodes. Development of oxynitride and DIPS photoanodes collaboration with NREL High-Throughput Experimental Thin-film Combinatorial Capabilities (Zakutayev) and High-Throughput Processing node (Ulsh).

Y2: Develop buried junction-type oxynitride thin-film. Optimize protection/catalyst layers for oxy-nitride photocathode and DIPS photoanodes. ***Outcome: novel buried junction-oxynitride photoabsorber, stable operation in alkali, DIPS thin-film photoabsorber/photoelectrode.***

Y3: Stability tests under solar concentration, plus H2A and LCA modelling employing HydroGEN node.

- Direct comparison of cost-benefit analysis for HV and HP devices from same team for ultimately achieving DOE targets.

Project Summary

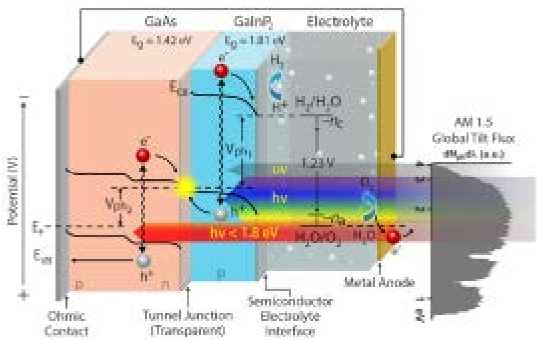
Q1 (end of 2017) — **Milestone #1 ✓ (HP anode)**

Q2 — **Milestone #2 ✓ (HP photoabsorber)**

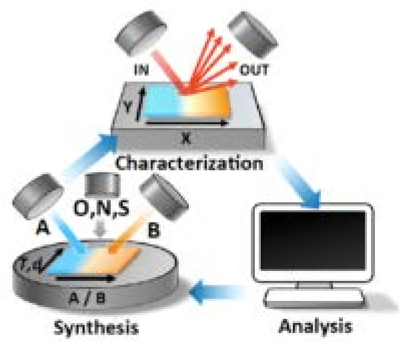
Q3 — **Milestone #3 (HV synthesis photoabsorber)** — **On-track**

Q4 Go/No-Go decision

Achieved and exceeded all millstones; on-track to achieve Go/No-Go decision

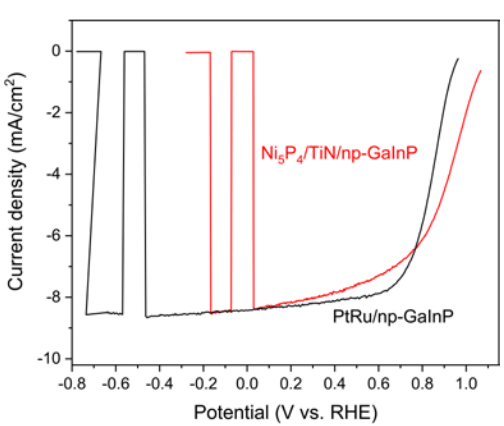


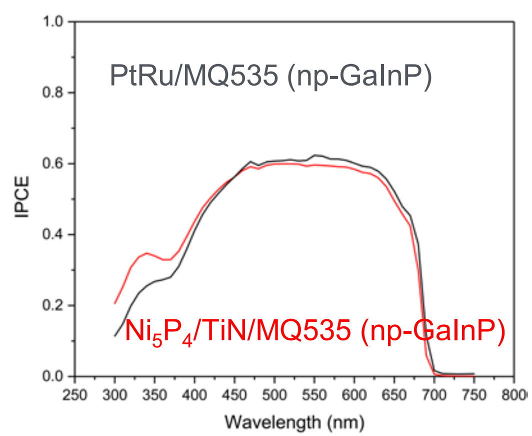
NREL: III-V semiconductor & semiconductor characterization nodes



NREL: High throughput experimental thin-film node

Effective utilization of HydroGEN nodes (6 meetings over 6 months)





Benchmarking test at NREL

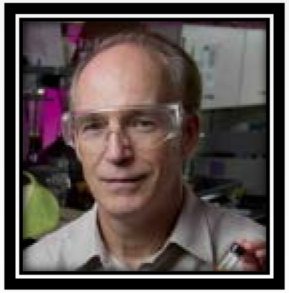
Thank you for your attention

1766-2016 RUTGERS 250

iAMDN Institute for Advanced Materials, Devices, and Nanotechnology

RUTGERS Energy Institute

Eric Garfunkel



Charles Dismukes

Martha Greenblatt

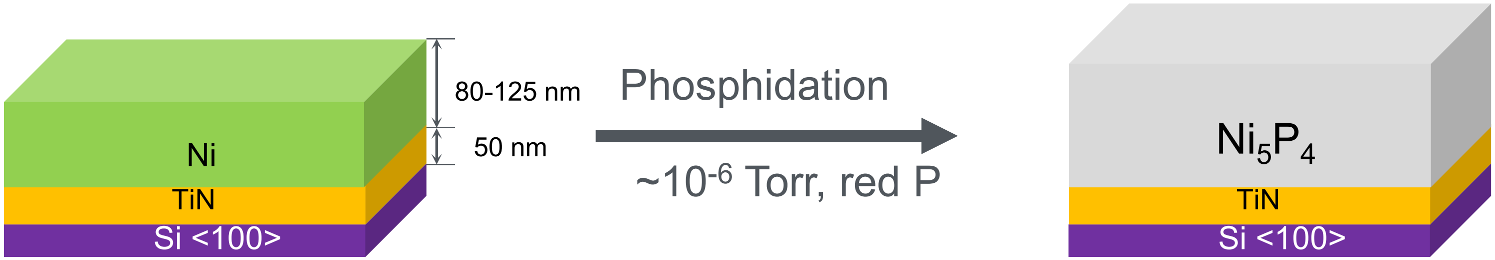
Anders Laursen

Shinjae Hwang

Technical Back-Up Slides

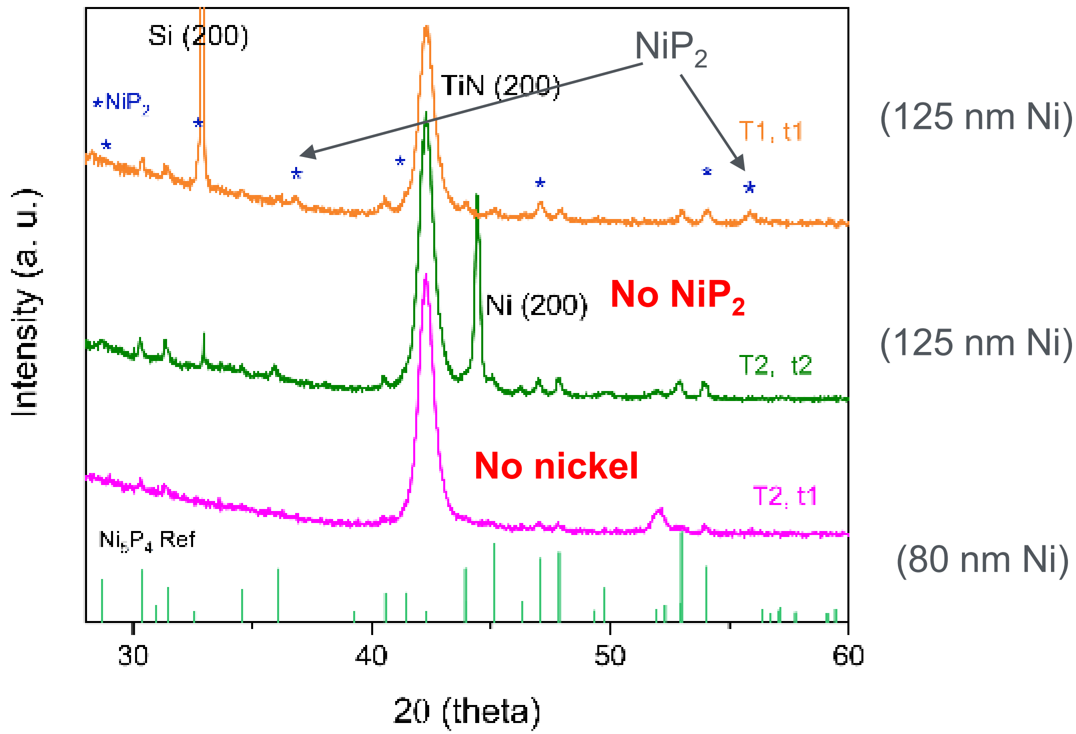
Accomplishments:
Low-temperature Ni_5P_4 thin-film synthesis

Using Si-PV model for catalyst synthesis optimization

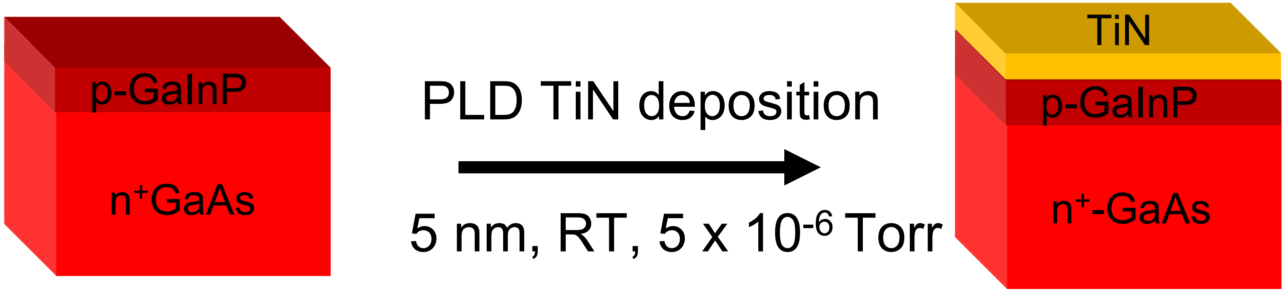


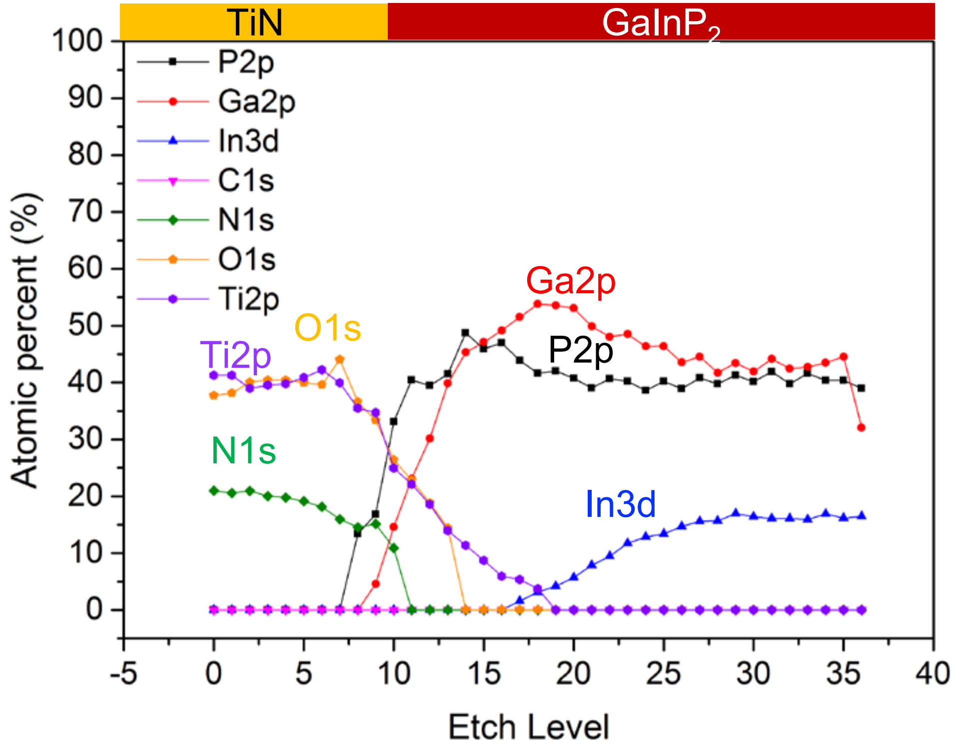
A thick layer is on purpose for getting X-ray diffraction

Phase-pure crystalline Ni_5P_4 can be obtained with choice of temperature and time.



Accomplishments:
Low-temperature fabrication TiN thin-film





XPS depth profile shows no significant atomic diffusion was detected