Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Highly efficient solar water-splitting using 3D/2D hydrophobic perovskites with corrosion resistant barriers

Aditya Mohite
Rice University

DOE Project Award: DOE-EERE 0008843
P193

Award #	DOE-EERE 0008843
Funding	**$1 M**

NREL NATIONAL RENEWABLE ENERGY LABORATORY
BERKELEY LAB
Sandia National Laboratories
INL Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

Project Overview

Project partners

Aditya Mohite (PI), Rice University
Michael Wong (Co-PI), Rice University
EMN Partners: LBNL: Francesca Toma
NREL: Todd Deutsch, Kai Zhu, James Young

Award #	DOE-EERE 0008843
Timeline	*01/01/20-01/01/23*
Funding	**$1 M**

Project Vision

Combine high-efficiency low-cost halide perovskite (HaP) solar cells with HER and OER catalysts made from earth abundant materials to demonstrate an integrated HaP-PEC

Project Impact

Develop a durable and efficient water splitting system for H_2 production using low-cost abundant materials to move towards the DOE goal of $1/kg

Project Goal

Demonstrate stable high-efficiency (>20%) halide hybrid perovskite (HaP) solar cells to demonstrate a HaP-based photoelectrochemical cell (HaP-PEC) with 20% Solar-to-Hydrogen (STH) efficiency and 500 hours of operational durability.

The main objectives of this project are as follows:

- *Developing high-efficiency water-resistant 3D/2D heterostructure perovskite solar cells (PCE>20%) with ultra-hydrophobic termination*
- *Fabrication of corrosion resistant barriers, integration of HER and OER catalysts and testing durability under electrolytes*
- *Understanding degradation mechanisms under operation and implementing strategies to mitigate corrosion*
- *Testing, benchmarking and optimization of PEC performance and stability*
- *Scaling-up PEC by increasing the active devices area to 5”x 5”*

Approach summary

Project history

Our team has published high-impact papers in optoelectronics, device integration of perovskites, as well as earth abundant catalysts, corrosion chemistry, and catalyst optimization which are relevant for developing low-cost, earth-abundant perovskite-PEC system.

Proposed targets for BP3

a. Optimize PECs for high-efficiency and durability
b. Techno-economic analysis
c. Scaling-up photocathode and photoanode
d. HaP-PEC large area module

Key barriers

Stability of perovskite solar cells in aqueous media

Develop corrosion resistance layers that are electronically transparent

Partnerships

LBNL: Degradation mechanisms, benchmarking PECs

NREL: Benchmarking PEC efficiency, outdoor testing

Accomplishments & progress

- Demonstrated world record efficiency solar-to-hydrogen efficiency of 20.8% using an integrated PEC with 100 hours of durability
- Demonstrated STH efficiency of 17.7% using Perovskite/Perovskite tandem
- High-efficiency was enabled by the use of the conductive adhesive barrier (CAB), which can perfectly translate electrons or holes to the reaction.
- Integrated design enabled harvesting lattice heat from the photoabsorber to the electrolyte.
- Developed low Ir containing and NiRu based OER catalysts, which demonstrate exceptional stability
- Developed a robust TEA model using our PEC design to achieve <$2/kg of H2.

Collaboration Effectiveness

- **Lawrence Berkeley National Laboratory** – **Francesca Toma**

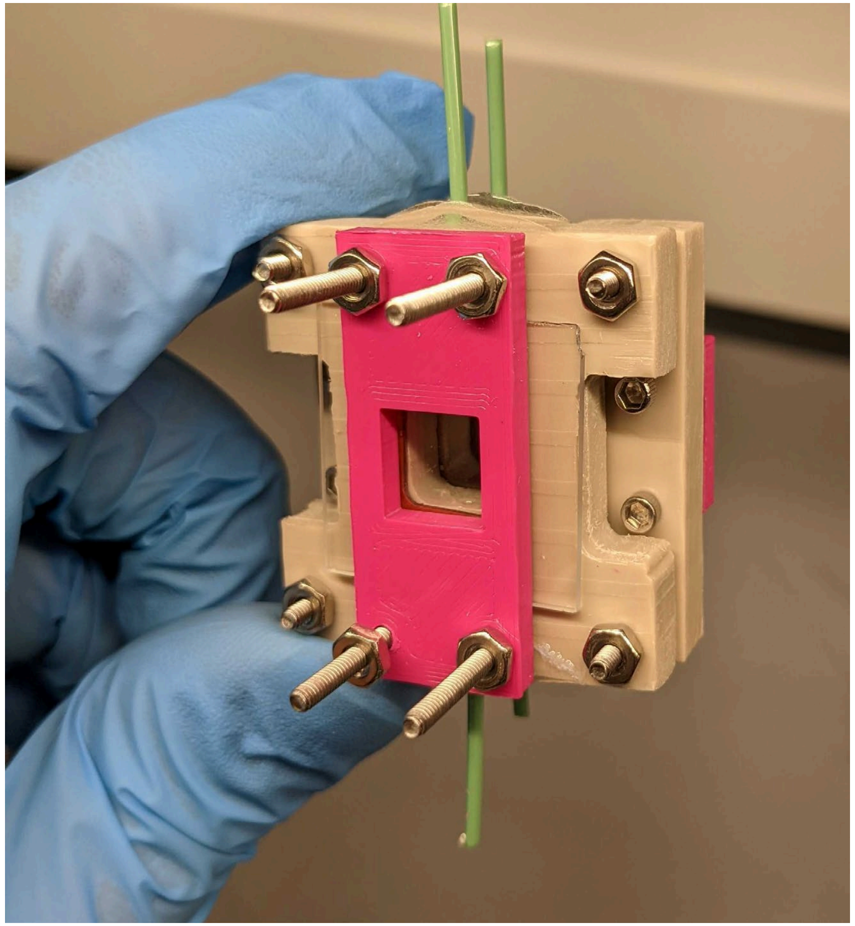
  Productive collaboration over three years on benchmarking, testing and characterization of PEC devices

  - Validated world record efficiency of 20.8% on 1 cm2 PECs
  - Testing Faradaic efficiency of catalysts
  - Testing half cell performance and degradation mechanisms
  - Measuring new Ir-free and low-Ir content catalysts

- **NREL – Kai Zhu, Todd Deutsch**

  - Provided pin and nip cells with 20% efficiency for testing half cells
  - Developing strategies of scale-up PECs
  - Understanding PEC data on CABs, photoanodes, measurement protocols
  - Inputs on TEA model developed by Rice on PECs

Approach: Components of the photoelectrochemical cell



1. Photoabsorber

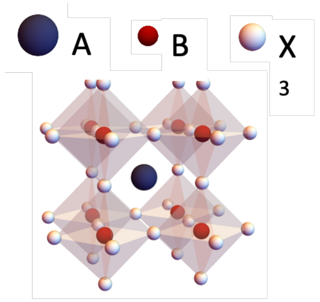
2. Corrosion barrier

3. Earth abundant catalysts (HER & OER)

Halide Perovskites: Solution processed photovoltaics

Chemical structure

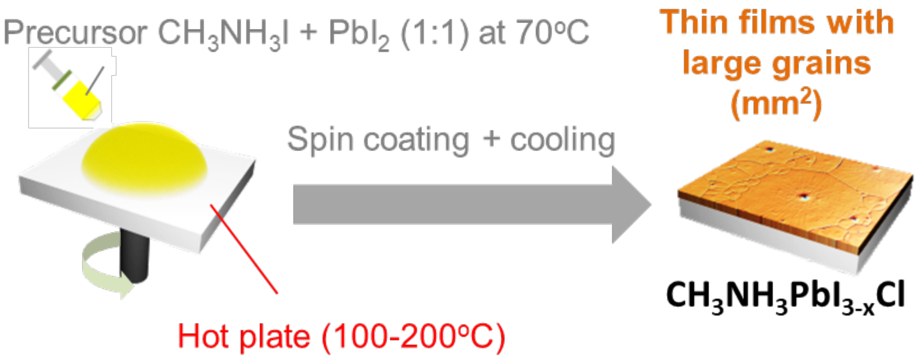
Perovskite: A B X_3

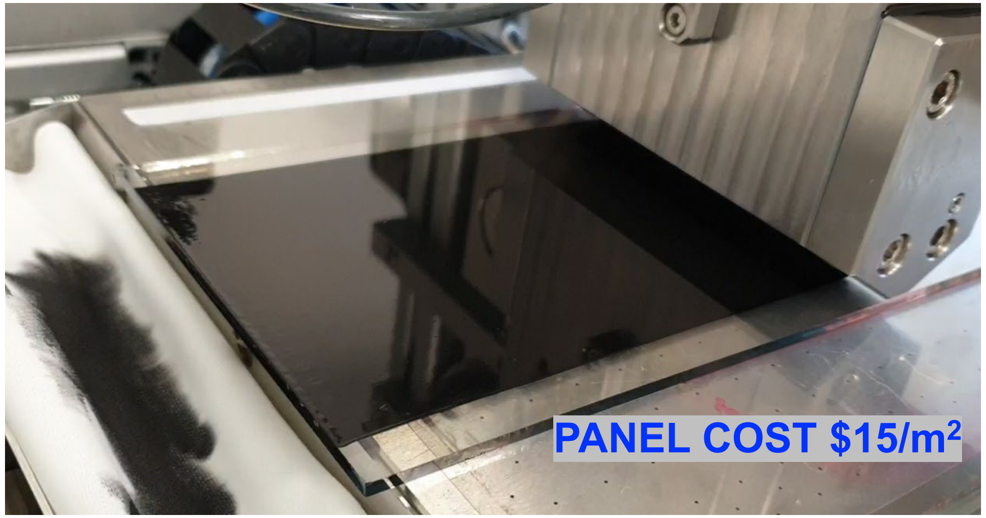


e. g., $MAPbI_3$, $CsPbBr_3$

Solution processed

SPIN-ON, PRINTING, SPRAYING, COATING





Advantages

Need 1000x times less material to absorb solar radiation

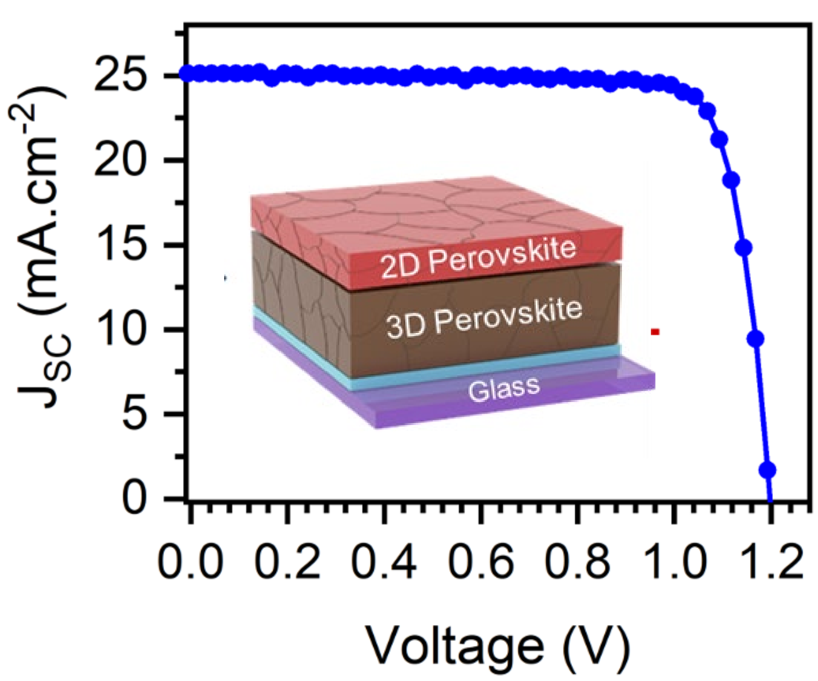
Easy to recycle- All components can be recovered at <100 °C

Can be recycled at ambient conditions

Can be recycled at ambient condition.

Achieved long-term durability

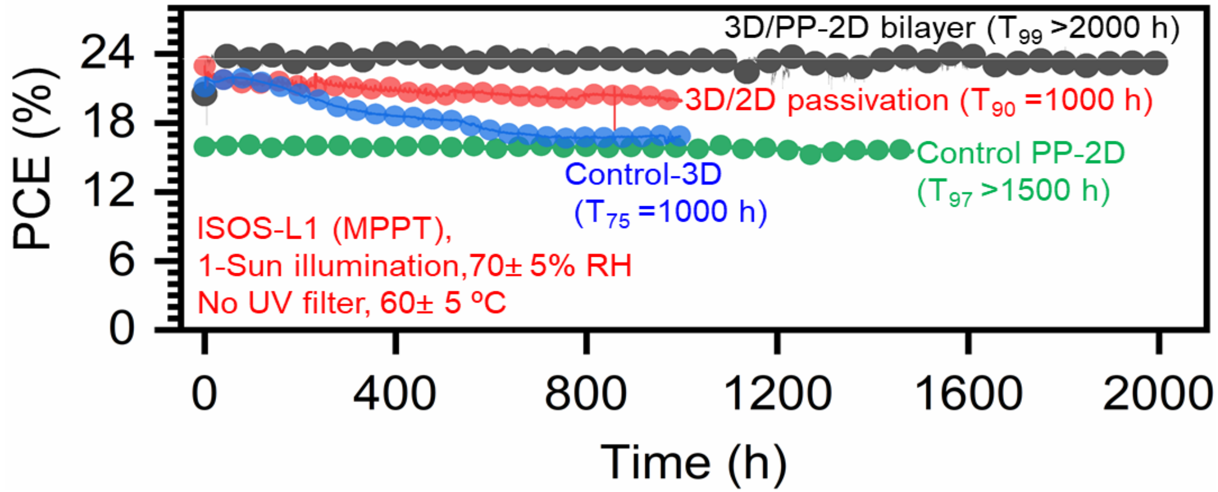
3D|2D stacks; η=25%



2 Rice Patents: First Solar interested in licensing

Proprietary processes and formulations developed at Rice

3D|2D perovskite stacks enables high-efficiency & durability

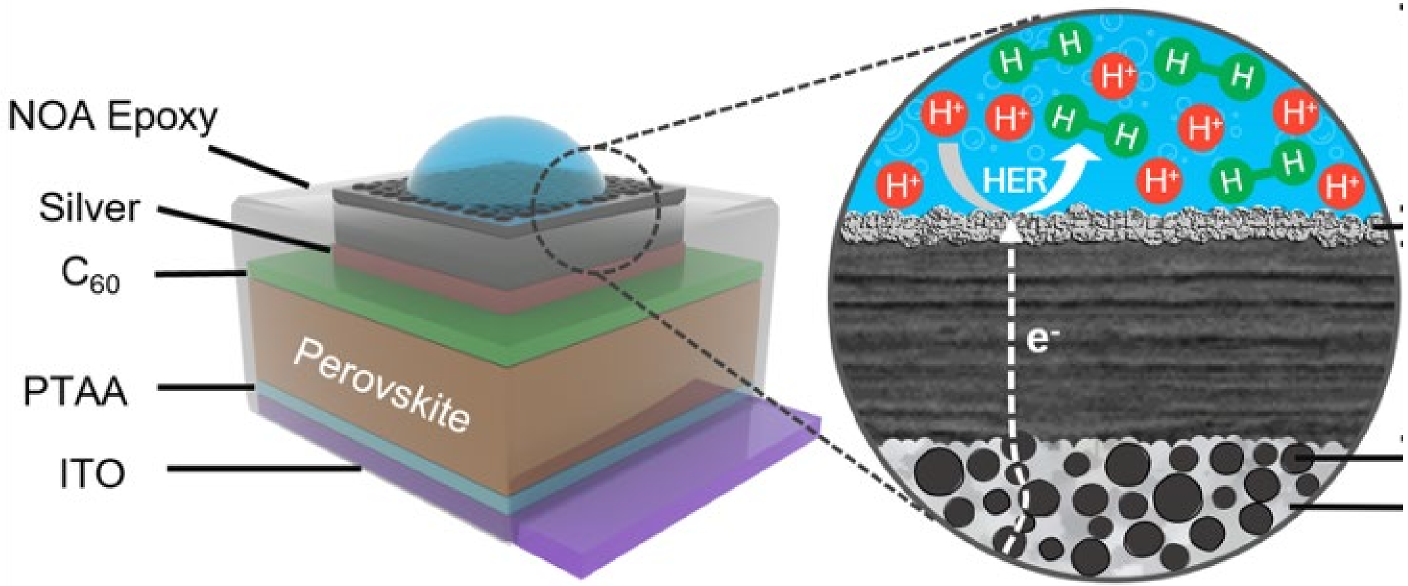


Science 2018, Nature Nano 2020, Nature Nano 2021, Science 2022, Nature Physics 2022

3 Rice Patents: First Solar interested in licensing.

Innovation: Conductive Adhesive Barrier

Near perfect (98%) conversion of electrical power to chemical energy



Modular, parallel processing

Catalyst or solar cell can be replaced and recycled

Non-trivial to get a low contact resistance – Most previous efforts lose device efficiency

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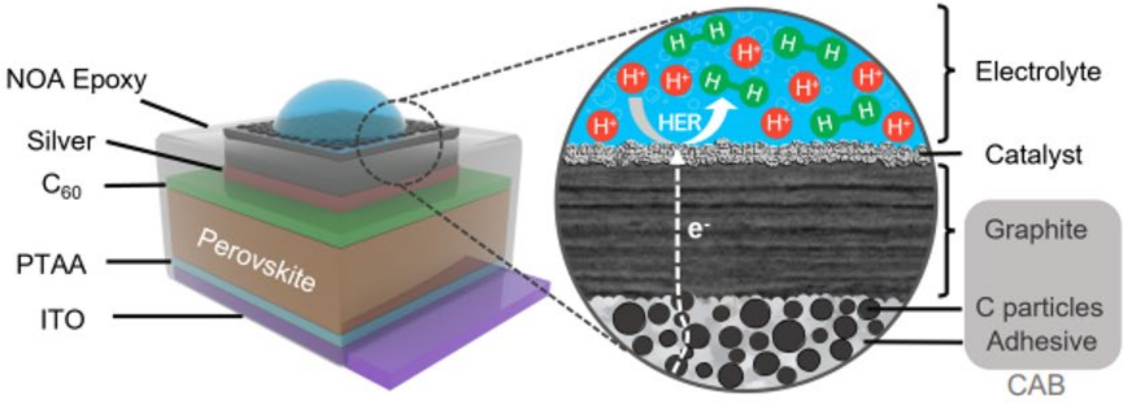
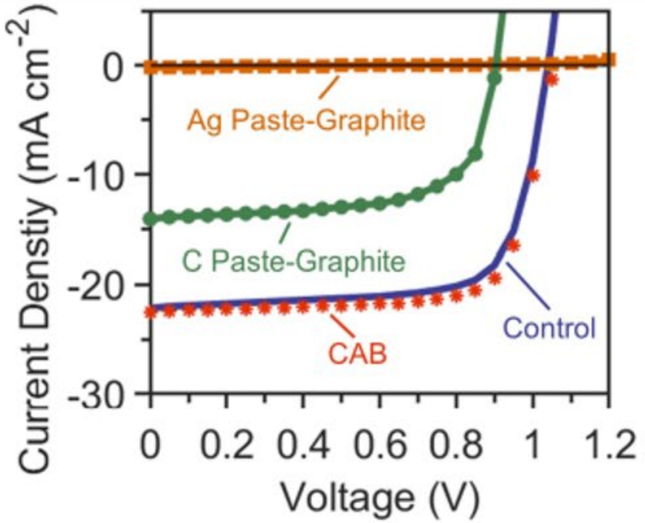
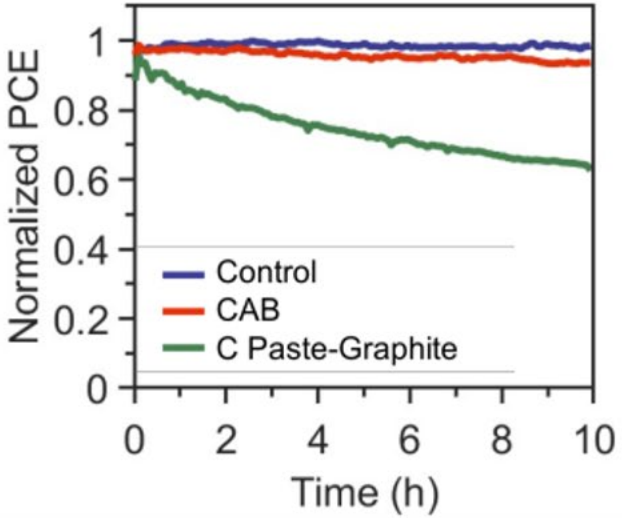
Innovation: Conductive-Adhesive Barrier (CAB)



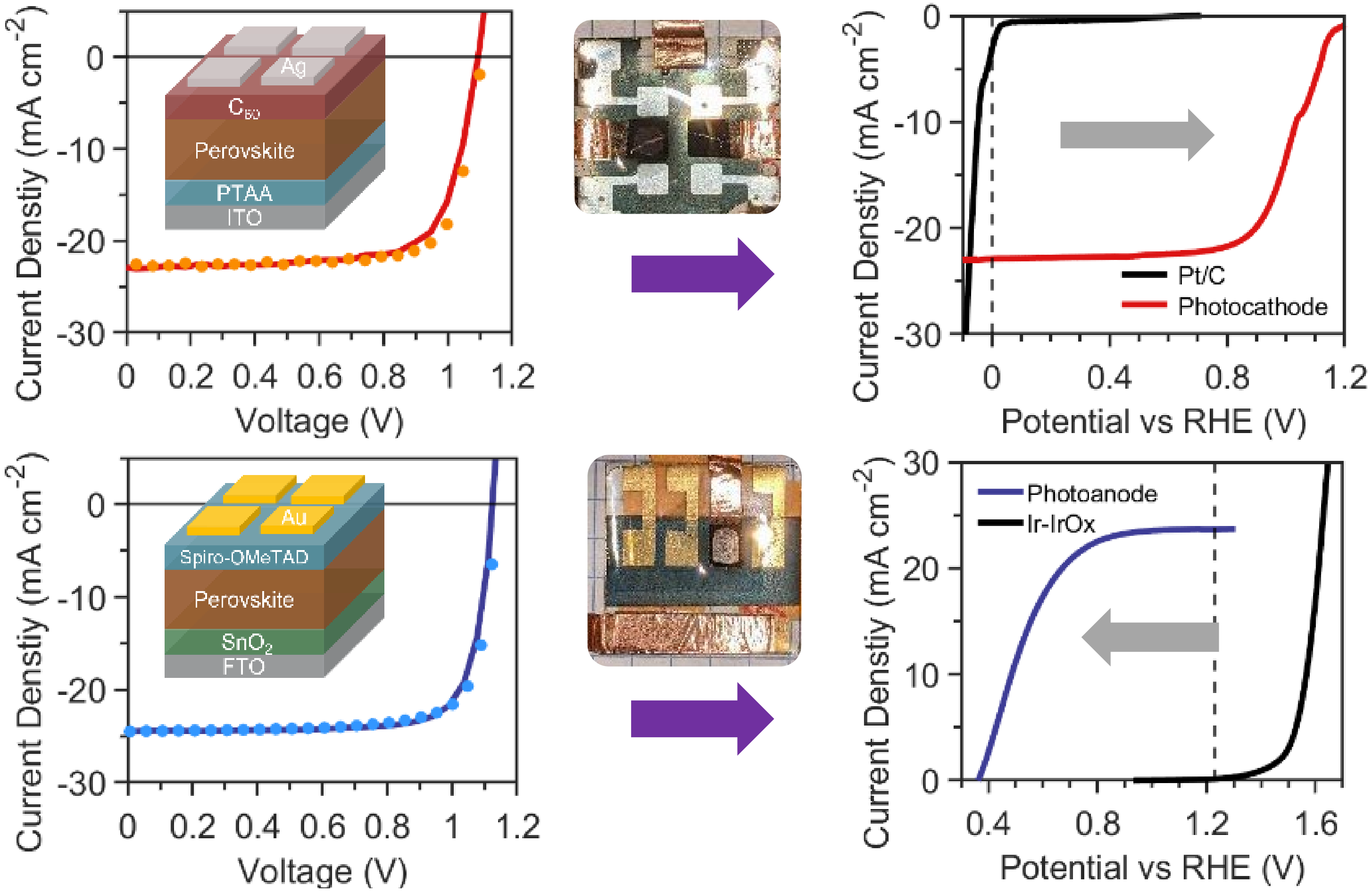




	Ag Paste	C paste	CAB	Control
V_{OC} [V]	-	0.90	1.07	1.06
J_{SC} [mA/cm²]	-	14.1	22.7	22.0
FF	-	0.67	0.73	0.76
Efficiency	-	8.5%	17.7%	17.7%

Milestone 2.2: Design of hydrophobic terminations and anti-corrosion barriers

Converting solar cells to photoelectrodes



CATHODE

PCE_{pin} = 19.1%

$\eta_{cathode}$ = 18.6%

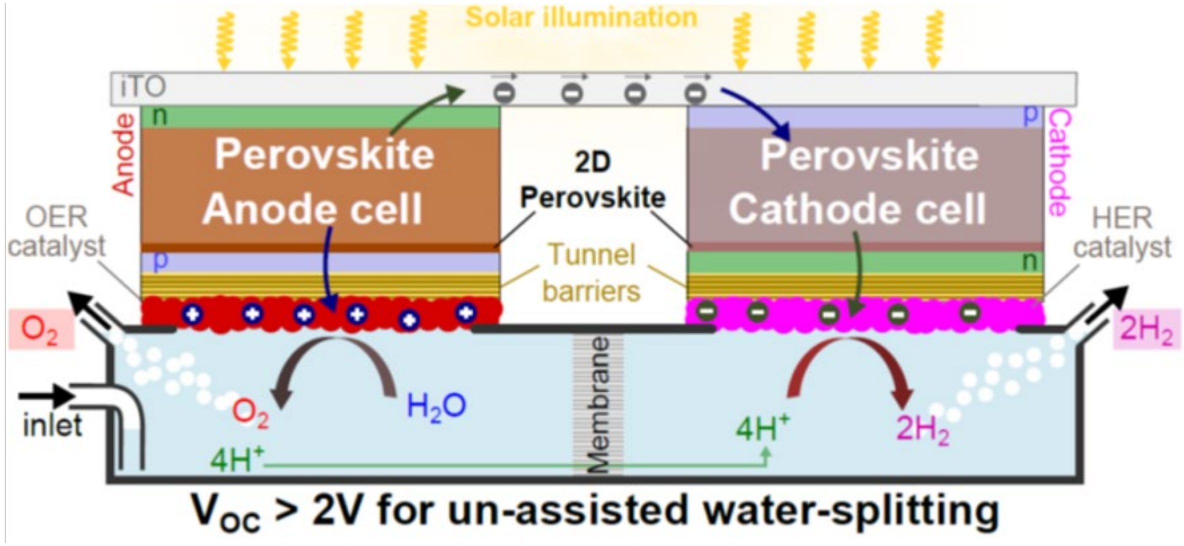
ANODE

PCE_{nip} = 20.9%

η_{anode} = 11.3%

Near-perfect conversion from solar cell to photoelectrode

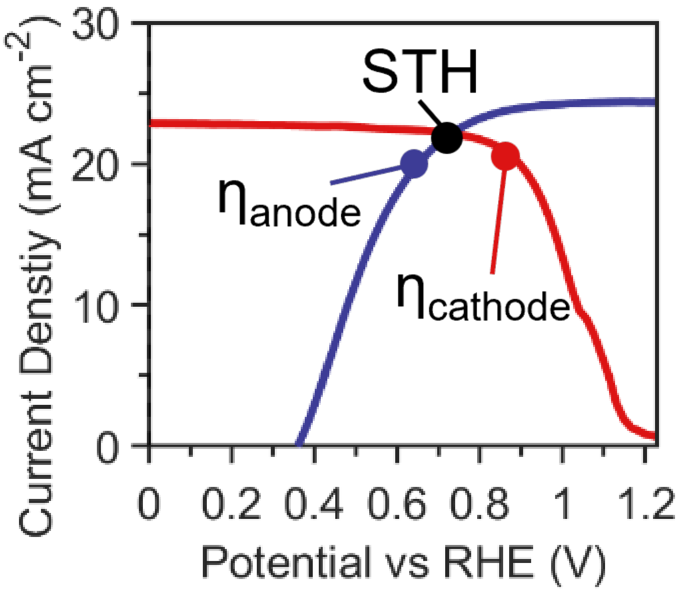
Our initial project concept (BP1)

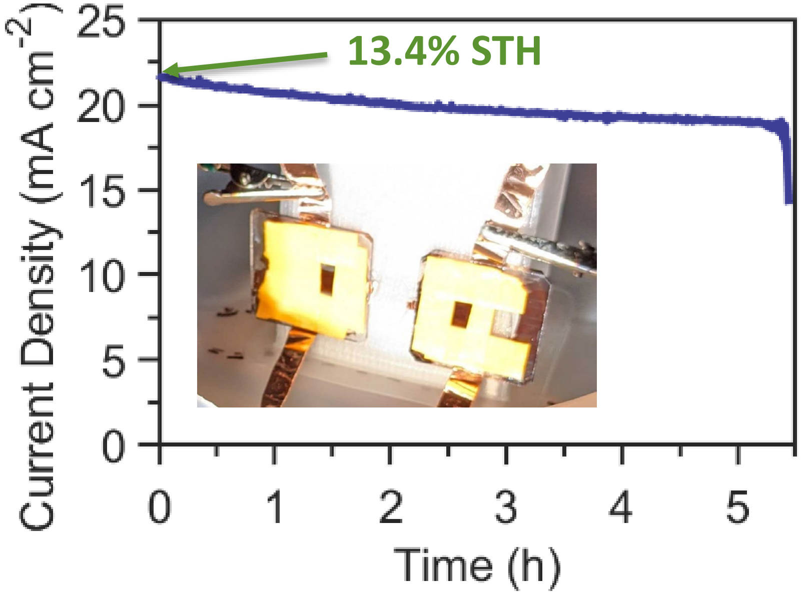


Three key components

- **High-efficiency PVs:** Exploit 3D/2D perovskite solar cells with regular and inverted architectures to fabricate photocathode and photoanode
- **Barriers:** hydrophobic polymers, carbons, ALD oxides (Al_2O_3, HfO_2)
- **Integration of catalysts:** Integrate with HER and OER catalysts to build an autonomous PEC platform

Autonomous solar water-splitting at 13.4%





Current density without bias

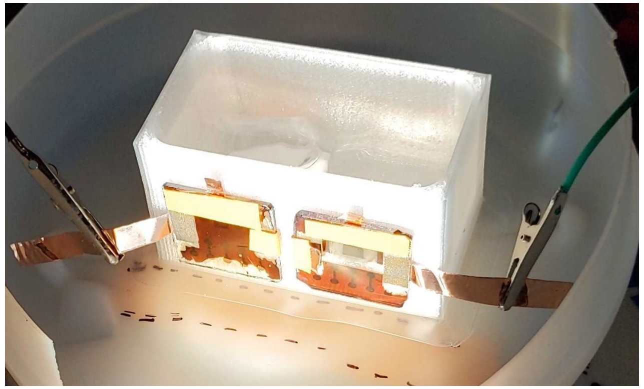
Thermodynamic water-splitting potential

Faradaic efficiency

$$STH = \frac{|J_{op}| \times 1.23V \times \eta_F}{P_{in}}$$

Bias-free solar-to-hydrogen efficiency

Solar illumination power density



Milestone 3.2: **Optimize PECs for high efficiency and durability**

BP 1 Objectives: Achieved

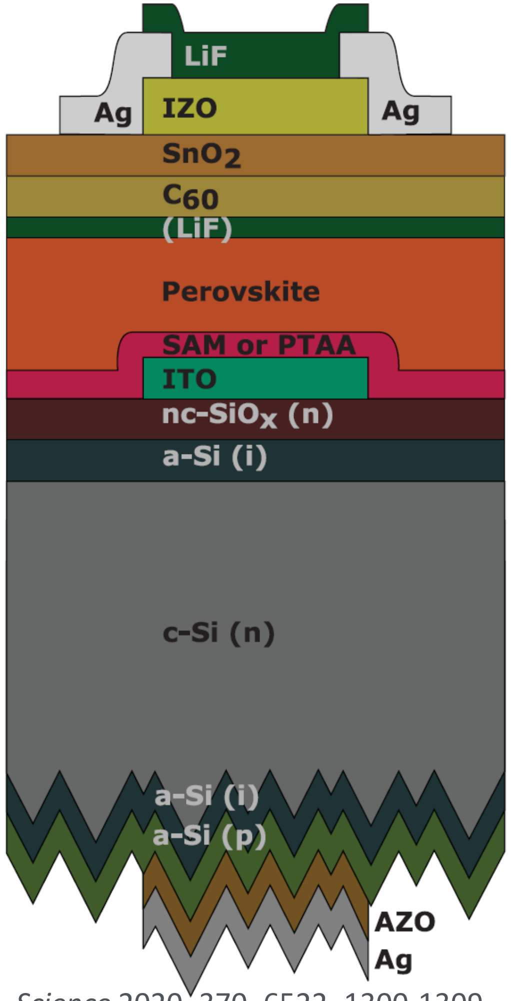
GNG: Proof of concept HaP-PEC demonstration with 10% STH efficiency and 1 hour stability

- ❖ Developed high-efficiency 3D solar cells with >20% efficiency – both p-i-n and n-i-p architecture
- ❖ Developed corrosion barrier protecting solar cell from electrolyte degradation retaining 99% of electrical power
- ❖ Demonstrated 12.4% STH with 2.5 hour stability

BP 2 Objectives: Achieved

- Design charge transport layers as barriers (Milestone 1.3)
- Design of ultra-hydrophobic terminations on the HaP layers and design of anti-corrosion barriers (Milestone 2.2)
- Optimize PECs for high efficiency and durability (Milestone 3.2)
- HaP-PEC for unassisted water splitting with 15% STH efficiency and with 100 hours stability under continuous operation (Decision Point 2)

Monolithic silicon-perovskite tandem



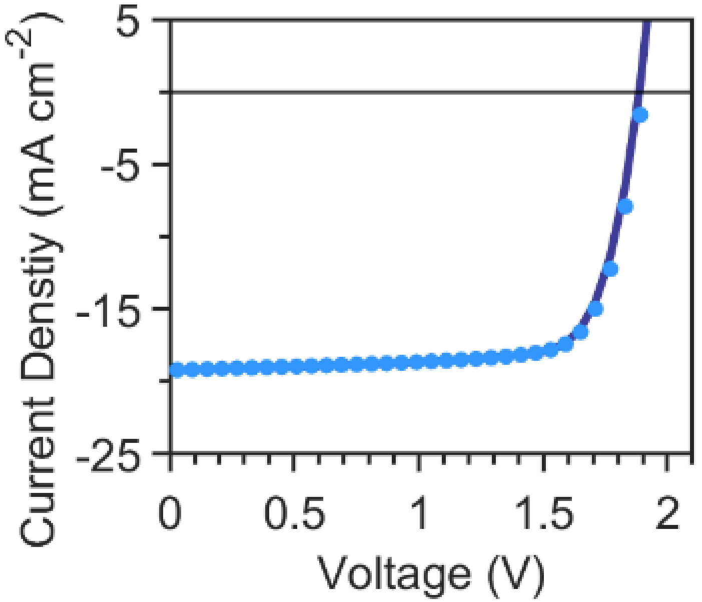
Science 2020, 370, 6522, 1300-1309.

$E_g \sim 1.6\text{-}1.7$ V
$V_{oc} \sim 1.1$ V

$V_{oc} \sim 1.8\text{-}1.9$ V

$E_g \sim 1.1$ V
$V_{oc} \sim 0.7$ V

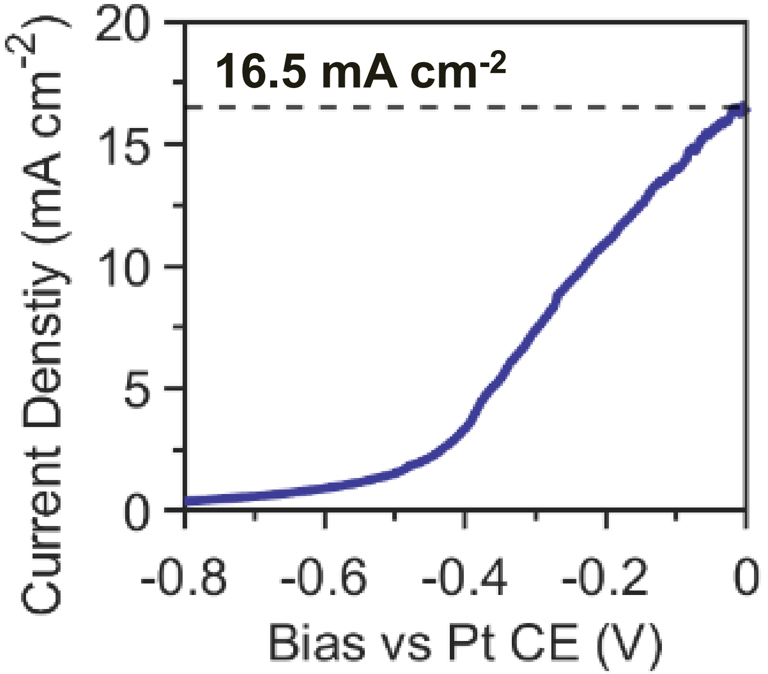
Enough for water splitting at J_{mpp}

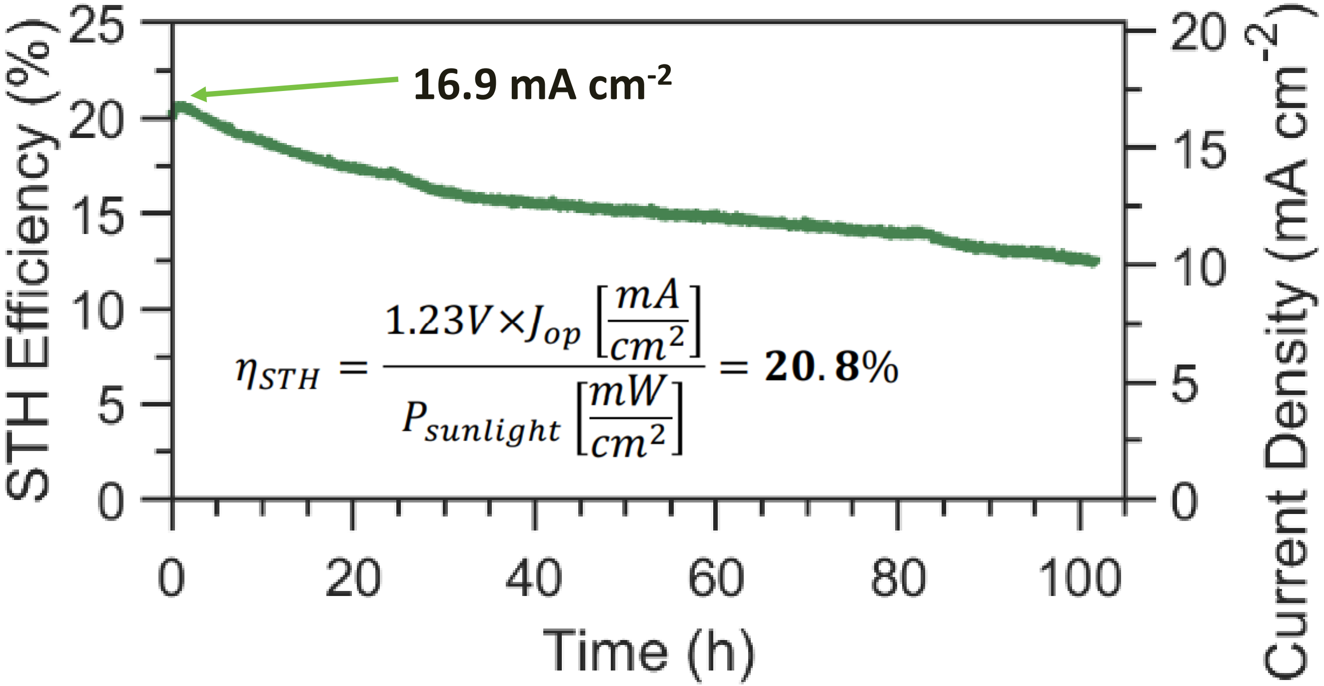


	Tandem
V_{OC} [V]	1.90
J_{SC} [mA/cm2]	19.2
FF	0.76
Efficiency	27.7%

Record efficiency unassisted water splitting

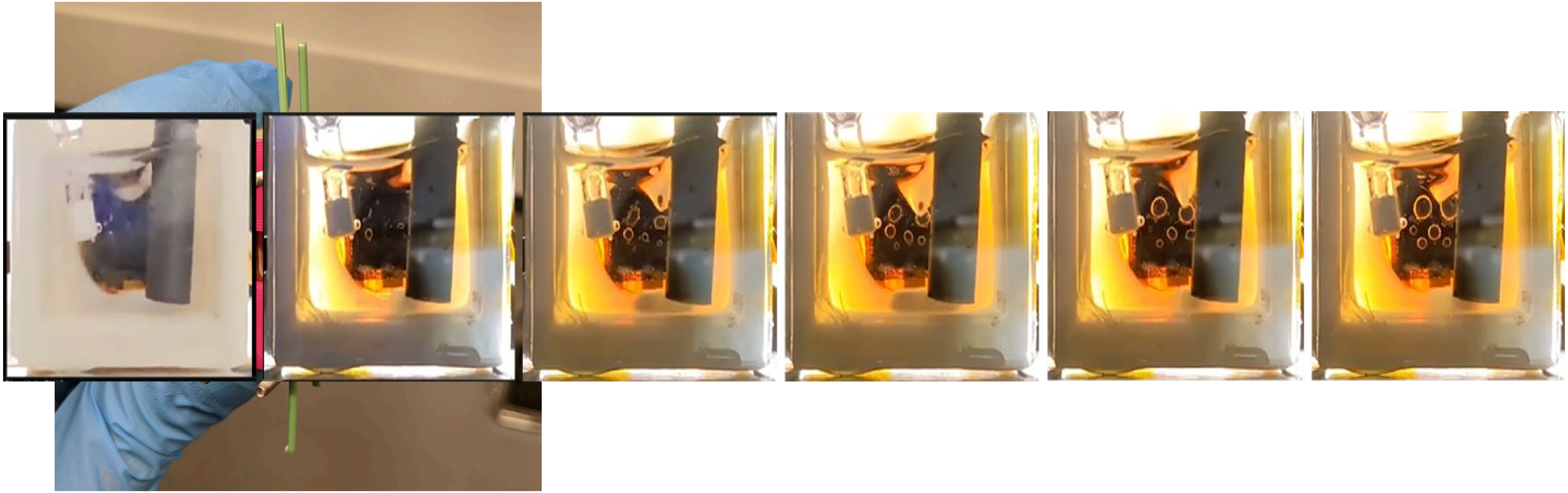
GNG for BP2: 15% STH for 100 hours



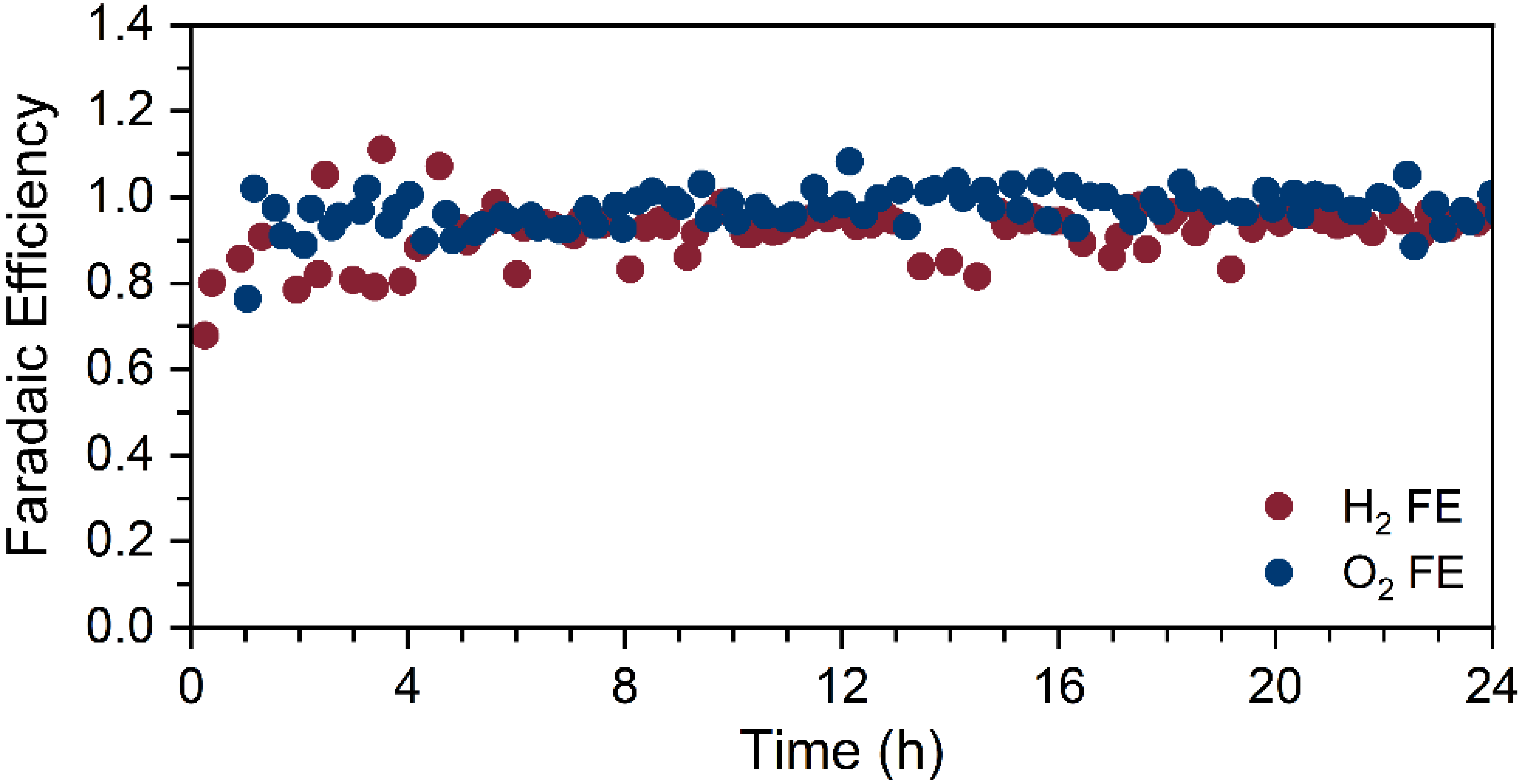


Same ink-based catalyst system as in co-planar system

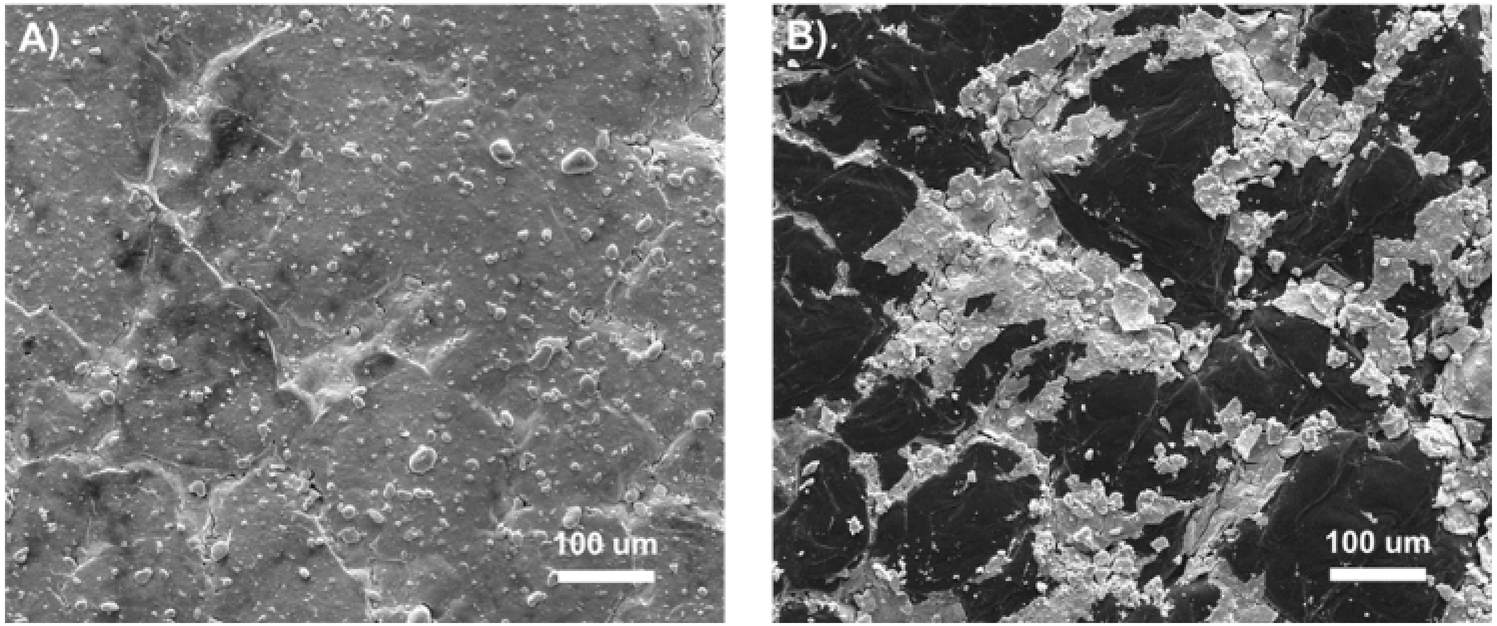
Validation: STH efficiency verified at Toma lab (LBL) node partner



Faradaic efficiency measurements at LBL

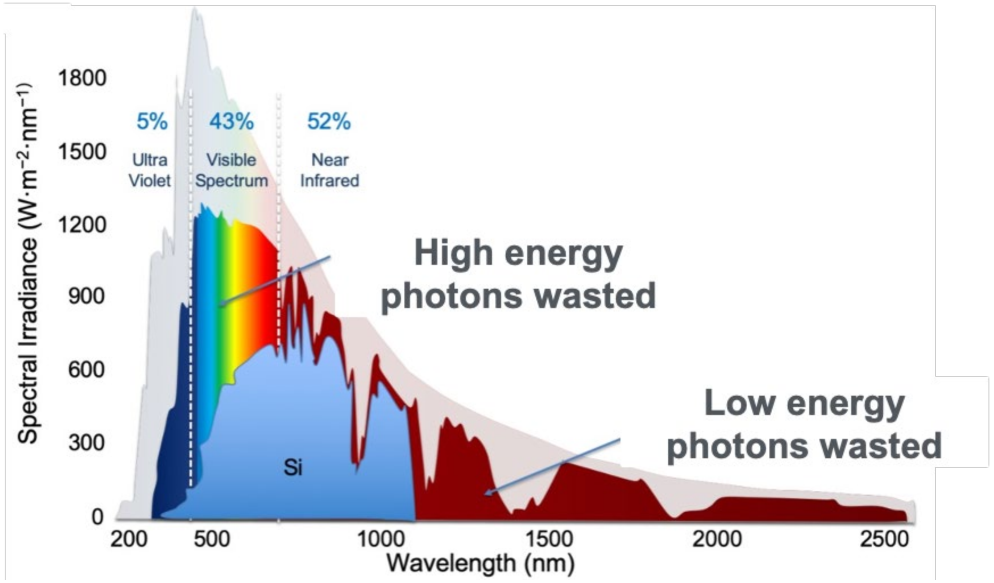


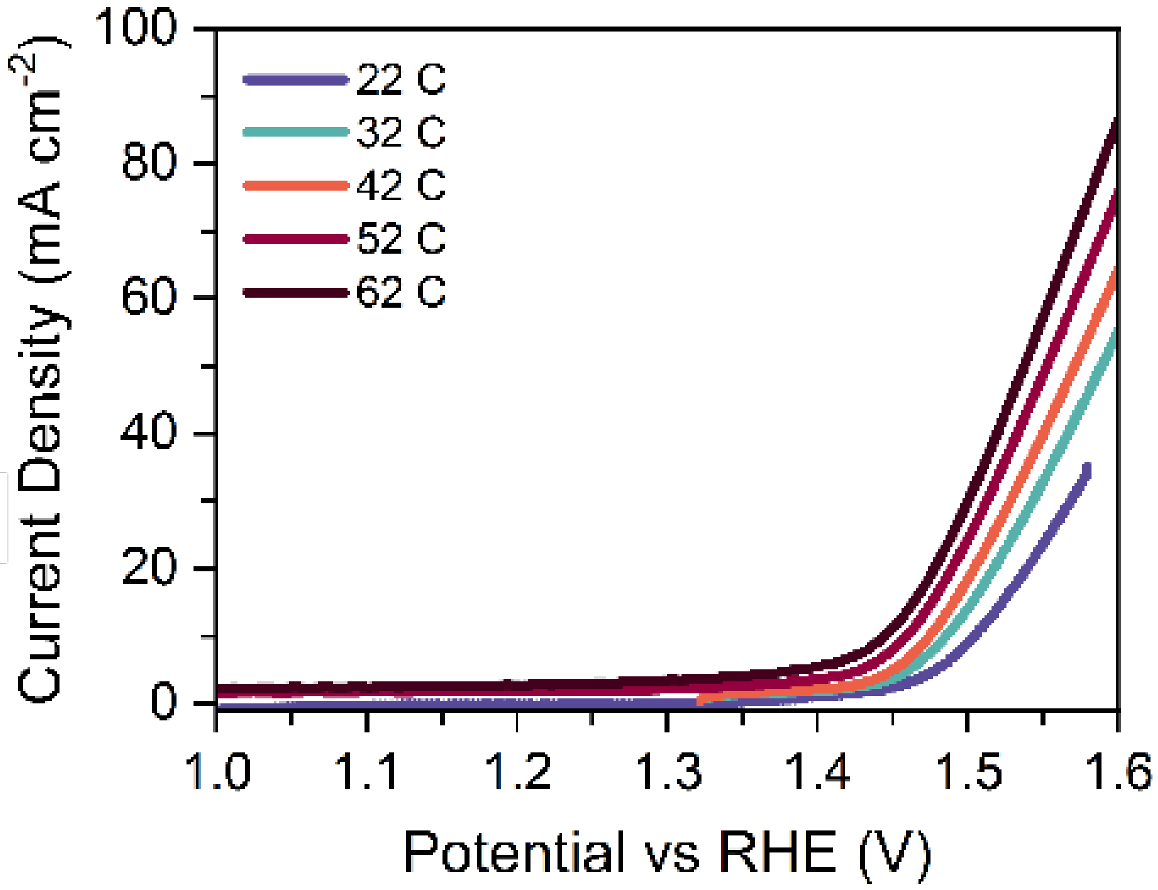
Catalyst delamination on surface of CAB



LBL Node (Toma): Understanding degradation mechanisms (XPS, FE measurements)

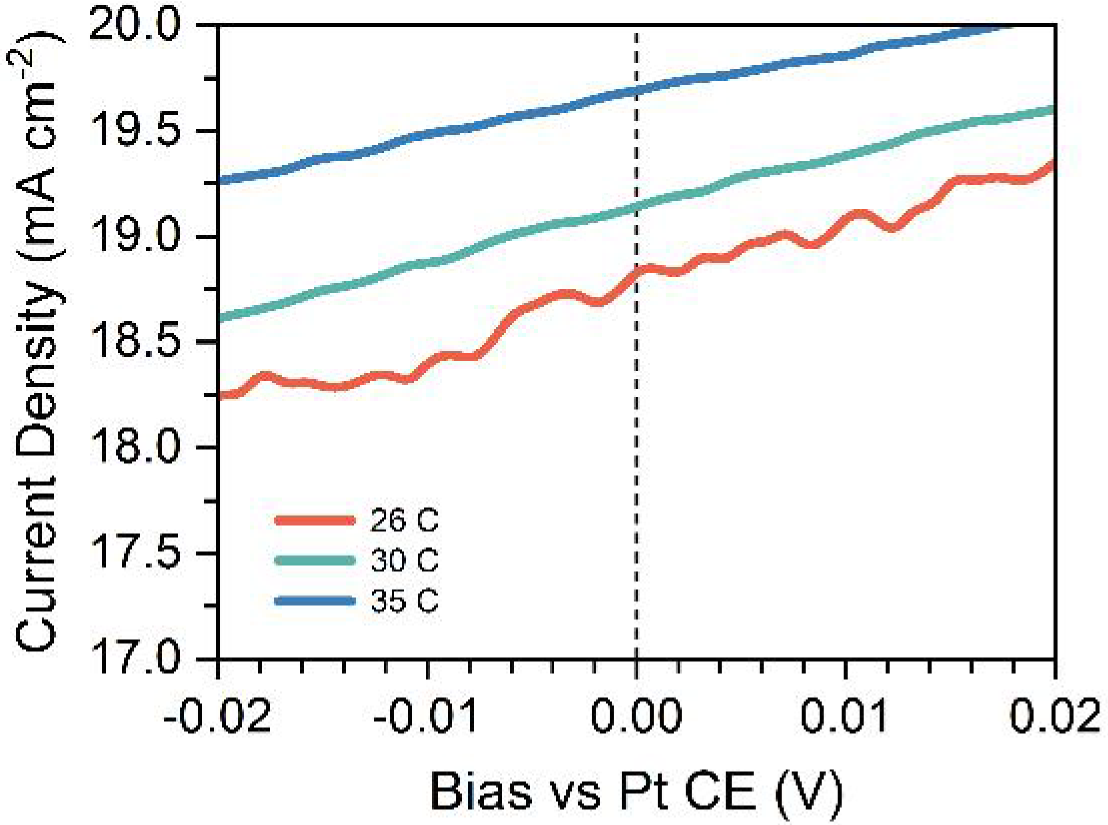
Temperature dependence of IrO_2 catalysts

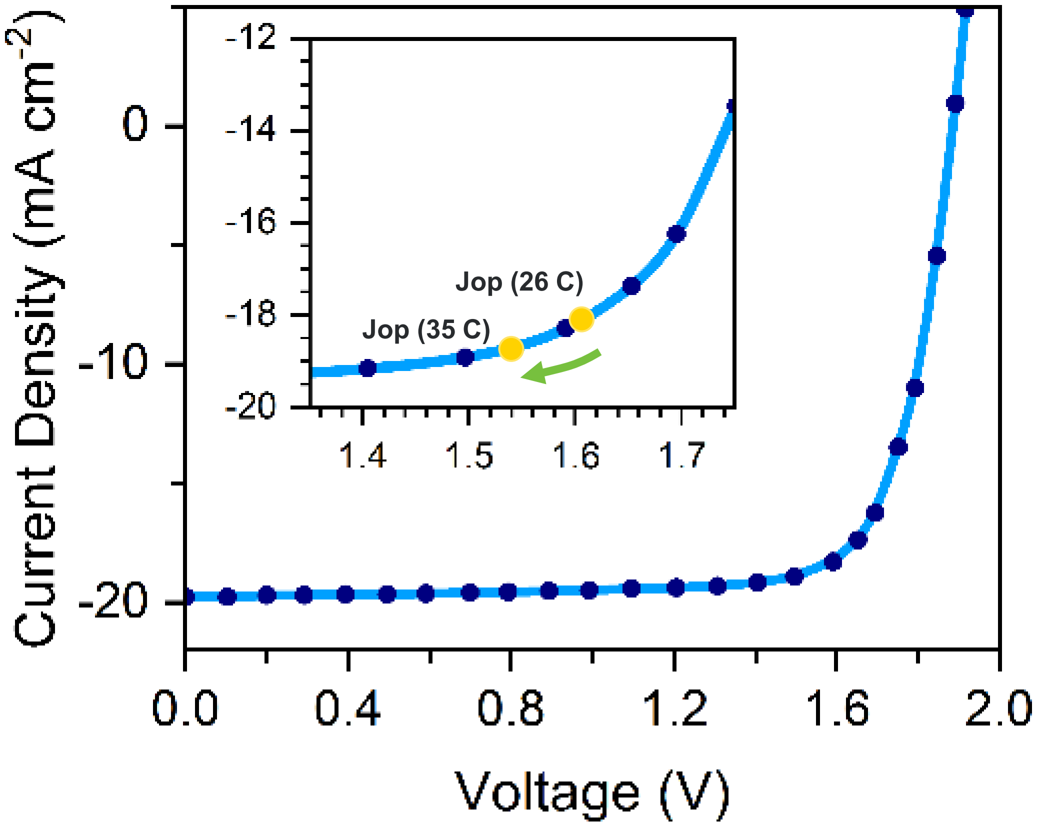




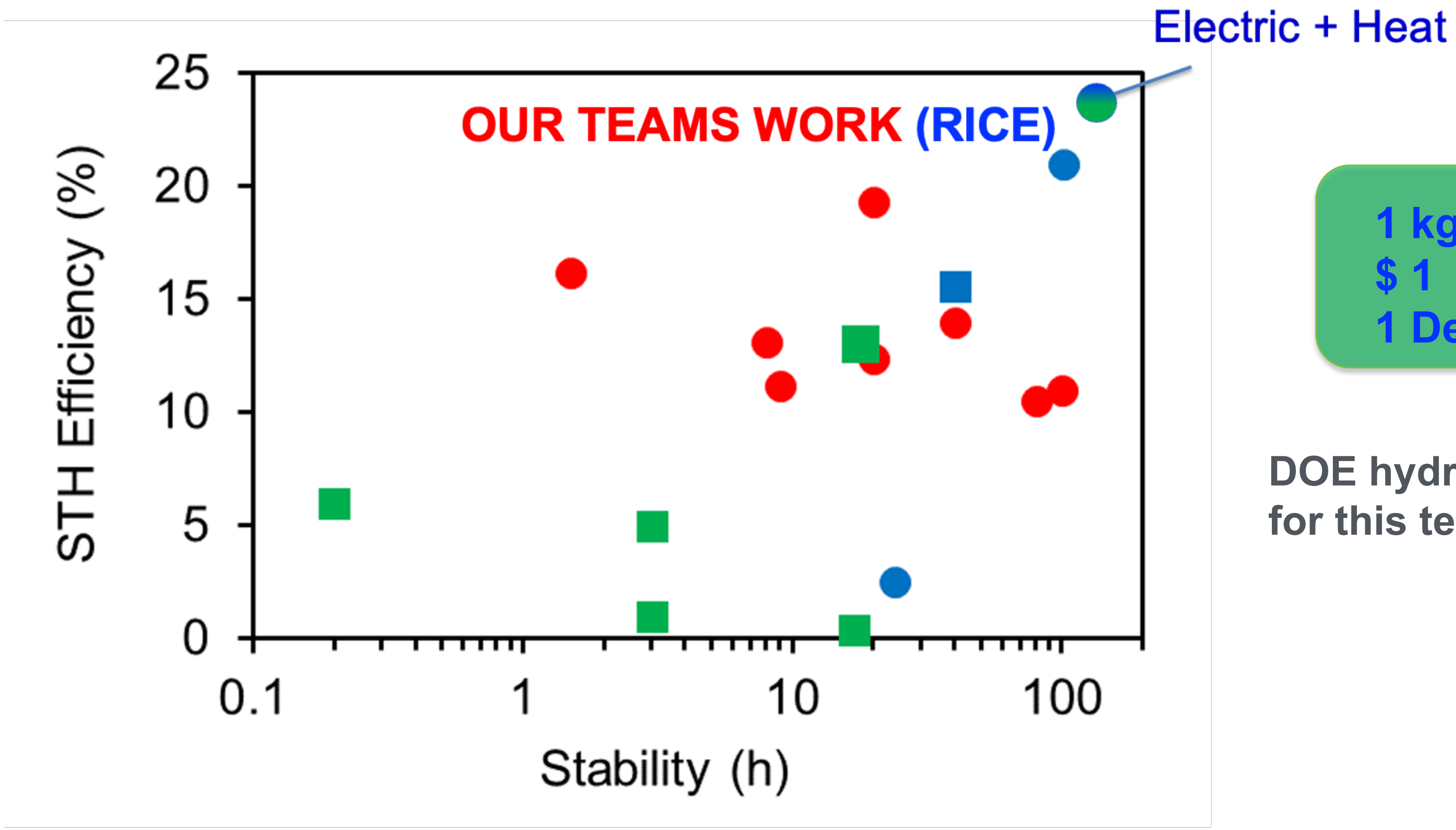
S. Siracusano et al. / Applied Catalysis B: Environmental 164 (2015)

Reaching STH efficiency >24% STH





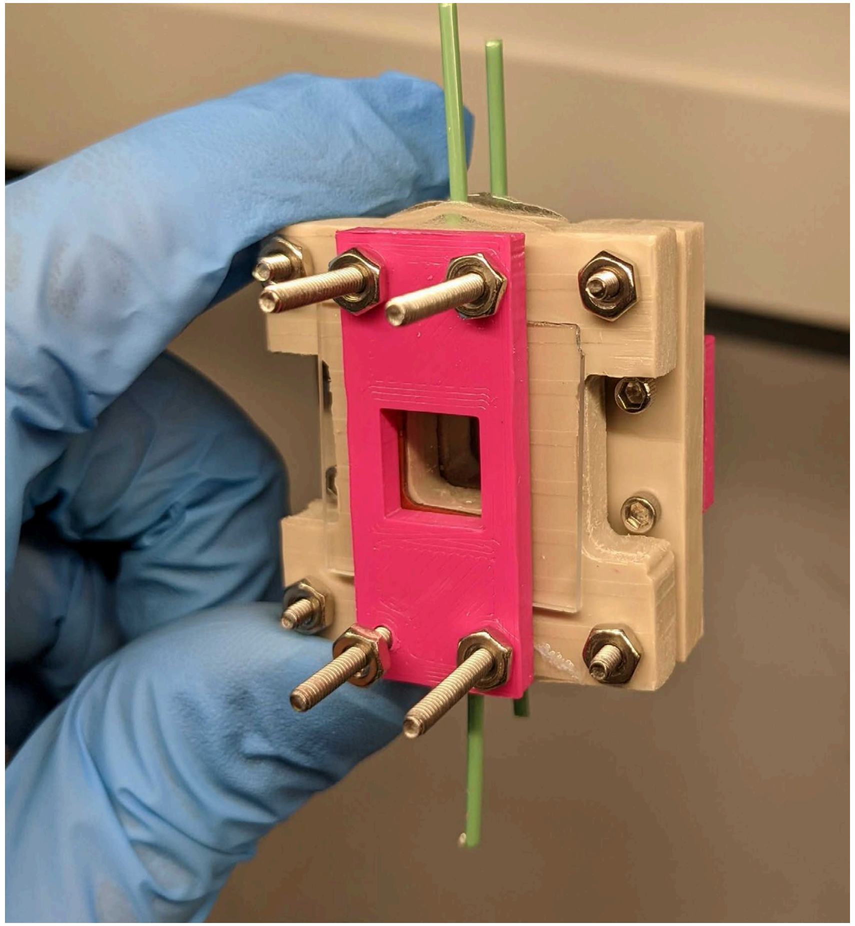
Impact: Comparison to other integrated devices



1 kg of H_2
$ 1
1 Decade

DOE hydrogen shot goal for this technology !

Components of the photoelectrochemical cell



1. Photoabsorber

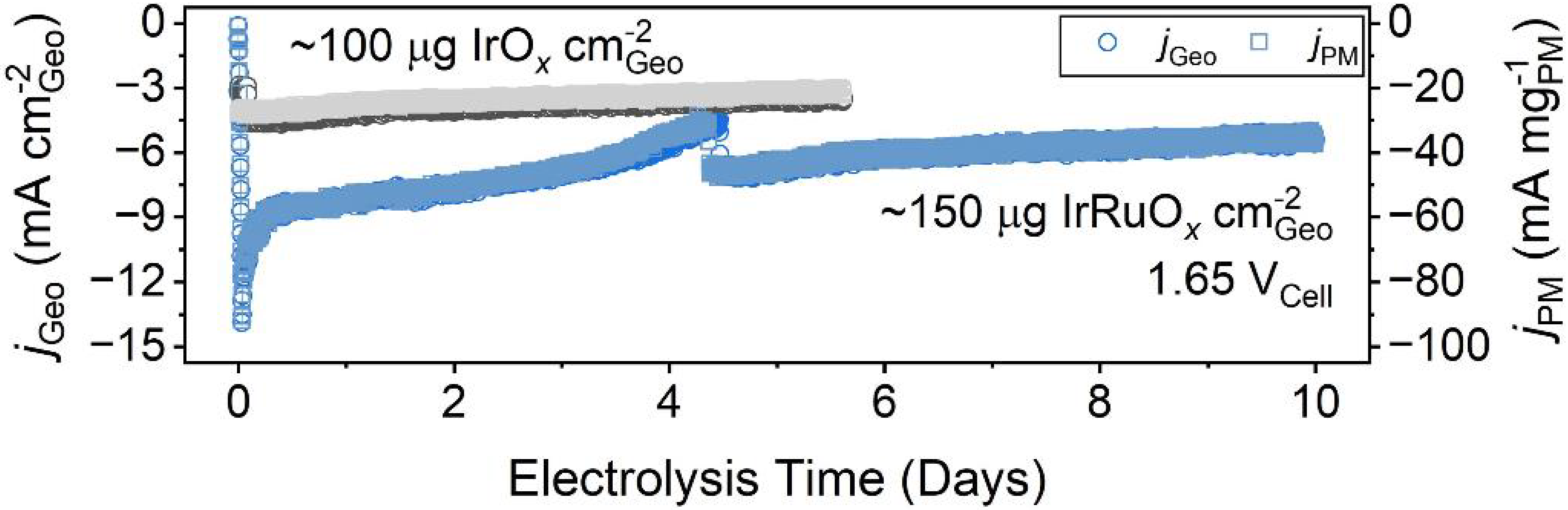
2. Corrosion barrier

3. Earth abundant catalysts (HER & OER)

A practical catalyst with 50% lower Ir

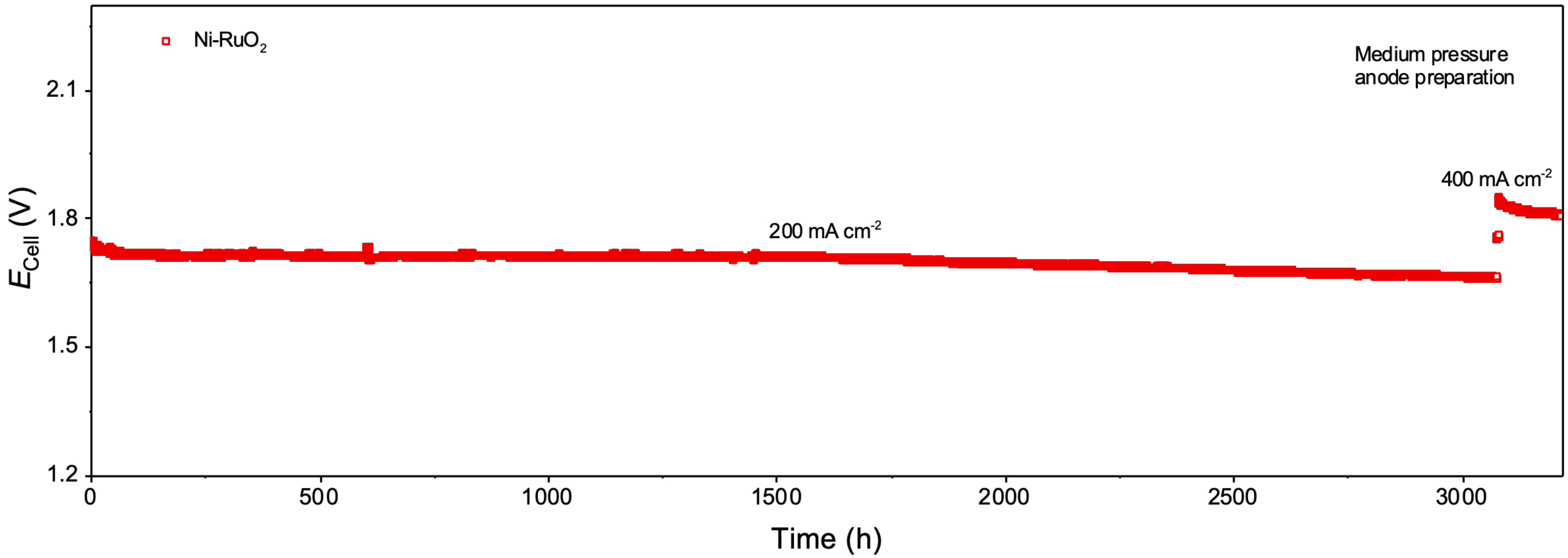
Using Ir-alloy catalysts (50% less Ir)

100 µg of IrRuO / cm² loading at 1.65 V

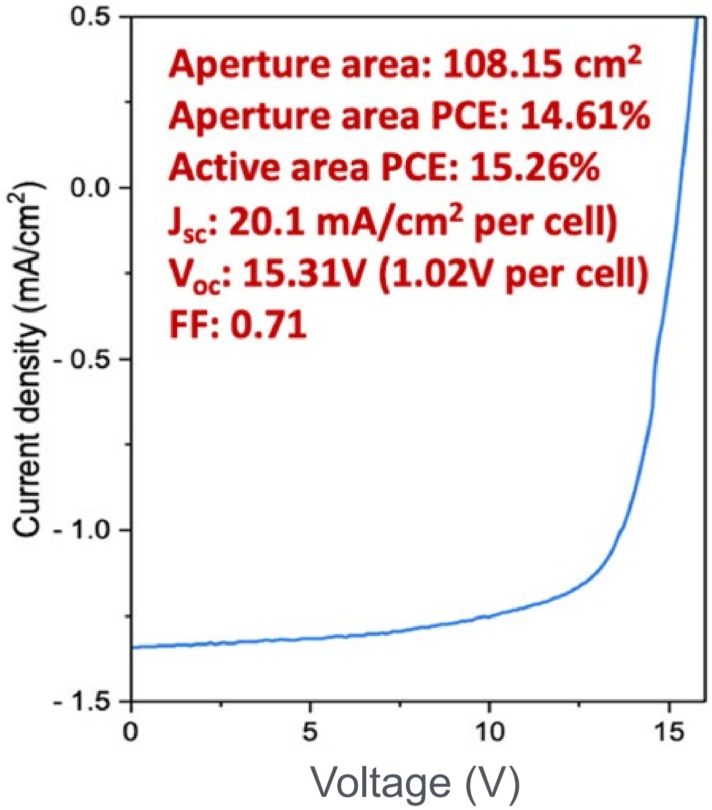


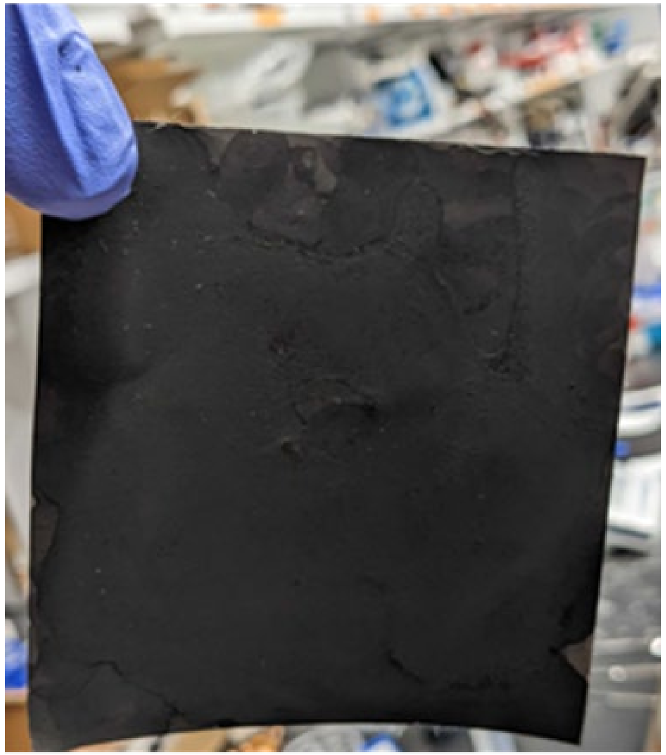
Longest Demonstration NiRu OER in PEM

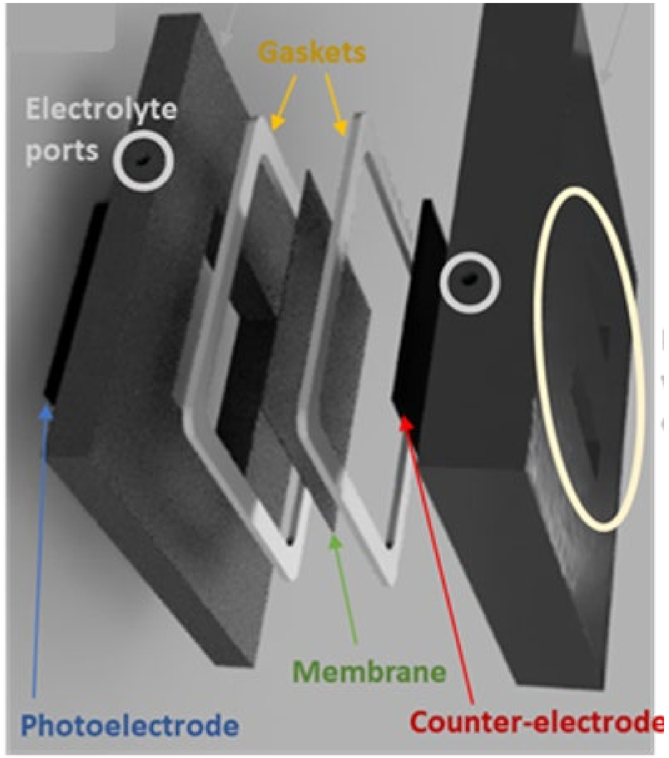
NiRu OER catalyst in PEM architecture



BP3: Scaling up of components

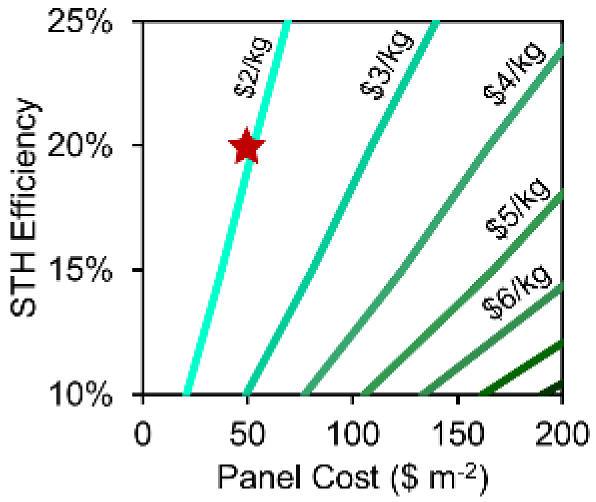


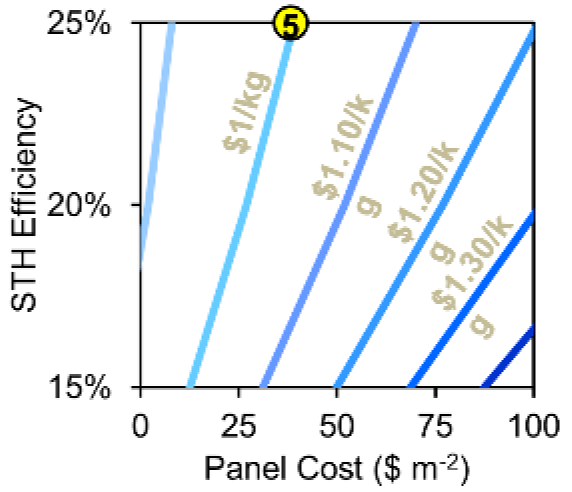


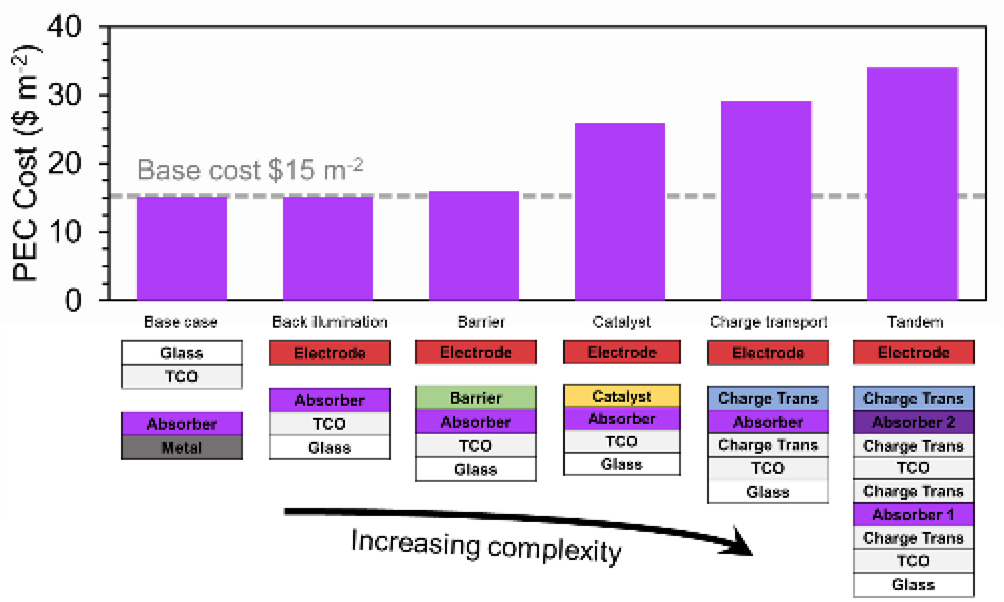


Scale up limited by availability of Si PV

Impact: Pathway for green H2 at $1/kg







Key assumptions:

- 1000 kg H_2/day production
- 20% STH (>25% PCE tandem PV, 80% efficient electrolysis)
- 10-year lifetime
- $50/m^2 panel – overestimated
  - Tandem PV panel
  - Precious metal catalyst loading 50-100 ug/cm^2

DOE hydrogen shot goal

1 kg of H_2
$ 1
1 Decade

Reviewer comments from 2021 AMR

- Lack of any cost targets or analysis is a weakness. The claim "demonstrated a near-ideal corrosion barrier" is not supported by the slides. It is not clear which barrier layer they are referring to. The rapid deterioration during the 2.5-hour solar-water-splitting test is described as OER catalyst degradation, but no explanation is given for its rapid and precipitous onset just after two hours.
- The project relies on a strategy that immediately reduces the theoretical efficiency by 50% compared to a stacked device. In addition, the cost of materials (owing to a doubling of the device size) is also going to increase the hydrogen price.
- Durability of the OER half reaction is a concern. The team should prioritize improving that or at least create a mitigation plan around it.
- There is a lack of modeling to complement the experimental approach.

Technology transfer & publications

Patents:

1. ***Conductive Adhesive-Barrier Enabling Integrated Photoelectrodes for Solar Fuels*** Aditya D. Mohite, Michael Wong, Austin Fehr, Ayush Agrawal, Faiz Mandani, **Provisional Application for U.S. Letters Patent** (22511 Patent Trademark Office)
2. Solution processed perovskite heterostructures Aditya D. Mohite, Siraj Sidhik. Provisional Application No. 63/365,822

Publications / Presentations:

1. ***Memory seeds control the crystal phase in 2D perovskite thin-films for high-efficiency photovoltaics*** Siraj Sidhik, Wenbin Li, Mohammad Samani, Hao Zhang, Yafei Wang, Justin Hoffman, Austin Fehr, Claudine Katan, Jacky Even, Amanda B. Marciel, Mercouri G. Kanatzidis, Jean-Christophe Blancon, Aditya D. Mohite****,*** ***Advanced Materials*** 33(29) 2007176, 2021.
2. ***Water-Stable 1D Hybrid Tin (II) Iodide Emits Broad Light with 36% Photoluminescence Quantum Efficiency*** Ioannis Spanopoulos, Ido Hadar, Weijun Ke, Peijun Guo, Siraj Sidhik, Mikael Kepenekian, Jacky Even, Aditya D. Mohite, Richard D. Schaller, Mercouri G. Kanatzidis, ***Journal of the American Chemical Society*** 142(19) 9028-9038, 2020.
3. ***Interfacial Electromechanics Predicts Phase Behavior of 2D Hybrid Halide Perovskites*** Christopher C. Price, Jean-Christophe Blancon, Aditya D. Mohite, Vivek B. Shenoy, ***ACS Nano*** 14, 3353-3364, 2020.
4. ***Sidhik et al Deterministic fabrication of 3D/2D perovskite bilayer stacks for durable and efficient solar cells Science 2022 Vol 377, Issue 6613 pp. 1425-1430***
5. ***Integrated halide perovskite photoelectrochemical cells with solar-driven water-splitting efficiency of 20.8%*** Austin M.K. Fehr, Ayush Agrawal, Faiz Mandani, Christian L. Conrad, Qi Jiang, So Yeon Park, Olivia Alley, Bor Li, Siraj Sidhik, Isaac Metcalf, Christopher Botello, James Young, Jacky Even, Jean-Christophe Blancon, Todd G. Deutsch, Kai Zhu, Steve Albrecht, Francesca M. Toma, Michael Wong, Aditya D. Mohite, ***Nature Comm.*** (accepted).

Timeline/Milestones summary

M1.1	Selection of the photo-absorbing HaP materials	Milestone	M3			100%	Complete
M1.2	Fabrication of high-efficiency and stable HaP solar cells	Milestone	M9			100%	Complete
M1.3	Design charge transport layers as barriers	Milestone	M15	M21		100%	Complete
M2.1	Understand the mechanisms of corrosion	Milestone	M12	M18		100%	Complete
M2.2	Design of ultra- hydrophobic terminations on the HaP layers and design of anti- corrosion barriers	Milestone	M18			100%	Complete
M3.1	Design and integration of HaP-PEC	Milestone	M12			100%	Complete
D1	**Integration of all components in a proof of concept HaP-PEC and demonstration of unassisted water splitting with 10% STH efficiency for 1 hour**	**Go/No-Go Decision Point #1**	**M12**			100%	Complete
M3.2	Optimize PECs for high-efficiency and durability	Milestone	M24			100%	Complete
D2	**HaP-PEC for unassisted water splitting with H_2 STH efficiency of 15% and with 100 hours stability under continuous operation**	**Go/No-Go Decision Point #2**	**M24**			100%	Complete
M3.3	Optimize PECs for high-efficiency and durability	Milestone	M33			80%	In progress
M3.4	Techno-economic analysis	Milestone	M33			100%	Complete
M4.1	Scaling-up photocathode and photoanode	Milestone	M30			70%	In progress
M4.2	HaP-PEC large area module	Milestone	M36			25%	In progress
D3	**Demonstration STH efficiency 20% and 500 hours stability in HaP-PECs**	**End of Project Goal**	**M36**			80%	On Schedule

Our team


Austin Fehr


Ayush Agrawal


Chris Botello


Jean-Christophe Blancon


Faiz Mandani


Chris Conrad

RICE
Unconventional Wisdom