



Active and Stable Electrocatalyst Supports and Microporous Layers for Anode Applications in PEM Electrolyzers

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- 04/30/2019

Overview



Timeline

- Project Start Date: 10/01/2018
- Project End Date: 03/31/2019
- Percent complete: 83%

Budget

- Total Project Budget: \$ 50K
 - Total Recipient Share: \$ 0K
 - Total Federal Share: \$ 50K
 - Total DOE Funds Spent*: \$ 35,500

* As of 02/28/19

Barriers

- Barriers addressed
 - Capital Cost
 - By reducing the PGM loading
 - System efficiency
 - By improving the cell efficiency through engineering the catalyst layer/transport layer interface

Relevance

DOE Hydrogen & Fuel Cell Program is targeting cost-effective production of H₂ from diverse domestic sources, including renewable, fossil, and nuclear energy resources. H₂ production from electrochemical water splitting is part of DOE vision to enable future energy scenarios where H₂ is sustainably produced using all the diverse domestic resources.

- Reducing precious group metal (PGM) loading will lower the unit cost of H₂.
- Stable conductive oxygen evolution reaction (OER) catalyst supports and microporous layer (MPL) fillers reduce the PGM loading in the catalyst layer without compromising performance.

Specification	Baseline FC	Baseline Electrolyzer	Baseline Umicore Catalyst	Proposed Supports
Total Support PGM loading (wt%)	50	2	75	50
Catalyst layer PGM loading (mg/cm ²)	0.3	2	1.5	0.3
Activity (mA/cm _{Ir} ² @ 1.55V)	n/a	1.00	0.43	>1.00
Durability (% reduction)	n/a	9%*	9.3%*	<9%

* *Journal of The Electrochemical Society*, 163 (11) F3105-F3112 (2016)

Approach

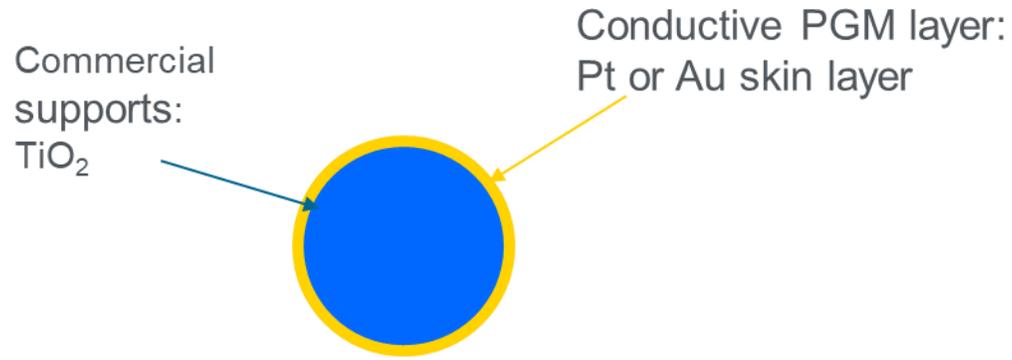
Show feasibility that thin layer of Pt or Au nanoparticles can be deposited on TiO_2 nanoparticles using facile and scalable methods to generate OER catalysts with low PGM metal loadings without increase in overpotentials to exceed $1 \text{ mA/cm}_{\text{Ir}}^2$ activity.

- The conductive Au or Pt layer between filler, TiO_2 , and OER catalyst, IrO_x , reduces required potentials to achieve desired electrochemical activities.
- Synthesis of conductive and stable fillers for electrolysis is relevant to multiple technologies Hydrogen and Fuel Cell Program is exploring towards diversification of hydrogen production.

Activity	Approach
Synthesis	Identify facile and scalable synthesis routes to prepare TiO_2 nanoparticles decorated with Pt or Au.
Characterization: Materials	Employ XRD, SEM, TEM, EDS and XRF to characterize the structure, distribution and quantify total PGM loadings on TiO_2 .
Characterization: Electrochemical	Investigate activity and stability towards OER in 0.1 M HClO_4 and compare with state-of-the-art catalysts.

Approach

Stable Conductive Support or MPL Filler



- Scalable synthesis
- Gold or platinum as PGM protective layer
- TiO_2 as core is stable

OER catalyst on Support



Task	Name	Period	Cost/Organization
1	Supported Catalyst/MPL Filler Development	Q1-Q2	LBNL: 50K

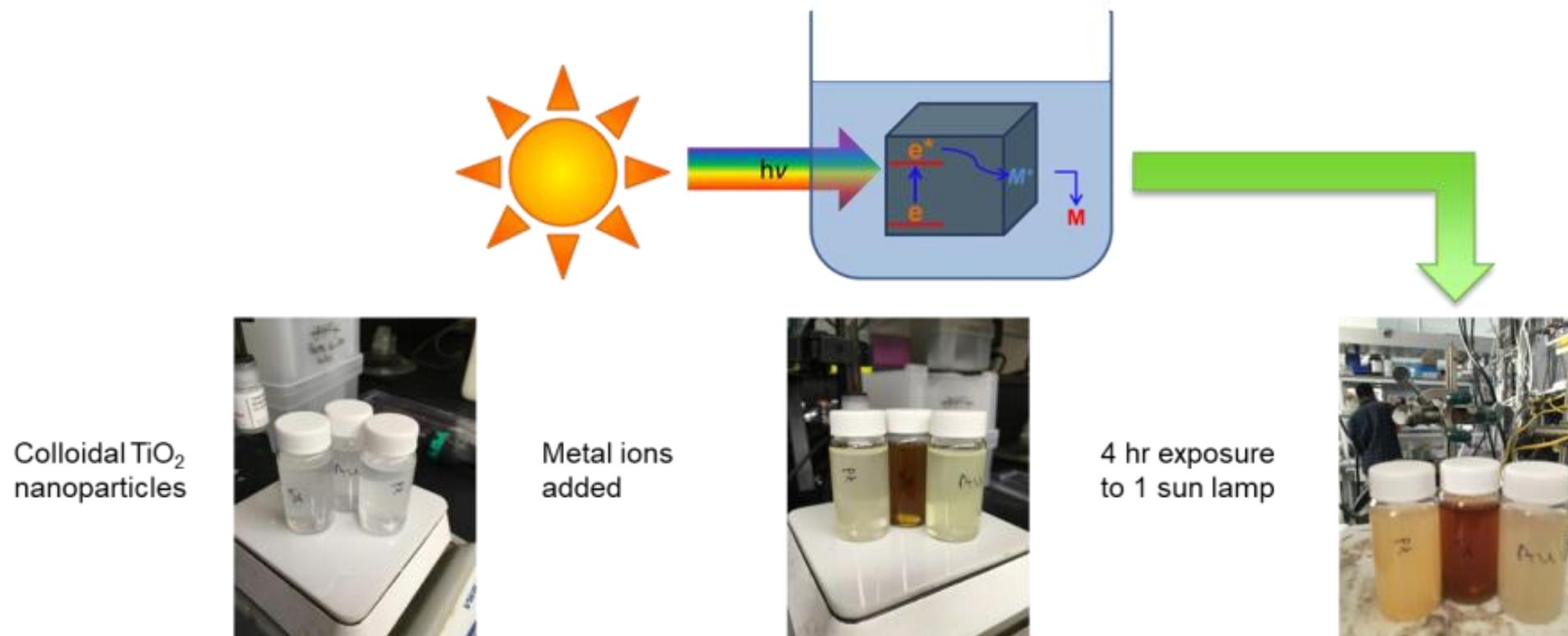
Support material (TiO_2) decorated with conductive barriers and electrocatalysts, and evaluated using electrochemical methods, and chemical and physical characterization tools.

Approach

Progress measures	Type	Deliverable	Status
Q1- 12/31/2018		Show feasibility for Pt or Au decoration on TiO ₂ supports.	
Q2- 3/31/2019		Show feasibility for Au and Pt decorated supports with Ir electrocatalysts are to meet target performance and durability metrics.	On track: PGM normalized OER activity in acid exceeds corresponding activity of commercial state-of-the-art catalysts. Stability studies underway.
Q2- 3/31/2019			

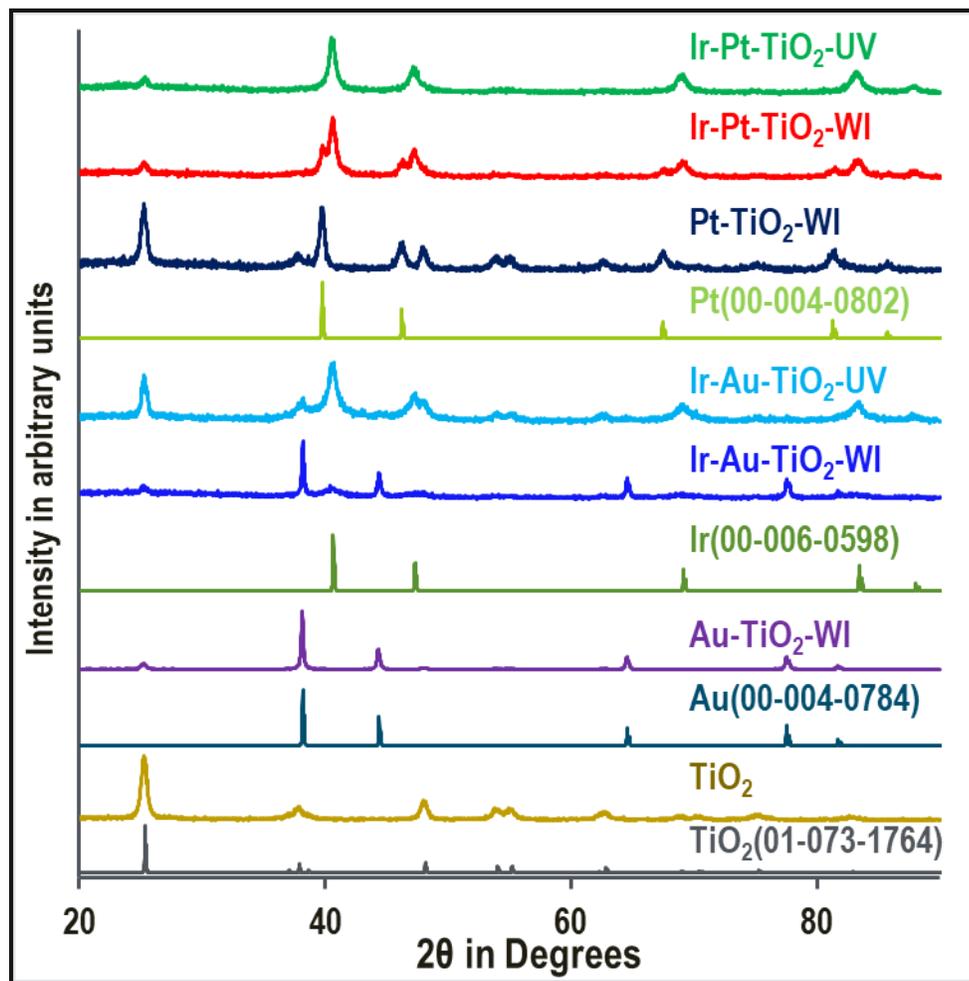
Accomplishment - Synthesis

1. Semiconductor properties of TiO_2 supports exploited to reduce chlorometallic precursors and generate metal nanoparticles on TiO_2 surfaces. (**UV method**)



2. Wetness impregnation of TiO_2 nanoparticles with solution of chlorometallic salts followed by reduction at $400\text{ }^\circ\text{C}$ in 2% hydrogen in argon environment. (**WI method**)
3. Iridium was loaded on all the filler nanoparticles thus generated via the WI method.

Accomplishment: Materials Characterization (XRD)

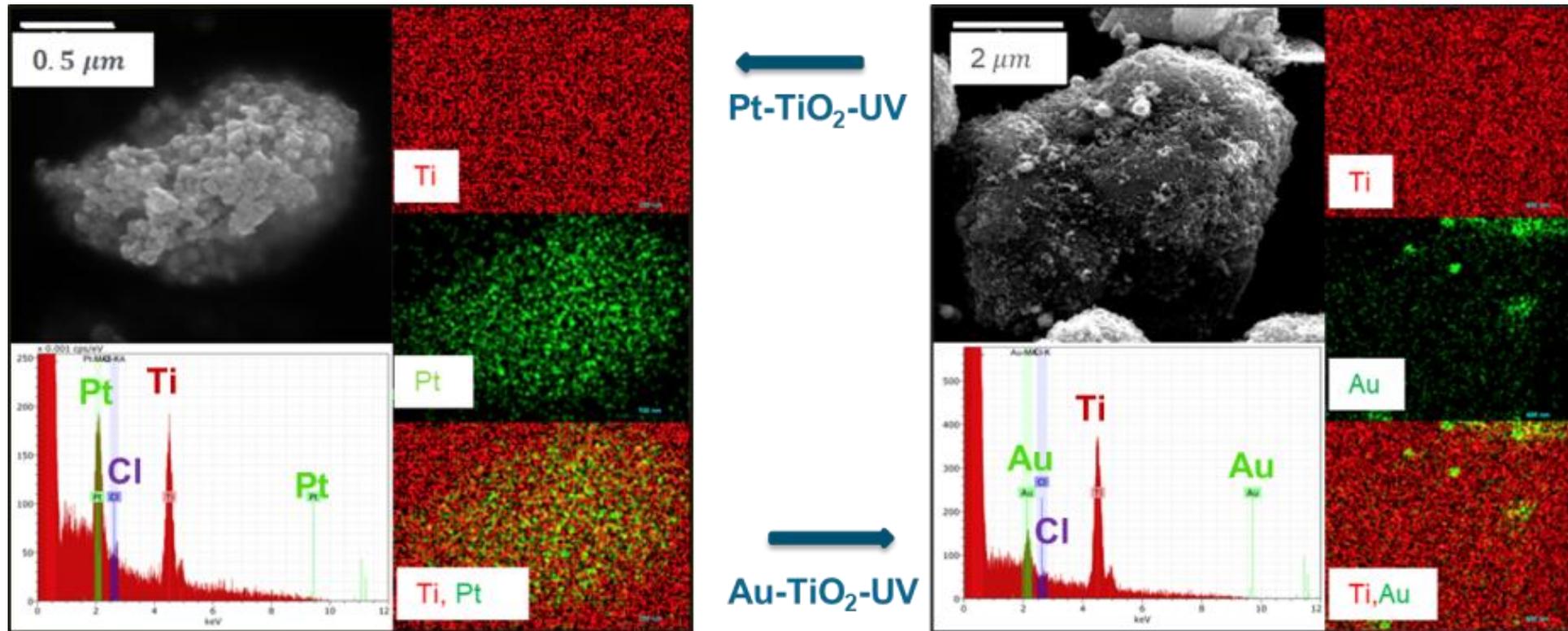


UV – photochemical reduction

WI – wet impregnation mediated reduction

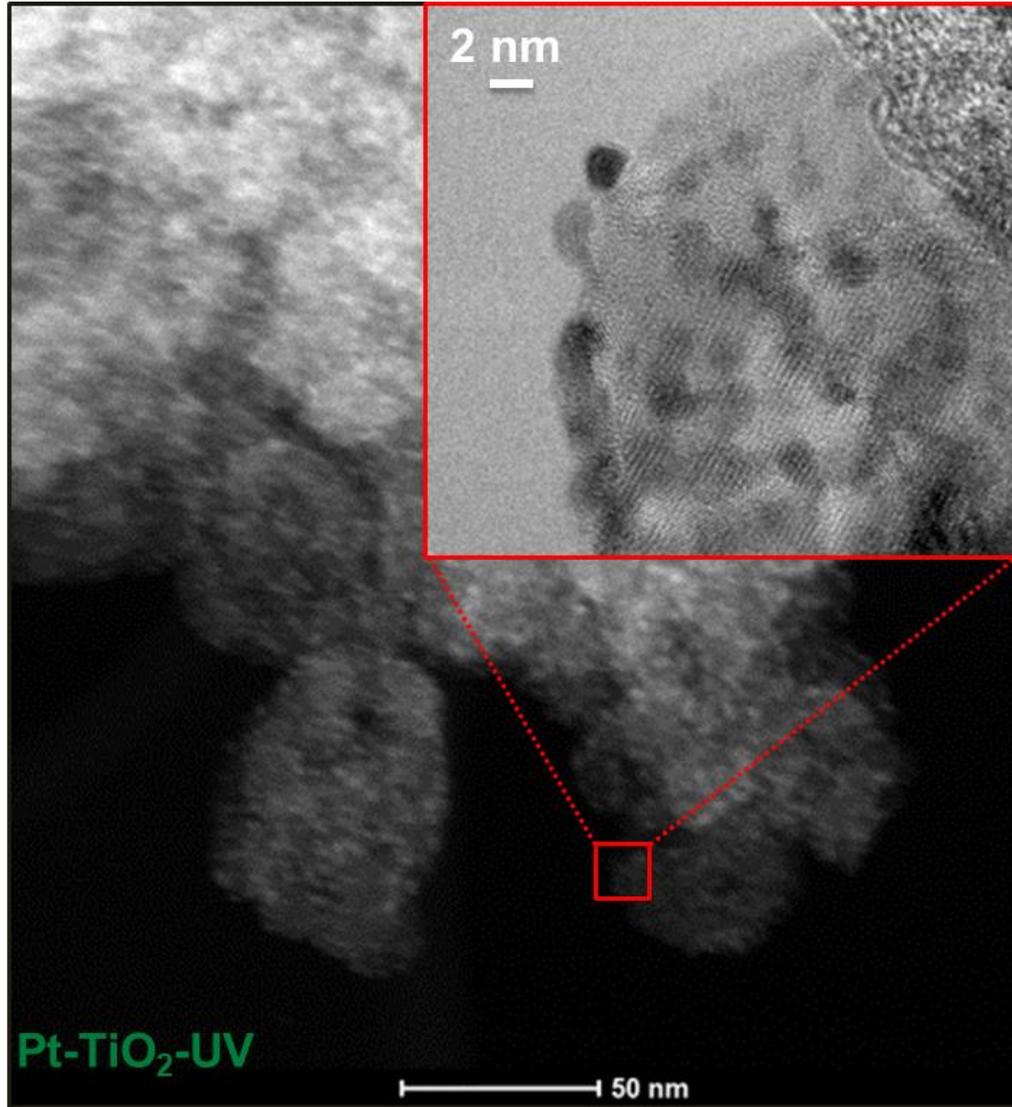
- Phase pure crystalline Pt, Ir and Au successfully synthesized using wetness impregnation (WI) method.
- Photochemical reduction (UV) method successfully generated phase pure gold, but less obvious for Pt either due to ultra small Pt nanoparticles or amorphous phase.
- Crystalline Ir obtained via WI method are in the range of 40-50 nm based on Scherrer Equation analysis of the XRD peaks.
- Ir nanoparticles crystallite size similar to TiO₂ substrate (~50 nm) based on Scherrer equation analysis.

Accomplishment Materials Characterization (SEM/EDS)



- Pt distribution from UV assisted method is homogenous in the matrix (left) while the gold distribution shows large aggregates (right).
- Post-synthesis processing successfully removes all the chloride ions from the matrix.

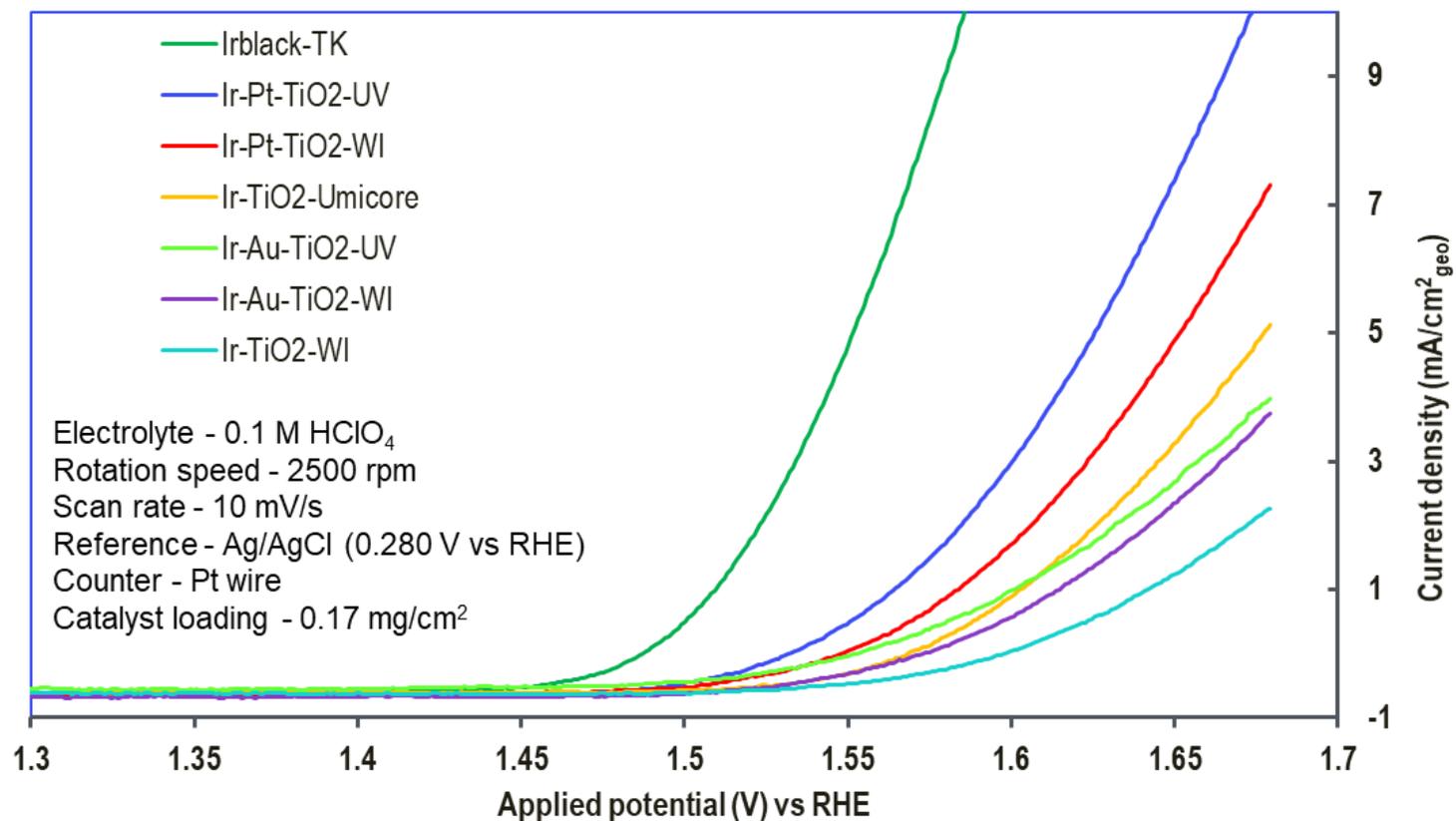
Accomplishment Materials Characterization (TEM)



- Taken together with evidence from XRD and SEM, UV assisted method generates ultra-small Pt nanoparticles.
- TiO₂ nanoparticles (50-100 nm) are evenly covered with much smaller Pt nanoparticles (2-3 nm).
- Pt nanoparticles do not aggregate significantly during the wet impregnation assisted Ir deposition on filler nanoparticles.
- Distribution of Pt nanoparticles on TiO₂ is more homogenous for UV assisted method compared to WI method.

Accomplishment

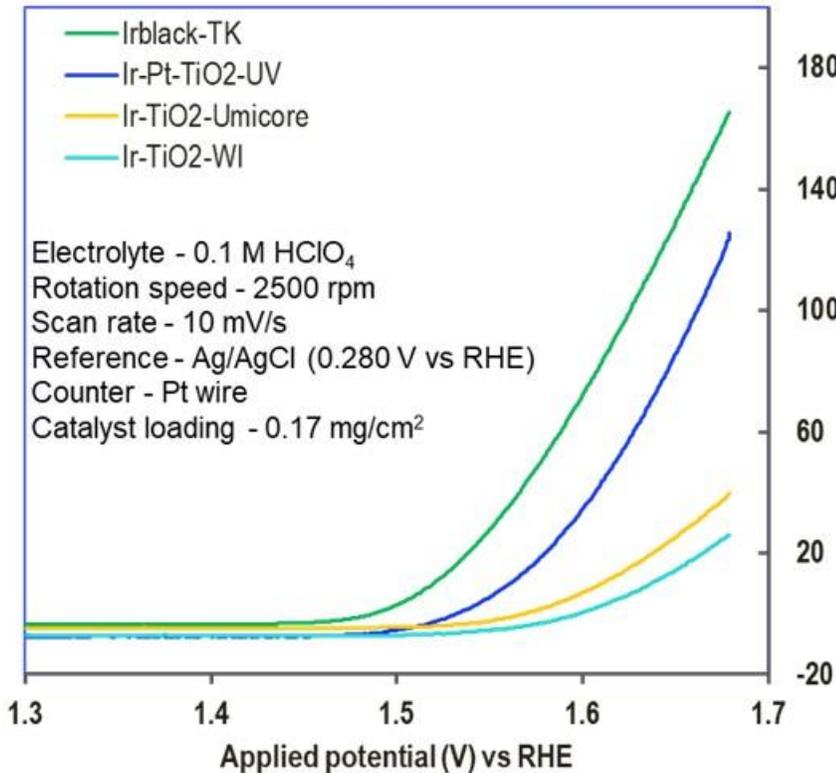
Electrochemical Characterization



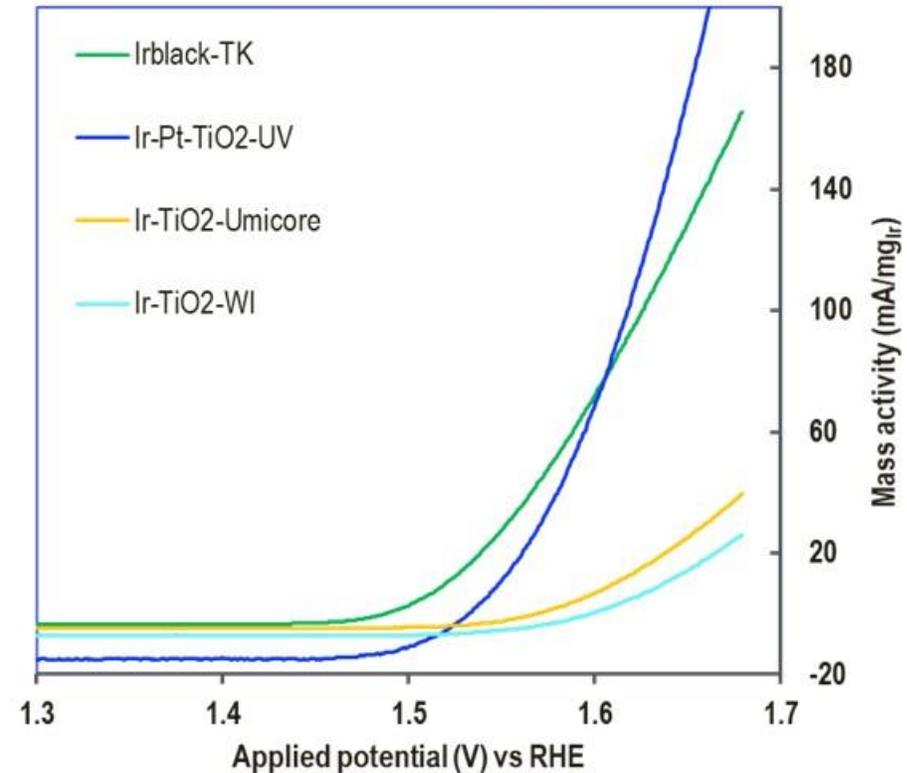
- Ir-Pt-TiO₂ outperforms the industrial high surface area oxide supported IrO_x catalyst Ir-TiO₂-Umicore at total PGM loading reduction on the support.
- UV-generated catalysts outperform WI generated catalysts with the same Ir loading.
- Homogenous distribution of particles in conductive layer leads to higher OER activity.

Accomplishment Electrochemical Characterization

Total PGM mass normalized



Total Ir mass normalized



- When the activities are normalized to mass of PGM (left) and iridium (right) the effect of conductive layer is more apparent
- Presence of conductive layer on filler materials results in the catalysts (Ir-Pt-TiO₂-UV) outperforming even the unsupported iridium catalysts (Irblack-TK)

Response to Previous Years Reviewers' Comments

- Project not reviewed previous years

Collaboration & Coordination



Partner	Project Roles
Molecular Foundry Lawrence Berkeley National Laboratory	
Barr Zulevi Pajarito Powder	
Francesca M. Toma Lawrence Berkeley National Laboratory	
Eden Tzanetopoulos Undergraduate Researcher, Lawrence Berkeley National Laboratory	
Adam Z. Weber Lawrence Berkeley National Laboratory	

Remaining Challenges and Barriers

Activity	Description
Activity degradation	Assess OER activity loss over 2 hour at 1.55 V vs RHE. Compare with high surface area oxide supported Umicore catalyst as well as unsupported Tanaka catalyst.
Catalyst dissolution	Quantify catalyst degradation from the 2 hour holds using ICP-MS.
Gold nanoparticle distribution on TiO₂	Optimize UV assisted and wet impregnation methods to improve distribution of gold nanoparticles.

Proposed Future Work



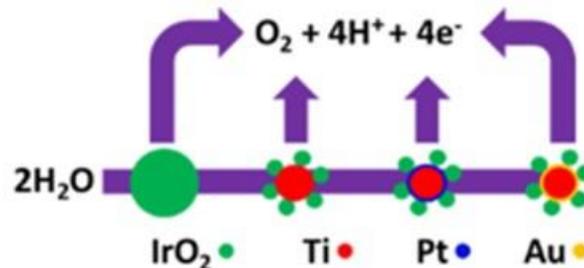
Duration	Description
Remainder FY2019	Complete activity loss and catalyst degradation studies and continue optimizing synthesis of homogenously distributed gold nanoparticles.
Beyond grant period	Consult with industrial collaborators and funding agencies to test materials in membrane electrode assemblies to leverage future funding.
Long-term	<ul style="list-style-type: none">• Explore methods to prepare fillers with various architecture such as conformal thin films of Pt and Au instead of nanoparticles.• Optimize the ratio of conductive layers and OER catalyst (Ir) layer for maximal performance at minimal PGM loadings.• Investigate effects of post-synthesis treatments such as heat on performance.

Technology Transfer Activities

- Patent Disclosure Agreements signed with Lawrence Berkeley National Lab to pursue filing a patent titled “Conductive and stable catalyst supports and microporous layer materials for high voltage applications”.

Project Summary

- Objective:** Demonstrate that conductive layer of platinum or gold makes it feasible to lower precious metal loading without compromising performance in using TiO_2 as filler materials in water oxidation catalyst layers.
- Relevance:** Replacing precious metal from the inactive bulk of the catalyst layer with conductive layer coated titanium dioxide fillers will lower the cost of hydrogen.
- Approach:** Utilize semiconductor properties of TiO_2 to reduce gold and platinum metal salts and use the resulting materials as fillers.
- Accomplishments:** Mass activity of Pt coated filler supported Ir is superior to state-of-the-art Iridium OER catalysts.
- Future Goals:** Demonstrate superior performance in membrane electrode assemblies.



Acknowledgments



Department of Energy for support