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School of Engineering
University of California, Irvine

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OF NORTH AMERICA

Corrosion-Resistant Non-Carbon Electrocatalyst Supports for PEFCs

PI: Vijay K. Ramani
Washington University in St. Louis

Project # FC145

Overview

Timeline and budget

Competitively selected project

- Project start date: 03/01/16
- Project end date: 02/28/21
- Total project budget: $ 3,397,431
  - Total recipient share: $ 397,431
  - Total federal share: $ 3,000,000
  - Total DOE funds spent**: *ca*.$ 2,700,000

* ** As of 4/30/20.

Barriers to be addressed:

- A. Durability
- C. Performance
- B. Cost

	2020 Target
Loss in catalytic (mass) activity^{a,b}	<40% loss
Loss in performance at 0.8 A/cm^2 ^{a}	30mV
Loss in performance at 1.5 A/cm^2 ^{b}	30mV
Mass activity @ 900 mV$_{iR\text{-}free}$^{c}	0.44A/mg$_{PGM}$

Partners

- Project lead: Washington University in St. Louis
- Partners (sub-contractors):
  - – Nissan Technical Center, North America
  - – University of California, Irvine

Impact of carbon corrosion on PEFCs

Carbon is mainly used as an electrocatalyst support due to its:

- High electrical conductivity (> 20 S/cm)
- High BET surface area : 200 - 300 m^2/g
- Low cost

Electrochemical oxidation of carbon occurs during fuel cell operation

- $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ $E^o = 0.207$ V vs. SHE

Carbon corrosion is accelerated:

- During start/stop operation (cathode carbon corrosion)
- Under fuel starvation conditions (anode carbon corrosion)

Kinetic and ohmic losses result due to:

- Pt sintering and loss of contact between Pt and C

Mass transport losses occur due to

- Formation of hydrophilic groups => flooding

Relevance

Research objectives: Technical targets

- Conducting, doped, non-PGM metal oxides (electron conductivity >0.2 S/cm)
- High surface area(>70 m^2/g)
- Exhibits SMSI with Pt
- Corrosion resistant (DOE 2020 targets)
- High electrocatalyst performance (DOE 2020 targets)

Metric	Units	SoA (Pt/C)*	SoA (Pt/RTO)	Proposed approach status (Pt/TiO_2-Ta)**	Project target
Total PGM content	$g\ kW^{-1}$	0.55	0.55	Not Available	0.25
Total PGM loading	$mg\ cm^{-2}$	0.4	0.4	0.6	0.25
Voltage at 1.5 $A\ cm^{-2}$ (air)	V	0.45	0.48	0.3	0.55
Loss in mass activity [a,b]	% loss	32	33	<10%	<5%
Voltage loss at 0.8 $A\ cm^{-2}$ [a]	mV	81	9	< 15	<10
Voltage loss at 1.5 $A\ cm^{-2}$ [b]	mV	182^{+}	20	N/A; 20 mV at $1 A cm^{-2}$	<20
Mass activity@900 $mV_{iR\text{-}free}$ [c]	$A\ mg^{-1}_{PGM}$	0.07	0.07	ca. 0.05	0.3

[a]-Table E1, [b]-Table E2; Appendix E of FOA; [c] DOE protocol per appendix E of FOA; **Pt/C refers to Pt/Graphitized Ketjen Black tested at NTCNA*; ***Results from entirely un-optimized MEAs run primarily to test stability*. $^{+}$*Pt/HSAC durability is much worse – MEA does not run beyond 0.5 $A\ cm^{-2}$ after start-stop cycling*. Data from MEA in a PEFC

Approach

Milestones

2nd Year	Q5	Demonstrate SMSI as ascertained by Pt d-band filling (XPS) Meet durability target in RDE (ECSA Loss <5% - 10,000 start-stop cycles)	(100%) (100%)
	Q6	Demonstrate 10% increase in mass activity (BoL in RDE) at 0.9V over Pt/C benchmark	(100%)
	Q7	B.E.T. Area>70 m^2 g^{-1} ;Particle size <70nm; conductivity of at least 0.2S cm^{-1} Meets stability and durability in RDE per DOE metrics (ECSA Loss <5%)	(100%) (100%)
	Q8	20-40wt%Pt; Surface area> 70 m^2 g^{-1} Pt particle size 3-6nm; Meets DOE 2020 durability targets in RDE and MEA	(100%) (100%)
3th Year	Q9	Demonstrate “End Project” durability metrics and at least 80% of “end project” mass activity metric in MEA	(80%)
	Q2	In addition to Milestone 6.2.1, meet “End Project” BoL mass activity target (Table 2)	(80%)
	Q3	Specify cost of best 2 Pt/DS materials	(80%)
	Q4	Meet “End Project” durability, activity, and performance targets in Table 2	(80%)

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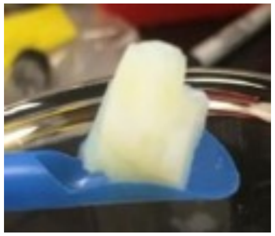
Approach

Support Synthesis and Pt deposition strategy

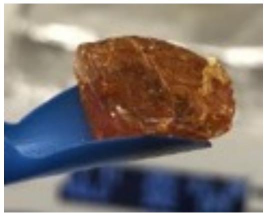
Wet gel



aerogel

Pros: High surface area and porosity

Cons: Lower conductivity can affect catalyst layer resistance



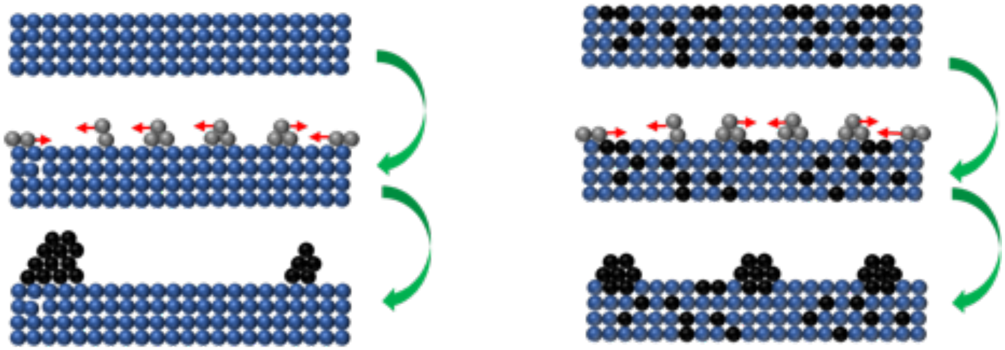
xerogel

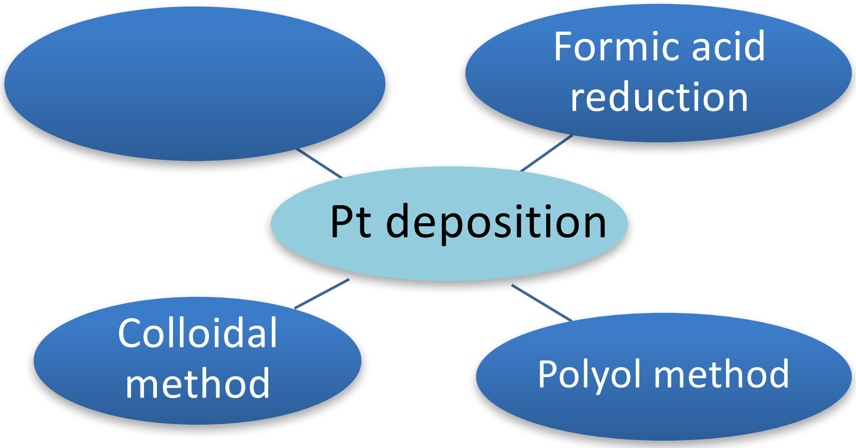
Pros: High conductivity

Cons: Lower porosity and partial agglomeration can affect MEA fabrication and increased mass transfer resistance in fuel cell

Optimize annealing temperature to achieve proper combination of conductivity, surface area and porosity in the support material

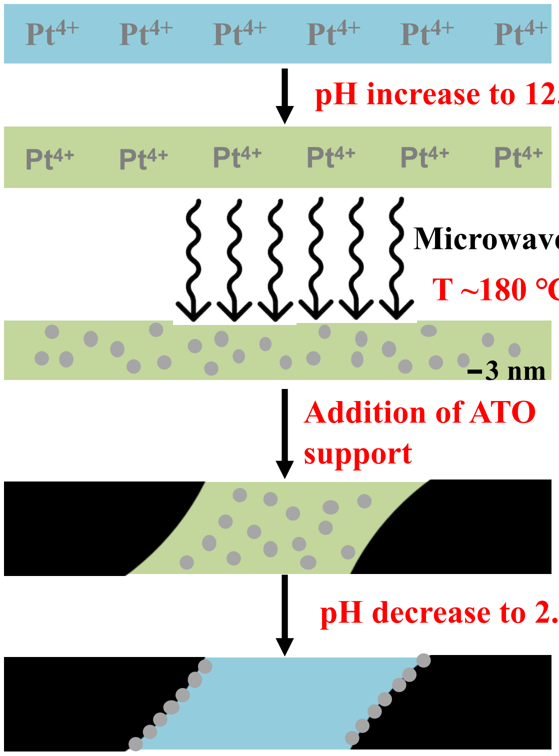
Pt seeded Support





Approach

Support Synthesis and Pt deposition strategy



Ethylene Glycol

Solvent + Reducing Agent

pH increase to 12.5

Glycolate Anion

Microwave Irradiation

T ~180 °C

Pt NPs formation

Addition of ATO support

pH decrease to 2.5

Pt NPs deposition

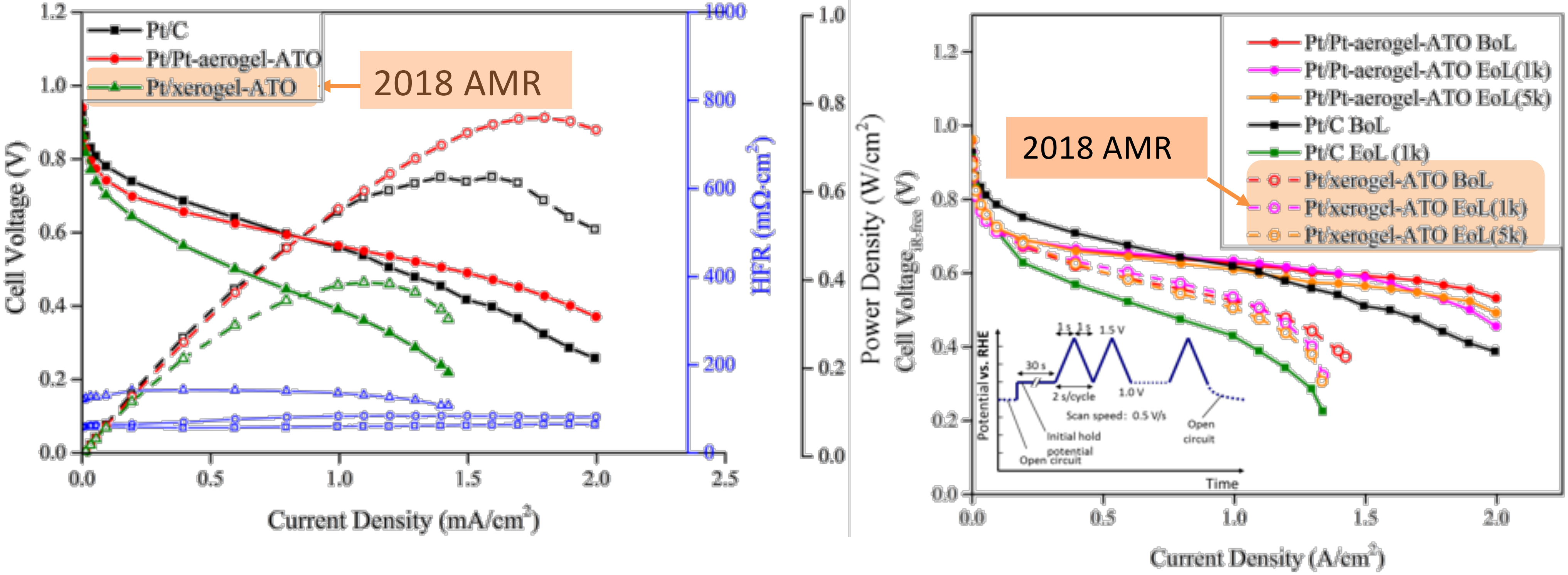
Colloid negative zeta potential vs. support positive zeta potential.

Schematic of Microwave assisted Polyol synthesis

Both Microwave-assisted Polyol Synthesis and ALD have also been used for alloy (e.g. Pt-Ni) deposition

Accomplishments and Progress (Prior)

Pt-aerogel-ATO MEAs exhibit excellent performance and durability



2018 AMR

2018 AMR

Comparison of fuel cell performance (H_2/Air) obtained for Pt/xerogel-ATO, Pt/Pt-aerogel-ATO and Pt/Vulcan Carbon before (BoL) and after (EoL) start-stop protocol for 1,000 **and 5,000 cycles** at 80°C, 90%RH and 200 kPa_{abs}. Pt loading at the cathode: 0.10 mg_{Pt}/cm^2. Pt loading at the anode: 0.10 mg_{Pt}/cm^2.

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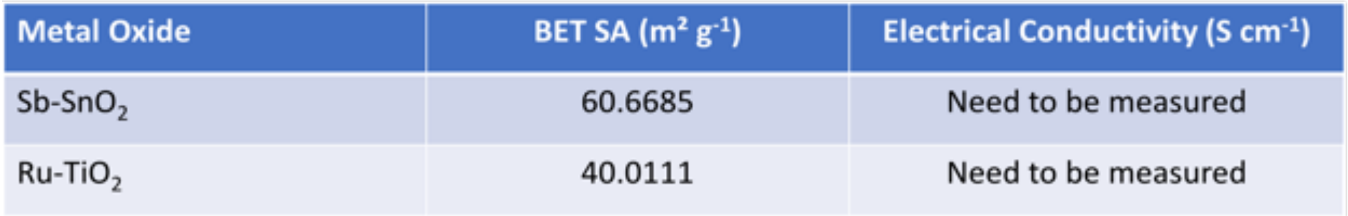
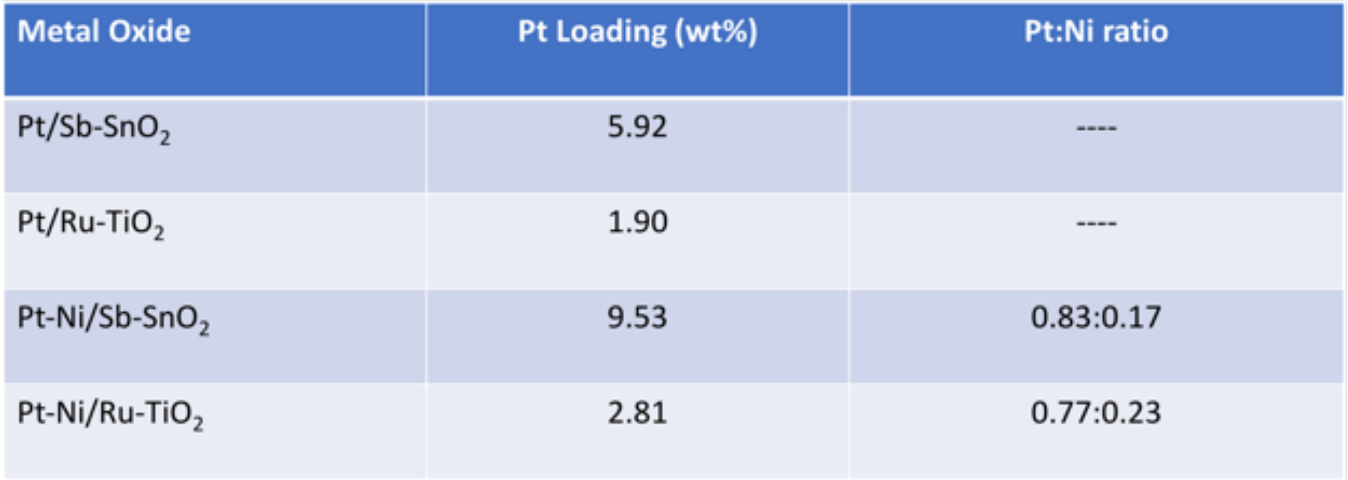
Accomplishments and Progress

Characterization results of various oxide supports and alloy catalysts:



Metal Oxide	BET SA (m² g^{-1})	Electrical Conductivity (S cm^{-1})
Sb-SnO_2	60.6685	Need to be measured
Ru-TiO_2	40.0111	Need to be measured

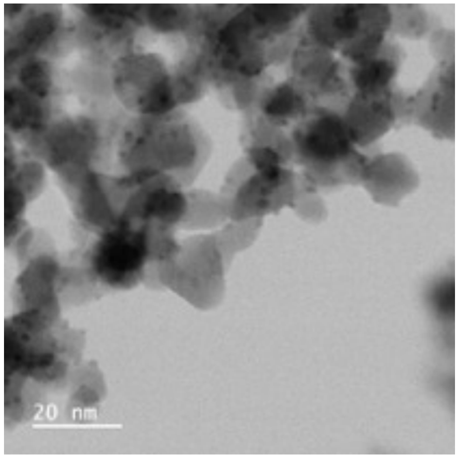


Metal Oxide	Pt Loading (wt%)	Pt:Ni ratio
Pt/Sb-SnO_2	5.92	----
Pt/Ru-TiO_2	1.90	----
Pt-Ni/Sb-SnO_2	9.53	0.83:0.17
Pt-Ni/Ru-TiO_2	2.81	0.77:0.23

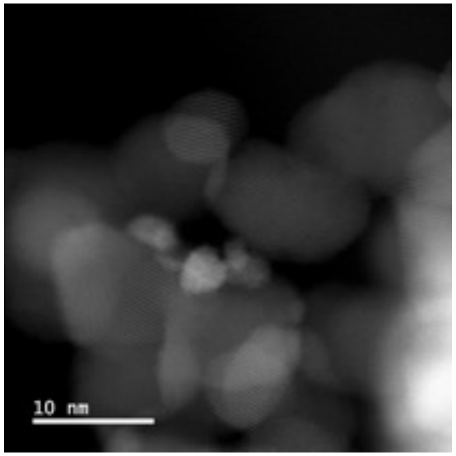
Accomplishments and Progress

Characterization results of various oxide supports and alloy catalysts:

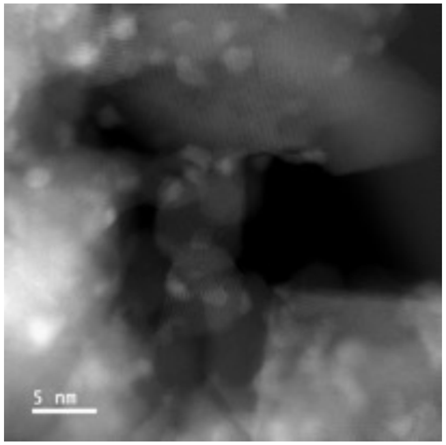
Pt-Sb-SnO_2



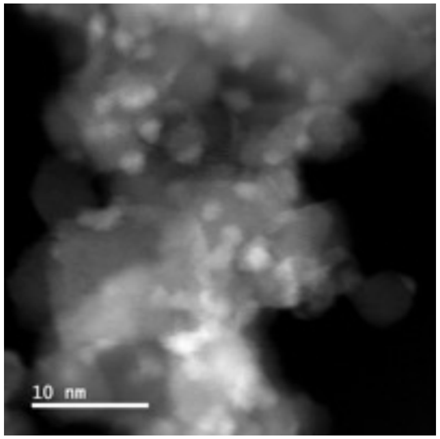
Pt-Ni/Sb-SnO_2



‘Pt-Ru-TiO2



Pt-Ni-Ru-TiO2

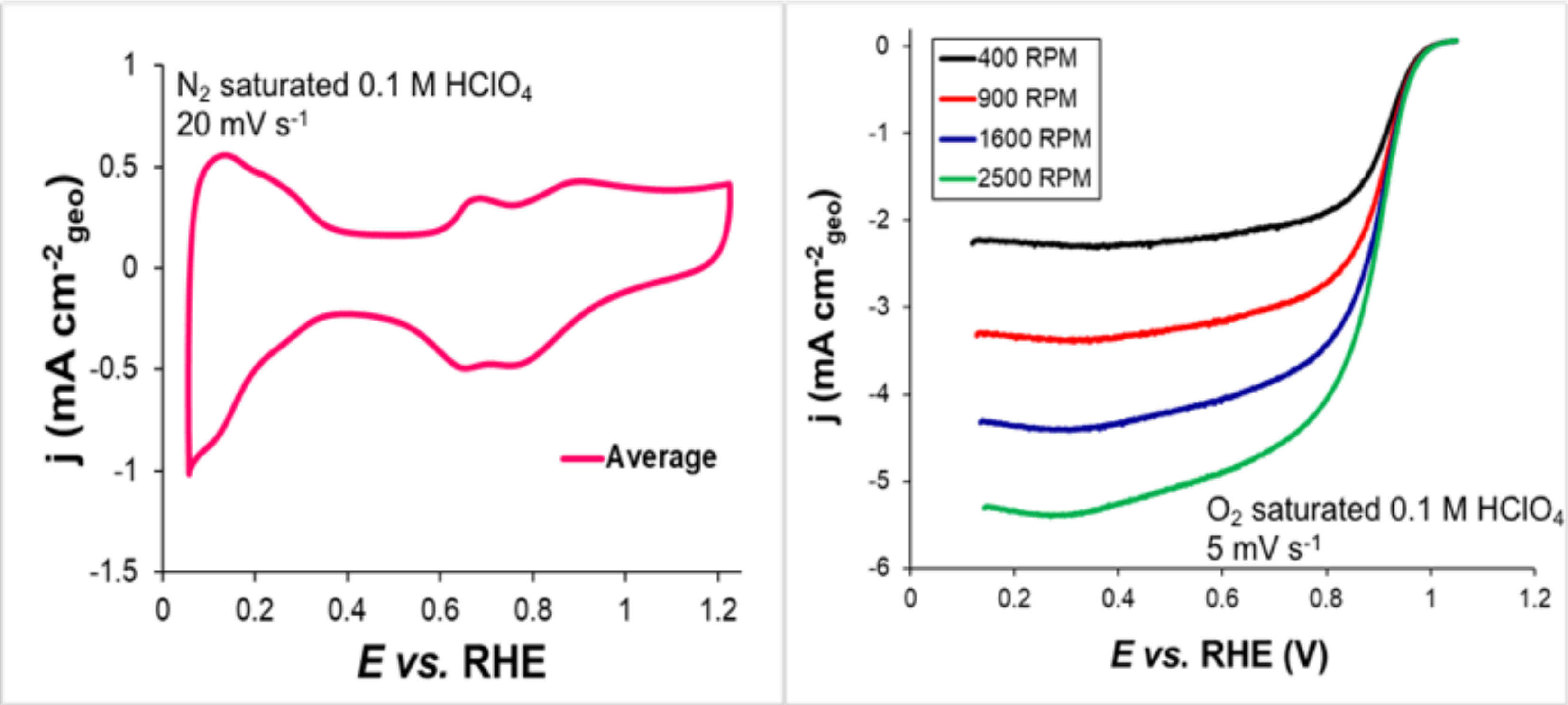


Well-dispersed alloy electrocatalysts obtained on our metal oxide supports
Further optimization of synthesis is ongoing

Accomplishments and Progress

Electrochemical Characterization

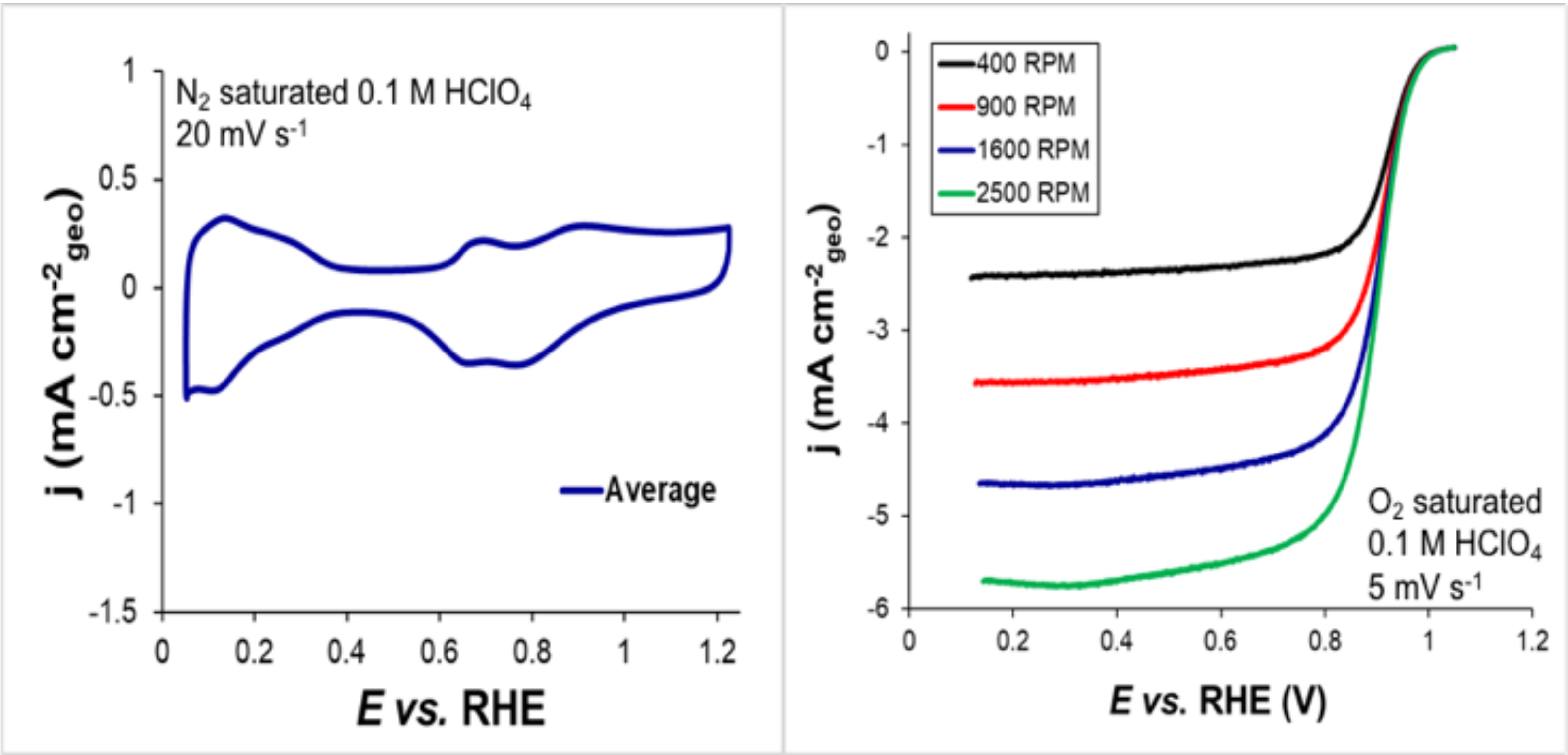
Pt/Sb-SnO_2



Accomplishments and Progress

Electrochemical Characterization

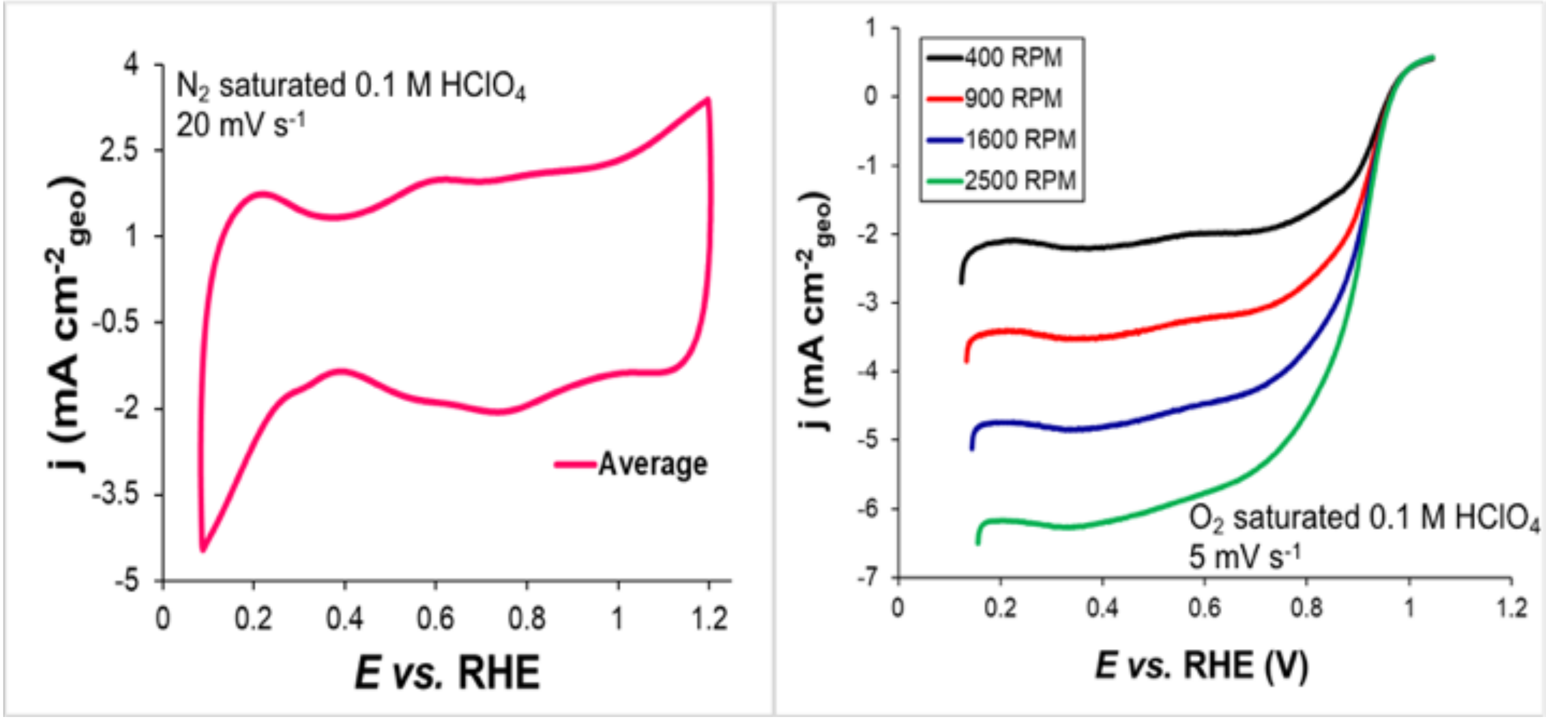
Pt-Ni/Sb-SnO_2



Accomplishments and Progress

Electrochemical Characterization

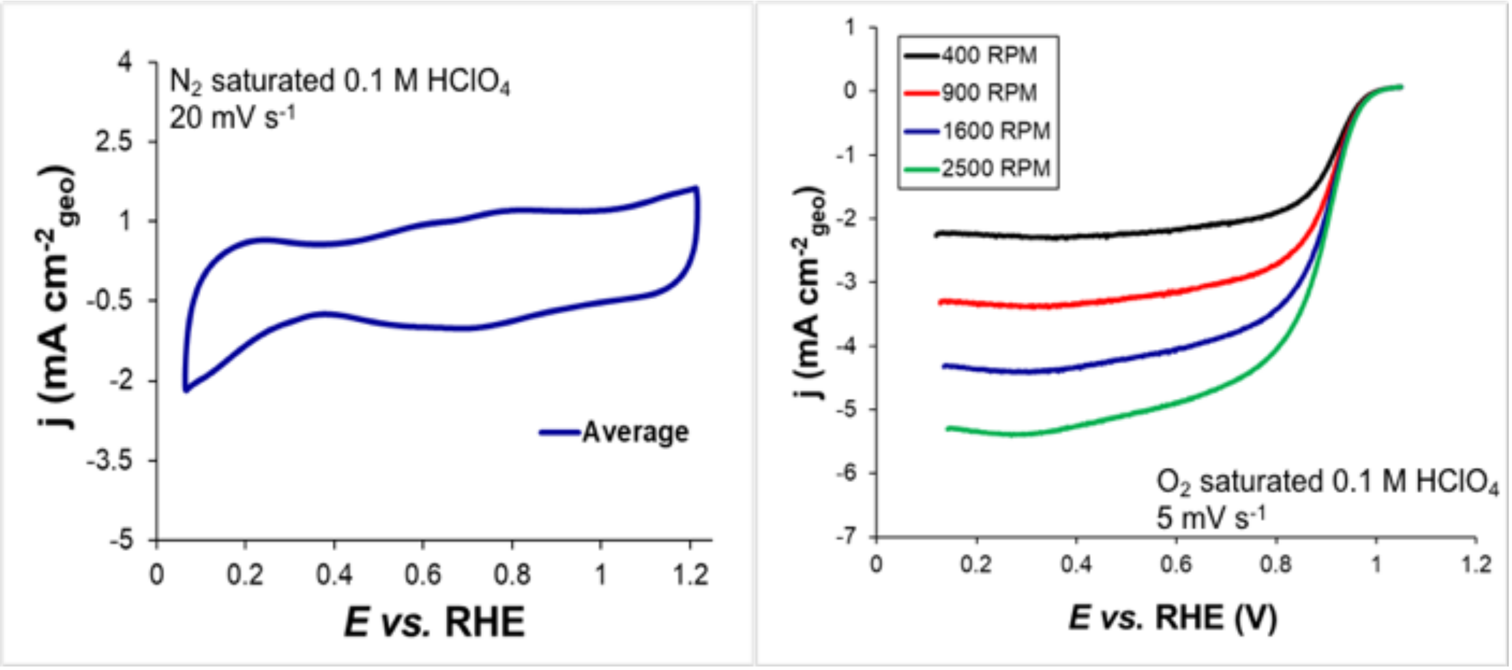
Pt/Ru-TiO_2



Accomplishments and Progress

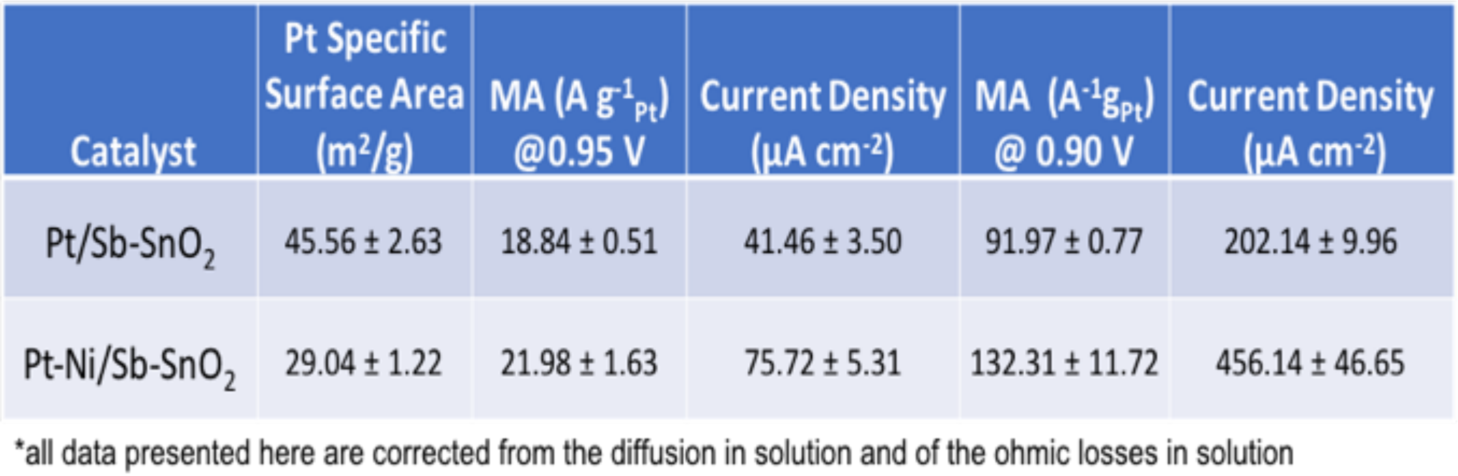
Electrochemical Characterization

Pt-Ni/Ru-TiO_2



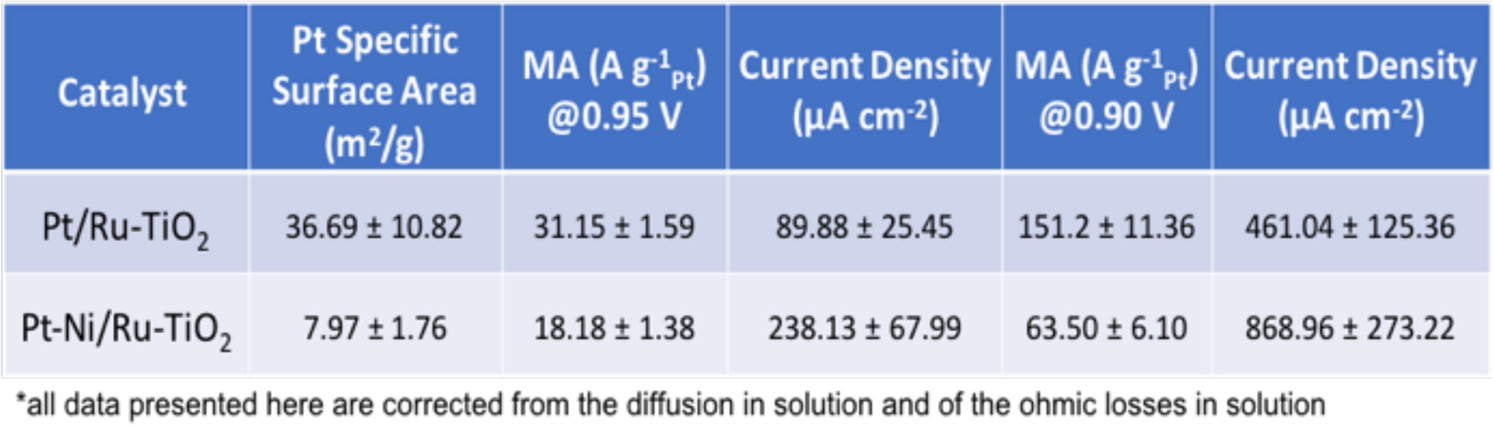
Accomplishments and Progress

Electrochemical Characterization: Analysis



Catalyst	Pt Specific Surface Area (m^2/g)	MA ($A\,g^{-1}_{Pt}$) @0.95 V	Current Density ($\mu A\,cm^{-2}$)	MA ($A^{-1}g_{Pt}$) @ 0.90 V	Current Density ($\mu A\,cm^{-2}$)
Pt/Sb-SnO_2	45.56 ± 2.63	18.84 ± 0.51	41.46 ± 3.50	91.97 ± 0.77	202.14 ± 9.96
Pt-Ni/Sb-SnO_2	29.04 ± 1.22	21.98 ± 1.63	75.72 ± 5.31	132.31 ± 11.72	456.14 ± 46.65

*all data presented here are corrected from the diffusion in solution and of the ohmic losses in solution



Catalyst	Pt Specific Surface Area (m^2/g)	MA ($A\,g^{-1}_{Pt}$) @0.95 V	Current Density ($\mu A\,cm^{-2}$)	MA ($A\,g^{-1}_{Pt}$) @0.90 V	Current Density ($\mu A\,cm^{-2}$)
Pt/Ru-TiO_2	36.69 ± 10.82	31.15 ± 1.59	89.88 ± 25.45	151.2 ± 11.36	461.04 ± 125.36
Pt-Ni/Ru-TiO_2	7.97 ± 1.76	18.18 ± 1.38	238.13 ± 67.99	63.50 ± 6.10	868.96 ± 273.22

*all data presented here are corrected from the diffusion in solution and of the ohmic losses in solution

Accomplishments and Progress

Electrochemical Characterization: Discussion

- Using appropriate synthesis methods, UCI is able to deposit Pt-Ni alloy catalysts on the WashU metal oxide supports to yield viable catalysts.
- Optimization remains to be done to further increase mass activity, but the first estimates of mass activity are quite promising
- Sb-SnO_2 supports are the primary target here given cost considerations.
- Nb-TiO_2 and Ta-TiO_2, two other candidates, had issues with electrical conductivity.

Reviewer Comments

Rotating disk electrode results show better mass activity for Pt/aerogel-NbTiOx. However, the MEA performance is well below that of Pt/C. Even worse, the durability of the Pt/aerogel is substantially worse. Comments were made that this is due to loss of conductivity, which is likely going to happen under other conditions as well. Thus, these materials do not seem overly promising for long-term durability. Therefore, it seems like work can end on these materials.

We are on our way to down-selecting with ATO emerging as a prime candidate. Early alloy work also supports this choice.

In the future, load-cycling data should be discussed to confirm that these catalysts and supports are also effective for the drive-cycle requirements. It is good that the project is presenting cost modeling results; however, the team needs to consider the system mitigation cost, not a stack replacement, as the baseline. It is known publicly that Toyota and General Motors have system mitigation strategies that would not require a stack replacement. Determining the cost of this mitigation may not be easy, but some type of estimate should be derived to determine the real value of the non-carbon support.

The team will appreciate any DOE insight on the cost value of OEM mitigation system and associated mitigation cost. The team has no sources or resources to technically make these assumptions. Based on insights that we have received in private conversations with automotive OEMs (with people heavily involved in stack development), it would appear that the mitigation approaches are quite expensive (equivalent to stack cost or significant fraction thereof), and also that they can exacerbate anode catalyst corrosion. We continue to believe that a materials solution is the best approach.

Reviewer Comments

Pt alloy development should have started earlier in the project. It is doubtful the project will be able to accomplish good activity performance in such a short time before the final deliverable. There is no mention of catalyst durability testing. While the support stability seems reasonable, the Pt stability on the metal oxide supports might be affected.
It was NOT originally in the funded SOPO, we accepted modification without seeking additional funds, and with a NCE (due to moving) we will manage to do it!

Preparing Pt-alloy can lead to improved mass activity and meeting the project milestone of achieving 0.3 A/mgPGM. However, the PI did not specify the type of Pt-alloy catalysts that the project will prepare in the third year.
We will begin with Pt-Ni, as shown in our results.

Collaboration

Washington University in St. Louis

- *__Lead PI and Technical PoC__*: **Vijay K. Ramani**, Roma B. and Raymond H. Wittcoff Professor of Washington University in St. Louis
- Metal oxide synthesis and characterization, RDE testing (ORR activity and electrochemical stability), PEFC evaluation

Nissan Technical Center, North America

- PI and Technical PoC: **Nilesh Dale** (Manager-Fuel Cell and Business Research)
- Electrochemical evaluation of the catalysts in PEMFC

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- *__PI and Technical PoC__*: **Plamen Atanassov** (Chancellor's Professor)
- Modeling of doped MO conductivity and SMSI (DFT), scale-up of doped metal oxide synthesis

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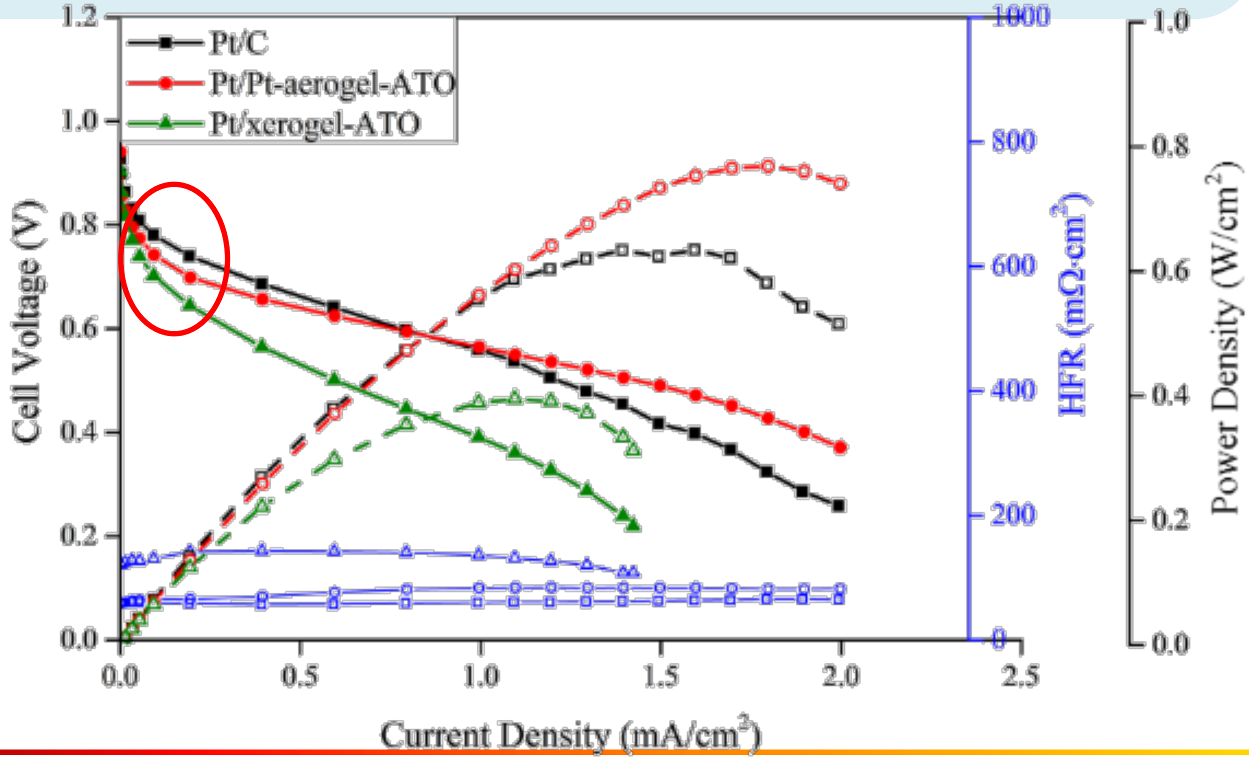
Remaining Challenges and Barriers

- Enhance the mass activity in low current region and retain stability at the same time.
- Optimize the ionomer loading in fuel cell for the metal oxide supported catalyst



Remaining Challenges and Barriers

- We will need to optimize the synthesis of Pt-alloy catalysts on our stable supports (likely Sb-SnO_2) – this was an addition to the project scope and we are underway to accomplish this with a NCE.

- Both Microwave-assisted polyol synthesis and ALD methods are in use to accomplish this task

- The alloy catalysts will provide a pathway to meeting remaining activity milestones.

Proposed Future Work

FY 2020/21

- WUSTL: Materials synthesis and characterization
  - ✓ Support UCI efforts to prepare Pt-Alloy/MO_x support catalysts by providing adequate quantities of support.

- Nissan North America Inc.: durability/performance testing
  - ✓ NTCNA role is concluded. But they will serve to prepare and evaluate Pt-alloy MEAs on a no additional cost basis.
- University of California, Irvine
  - ✓ Pt-alloy catalyst deposition on WUSTL supports using ALD and microwave-assisted polyol synthesis methods
  - ✓ Physico-chemical and electrochemical characterization of synthesiszed Pt-alloy catalysts
  - ✓ Providing catalyst to NTCNA for MEA fabrication and evaluation

Summary

- **Objectives and approach:**
  - Synthesize doped metal oxides and Pt seeded metal oxide for catalyst supports.
  - High conductivity, BET surface area, and high porosity.
  - Exhibits SMSI and corrosion resistance (attaining DOE 2020 targets)
- **Relevance**
  - Material-level mitigation strategies can solve cathode durability issues
- **Accomplishments**
  - Pt deposited on Niobium doped titanium oxides shown high mass activity in the fuel cell in kinetic region. NTO – not stable in MEA. ATO is highly stable.
  - Added 1wt% Pt as seed during aerogel ATO synthesis (Pt-aerogel-ATO) to engineer the morphology and crystal structure of the. Met durability target in fuel cell test.
  - **ALD and microwave-assisted poyol synthesis used to deposit Pt-alloy catalysts onto ATO supports**
- **Collaborations**
  - Washington University in St. Louis
  - Nissan Technical Center, North America
  - University of California, Irvine