Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

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

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Co-PI: Martha Greenblatt
Rutgers, the State University of New Jersey

Project ID # P160

NREL · Berkeley Lab · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

Project Overview

Partners

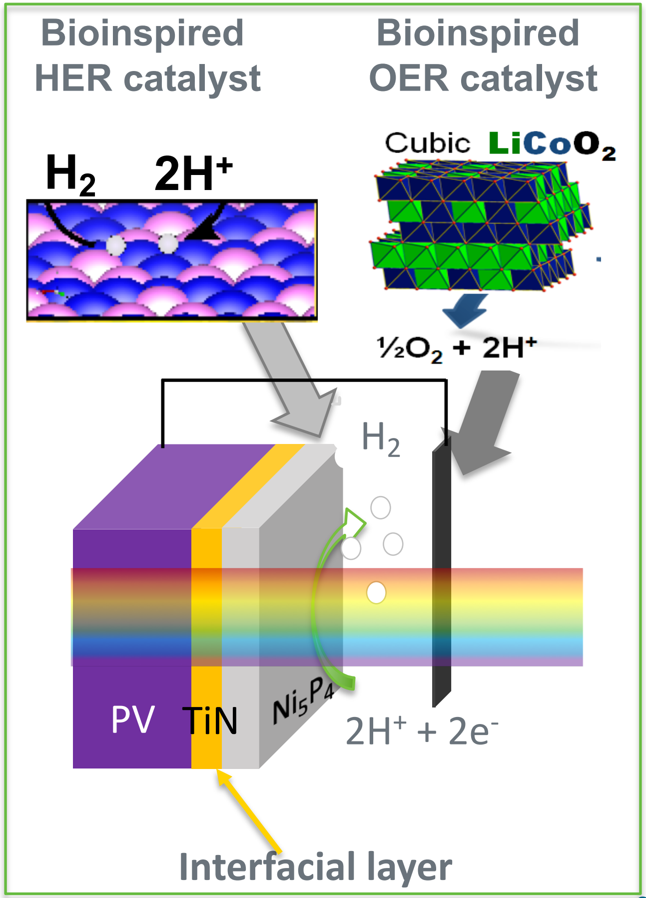
Rutgers PIs: E. Garfunkel & G. C. Dismukes,
coPI: M. Greenblatt

NREL 4 Nodes (MOVPE, PEC, HTE & HOIPS): T. Deutsch, J. Young, D. Friedman, M. Steiner, A. Zakutayev, K. Zhu, & J. Berry

Award #	EE0008083
Start/End Date	09/01/17 - 01/31/21
Yr 1-3 Funding	

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 recent HV PEC NREL & Rutgers perovskite oxynitrides and NREL Hybrid Organic-Inorganic Perovskites in tandem with Si
-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 RU PGM-free ECats.
- Identify & solve catalyst/PV interface problems.

Approach - Summary

Project Motivation

NREL

High-performance Photovoltaics: State of the art material competing with NREL HP III-V tandems (STH 16.7%)

High-value (HV) – emerging photoabsorbers: $SrNbO_2N$ and Hybrid organic-inorganic Perovskites (HOIPs) are potential efficient and low-cost with high potential impact on global energy economy. Both show many early development hurdles.

Rutgers

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

$LiCoO_2$ 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 – Year 2

- **HP tandem device** – Replace PGMs catalysts with non-noble metal thin-film catalysts without compromising STH efficiency.
- **HP tandem device –** Achieve stability > 24h with a tandem device at zero bias.
- **HV device –** Achieve high photocurrent density using low-cost semiconductors.

Key Impact – Year 2

Metric	State of the Art	Expected Advance
HP - STH	Non-PGM STH ~11.5%,(Rutgers, 2019)	*>12% STH*
HP - Stability	*Non-PGM ~ 100h (JCAP)*	*>48 h*
HV – Photoabsorber down-selection	*Si-W:$BiVO_4$*	*Si:HOIPs or Si:$SrNbO_2N$*

Partnerships

III-V semiconductor epi-structure, device, design, and fabrication. MOCVD GaInP/GaAs growth & engineering capabilities.

Daniel Friedman & Myles Steiner

On sun characterization of bulk and interfaces solar testing and benchmarking capabilities.

Todd Deutsch & James Young

High-throughput thin-film combinatorial capabilities multi-source and reactive sputtering capabilities.

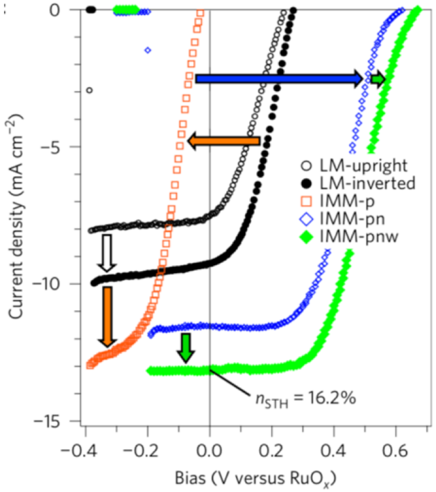
Andriy Zakutayev

Hybrid organic inorganic perovskites for water splitting.

Kai Zhu & Joseph Berry

Approach – Innovation: High Performance Device

NREL III-V semiconductors



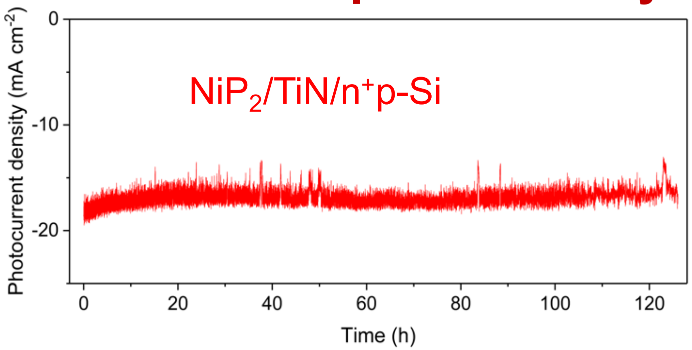
State of Art:

IMM structure III-V with PtRu catalyst, 16.2% STH, but unstable <0.5 h.

Nature Energy **2017**, 2, 17028.

+

Rutgers PGM-free OER+HER catalysts & durable thin film protection layer



high TOF among PGM-free HER catalysts & durability (>120 h) on a Si photocathode

J. Mat. Chem. A., **2019**, **7**, 2400-2411

Overall Project Goals:

>10% solar-to-hydrogen efficiency

- >100 hrs stability continuous light

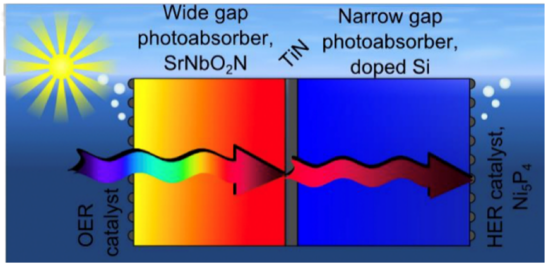
BP2 scope: Efficiency > 12% STH, and stable performance (>48 h)

- Introduce AR coating & 2nd GEN quantum well tandem device to increase STH
- Investigate strategy for long-term stable performance (protection layers/operating pH)

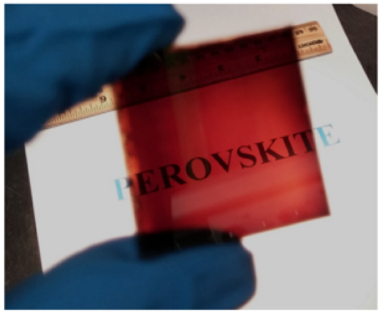
Approach – Innovation: High Value Device

Compare oxynitride to HOIPs

$Sr_{1-x}Nb_xO_2N$ vs. Perovskite

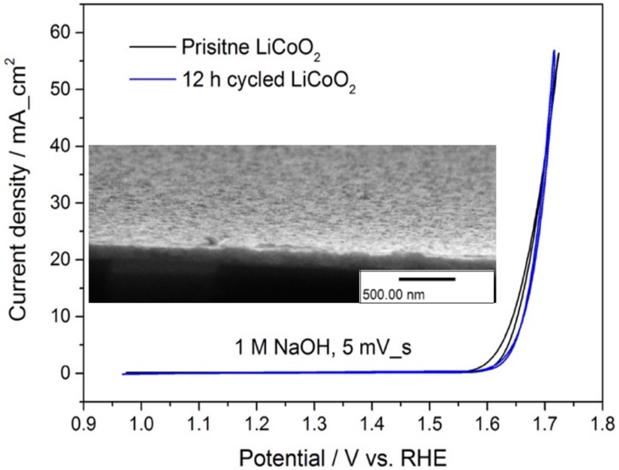


ECS Trans. **2016**, *72* (37), 1.



Nature Energy **2,** 17038 (2017).

Rutgers thin-film catalyst



S. Hwang, *et al.*, *ECS Trans.* 2016, *72*, 31–51.

BP2 - Semiconductor down selection

Project Goals:

- Reduce PEC cost enabling lower H_2 ~10% STH (~ to HP device)

BP 2 scope: $Sr_{1-x}Nb_xO_2N$

- Synthesize thin-film on silicon
- Use lower temperature (< 600 °C)
- Optimize photocurrent density by tuning Sr/(Sr+Nb) ratio

BP 2 scope: HOIPs

- Evaluate wide bandgap efficiency
- Compare two device architectures
- Evaluate PCE stability

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

- Compare two competing device designs (HV vs HP) using techno-economic analysis to evaluate the better route to lower H_2 cost <$2/kg

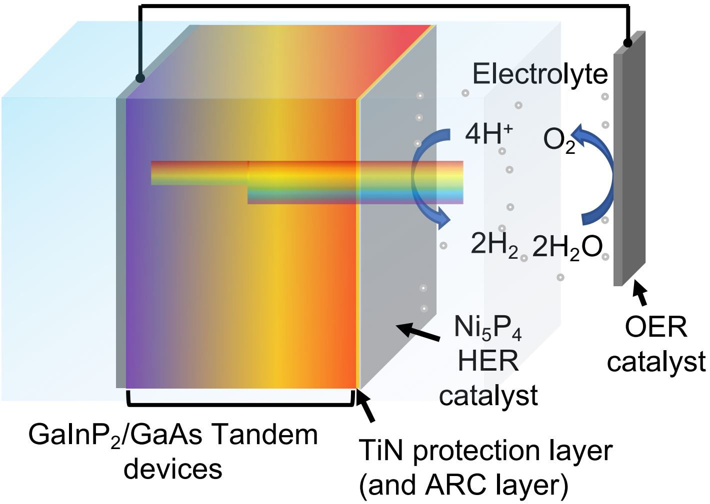
- **HydroGEN consortium**
  HP strategy: combine high efficiency III-V photoabsorbers & EMN expertise of the MOPVE, PEC, and ON-SUN nodes with Rutgers PGM free Ecats and thin film technology to produce a more stable HP PEC device

- **HV strategy:** Compare $SrNbO_2N$ vs. HOIPs as low-cost photoelectrodes. Rutgers to develop both protection and catalyst layers for PEC operation of both devices.

- Utilize NREL HTP-Synthesis node expertise to make thin-film $Sr_{1-x}Nb_xO_2N$. Evaluate PEC

- Utilize NREL HOIPs node expertise to fabricate tandem PV junction. Evaluate PEC

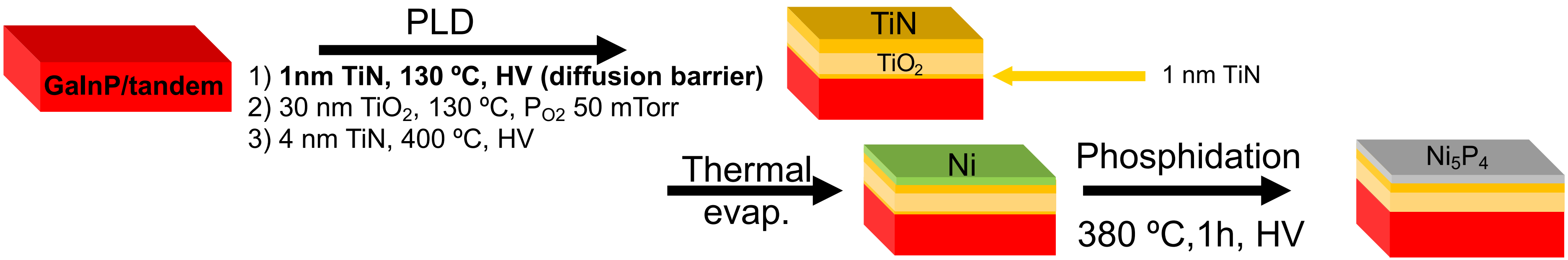
Accomplishments: High performance device (III-V PEC)

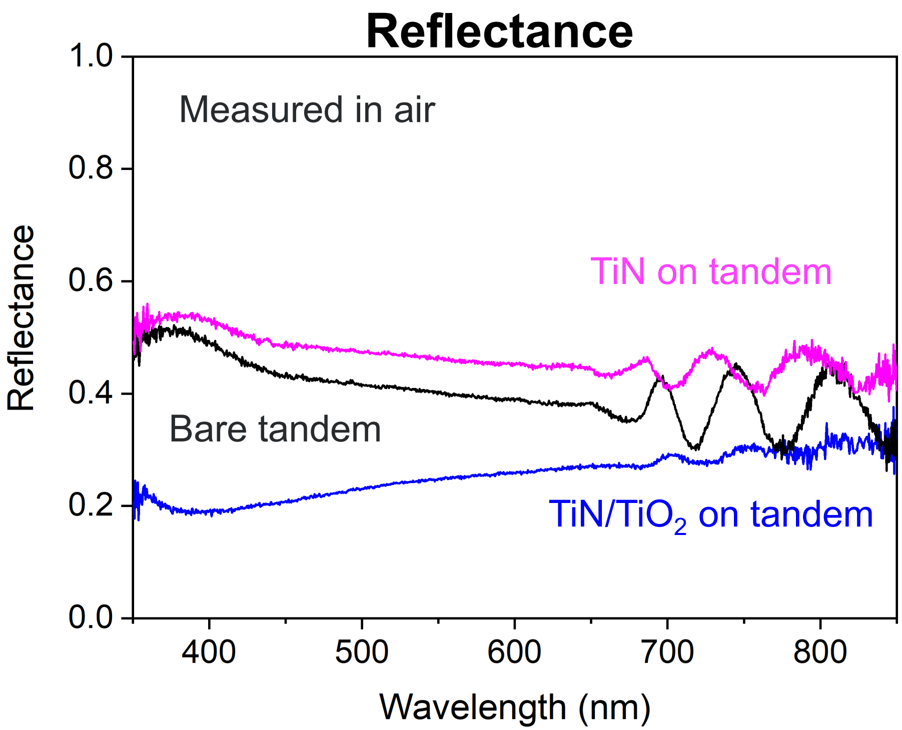


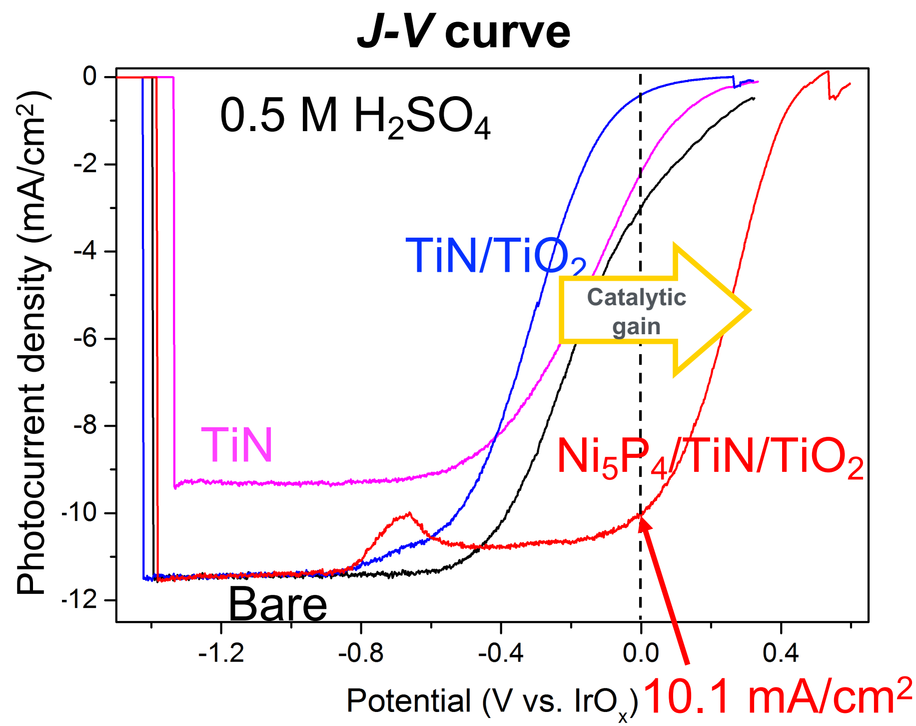
Year 2 Target (GNG)	Year 2 Result
2nd GEN Tandem device: STH > 12%	2nd GEN Tandem device: STH >12.8%
>48h durability	>200 h durability

1. Add TiO_2 anti-reflective coating on TiN protection layer to increase STH 12.4% using 1st GEN n^+p-$GaInP_2$/n^+p-GaAs tandem device (Go/No-Go decision point metric) ✓
2. Further increase STH (12.8%) using 2nd GEN n^+p-$GaInP_2$/n^+p-GaAs tandem device with Multi-quantum well (Milestone 6) ✓
3. Simultaneously achieved STH >12% and > 200h durability in pH7 electrolyte using n^+p-$GaInP_2$/n^+p-GaAs tandem (Milestone 5, Go/No-Go decision point metric) ✓

Accomplishments:
HP device – Develop Anti-reflective coating (ARC) interfacial layer





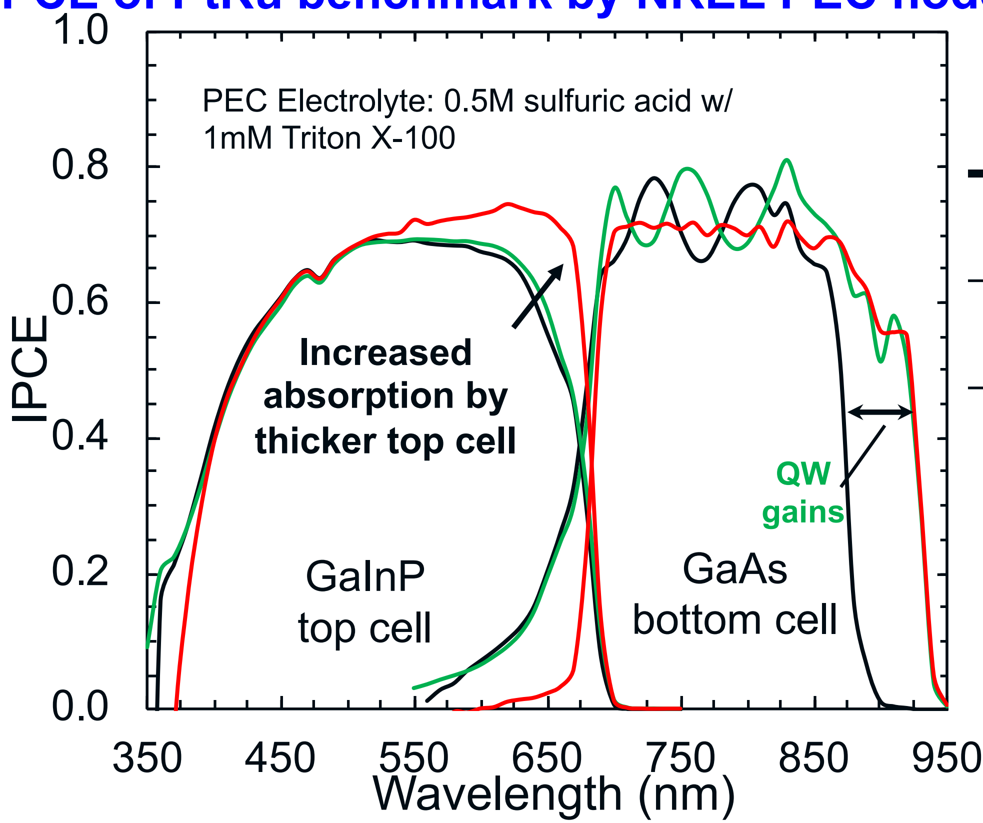


- **Adding TiO_2 (ARC) substantially decreased the reflectance and achieved similar J_{sat} with bare III-V tandem (recovered loss from TiN layer, STH 12.4%)**

HP device -2nd GEN - Quantum well (QW) bottom junction

Introduced quantum wells (QWs) into a mechanically and thermally stable lattice-matched (LM) upright structure to increase light absorption at longer wavelengths

IPCE of PtRu benchmark by NREL PEC node using QW device (NREL MOVPE node)



Device name	Top cell	Bottom cell	*IPCE (mA/cm2 top)*	*IPCE (mA/cm2 botttom)*
Baseline	1-μm GaInP	GaAs	10.98	10.21
Ctrl 1	1-μm GaInP	GaAs+QW	11.28	12.28
QW	3-μm GaInP	GaAs+QW	12.06	10.71

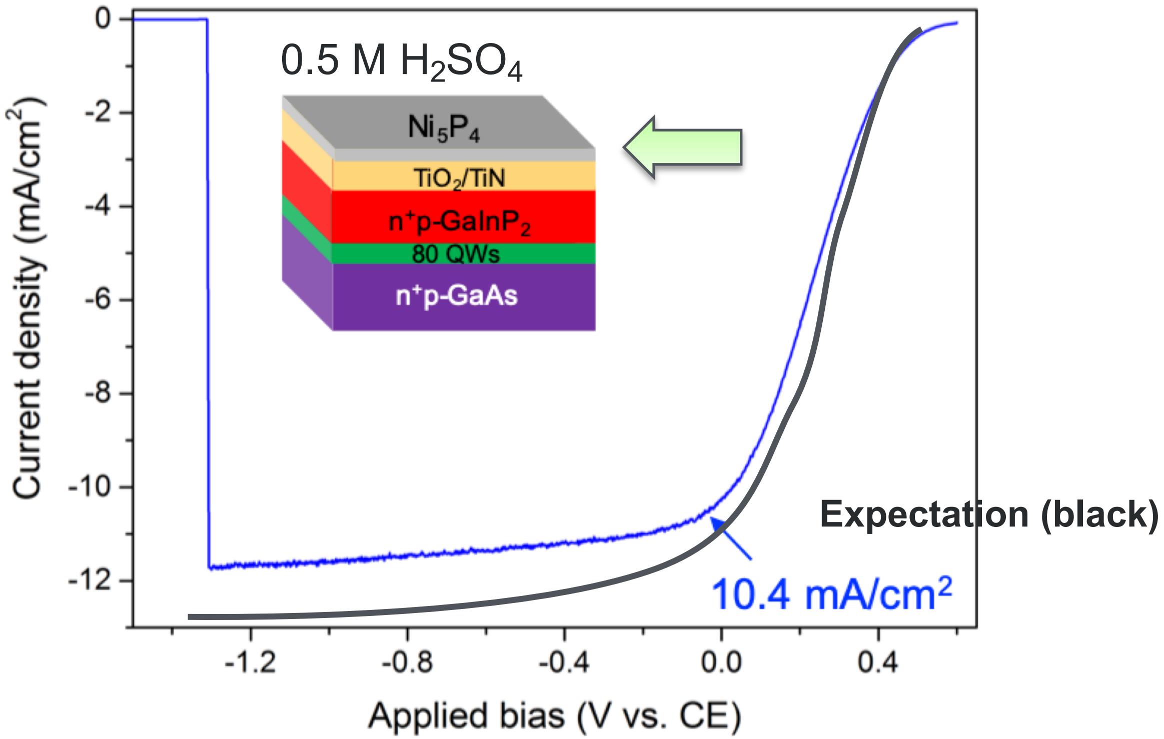
- Adding QW & adjusting the top junction thickness improves total (tandem) junction photocurrent density

- Combined changes give 11.28 mA/cm^2 (STH 13.8%) = 10% improvement, compared to benchmark = PtRu Ecat on 1st GEN tandem (**black line**)

M. A. Steiner, C. D. Barraugh, C. W. Aldridge, I. B. Alvarez, D. J. Friedman, N. J. Ekins-Daukes, T. G. Deutsch and J. L. Young, *SUSTAIN. ENERG. FUELS*, 2019.

Milestones 6:
STH > 12% using Ni_5P_4 catalyst (on part with PtRu benchmark catalyst) ✓

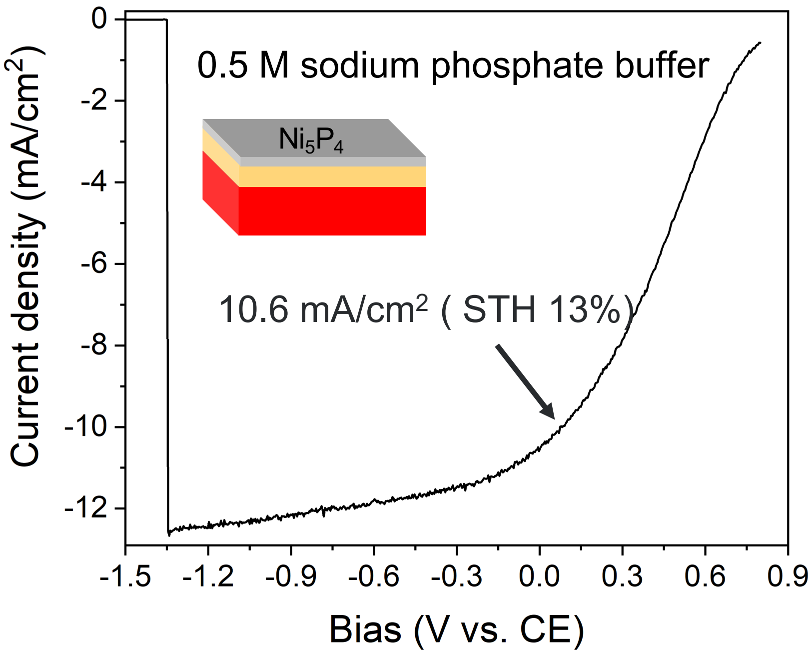
J-V of $Ni_5P_4/TiN/TiO_2$/2nd GEN tandem



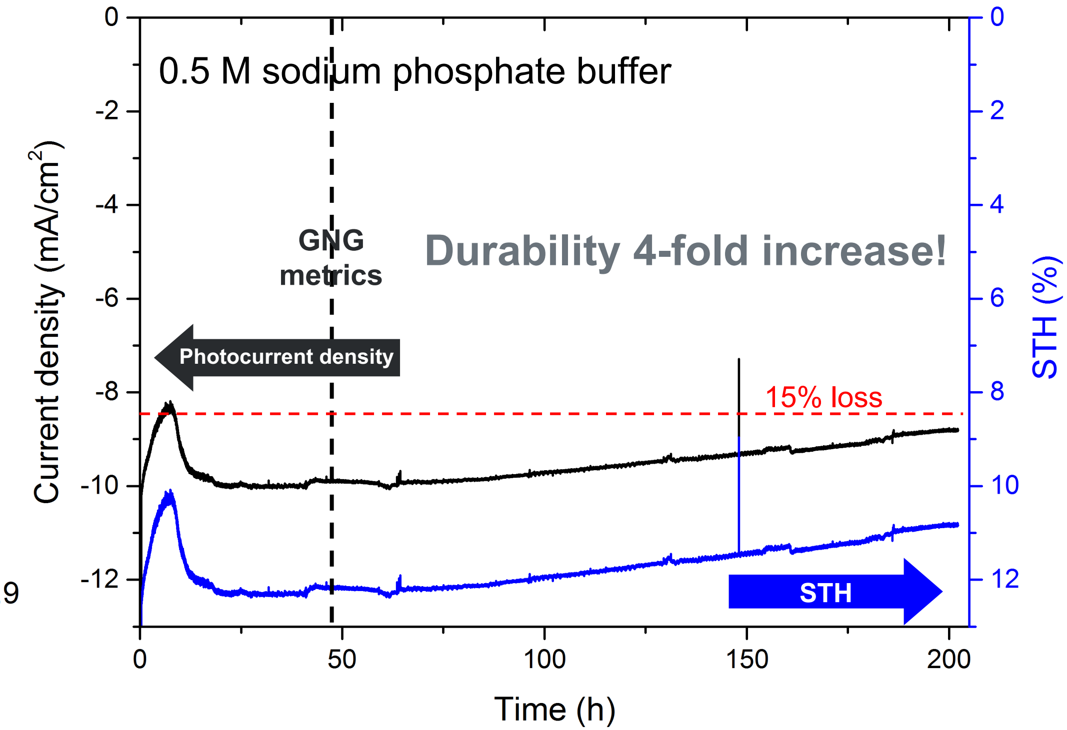
- **Apply $Ni_5P_4/TiN/TiO_2$ on 2nd GEN tandem device, achieve 10.4 mA/cm^2 (STH 12.8%) using 1.5 μm thick top junction**
- **Current density matching of top and ARC thickness can further increase photocurrent**

Accomplishments:
HP device - Efficiency and Durability in pH7

J-V curve



Durability



- **Change the operating pH to neutral for stable performance***
- **Durability test shows >200h of stable performance with >10% STH, which exceeded the GNG metrics:** *Evaluation of high-performance PEC device with renewable catalysts under optimum solar flux.* Achieve >12% STH, and 48h stability (< 15% loss of photocurrent)

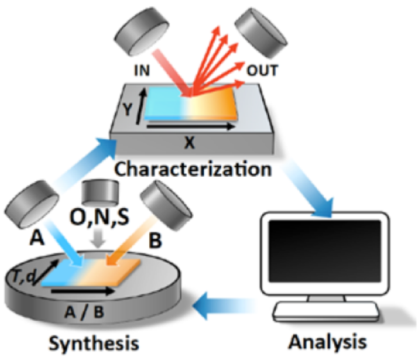
*Details in technical back-up slides

Accomplishments
High-Value Devices Overview

$Sr_{1-x}Nb_xO_2N$ photoanode (Year 2)

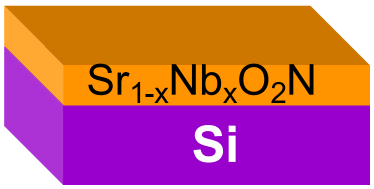
NREL: High throughput experimental thin-film node

Low T co-sputter and spatially resolved characterization capability



Year 2

Crystalline $Sr_{1-x}Nb_xO_2N$ on Si



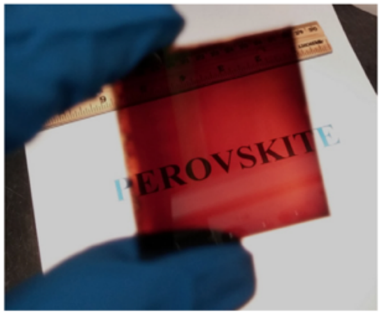
Milestone 7 ✓

$J_{at\ 1.23\ V}$: 0.2 mA/cm²(milestone) → 0.53 mA/cm²

Hybrid Organic-Inorganic Perovskites (HOIPs) (Year 2)

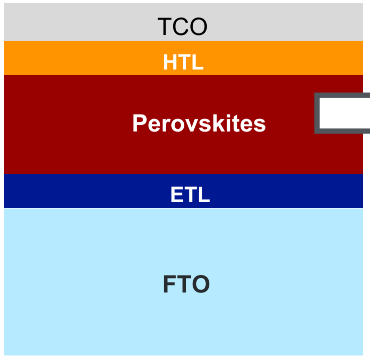
NREL: Hybrid Organic-Inorganic Perovskites node

High efficiency with Large area HOIPs capability



Nature Energy **2**, 17038 (2017).

Year 2



Create Wide bandgap (1.6 – 1.7 eV)

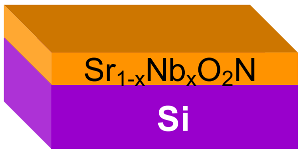
Milestone 8 ✓

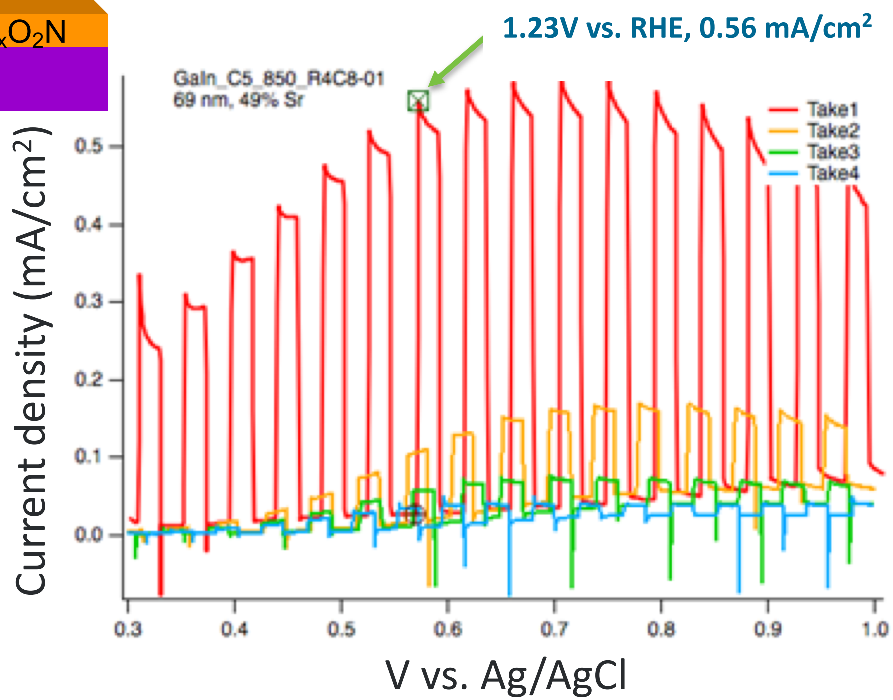
Power density (stability & eff): 240 mWh/cm² (milestone) → 10,000 mWh/cm² Surpassed by 40X

Accomplishments (technical slide):

HV device 1 - $Sr_{1-x}Nb_xO_2N$ photoanode PEC performance

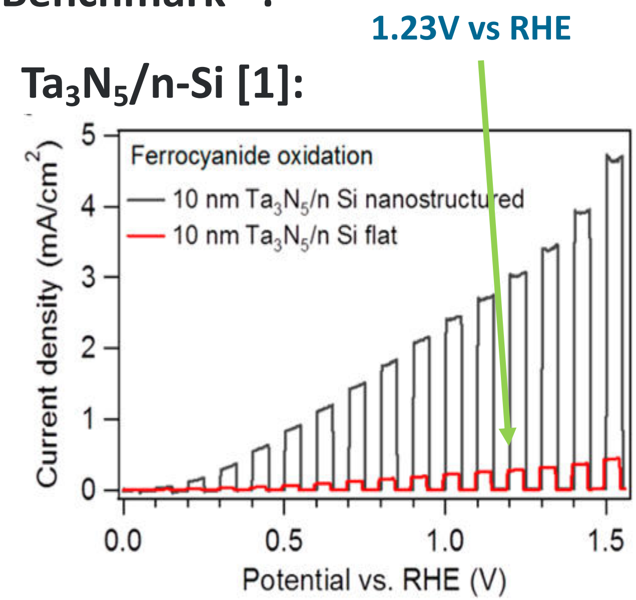
PEC performance of $Sr_{1-x}Nb_xO_2N$/Si thin film (x=0.49, 69nm thickness) without catalyst:





Benchmark *:

Ta_3N_5/n-Si [1]:



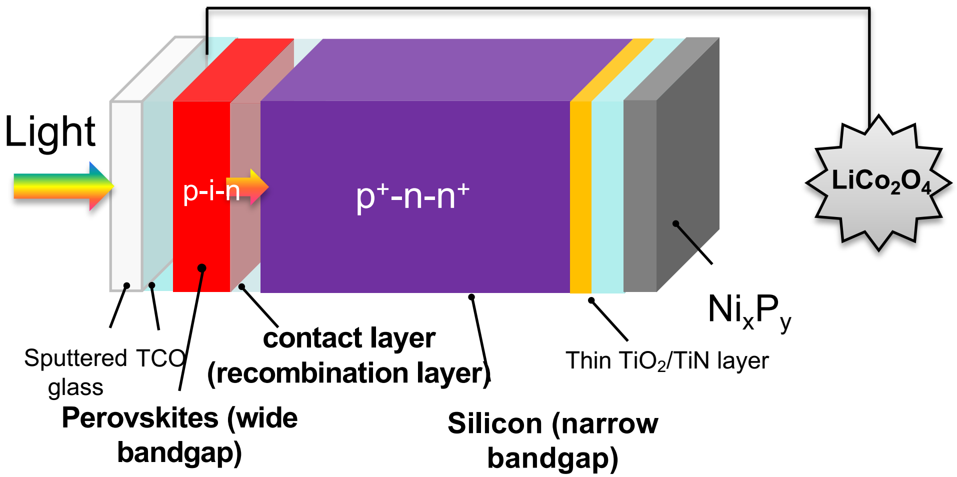
- **$Sr_{0.49}Nb_{0.51}O_2N$: J_{sc} = 0.56mA/cm^2 @ 1.23V vs RHE**

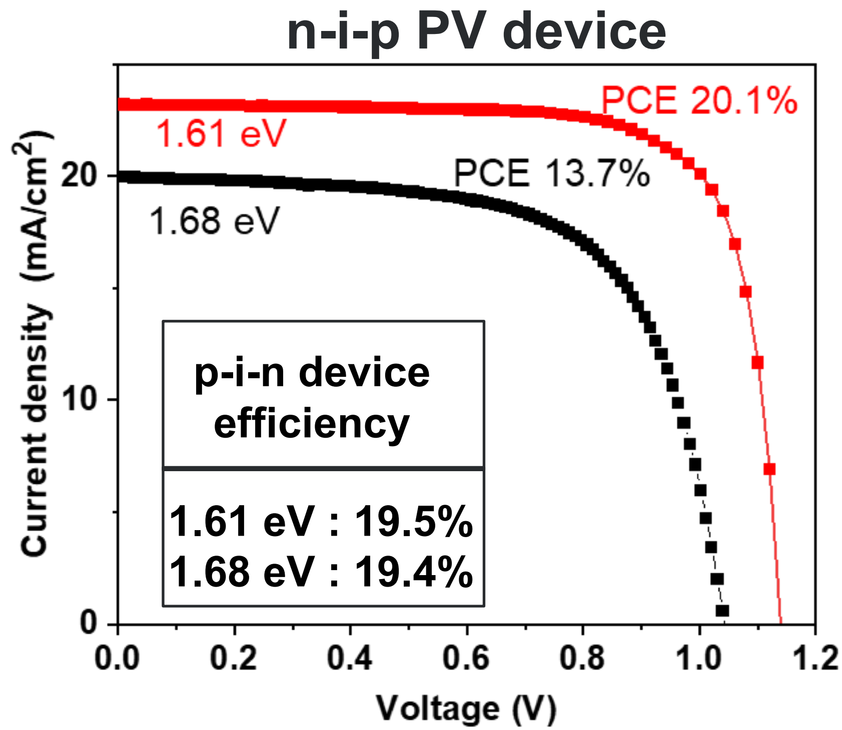
Exceeded Milestone 7: Produced a range of composition $Sr_xNb_{1-x}O_{3-y}N_y$ compounds photocurrent on par with benchmark planar Ta_3N_5 *
J_{sc} > 0.2 mA/cm^2 @ 1.23V vs RHE in ferri/ferrocyanide solution.

*Narkeviciute et al *Nano Lett.* **2016**, *16* (12), 7565–7572.

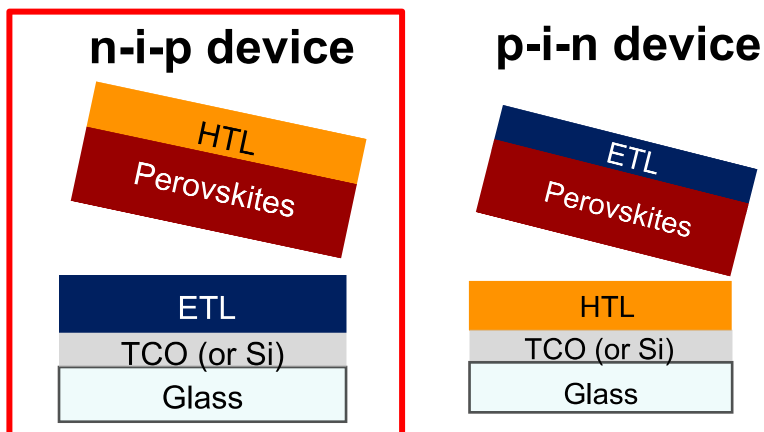
Accomplishments (technical slide):
HV device: HOIPs/Si tandem structure (NREL HOIPS node)

Which orientation to use? p-i-n or - n-i-p ?





- 1.61 eV bandgap HOIPs n-i-p device shows slightly better performance than p-i-n device.
- Due to material compatibility issues (ETL vs. HTL on Si), we chose the n-i-p device structure



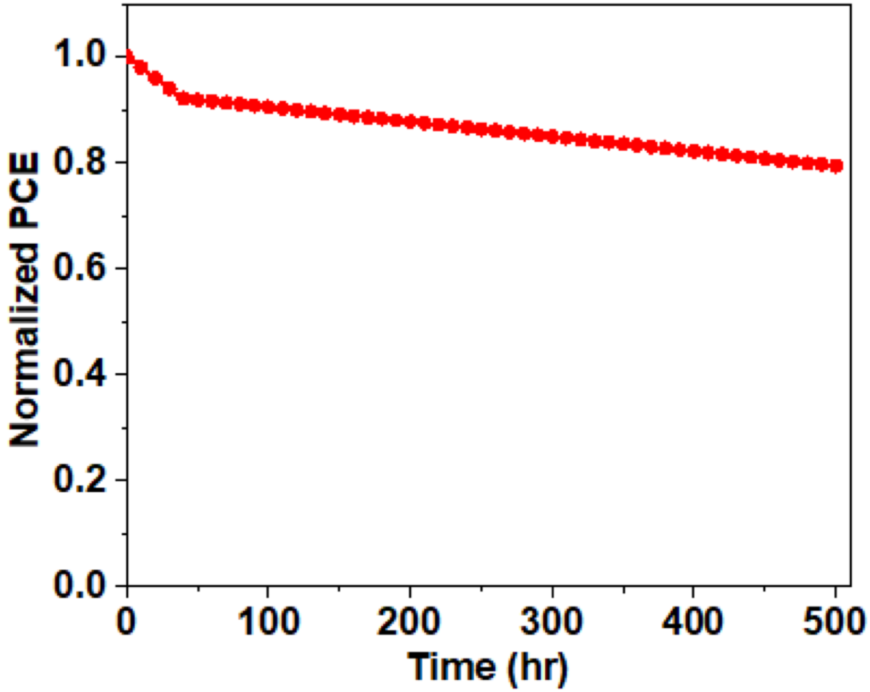
Accomplishments (technical slide):

HV device: Wide bandgap HOIPs PV stability (NREL HOIPS node)

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Milestone 8: Evaluate the PV and stability performance of HOIPS thin film. Achieve overall power generation of > 240 mWh/cm^2 (equal to 10 mA/cm^2 for 24h for a photoabsorber producing 1V photovoltage).

Stability test of HOIPs PV cell (N_2, continuous light)



- **n-i-p 1.61 eV bandgap photoabsorber gives stable PCE and less than 20% loss over 500 h. - Power generation > 10,000 mWh/cm^2**

Project outcomes

Milestones	Planned	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Status
#5	BP2-Q1	Achieve stable performance over 24h using Ni_5P_4/TiN on 1st GEN upright tandem photoabsorber (< 15% loss of photocurrent).	STH (initial) 13%, stable for 200h with >10% STH (< 15% loss of photocurrent) in pH7, NREL, Rutgers	**complete**
#6	BP2-Q2	Develop 2nd GEN upright tandem photoabsorber with > 12 % STH, which is on par with PtRu benchmark catalyst	Achieved 12.4% STH with anti-reflective coating with 1st GEN; Achieved 12.8% STH with 2nd GEN III-V tandem, NREL, Rutgers	**complete**
#7	BP2-Q2	Using selected composition among of $Sr_xNb_{1-x}O_{3-y}N_y$ compounds, achieve photocurrent on par with benchmark planar Ta_3N_5	Achieved 0.56mA/cm^2 photocurrent density @1.23V vs RHE with $Sr_{0.49}Nb_{0.51}O_xN_y$, NREL, Rutgers	**complete**
#8	BP2-Q3	Evaluate the PV and stability performance of 2D/3D HOIPS thin film. Achieve overall power generation of > 240mWh/cm^2	Stable PCE (> 10,000 mWh/cm^2) with less than 20% loss over 500 h with n-i-p 1.61 eV bandgap photoabsorbers, NREL	**complete**
Go/No-go Criteria for Thrust 1	BP2-Q4	Evaluate of high-performance PEC device with renewable catalysts under optimum solar flux Achieve >12% STH, and 48h stability (< 15% loss of photocurrent)	STH (initial) 13%, stable for 200h with >10% STH (< 15% loss of photocurrent) in pH7 with 1st GEN III-V tandem, NREL, Rutgers	**complete**

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

Collaboration: Effectiveness
Multiple interactions with HydroGEN nodes

NREL: III-V semiconductor & semiconductor characterization nodes

NREL: High throughput experimental thin-film node

NREL: Hybrid Organic-Inorganic Perovskites node

Date	Meetings w/	Presenter	Outcomes
5/23/2019	**NREL**	**NREL**	Updates on $Sr_xNb_{1-x}O_2N$ anode device and internal Go/No-Go **(Task 12, and Milestone 7)**
9/12/2019	**NREL**	**Rutgers**	Device structure plan for HOIPs/Si tandem device and first round sample exchange **(Task 13, and Milestone 8,9)**
10/8/2019	**NREL**	**Rutgers** **NREL**	First test follow-up **(Task 13, and Milestone 8,9)**
10/29/19-10/30/19	**HydroGEN**	N/A	2nd HydroGEN Workshop at ASU
May 2019 - Jan 2019 (**22 times**)	**NREL**	**Rutgers** **NREL**	One-on-one weekly update (S. Hwang – J. Young) **(Task 5,6,8, Milestone 6, and GNG)**
01/15/2020 (**3 times**)	**NREL/** **NREL/** **NREL**	**Rutgers**	**Milestones and GNG**

- Including the above teleconference, we have multiple email correspondence to deliver the Milestones on time.

Collaboration: HydroGEN consortium

Data sharing and interaction with 2B benchmark team:

- Verified data uploaded to HydroGEN site and Datahub. Quarterly reports with input from both RU and nodes shared in HydroGEN site and Datahub, and EMN nodes. This has allowed the continued sharing of progress, samples needed, problems encountered, and verification of experimental test procedures.

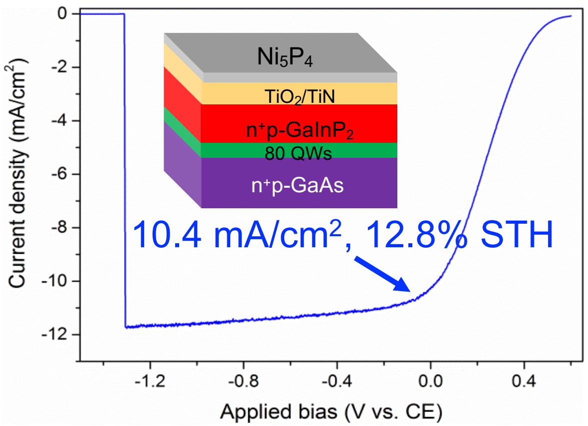
- Contributions were made for the 2B benchmark team including participation in AWSM workshop and reviewing the PEC SOP. Sharing the data to the water splitting R&D community is realized through publication as well as open access to the verified raw data in the datahub after the project period. Data shared in publications will be opened for sharing at the time of publication

- ## HydroGEN community interaction: (Since 2019 AMR)

Post-award	Means of communication	Node/point of Contact(s)
	Telecon	Todd Deutsch NREL
	Telecon for progress	Todd Deutsch, Andriy Zakutayev, and Kai Zhu NREL
	In-person (ASU 2^{nd} AWSM workshop)	HydroGEN community
	Telecon for weekly progress meeting	James Young NREL

Proposed Future Work

BP 3 plan – HP device



1. **Control ARC and top $GaInP_2$ thickness for current matching**
2. **Durability under simulated diurnal cycle**
3. **On-sun testing**

Goal: STH > 13.5%, 1 week stability under solar cycling

- *Achieve >13.5% STH suing better matching of junction current using ARC layer on 2nd GEN tandem device* (Y3Q1-Q3)
- *Diurnal cycle test to identify the STH and stability in neutral electrolyte* (Y3Q2-Y3Q4)

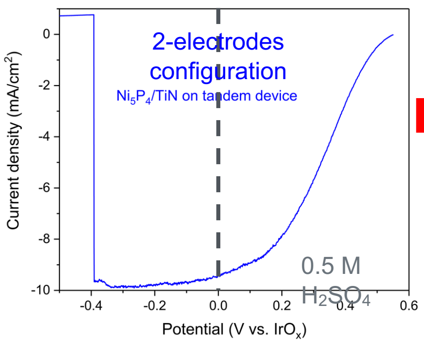
BP 3 plan – HV 2 device- HOIPs (Down selected HOIPs over $SrNbO_2N$)

- *Develop n^+p-Si photocathode for neutral/alkaline conditions* (Y2Q1-Y3Q1)
- *Half-cell HOIPs photoelectrode performance evaluation* (Y3Q1-Q3)
- *Assemble a full cell: HOIPs/Si tandem device and test under 1 sun illumination* (Y3Q2-Q4)

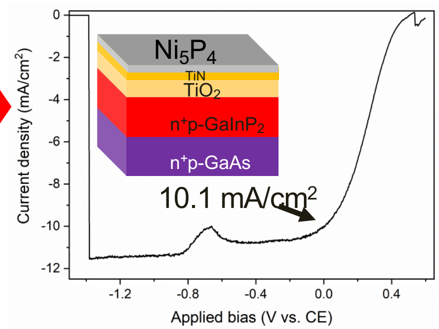
Goal: STH > 10%, > 24h stability

Project Summary

High-performance devices

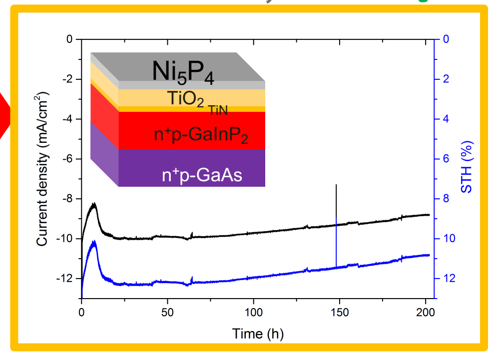


Year 1 results – STH 11.5%



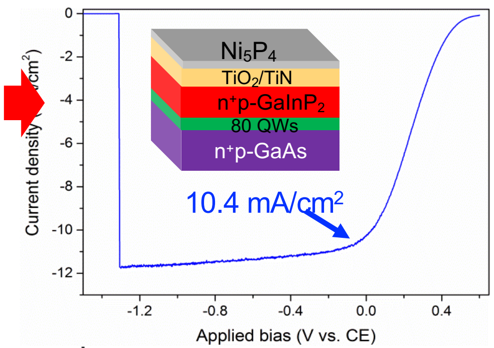
Anti-reflective coating with 1st GEN (STH 12.4%)

Milestone 5, GNG ✓



1st GEN III-V tandem in pH7, STH (initial) 12.6%

Milestone 6 ✓



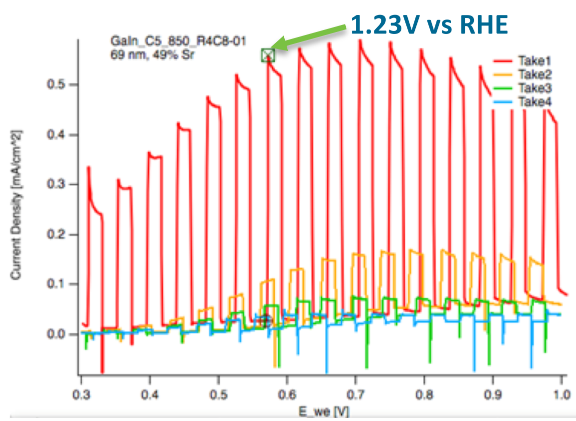
2nd GEN III-V tandem (STH 12.8%)

High-value devices

$ZnSnN_2$ photoabsorber

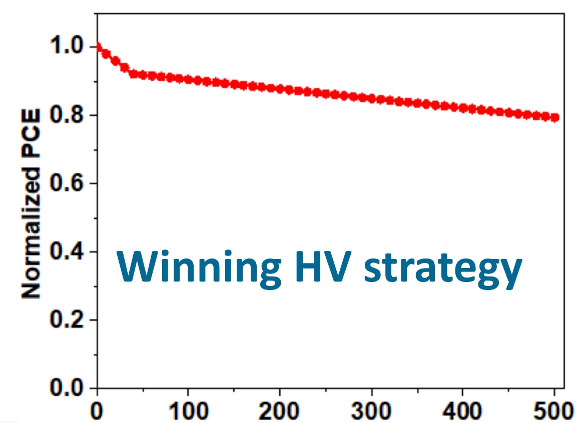
Year 1 - $ZnSnN_2$ instability

Milestone 7 ✓



HV device 1 - $SrNbO_2N$

Milestone 8 ✓



HV device 2 – HOIPs

Thank you for your attention

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Technical Back-Up Slides

Publications and Presentations

Publications (Year 2)

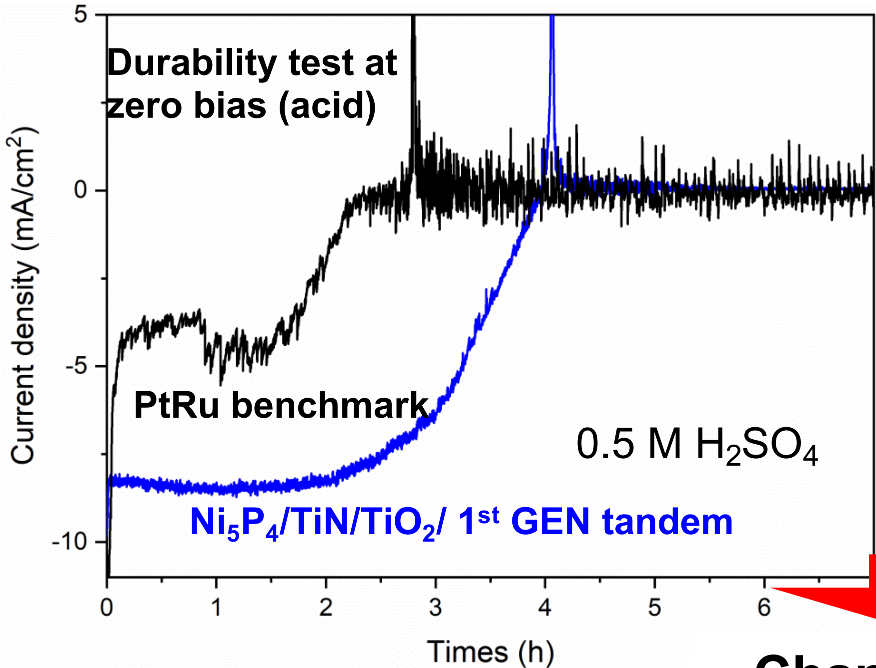
1. S. Hwang, J. L. Young, R. Mow, A. B. Laursen, M. Li, H. Yang, P. E. Batson, M. Greenblatt, M. A. Steiner, D. Friedman, T. G. Deutsch, E. Garfunkel, and G. C. Dismukes “Highly efficient and durable III-V semiconductor-catalyst photocathodes via a transparent protection layer” Sustainable Energy & Fuels, 2020, **4**, 1437-1442

2. S. Hwang, S.H. Porter, V. Manichev, M. Li, V. Amarasinghe, E. Taghaddos, A. Safari, M. Greenblatt, E. Garfunkel, and G. C. Dismukes, “$SrNbO_2N$ thin-film as a photoanode for solar-driven water oxidation” *manuscript submitted*

Presentation (Year 2)

1. K. Heinselman, S. Hwang, A. B. Laursen, K. Talley, J. Young, G. C. Dismukes, E. Garfunkel, and A. Zakutayev “Photoelectrochemical Applications of $SrNbO_2N$ Thin Films Synthesized via a Two-Step Process at Reduced Temperatures”, ECS meeting Atlanta GA Oct. 13-17 2019.

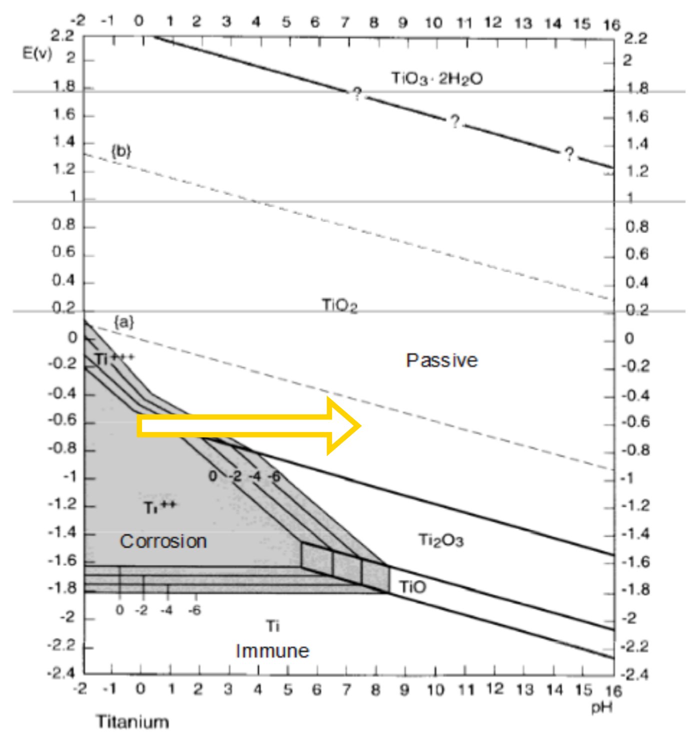
Accomplishments (technical slide):
HP device - Durability of HP device – Change the operating pH



- **Durability test of PtRu benchmark and $Ni_5P_4/TiN/TiO_2$ 1st GEN tandem device in acid at zero bias resulted in catastrophic failure after 2-4 h (sample dependent).**
- **Introducing the $Ni_5P_4/TiN/TiO_2$ layers improved the stability, but not sufficiently for the project milestones.**

Change the pH

- High aspect ratio of the defects of the $GaInP_2$ (or defects in underlying substrate) cannot be protected by **3-4 nm TiN in acid media.**
- Thicker TiN layer would reduce the light transmission.
- Relatively thick 30 nm of TiO_2 (ARC layer) proved chemically too unstable under the operating conditions.
- **Based on Pourbaix diagram, pH 7 (0.5 M sodium phosphate buffer)** that would not etch the TiO_2 layer.

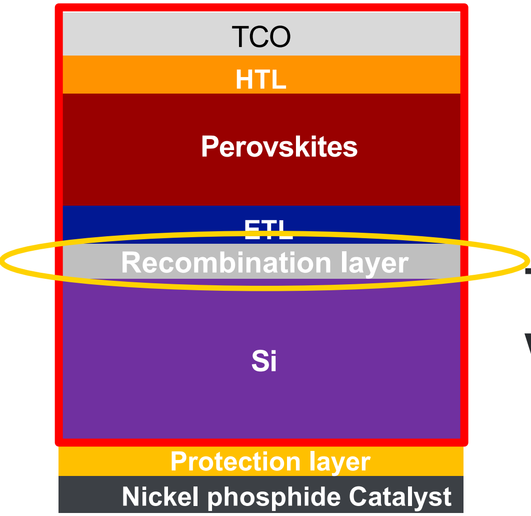


M Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, London: Pergamon Press Ltd, (1966).

Accomplishments (technical slide):

HV device 2 – HOIPs/Si junction – recombination layer

Selection of recombination layer for HOIPs/Si tandem junction



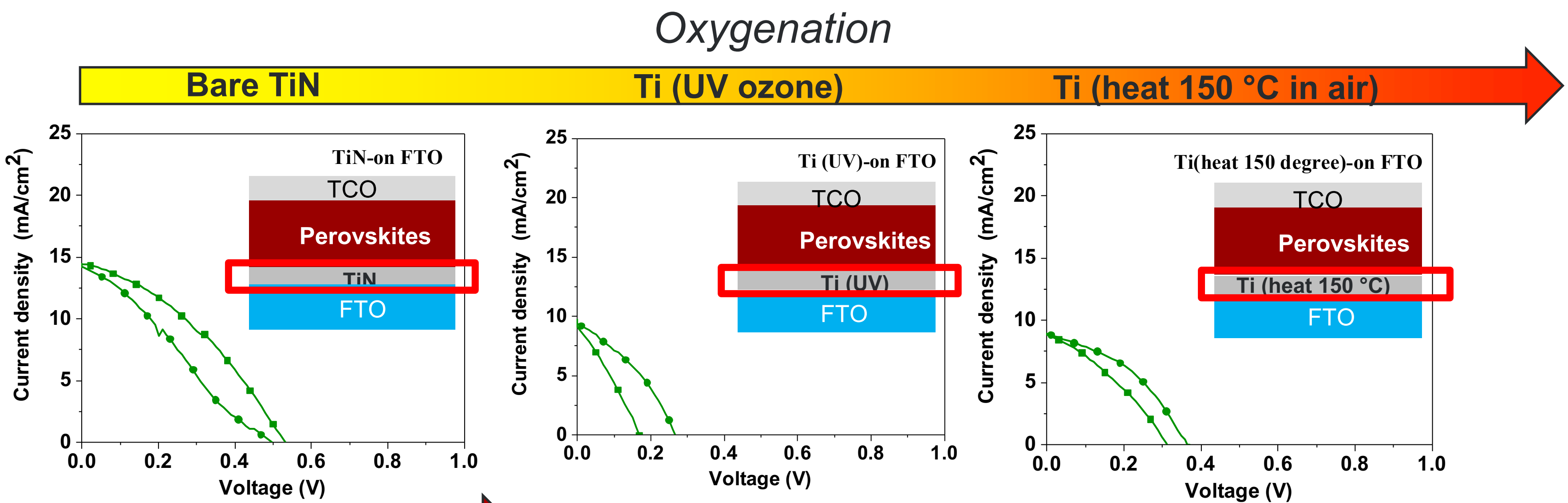
Requirements

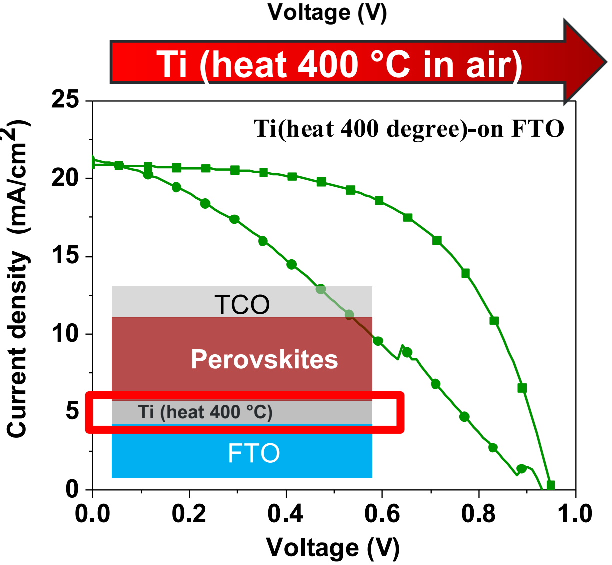
- **High conductivity**
- **High transparency**
- **Compatible with ETL and Si**

Ti and TiN were selected for testing due to the compatibility with ETL (TiO_2) and Si, and its high conductivity

	FTO	ITO	n^+-Si
Purpose	Model PV substrate	Model PV substrate	Model half-cell PEC substrate
Material properties	High T compatible (~ 500 °C)	Smooth surface, high conductivity	Native oxide formation

Accomplishments (technical slide): HV device 2 – HOIPs/Si junction – Selection of recombination layer





- **Based on TiN vs. various Ti precondition, increasing the oxygenation improve the PV performance probably due to the thicker layer of ETL (TiO_2) formation.**
- **Annealed Ti at 400 °C show similar current density (~ 20 mA/cm^2) and photovoltage (1 V) with optimized PV device**