Budget Period 1 Review

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

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Project number
DE-FOA-0002022-1652
Project ID # P193

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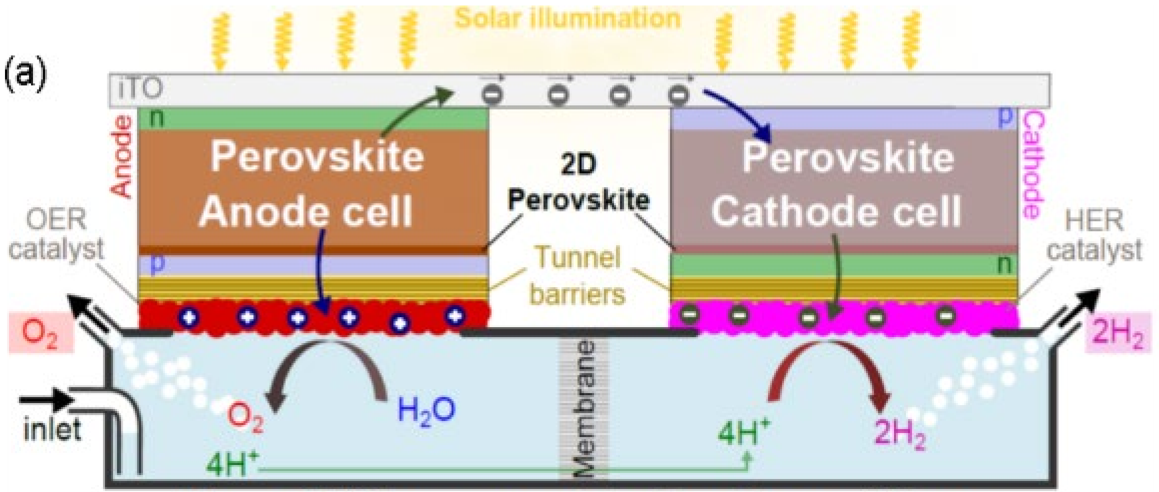
Aditya D. Mohite/ Rice University

Technology Summary

In this proposal , we will demonstrate an innovative concept with advanced materials for photo-electrochemical cells based on direct water splitting to produce hydrogen fuel by interfacing stable (under 1-SUN illumination and in humidity) layered 3D/2D perovskites with high performance catalysts for Hydrogen evolution and Oxygen evolution reactions (HER and OER) to realize a low cost, relative large PEC system with 500 hours of operation with hydrogen generation by water splitting (STH) efficiency 20%.

Concept of the project



V_{OC} > 2V for un-assisted water-splitting

Key Personnel

Prof. Michael Wong (Rice University)

Program Summary

Period of performance: 36 months

Federal funds: $ 1.0 Million
Cost-share: $ 200 K
Total budget: $1.2 Million

	Key Milestones & Deliverables
Year 1	• Fabrication of perovskites solar cells (>20% efficiency, 1000 hrs stability) • PEC with STH>10% and 1 hour stability (bias-free)
Year 2	• Fabrication of anti-corrosion barriers, understanding and mitigating corrosion • PEC:15% STH efficiency and 100 hr. stability
Year 3	• STH 20% with 500 hours durability • Scale-up HaP-PEC to 5x5 $inch^2$

Technology Impact

Two of the most developed technologies are based on (i) Titania (or metal oxides) and (ii) III-V semiconductors. Metal oxides are inefficient with STH efficiency ~1%. In contrast, III-V semiconductors such as GaAs have demonstrated STH >15% but their widespread use has been limited by their propensity to photo-corrosion of materials in aqueous environments and also high cost of fabrication.

Durable and efficient water splitting system for H_2 production

Vision, Impact and Partners

Project Vision

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

Award #	DE-FOA-0002022-1652
Funding	$1 M

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 $2/gg

Project partners

Aditya Mohite (PI), Rice University

Michael Wong (Co-PI), Rice University

EMN Partners (year 1): LBNL: Francesca Toma & Nemanja Danilovic
NREL: James Young and Todd Deutsch

Innovation and Objective

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 BP1

1. High-efficiency 3D/2D perovskite materials with ideal band-alignment
2. Develop corrosion resistant barriers
3. Integration of HER and OER catalysts with perovskite cells to build a proof-of-concept PEC technology with >10% STH efficiency with 2 h

Key challenges

Stability of perovskite solar cells in aqueous media

Develop corrosion resistance layers that are electronically transparent

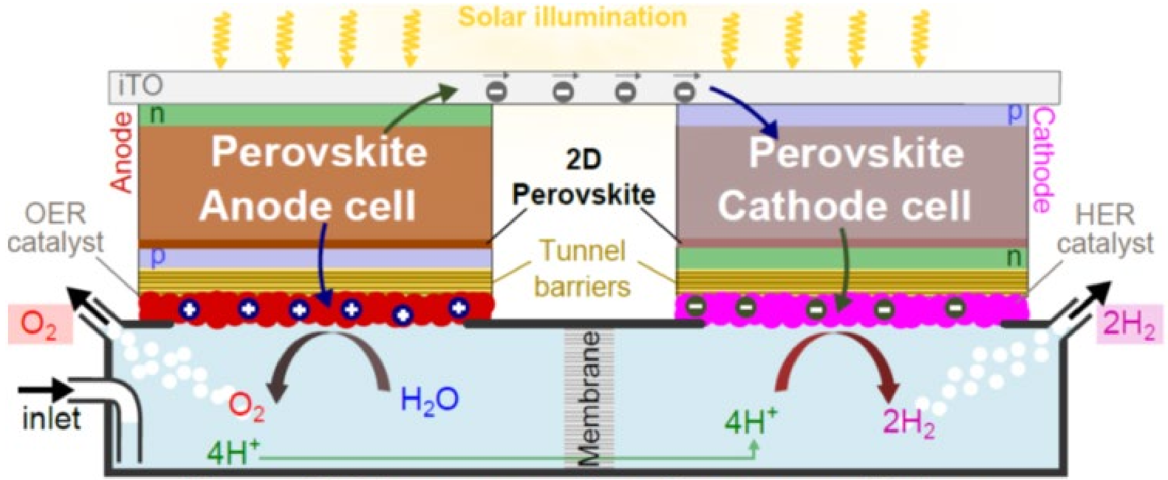
Partnerships

LBNL: Understanding degradation mechanisms in PECs through in-situ characterization techniques

PEC measurements – small area devices

NREL: Benchmarking PEC efficiency

Our project concept & innovation



V_{OC} > 2V for un-assisted water-splitting

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 a autonomous PEC platform

BUDGET PERIOD 1 Milestones & GO/NO-GO

- Selection, and optimization of 3D/2D perovskites with appropriate band alignment (Milestone 1.1)
- Demonstrate a 3D/2D perovskite solar cell with ~20% efficiency and 1000 hours stability, and <10% degradation in efficiency (Milestone 1.2)
- Understand corrosion in halide perovskite photocells (Milestone 2.1)
- Demonstrate integrated PEC with 10% STH efficiency for 1 hour (Milestone 3.1) GO/NO-GO

HIGH-EFFICIENCY & STABLE PEROVSKITE SOLAR CELLS

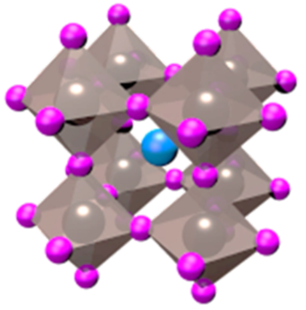
- 3D/2D p-i-n and n-i-p cells with >20% efficiency (M1.1)
- New method to obtain high-efficiency and stable 2D perovskites
- Developed high-efficiency 3D solar cells with >20% efficiency – both p-i-n and n-i-p architecture
- Synthesized and characterized first water-stable perovskite

Halide perovskites: A new class of semiconductors

3D Halide Perovskites

AMX_3

$CaTiO_3$



A: Organic cation
$CH_3NH_3^+$, Cs^+, FA^+, ..

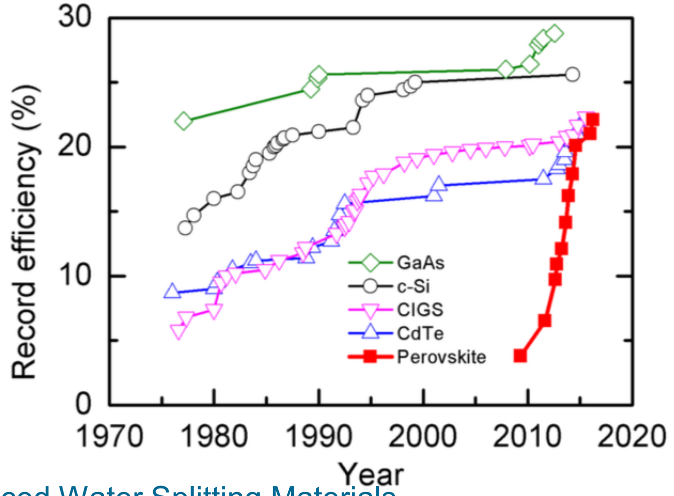
B^{2+}: Metal
Pb^{2+}, Sn^{2+}, Ge^{2+}, …

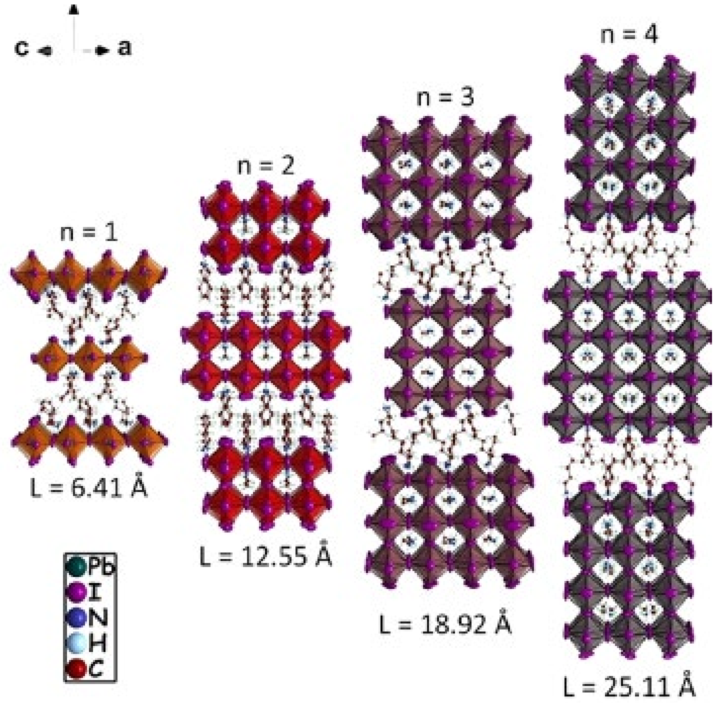
X_3: Halide
I^-, Cl^-, Br^-, …

Goldschmidt tolerance factor

$$t = (R_A + R_X)/\sqrt{2}(R_M + R_X) \ \& \ 0.8 \leq t \leq 1$$

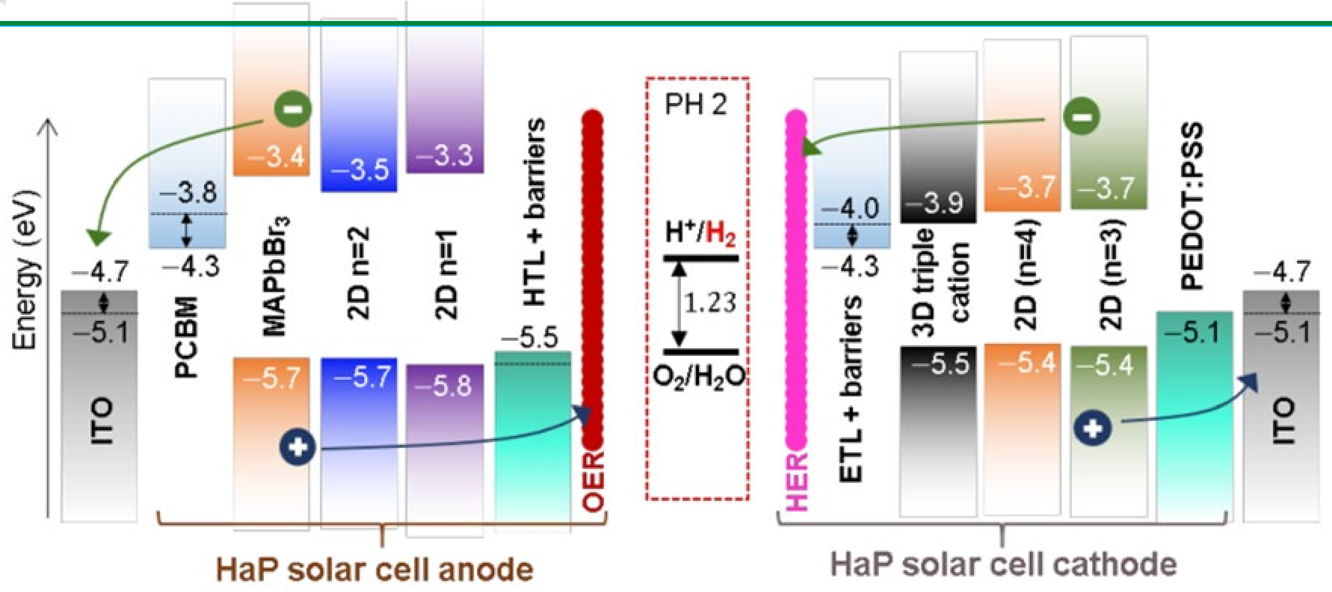
Record certified efficiency ~ 24.2%

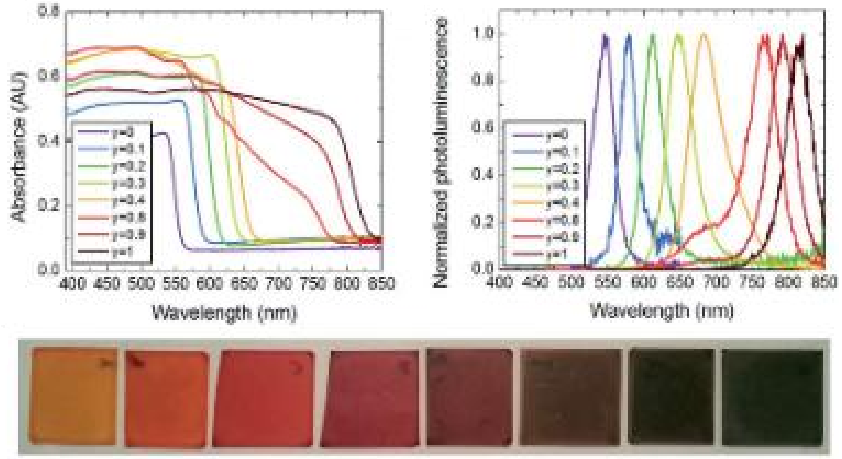




- ❖ **Near ideal properties for optoelectronic devices – record PV efficiencies**
- ❖ **Wide range of structural motifs, which can be tailored using solutions chemistry**
- ❖ **Earth abundant and low-cost**

Tunable band-alignment

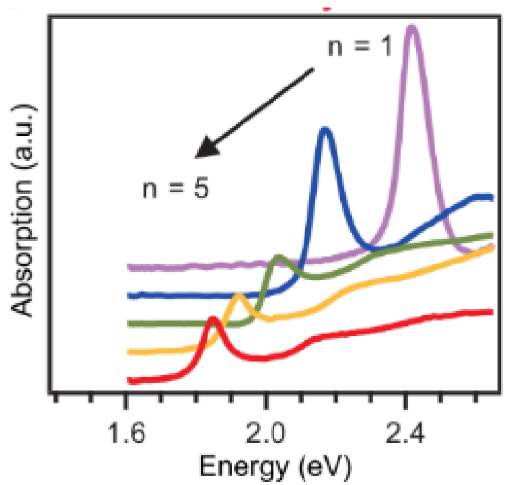




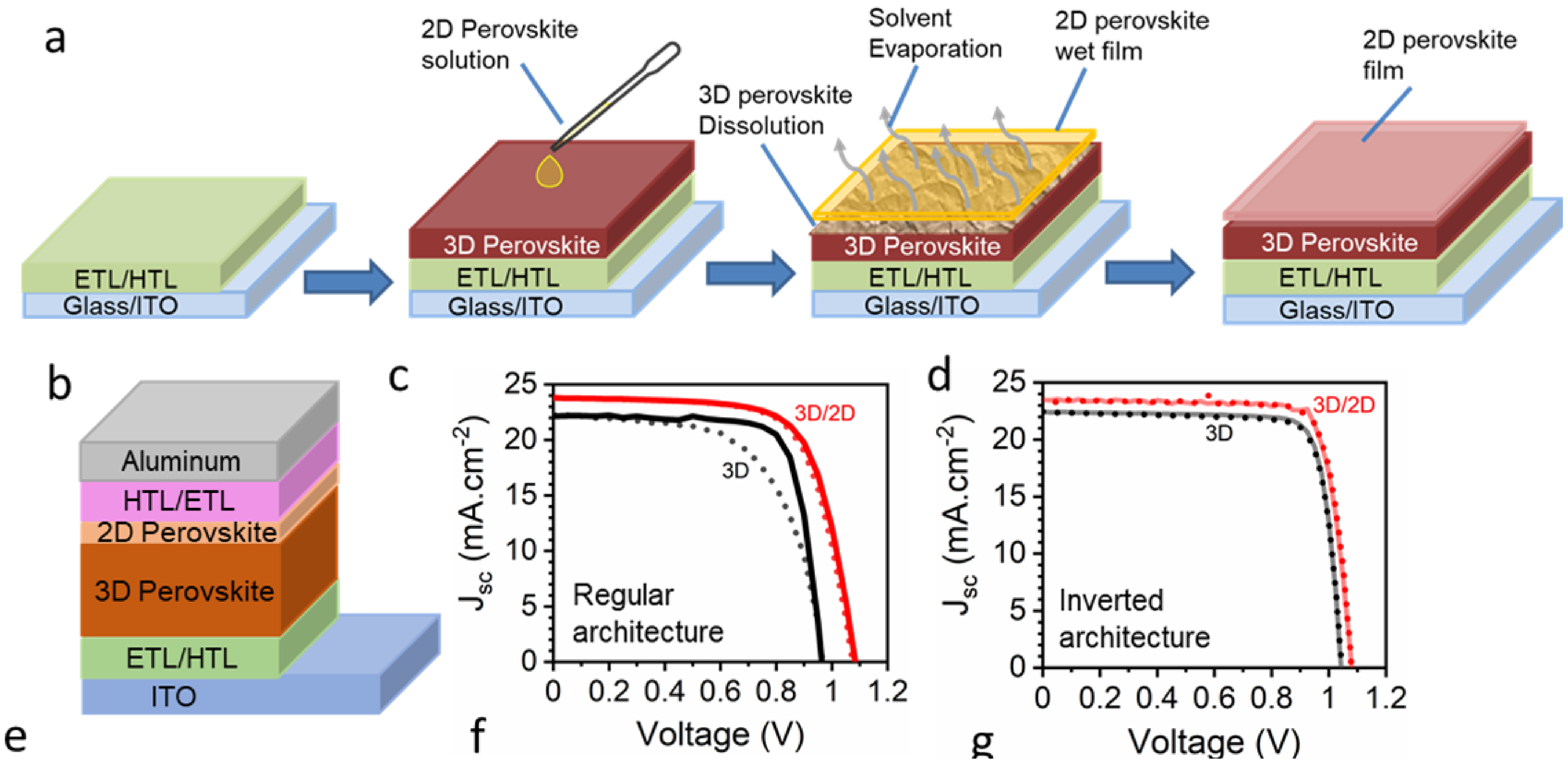
Esperon/Snaith, EES, 2014

- The band-gap can be tailored from 2.8 eV to 1.2 eV
- Band-alignment can be tuned match the redox potentials for HER and OER
- 2D HaP provide opportunities to create hydrophobic barriers using Fluorinated organic cations and molecules

2D Perovskites

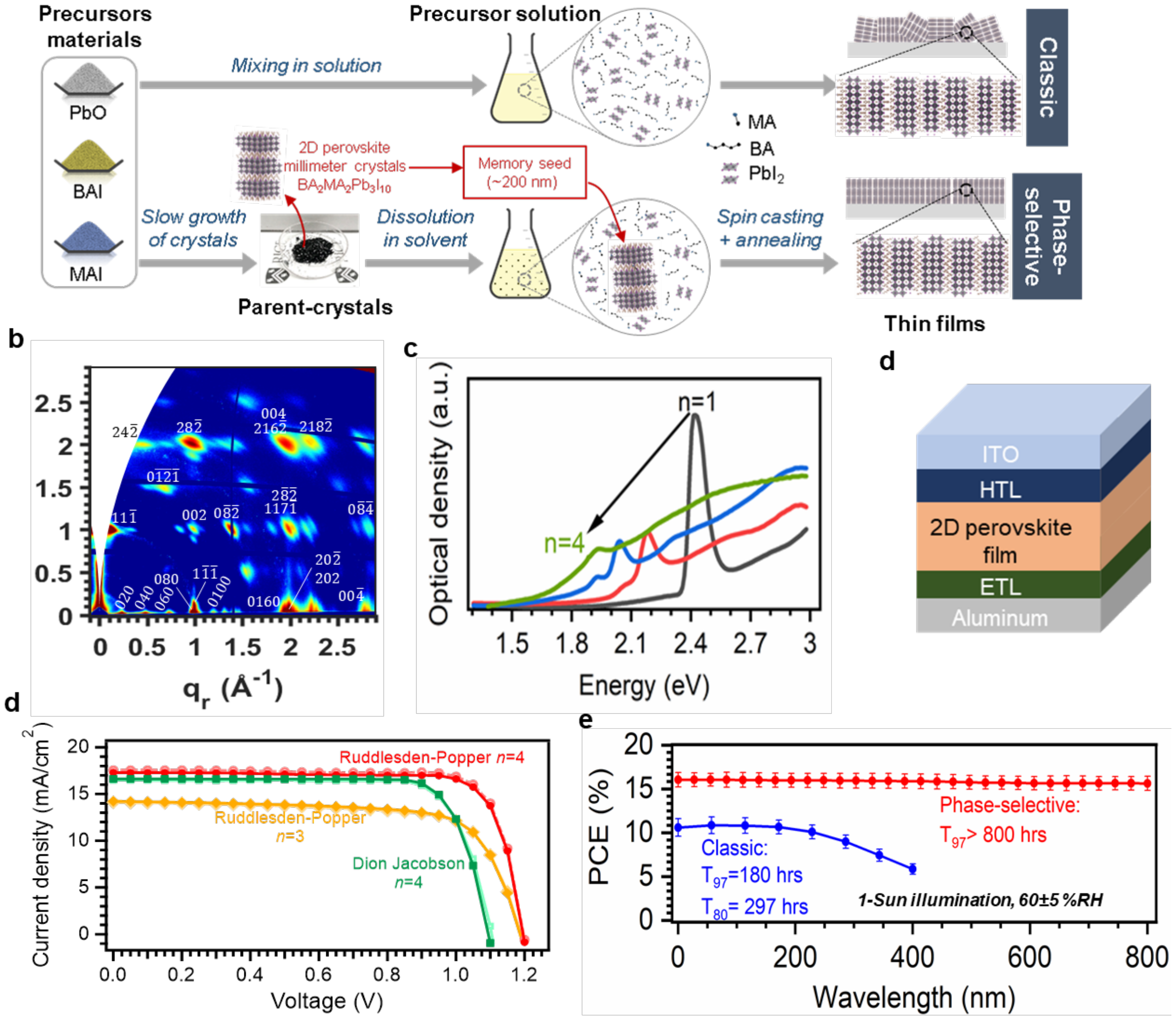


High-efficiency 3D/2D heterostructure solar cells



Milestone 1.1: **3D/2D cells with >20% demonstrated**

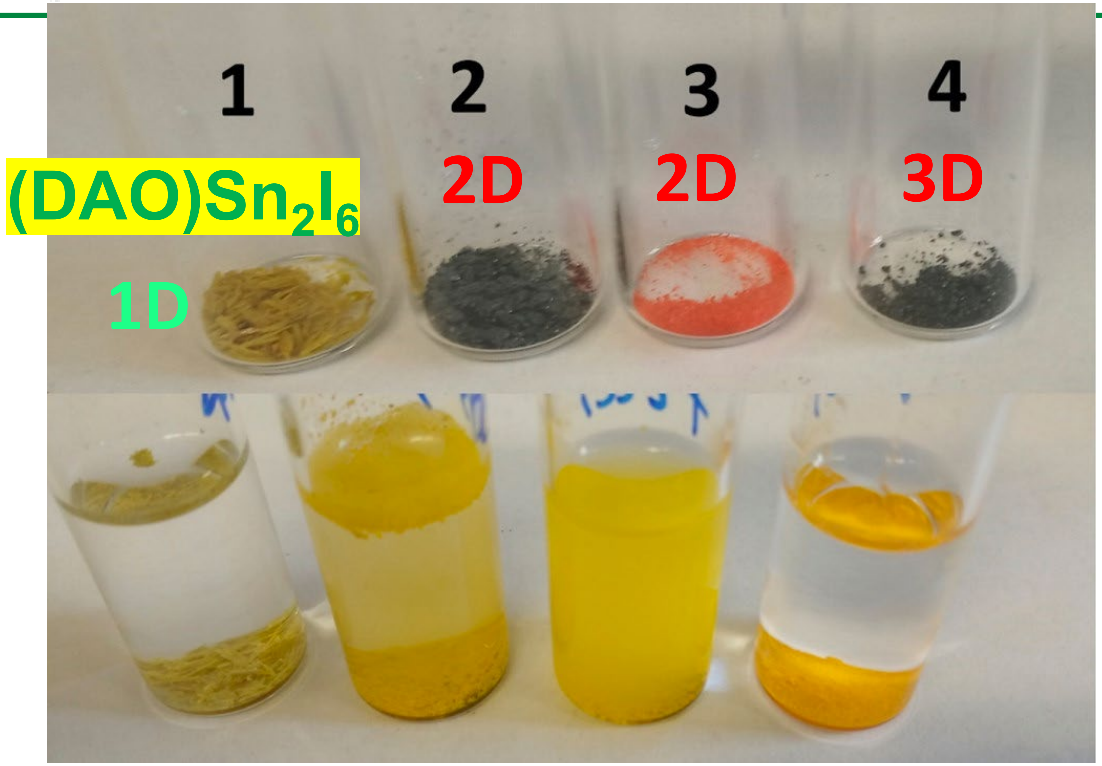
2D perovskite solar cells with 17.3% efficiency



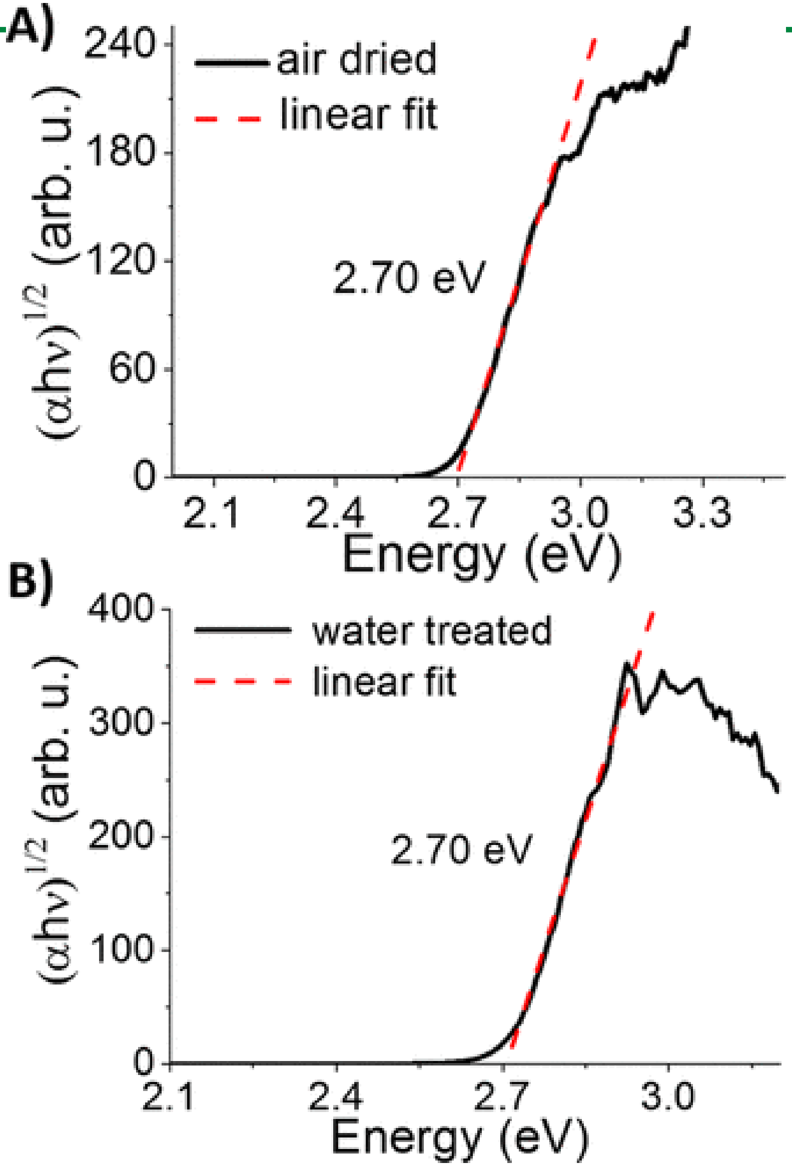
- New method to obtain phase-pure 2D perovskite films
- Enabled high V_{OC}
- Excellent stability
  T_{97}=800 hours
  T_{80} = 7000 hours
  (extrapolated)

Milestone 1.2: Solar cell stability

Synthesis of first water-stable perovskite



(DAO, 1,8-octyldiammonium)



- Demonstrated 24 hours stability in water
- No change in optical absorption

Milestone 1.2: Solar cell stability

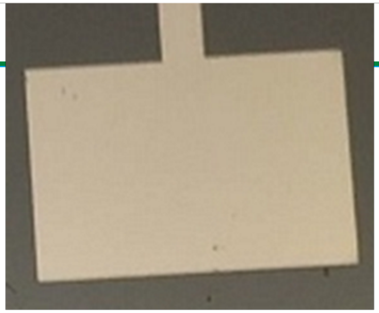
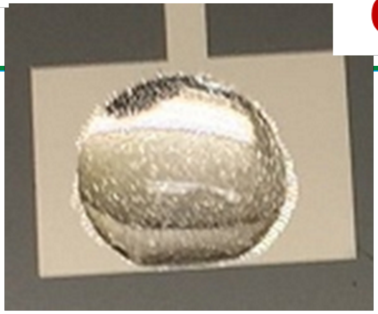
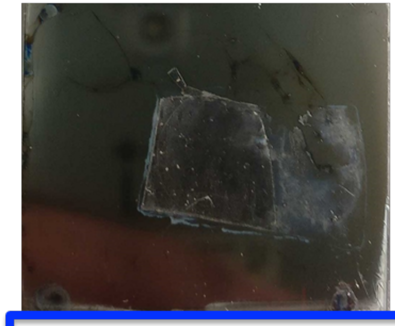
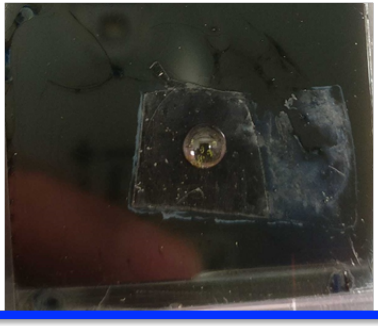
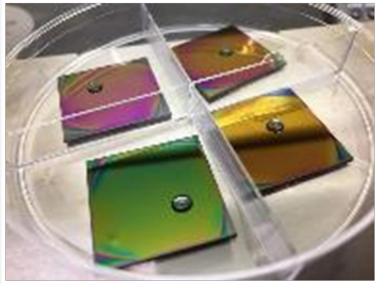
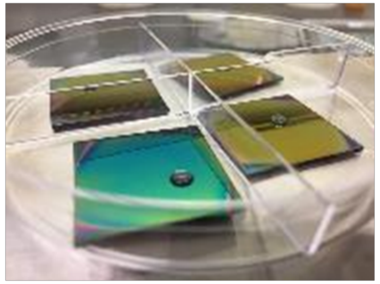
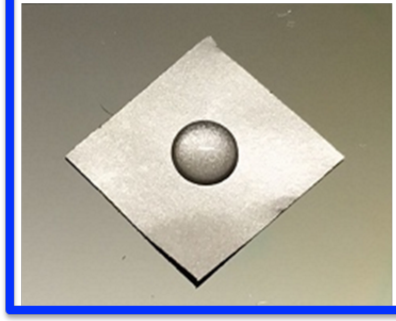
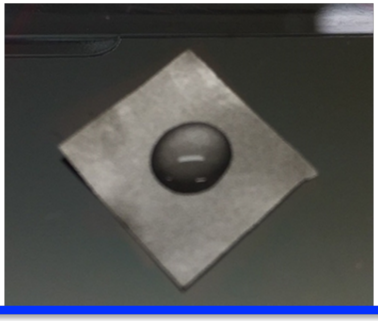
CORROSON MECHANISMS & BARRIER DESIGN

- **Screening of barrier candidates**
- **Testing and characterizing degradation**
- **Learning the design principles for a near-ideal ambipolar barrier**

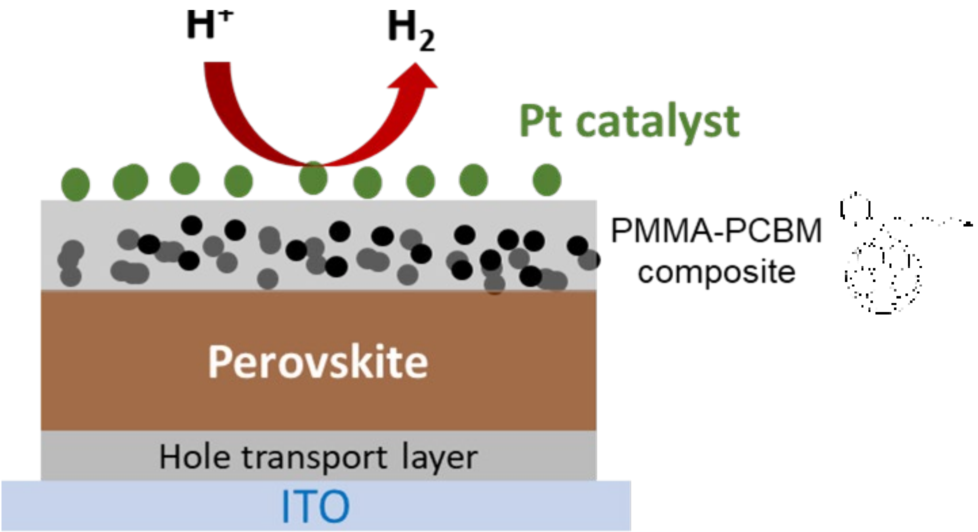
Approach for anticorrosion barriers

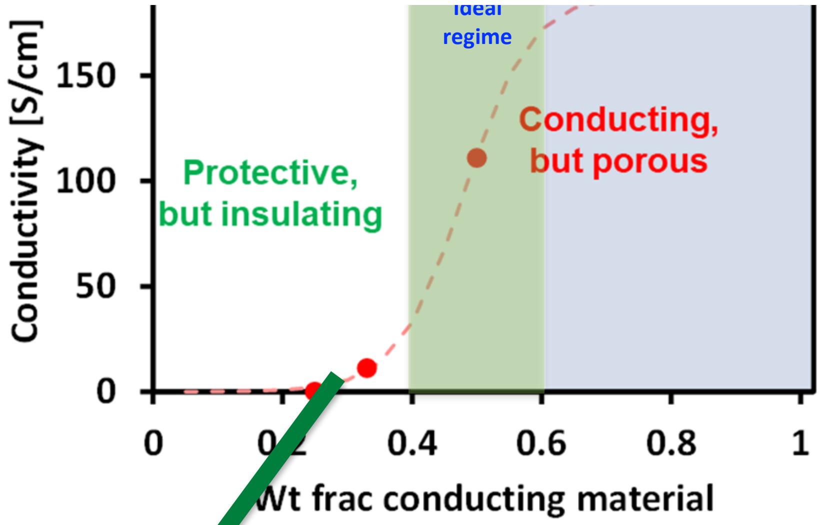
Visual testing followed by correlated optical imaging, PL and AFM imaging

1. High throughput screening of barriers ("drop test")
2. Identification of mechanisms of degradation in successful candidates
3. Suppression of mechanisms

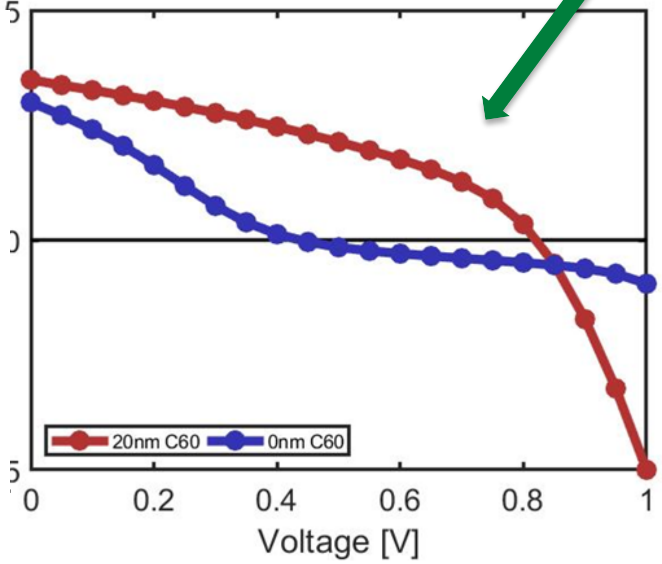
MATERIAL	REASONING	BEFORE	AFTER	OBSERVATION
Pt, 50nm sputtered	Inert Pt metal, conductive, thick enough to cover perovskite roughness			Dendritic growths originating with roughness from perovskite
Reduced Graphene Oxide SWNT films	Dense, ordered rGO should slow water diffusion and maintain conductivity			Imperfect transfer created visible pin-holes – degrades underlying perovskite
PMMA, spin-coated	Hydrophobic polymer shown to protect perovskite			**>24h with no morphology loss; 100 nm PMMA**
ML Graphene, Polymer-graphene composite, bilayer	Bifunctional – conductive and protective			**>24h with no morphology loss or color change**

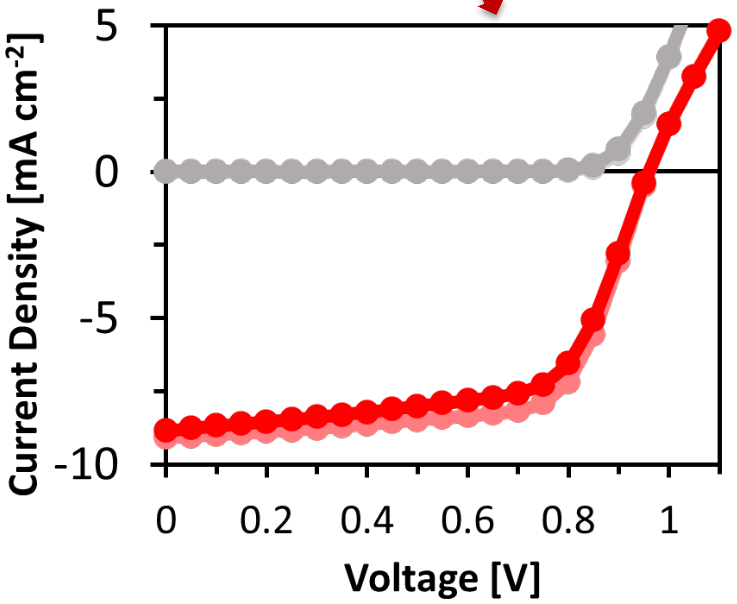
PMMA-PCBM as electron transport layer & corrosion barrier





Goal: realize charge transport while preventing degradation



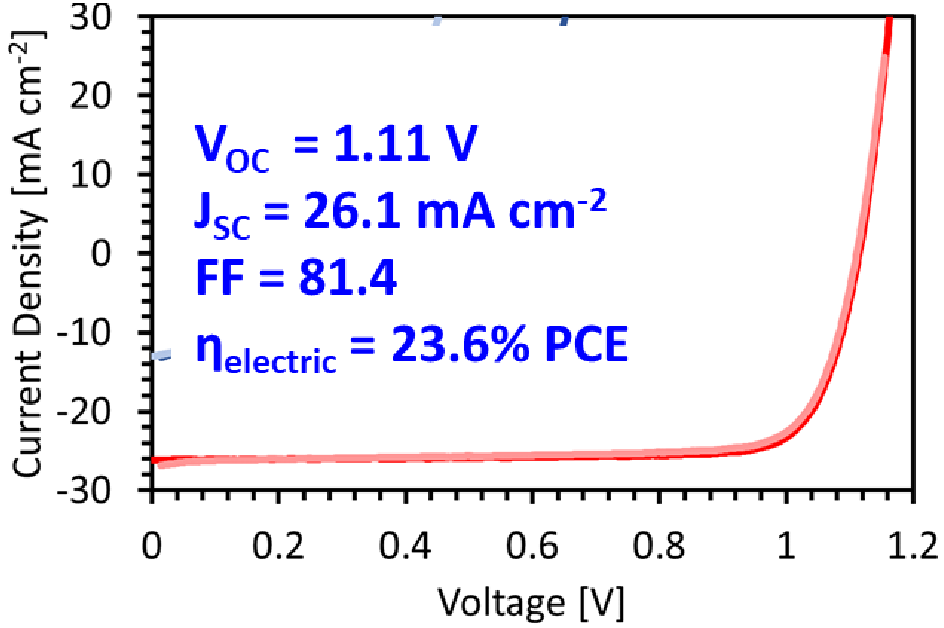


Charge transport significantly affect

Better transport but bad stability

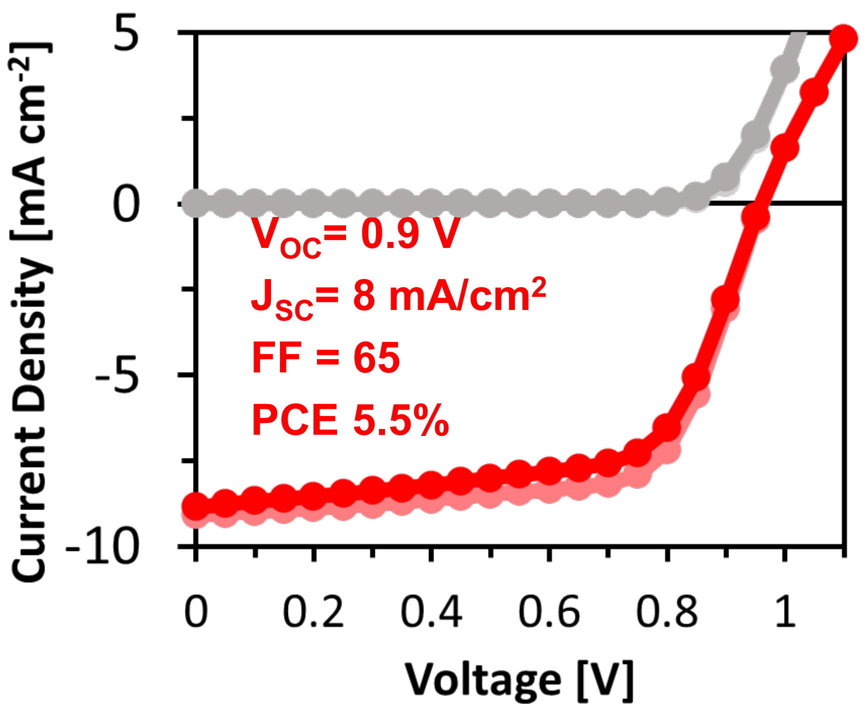
PMMA-PCBM as transport layer & barrier

Solar cell with NO barrier



FTO|NiO_x|Perovskite |PCBM|Ag

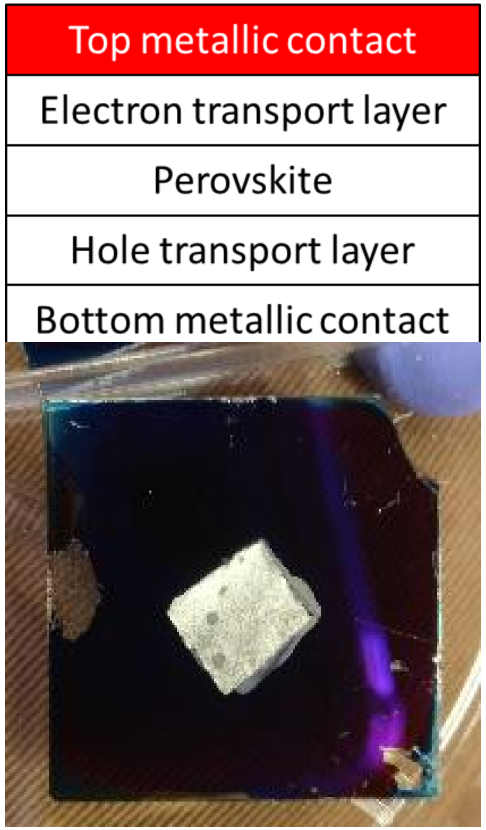
Solar cell with barrier



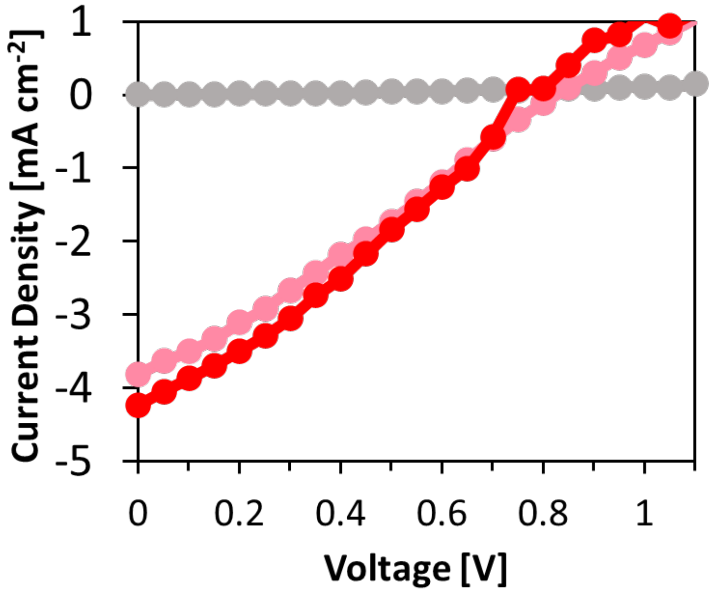
FTO|NiO_x|Perovskite |PMMA-PCBM|Ag

- ❖ Large (77%) loss in solar-cell efficiency using PMMA-PCBM barrier
- ❖ High contact resistance of the barrier
- ❖ Provides some protection but at a large cost in efficiency of PV

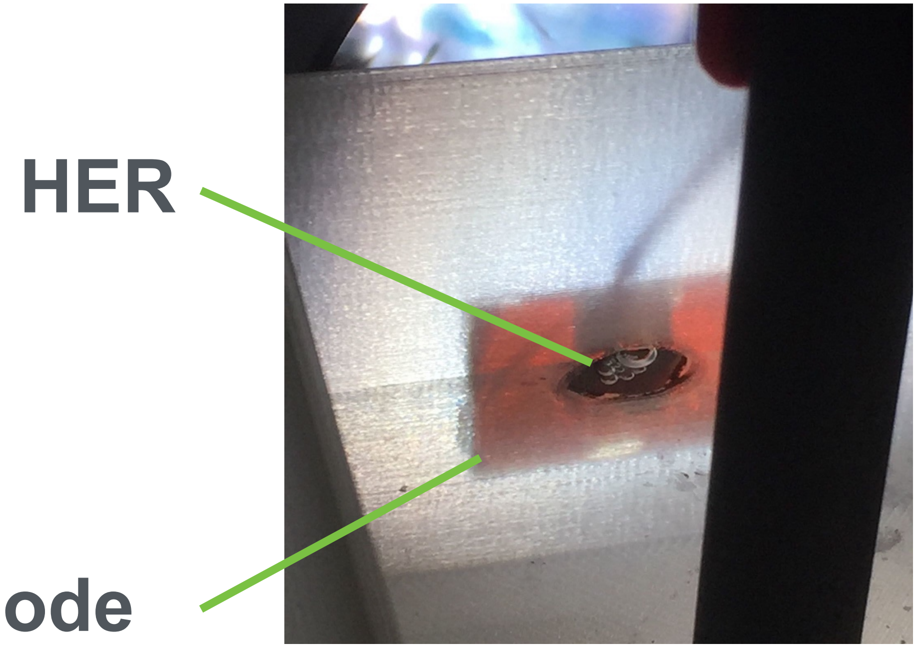
Graphene based barrier



FTO|NiO_x|perovskite|C_{60}|C paste|MLG sheet



V_{oc}	0.78 V
J_{sc}	3.1 mA/cm^2
FF	30.9
Efficiency	**0.74%**



Demonstrated photocathode but degrades PV performance due to high-contact resistance

Integrated photocathode

Photovoltaic device

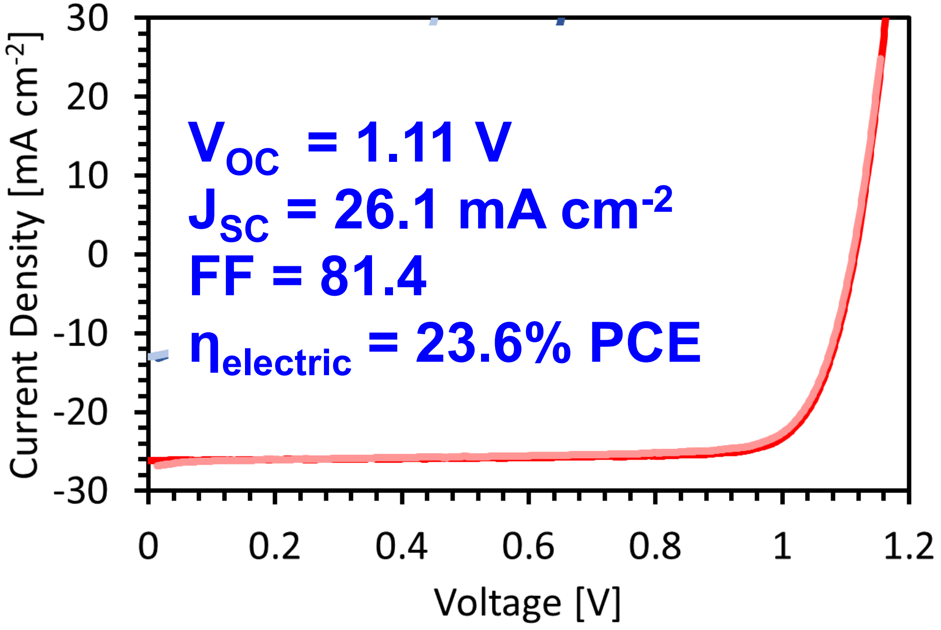
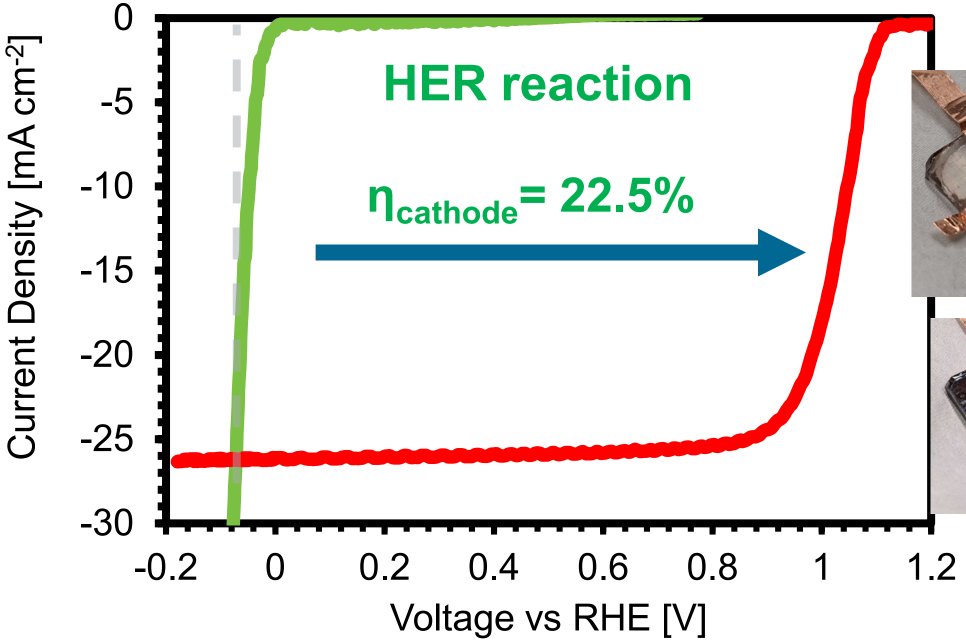
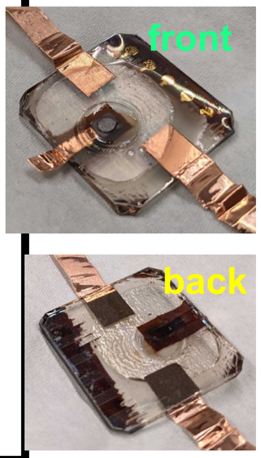


Photo-cathode





Milestone 3.1 Design and integration of PEC (photocathode, photoanode)

$$ABPE = \frac{|J_{mpp}| \times |V_{mpp} - V^{0}_{rxn}|}{P_{in}}$$

- J_{mpp}: Current density at MPP from LSV
- V_{mpp}: Potential at MPP from LSV
- V^{0}_{rxn}: Standard potential for half-reaction
- ABPE: Applied Bias Photocurrent Efficiency, sometimes called "photoelectrode efficiency"
- P_{in}: Solar illumination power density

Near-perfect conversion from electrical to catalytic

Integrated photoanode

Photovoltaic device

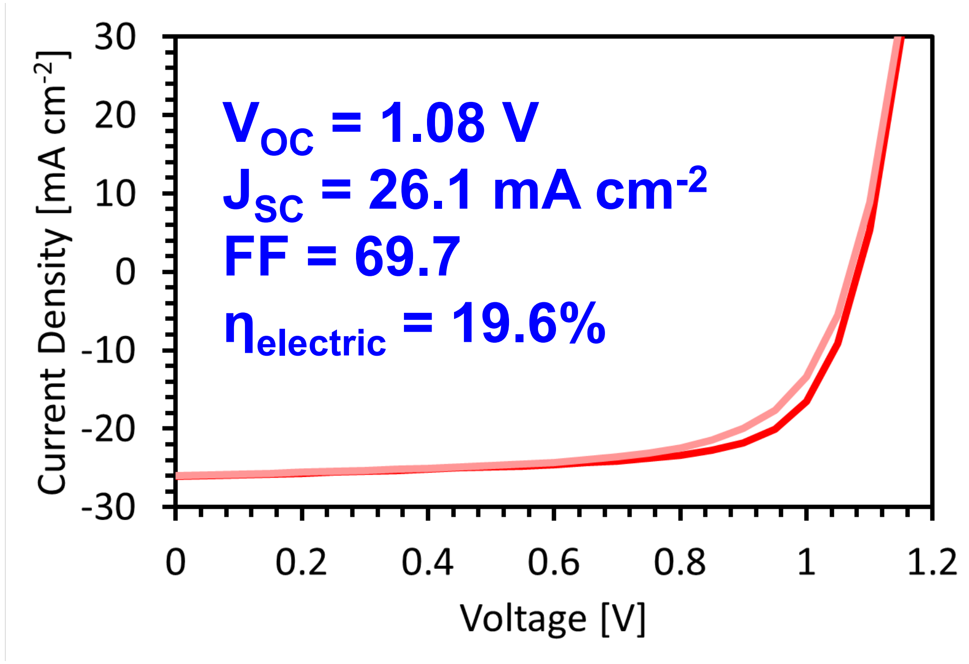
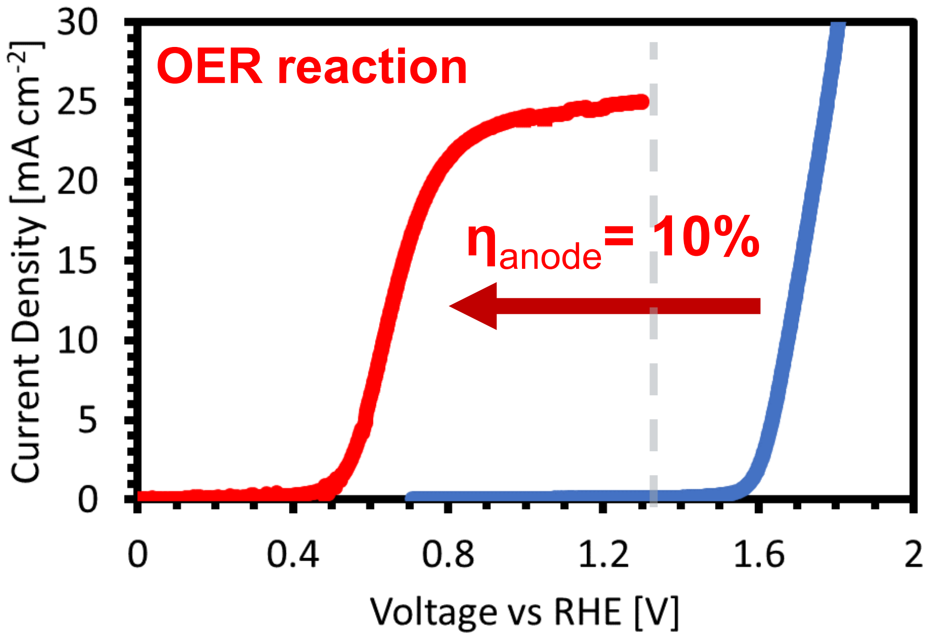


Photo-anode



Performance of photoanode is limited by the OER catalyst performance (IrO_2 in 0.5M H_2SO_4)

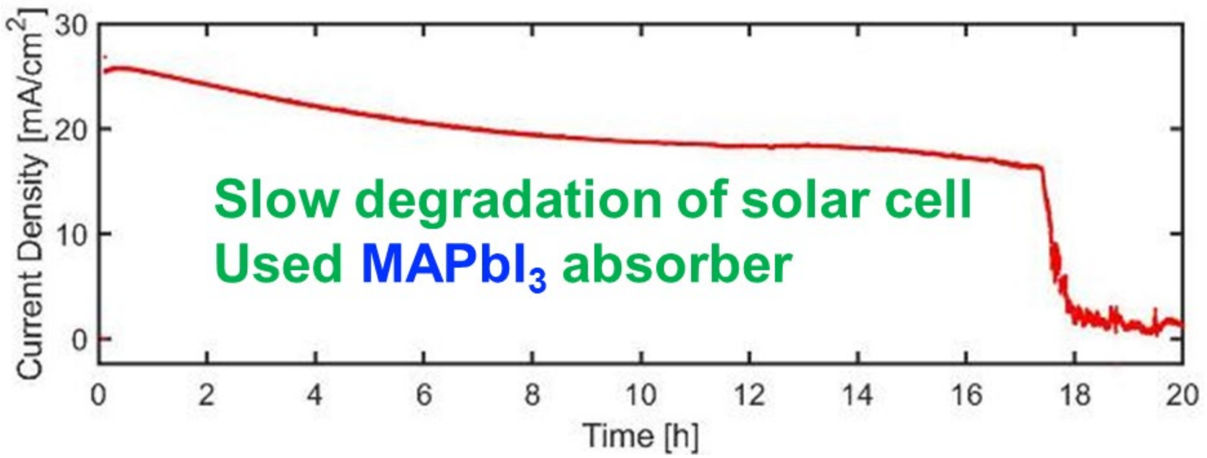
Corrosion barrier is ambipolar

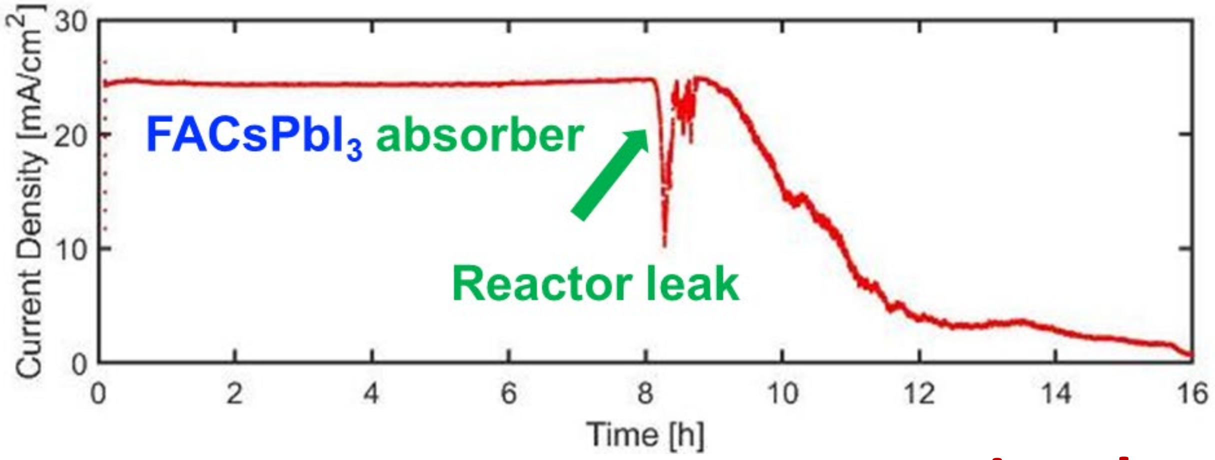
Milestone 3.1 Design and integration of PEC (photocathode, photoanode)

Stability of photocathode

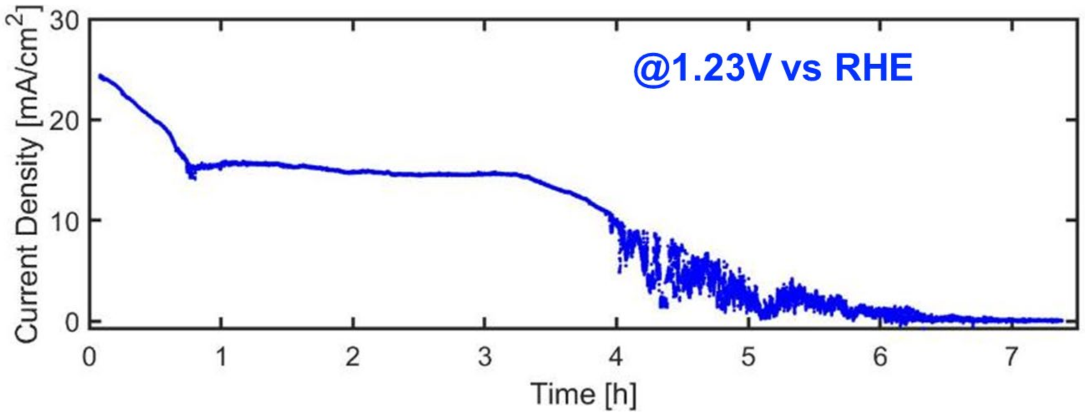
3-terminal measurements

Photocathode degradation





Photoanode degradation

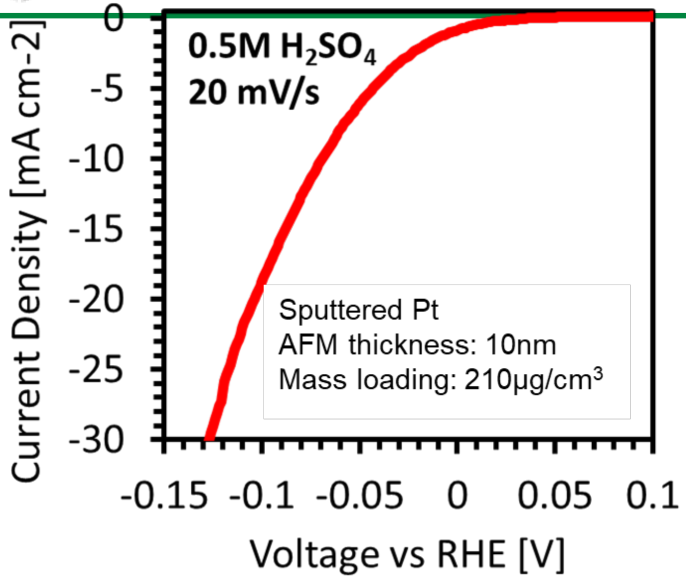


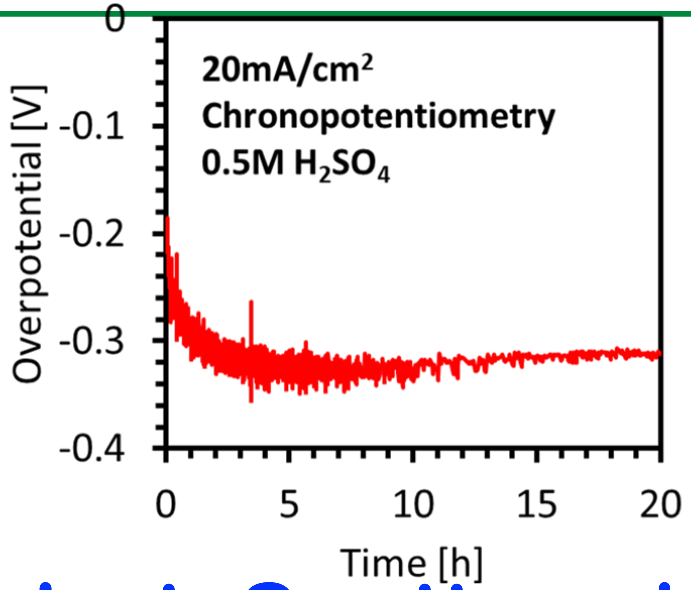
Stability of photoanode limited by OER catalyst degradation

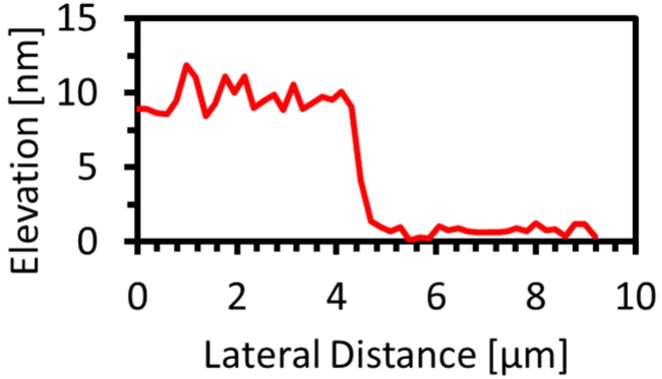
(IrO_2 in 0.5M H_2SO_4)

Requires better engineering of the components

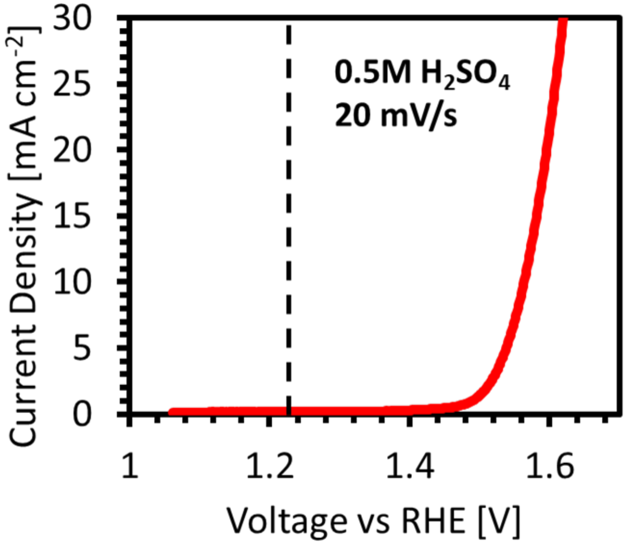
HER catalyst: Sputtered Pt (5 nm)

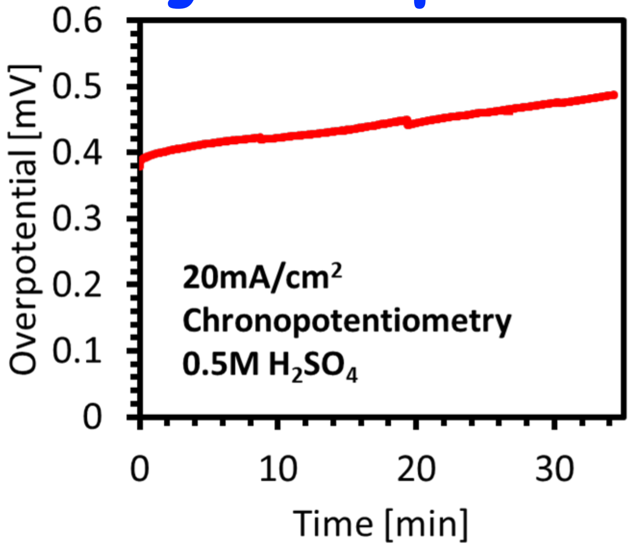






OER catalyst: Sputtered Pt (5 nm)

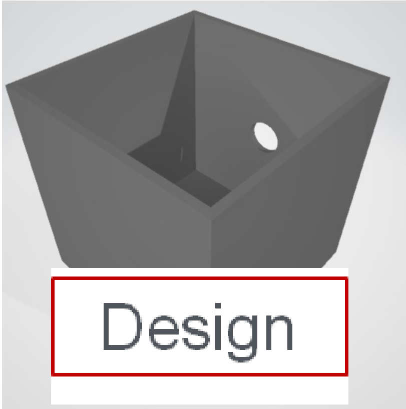


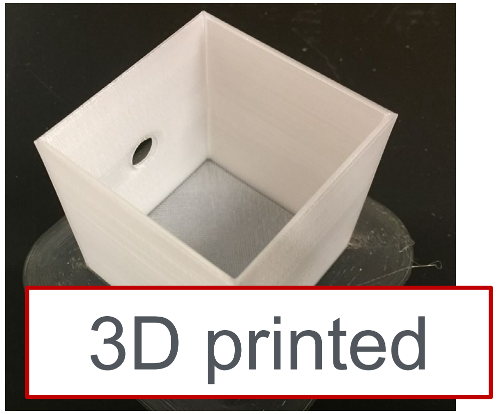


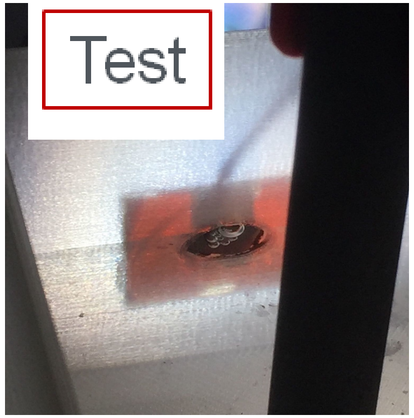
- Pt shows low overpotential and good current density as anticipated
- Slight degradation (100 mV) in overpotential likely due to bad adhesion
- Stable up to 20 hours and then measurement stopped
- Overpotential of 1.6V at 20 mA/cm^2
- Fast degradation in overpotential within minutes

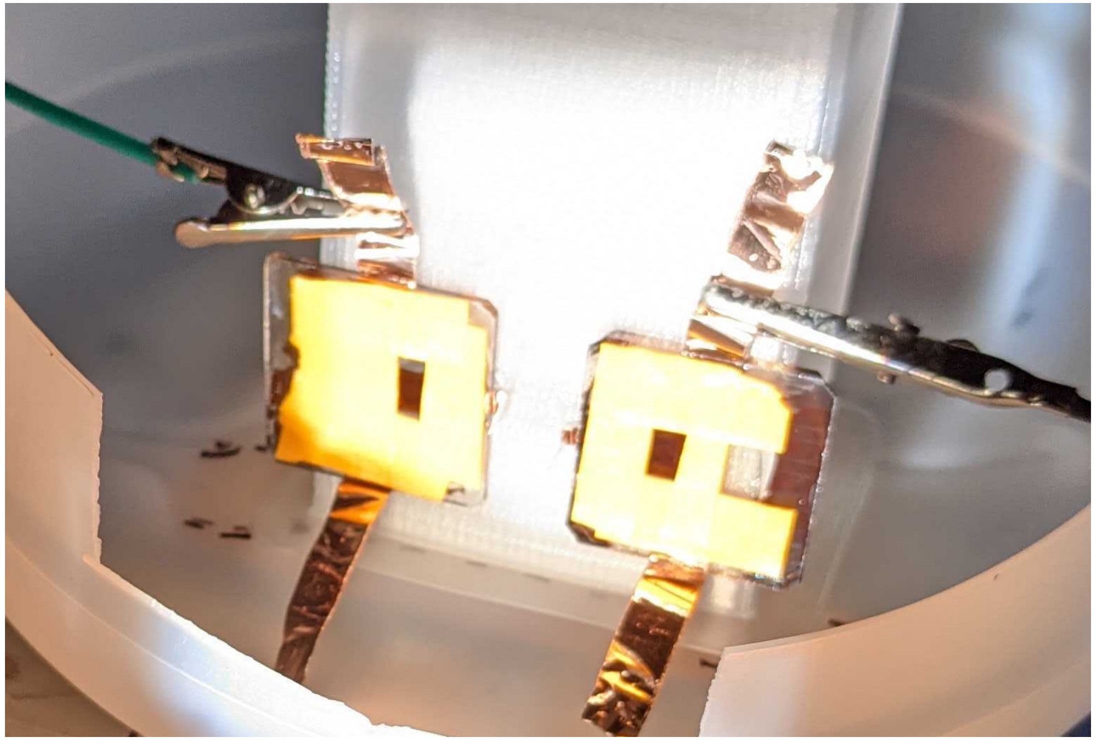
Novel 3D printed PEC reactor design

Polypropylene





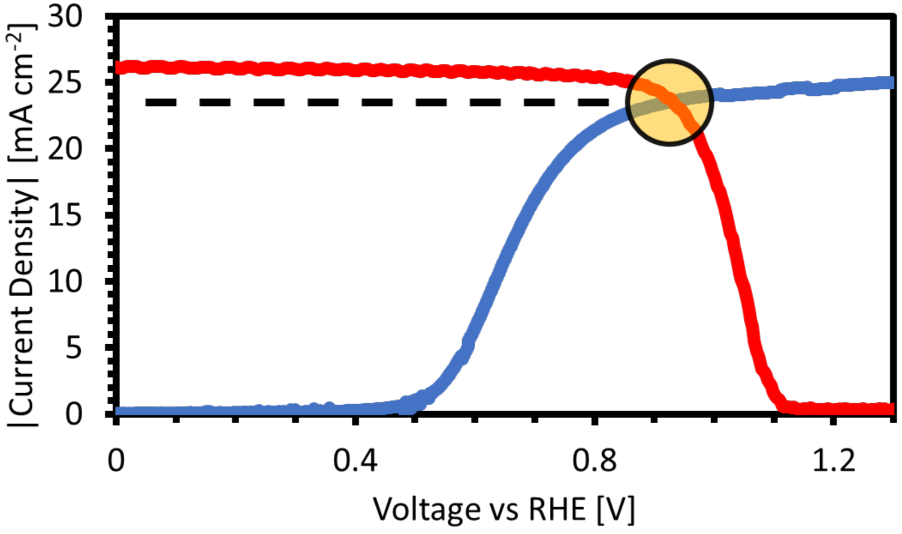


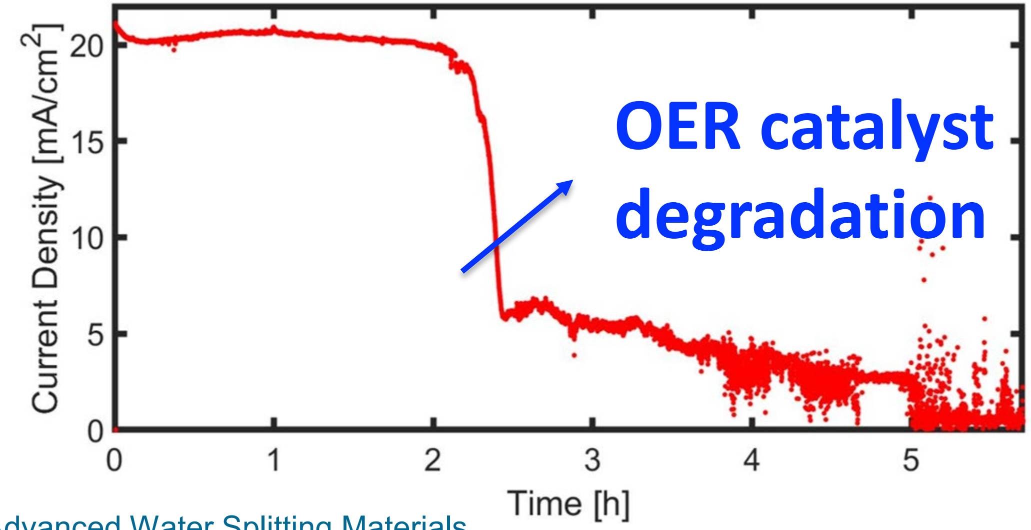


Milestone 3.1 Design and integration of PEC (photocathode, photoanode)

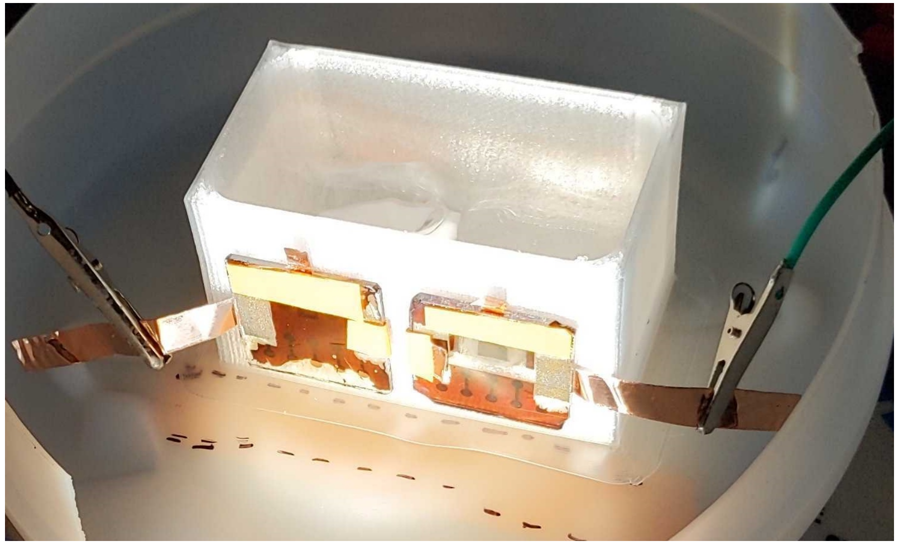
Autonomous solar water-splitting 2.5 hours

Solar-to-Hydrogen η_{STH} = 12.4%





Two-terminal measurement

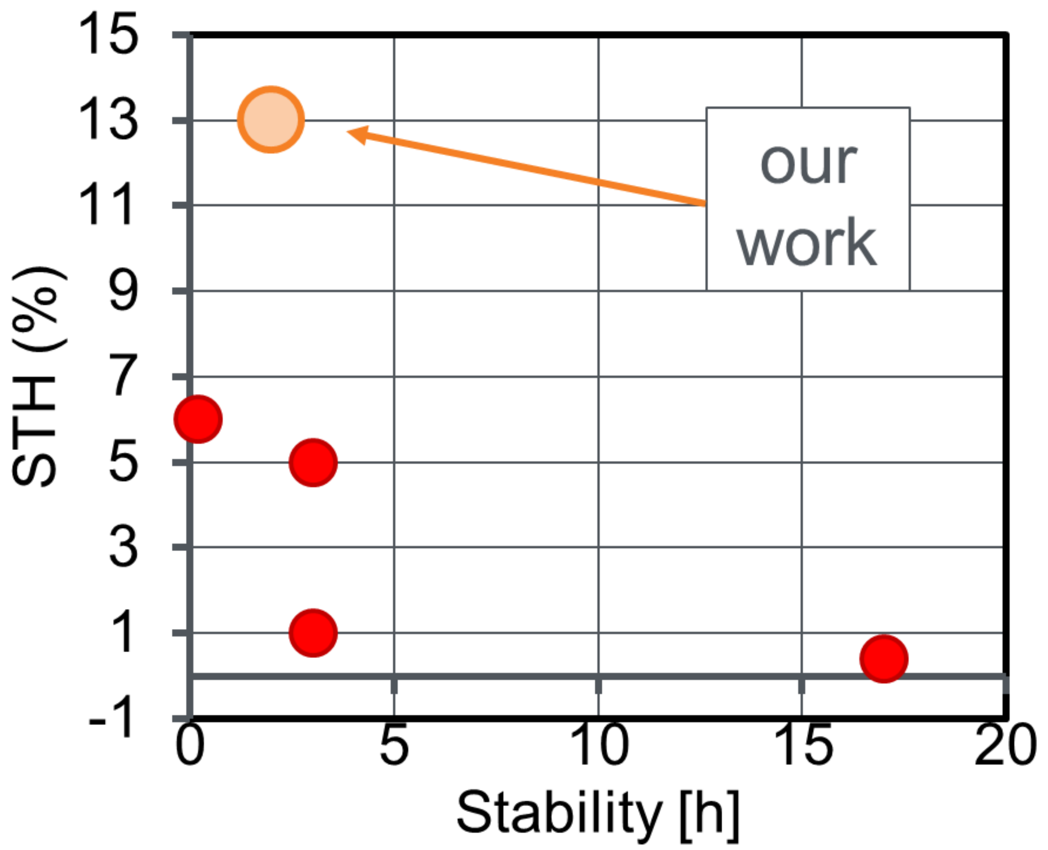


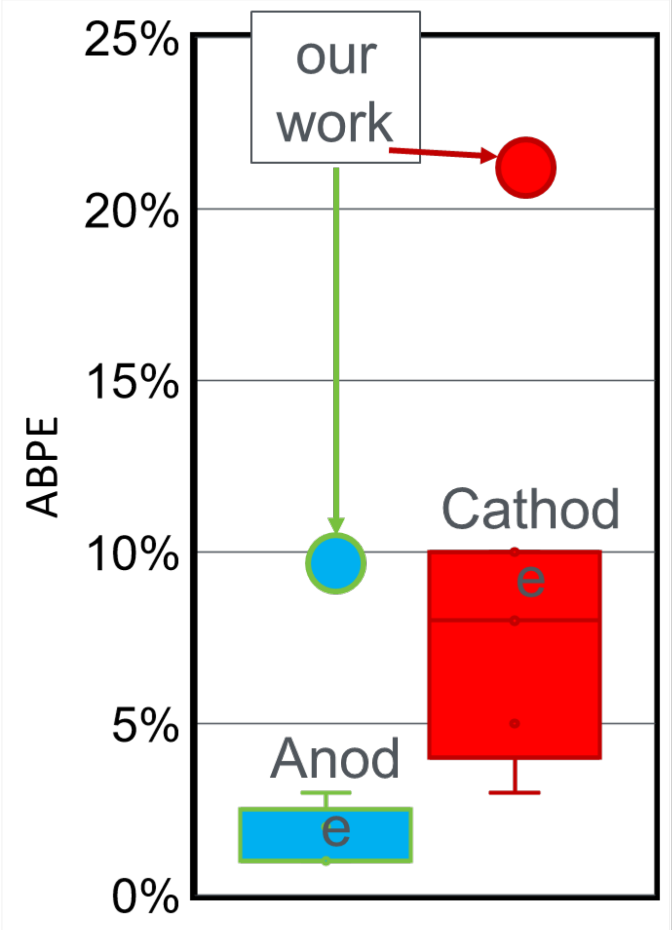
$$STH = \frac{|J_{op}| \times 1.23V \times \eta_F}{P_{in}}$$

- Current density without bias → $|J_{op}|$
- Thermodynamic water-splitting potential → $1.23V$
- Faradaic efficiency → η_F
- Solar illumination power density → P_{in}
- Bias-free solar-to-hydrogen efficiency → STH

GO/NO-GO for BP1: 10% STH for 1 hour

Comparison with other results on HaP-PECs





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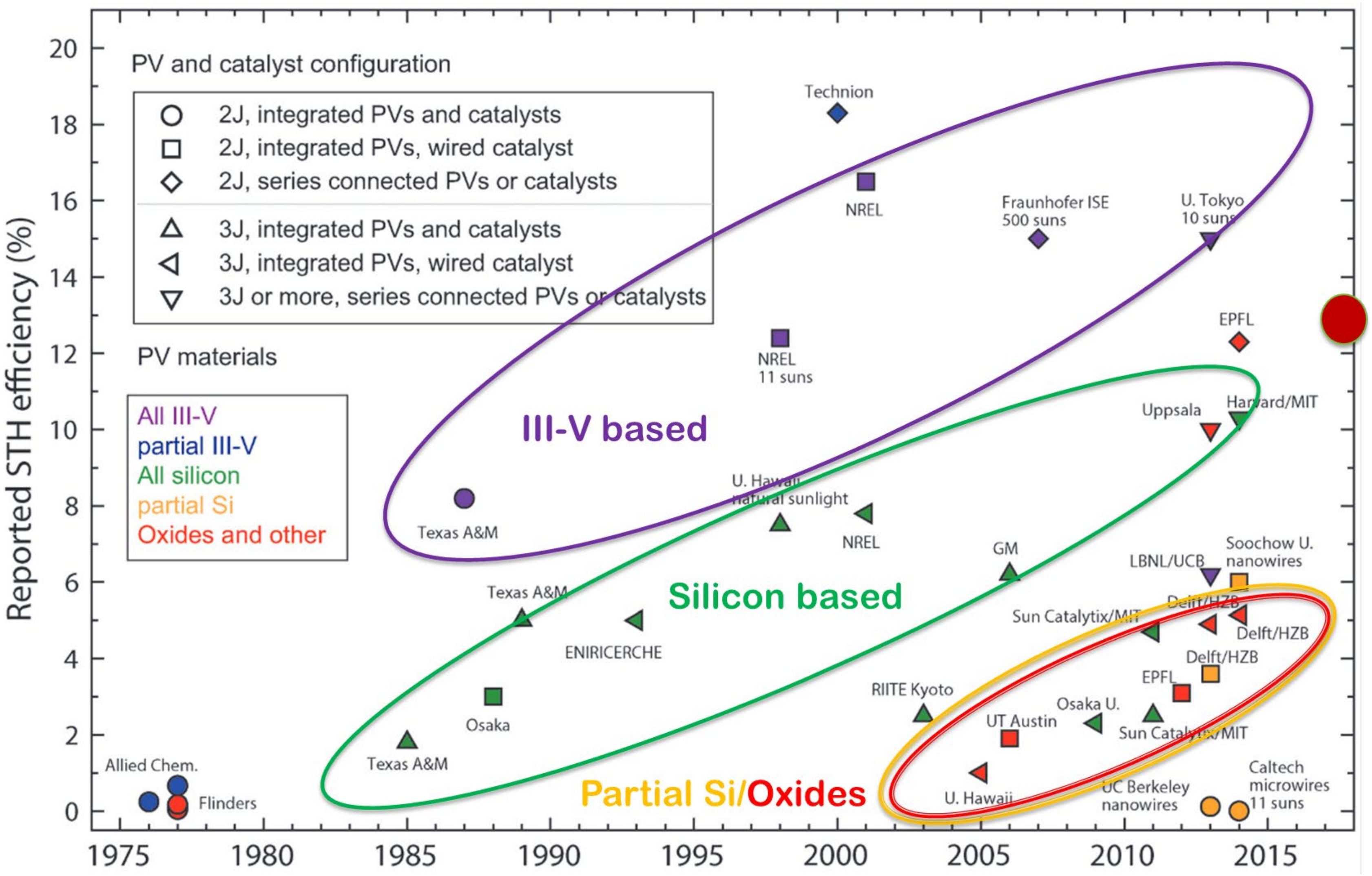
Perovskites have made their mark for PECs…



Collaboration Effectiveness with NODES

- **LBNL: Consultations for PEC measurements and benchmarking**

  Francesca Toma

  1. Consultation of protocols for hybrid perovskite PEC measurements
  2. Sample exchanges for testing and validation of efficiency
  3. Samples shipped for testing faradaic efficiency

- **LBNL: Understanding degradation mechanisms in PECs through in-situ characterization techniques – Dr. Francesca Toma**

  Planed work to perform XPS, AFM on degraded cathodes and anodes and ICPMS on used electrolytes

Impact on project: Critical for development of first of its kind perovskite-based PEC platform for testing, characterization and benchmarking performance and stability.

NREL: Todd Deutsch and James Young

- **Once a month calls to discuss specific recipes for catalyst deposition**
- **Consultation for PEC measurement protocols**
- **Consultation on OER catalyst stability**

Impact on project: Accelerated the knowledge gap for measurements on PECs and their characterization.

Publications & Presentations

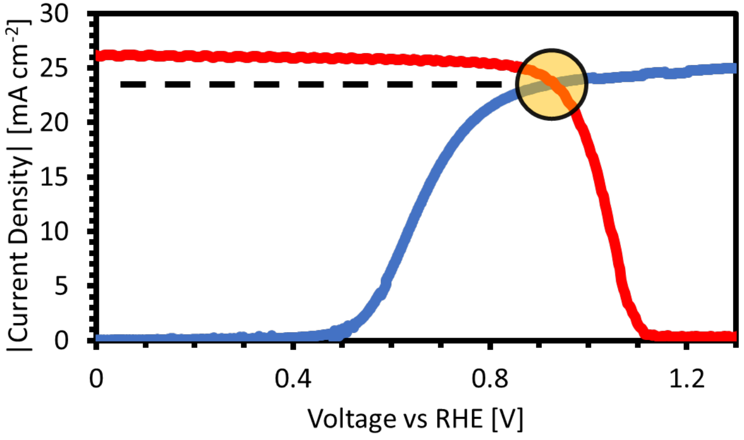
Milestone Schedule							
Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
M1.1	Selection of the photo-absorbing HaP materials	Milestone	M3			100%	Completed
M1.2	Fabrication of high-efficiency and stable HaP solar cells	Milestone	M9			100%	On Schedule
M1.3	Design charge transport layers as barriers	Milestone	M15			80%	On Schedule
M2.1	Understand the mechanisms of corrosion	Milestone	M12			85%	On Schedule
M2.2	Design of ultra- hydrophobic terminations on the HaP layers and design of anti-corrosion barriers	Milestone	M18			50%	On Schedule
M3.1	Design and integration of HaP-PEC	Milestone	M12			100%	On Schedule.
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%	On Schedule.
M3.2	Optimize PECs for high-efficiency and durability	Milestone	M24			15%	On Schedule.
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**			10%	Not started.
M3.3	Optimize PECs for high-efficiency and durability	Milestone	M33			0%	Not started.
M3.4	Techno-economic analysis	Milestone	M33			0%	Not started.
M4.1	Scaling-up photocathode and photoanode	Milestone	M30			5%	Not started.
M4.2	HaP-PEC large area module	Milestone	M36			0%	Not started.
	Demonstration STH efficiency 20% and 500 hours stability in HaP-PECs	**End of Project Goal**	**M36**			0%	Not started.

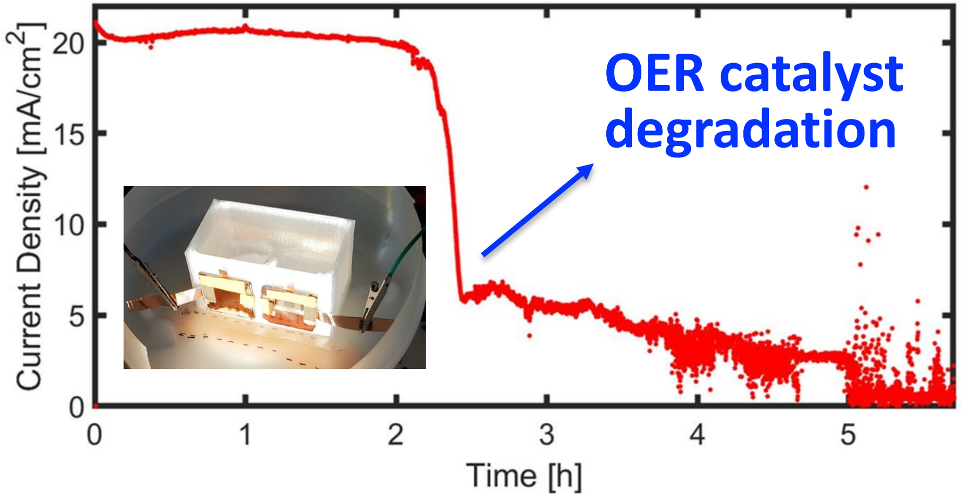
Project summary

Award #	DE-FOA-0002022-1652
Funding	$1 M

Two-terminal measurement

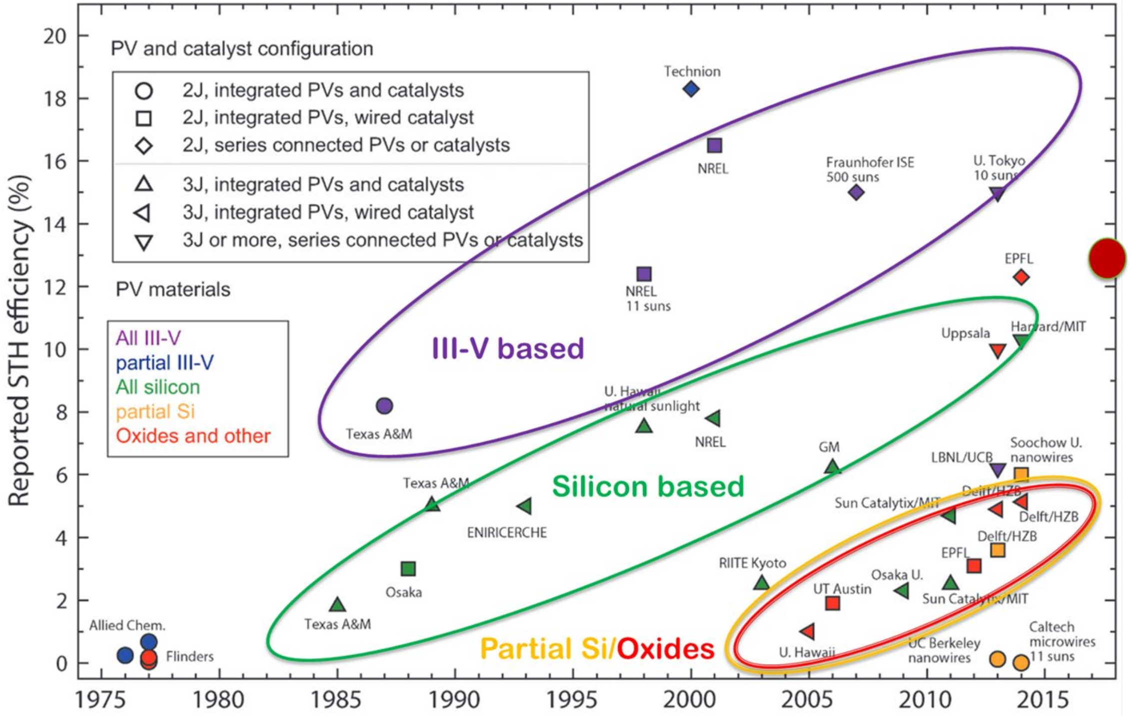
Solar-to-Hydrogen η_{STH} = 12.4%





1. Demonstrated a near-ideal corrosion barrier that translates the PV efficiency to the chemical reaction

2. Demonstrated integrated perovskite-PEC with >12.4% with 2.5 hours of stability



Future work

1. Demonstrated integrated perovskite-PEC with STH efficiency 15%

2. Demonstrate two-terminal stability of 100 hours

3. Demonstrate HaP-PEC devices with 3 cm2 device area

4. Demonstrate PEC performance and stability with light concentration

Our team

MOHITE group

Austin Fehr

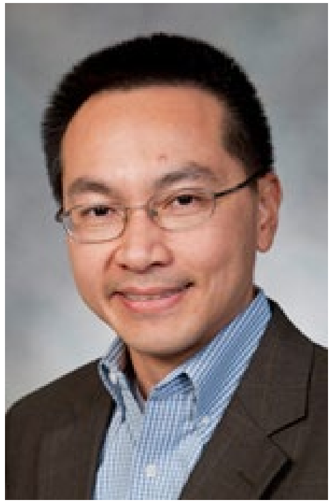
Ayush Agarwal

Chris Botello

Jean-Christophe Blancon

Isaac Metcalf

WONG group



Austin Fehr

Key Accomplishments

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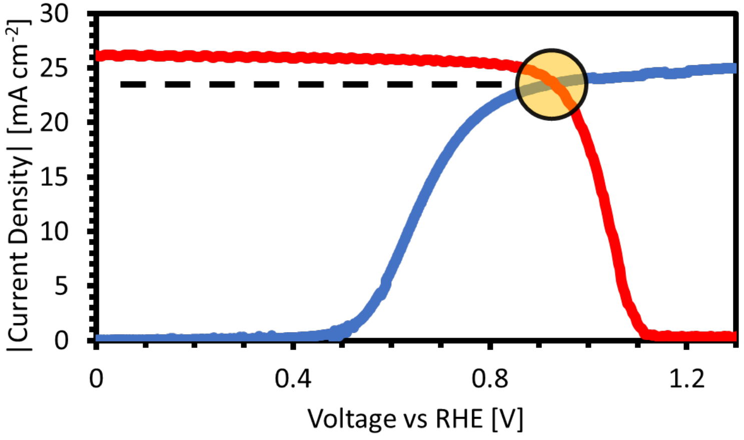

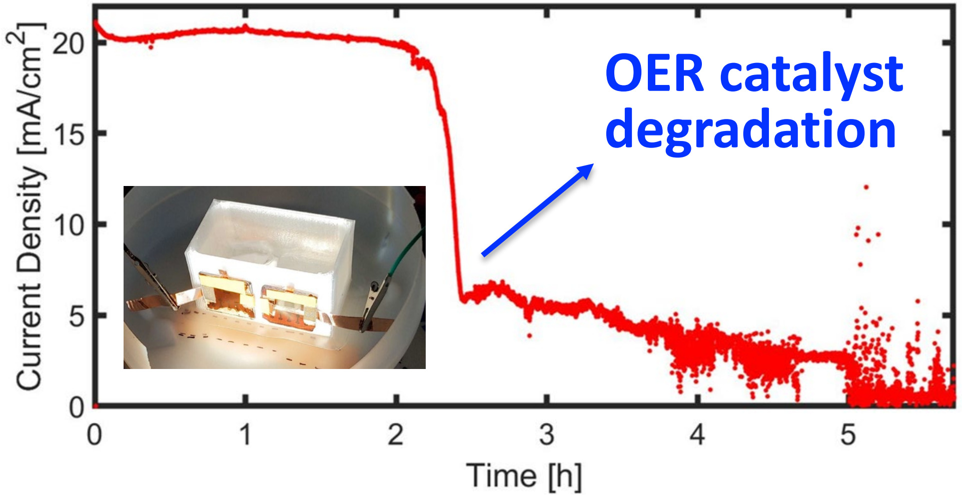

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