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Corrosion-Resistant Non-Carbon Electrocatalyst Supports for PEFCs

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

Project # FC145

Date: 05/01/2019

Overview

Timeline and budget

Competitively selected project

- Project start date: 03/01/16
- Project end date: 03/31/20
- Total project budget: $ 3,397,431
    - Total recipient share: $ 397,431
    - Total federal share: $ 3,000,000
    - Total DOE funds spent**: $ 1,950,000

* ** As of 2/28/19.

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

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Collaboration

Washington University in St. Louis

- *<u>Lead PI and Technical PoC</u>*: **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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- *<u>PI and Technical PoC</u>*: **Plamen Atanassov** (Chancellor's Professor)
- Modeling of doped MO conductivity and SMSI (DFT), scale-up of doped metal oxide synthesis

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Relevance

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 1Acm^{-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

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Approach

Milestones

2nd Year	Q5	Demonstrate SMSI as ascertained by Pt d-band filling (XPS)	(100%)
		Meet durability target in RDE (ECSA Loss <5% - 10,000 start-stop cycles)	(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}	(100%)
		Meets stability and durability in RDE per DOE metrics (ECSA Loss <5%)	(100%)
	Q8	20-40wt%Pt; Surface area> 70 m^2 g^{-1} Pt particle size 3-6nm;	(100%)
		Meets DOE 2020 durability targets in RDE and MEA	(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)	(ongoing)
	Q3	Specify cost of best 2 Pt/DS materials	(ongoing)
	Q4	Meet “End Project” durability, activity, and performance targets in Table 2	(ongoing)

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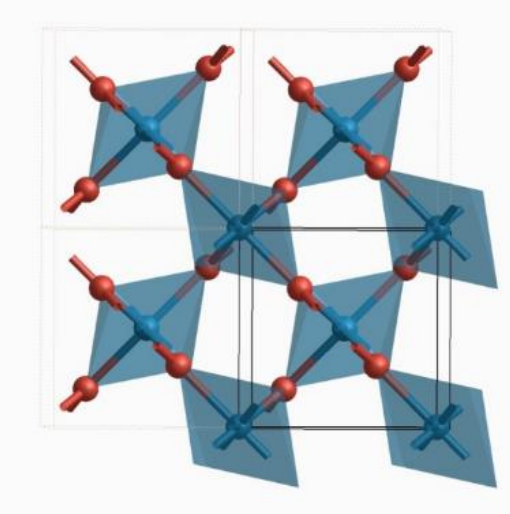
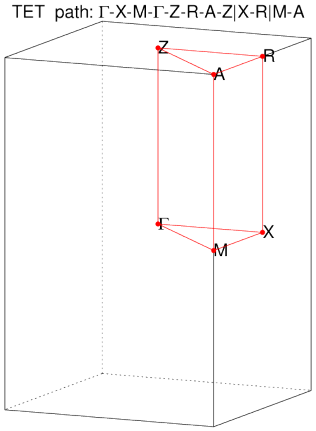
Approach

Density Functional Theory - Doping of TiO_2 with Ta

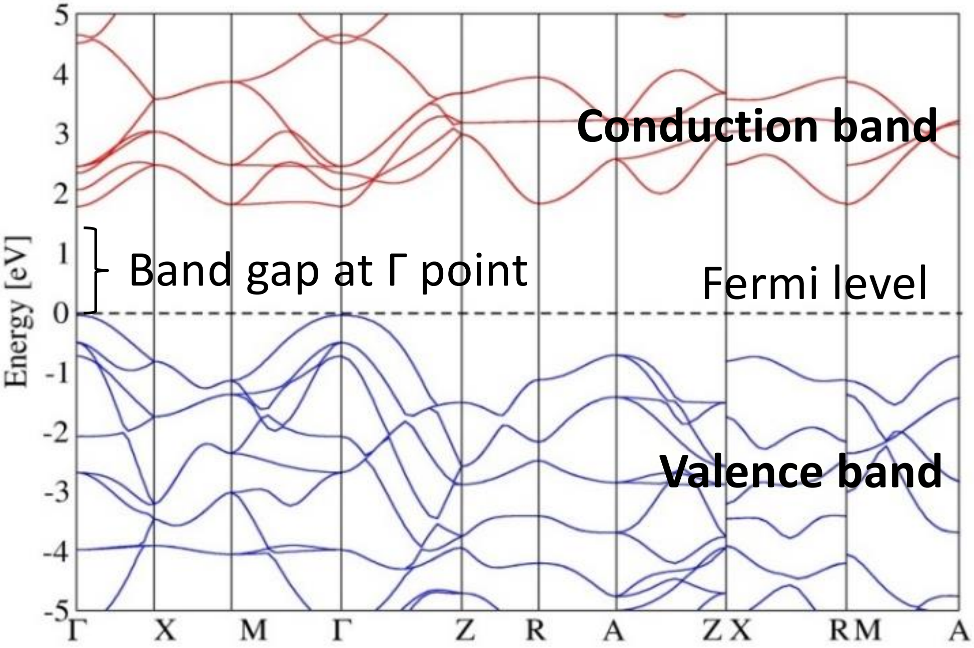
Change in the electronic structure of supports as a result of doping





DFT optimized structure of TiO_2 (PBEsol functional). Cell parameters *a*=4.56, *b*=4.56, *c*=2.93 Å

red – O, blue - Ti

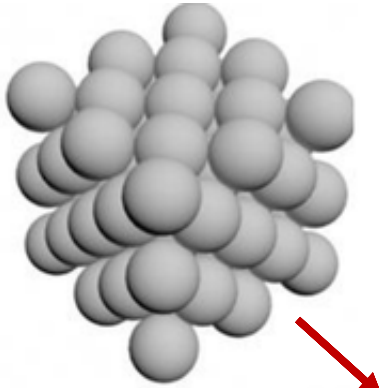


DFT calculated band structure of TiO_2. Top HSE06 level, bottom PBEsol level

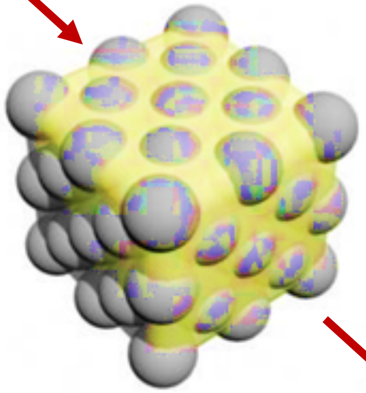
- TiO_2 is **a semiconductor, absorbs in UV.**
- Direct B-G of 1.82 eV at PBEsol level, 3.44 eV at HSE06 level (hybrid functional needed).
- Experimental reports 3.3-3.6 eV (UPS-IPS spectroscopy).

Approach

Design Porous TiO_2 supports



Silica template



Infiltration of TiO_2 support via ultra sonication, followed by pyrolysis

Leaching the sacrificial silica support: Porous TiO_2 support

Synthesis and characterization of high surface area TiO_2 supports.

(i) Synthesis of TiO_2 support.

- sol−gel technique
- alkoxides titanium as precursors

ii Sacrificial support method (Templating)

- Cab-O-Sil L90 surface area ~90 m^2 g^{-1}, 0.22 μm
- Cab-O-Sil EH5, surface area ~400 m^2 g^{-1}, 0.14 μm
- pyrolyzed at 850°C followed by leaching with 40 wt.% HF

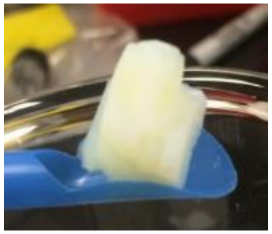
iii Characterization of TiO_2 support

- Morphology: SEM, N_2-sorption BET surface area, pore size analysis
- Composition: EDS, XPS, Elemental Mapping
- Structure : XRD
- electron conductivity (in-house test cell)

Approach

Support Synthesis and Pt deposition strategy

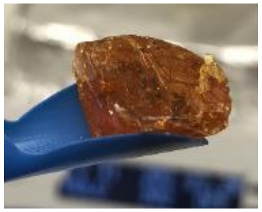
Wet gel



aerogel

Pros: High surface area and porosity

Cons: Lower conductivity can affect catalyst layer resistance



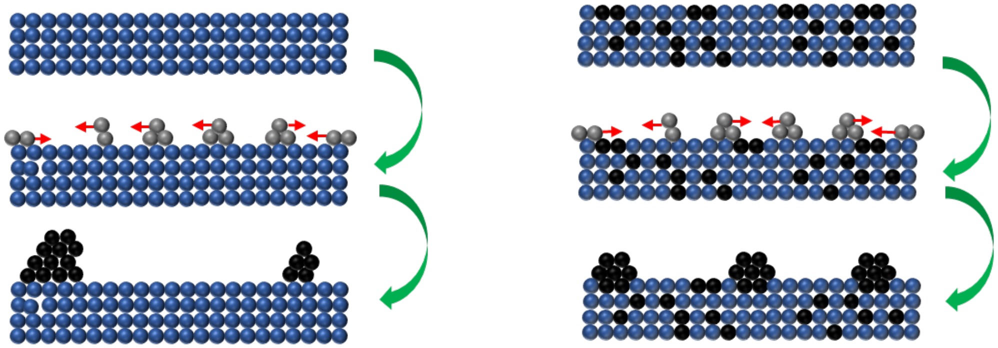
xerogel

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

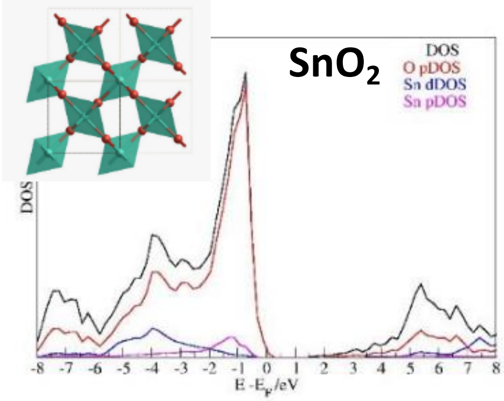


Pt deposition

- Atomic layer deposition
- Colloidal method
- Polyol method

Accomplishments and Progress

Pt on Sb-doped SnO_2 - electronic structure, reactivity, and durability



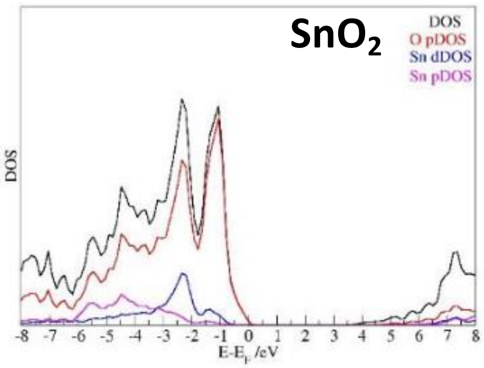
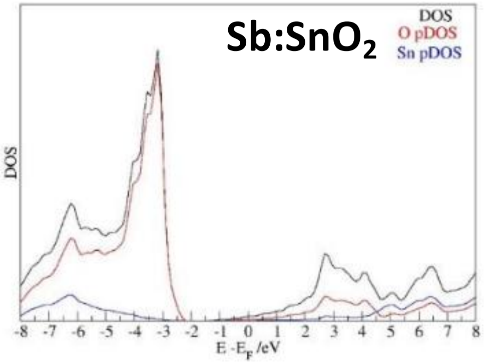


Figure. DFT calculated electronic structure of SnO_2 and SnO_2 doped with 4% Sb. Left PBE functional; Right PBE+U (U=7.7)



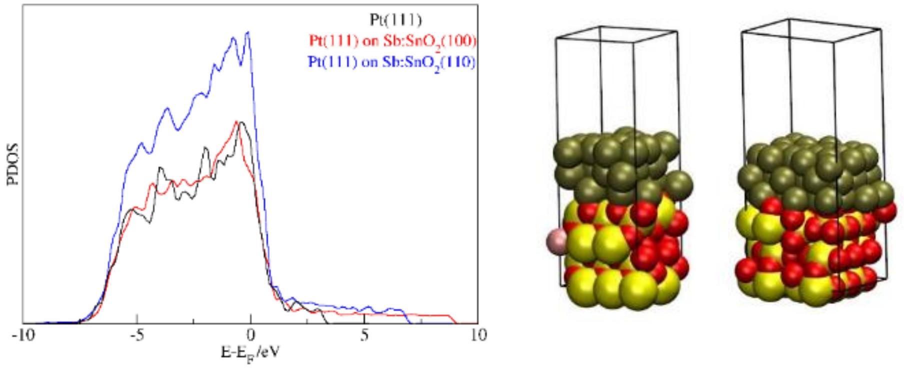


Figure. Projected Density of States of Pt(111) supported on $Sb{:}SnO_2$(100) and $Sb{:}SnO_2$(110).

d-band center relative to the Fermi level

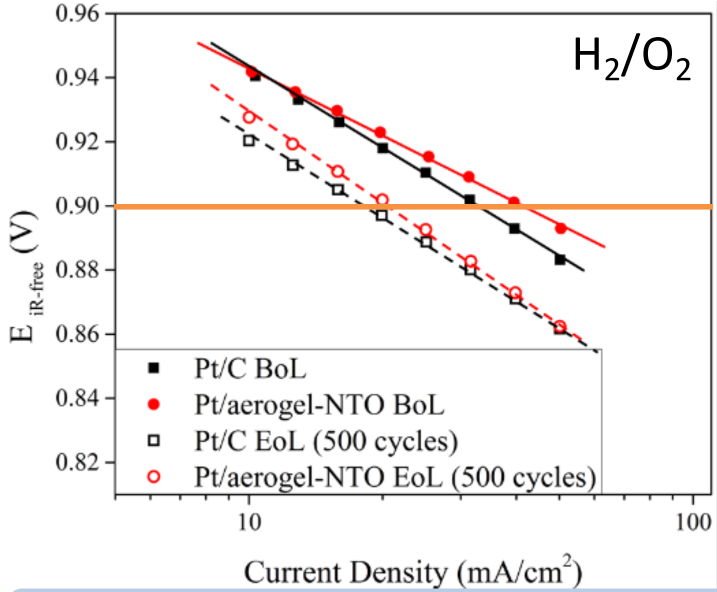
ε_d-E_F= -2.02 eV for Pt(111)
ε_d-E_F= -1.96 eV for Pt(111) on $Sb{:}SnO_2$(100)
ε_d-E_F= -2.06 eV for Pt(111) on $Sb{:}SnO_2$(110)

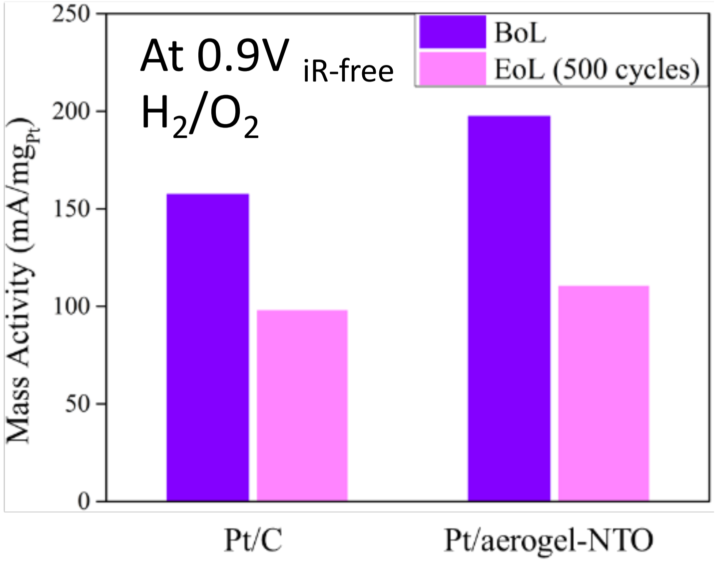
- SnO_2 is **a semiconductor,** with a band gap of 3.5 eV at PBE+U level (exp value 3.6 eV);
- Sb:SnO2 (4% doping) is a **n-type semiconductor** → good agreement with experiment and previous theoretical calculations

- Strong interaction between Pt(111) and $Sb{:}SnO_2$ predicted, -0.13 eV/atom
- ORR overpotential on supported Pt(111) similar to that of unsupported Pt(111); larger stability expected

Accomplishments and Progress

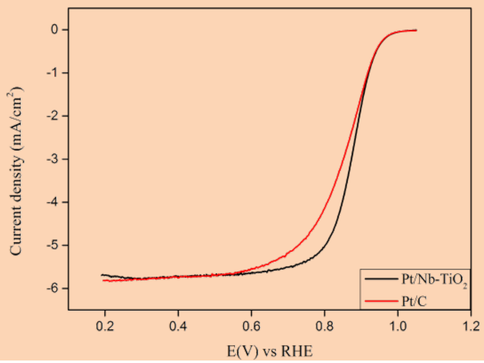
Fuel cell evaluation at 80°C for MEA with Pt/aerogel-NTO at cathode





Comparison of IV performance obtained Pt/C and Pt/aerogel-NTO at 80°C with 100kPa back pressure, 100%RH. Cathode loading: 0.2 mg_{Pt}/cm^2

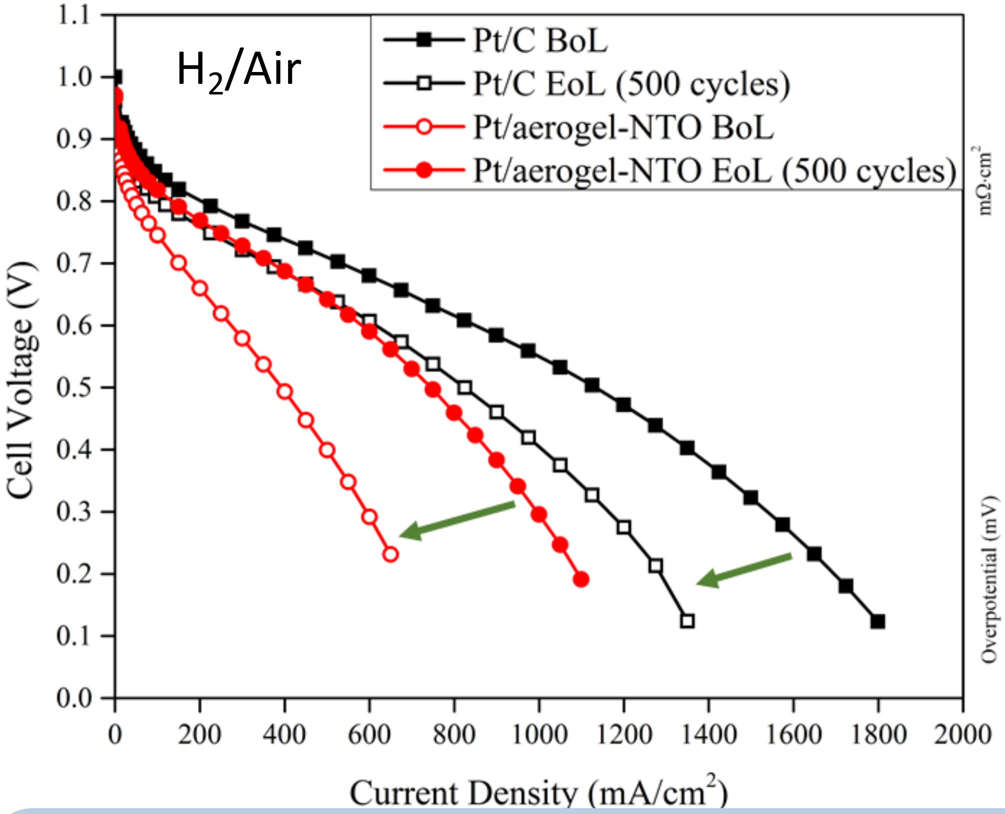
2018AMR

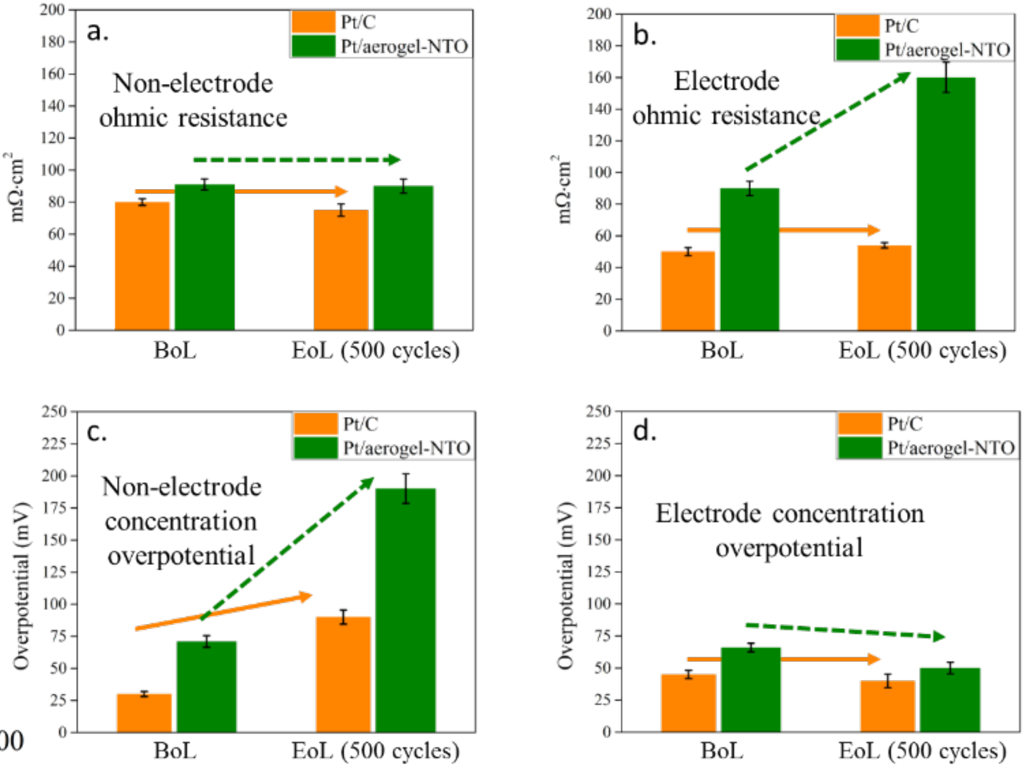


The better mass activity of Pt/aerogel-NTO has been successfully transferred from RDE to fuel cell

Accomplishments and Progress

Fuel cell evaluation at 80°C for MEA with Pt/aerogel-NTO at cathode(H_2/Air)





Comparison of IV performance obtained Pt/C and Pt/aerogel-NTO before (closed symbols) and after (open symbols) start-stop protocol 500 cycles (for Pt/ATO) at 80°C with 100kPa back pressure, 100%RH. Cathode loading: 0.2 mg_{Pt}/cm^2

- Pt/aerogel-NTO is not as stable as Pt/C under start-stop stability test condition
- The loss of aerogel-NTO conductivity affects fuel cell stability

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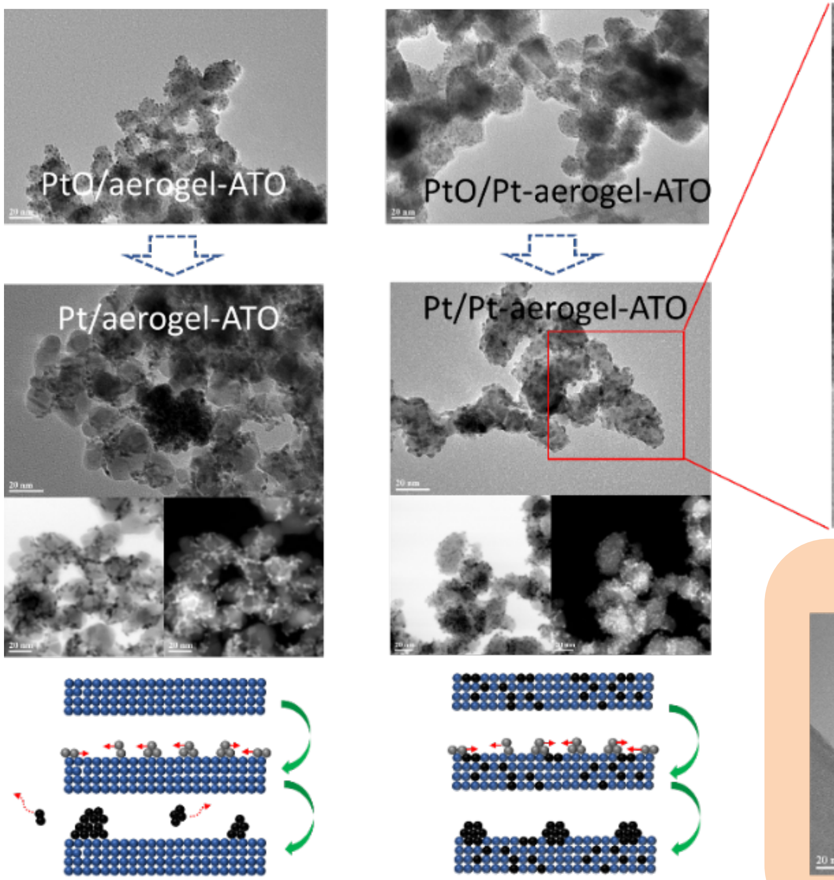
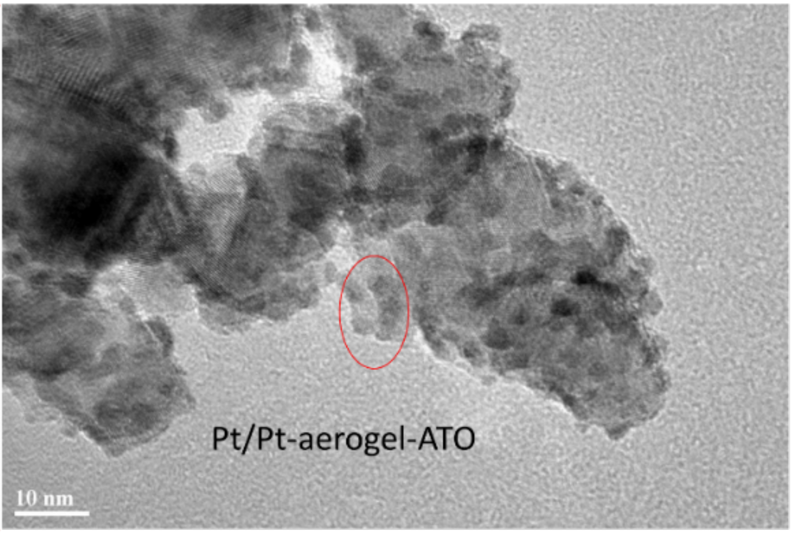
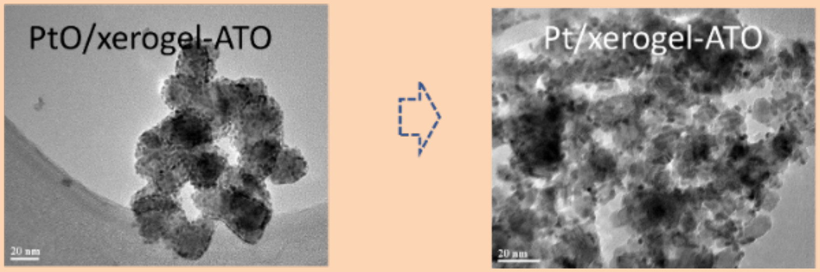
Accomplishments and Progress

Physical characterization of ATO based support





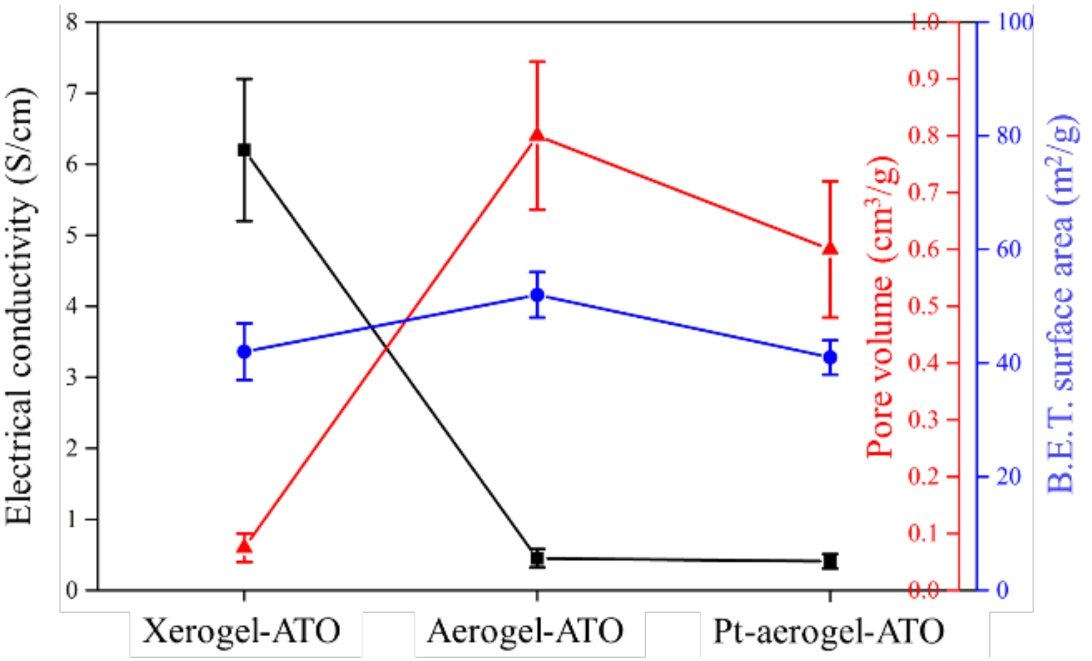
AMR 2018 sample

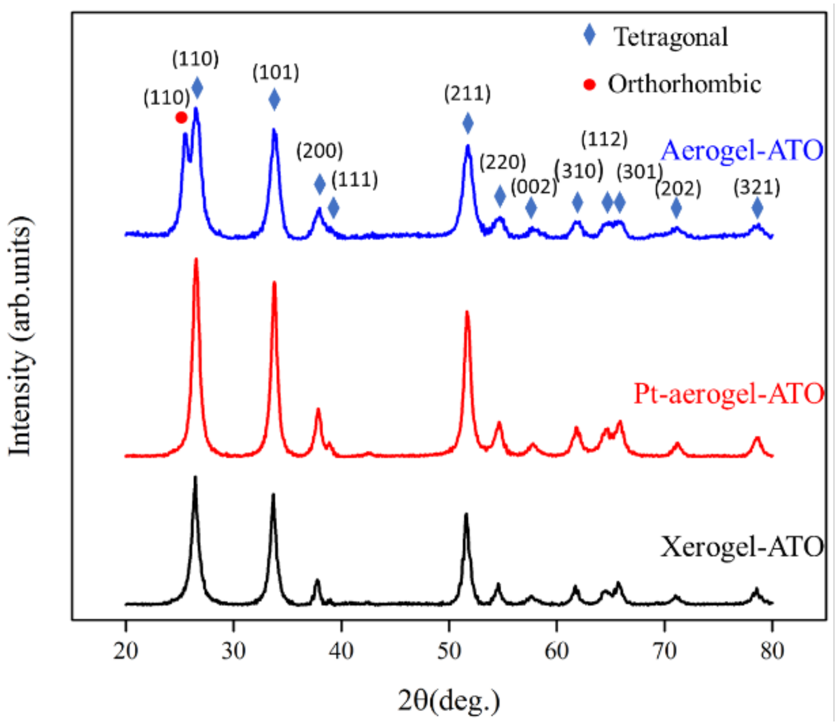


1wt% Pt was added as seed during aerogel ATO synthesis (Pt-aerogel-ATO) to engineer the morphology of the surface.

Accomplishments and Progress

Physical characterization of ATO based support

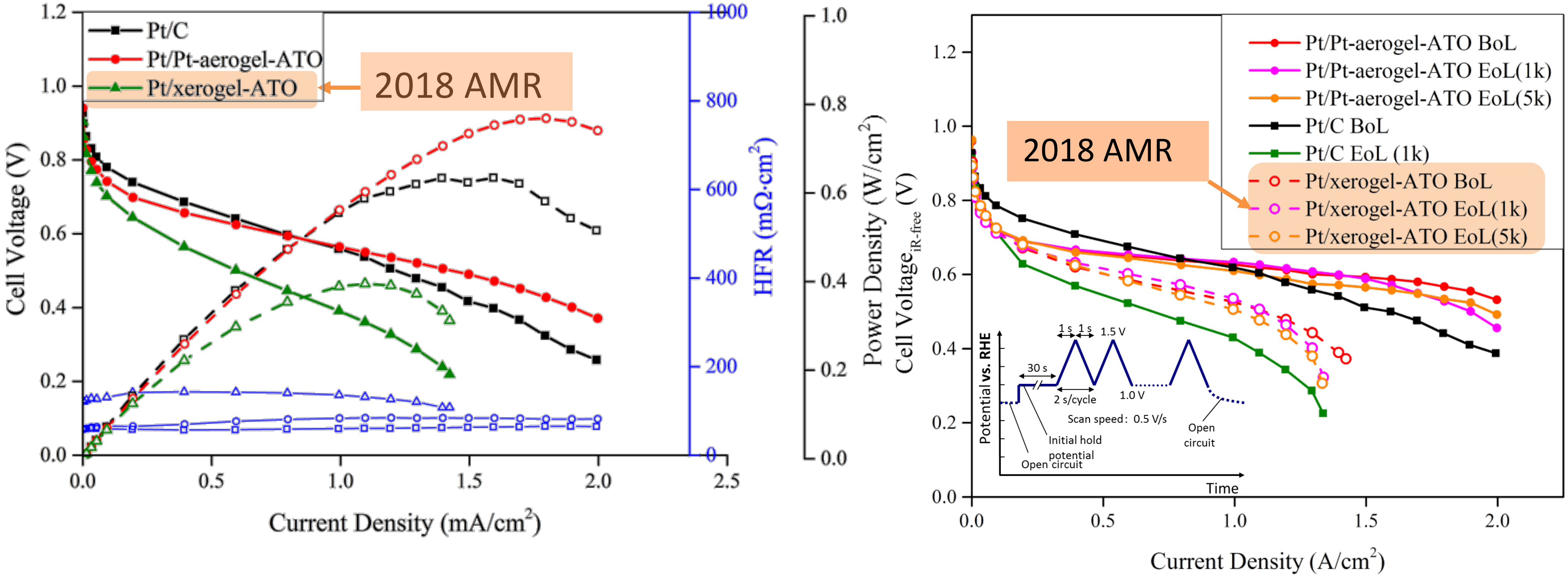




- We added 1wt% Pt as seed during aerogel ATO synthesis (Pt-aerogel-ATO) to engineer the morphology of the support.
- The big difference in lattice constants and diffraction peaks between aerogel-ATO and Pt-aerogel-ATO indicated that Pt seed affected the ATO nucleation during the annealing process and modified the crystal structure of the material.

Accomplishments and Progress

Pt-aerogel-ATO MEAs exhibit excellent performance and durability



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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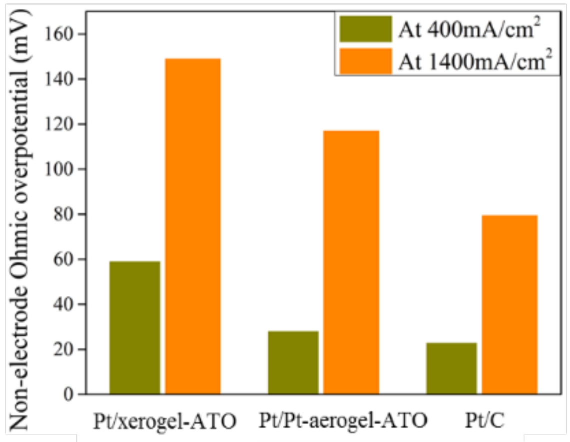
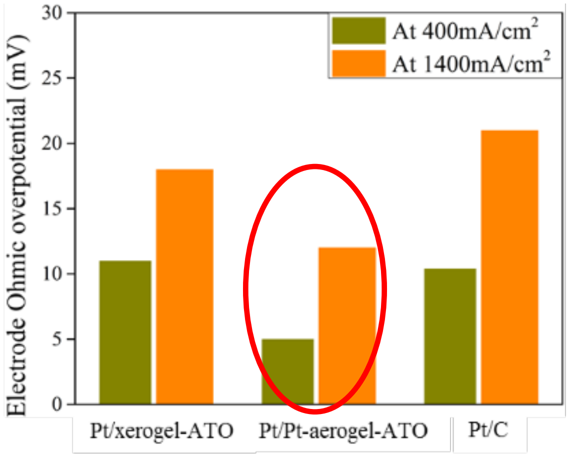
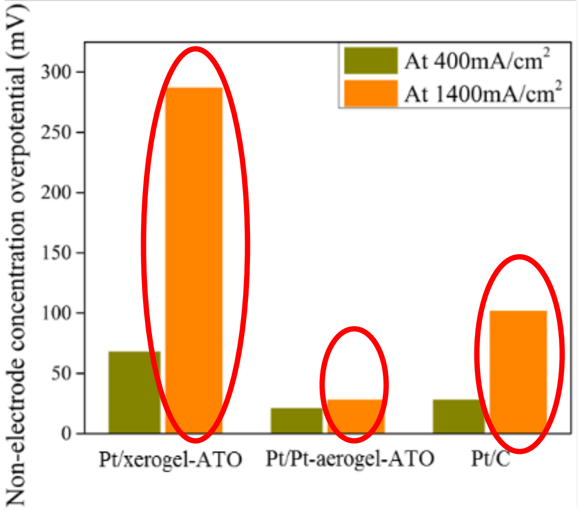
Accomplishments and Progress

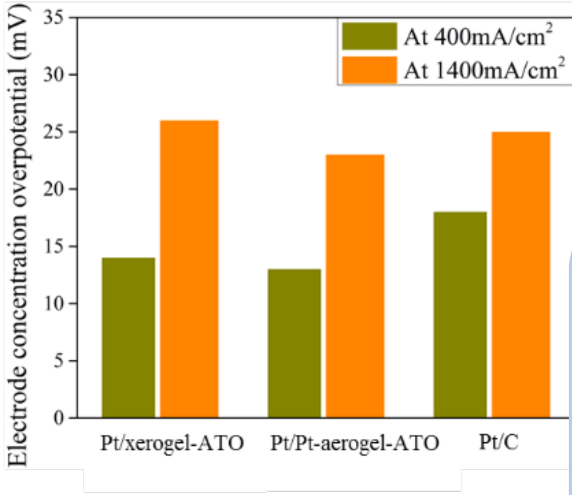
Fuel cell overpotential loss analysis

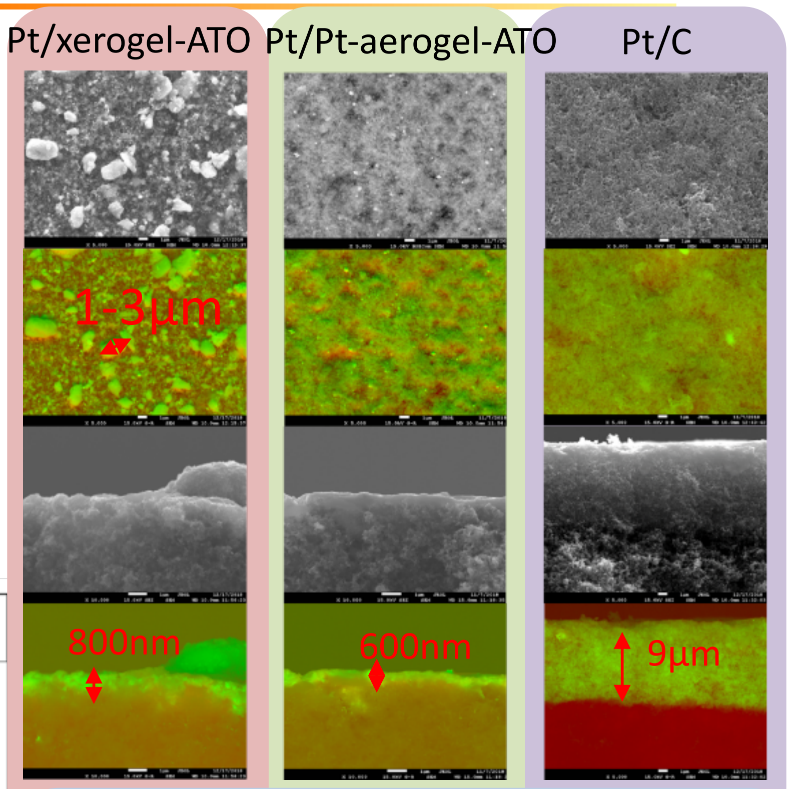
Pt-aerogel-ATO minimized mass transfer resistance and electrode Ohmic resistance











- Lower electrical conductivity of ATO support didn't affect the fuel cell performance.
- Uniform catalyst layer with optimized ionomer coverage will help solve the mass transfer issues at high currents.

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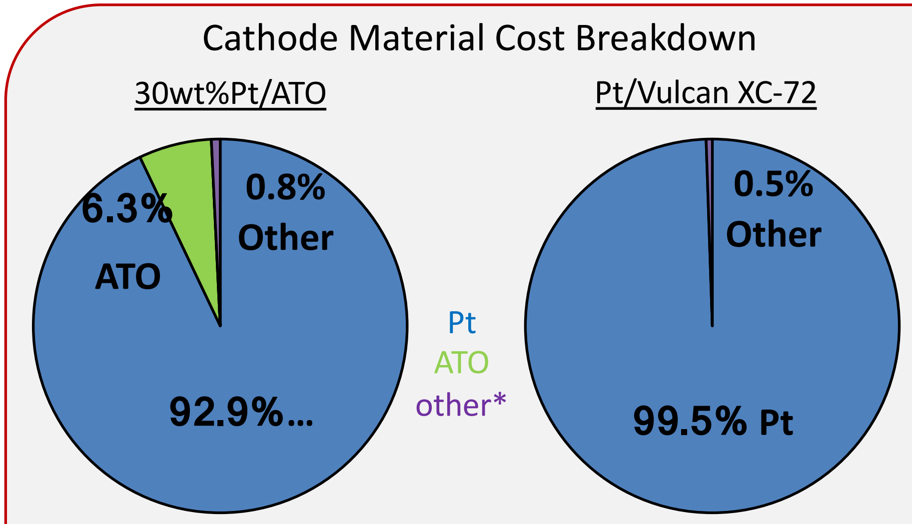
Accomplishments and Progress

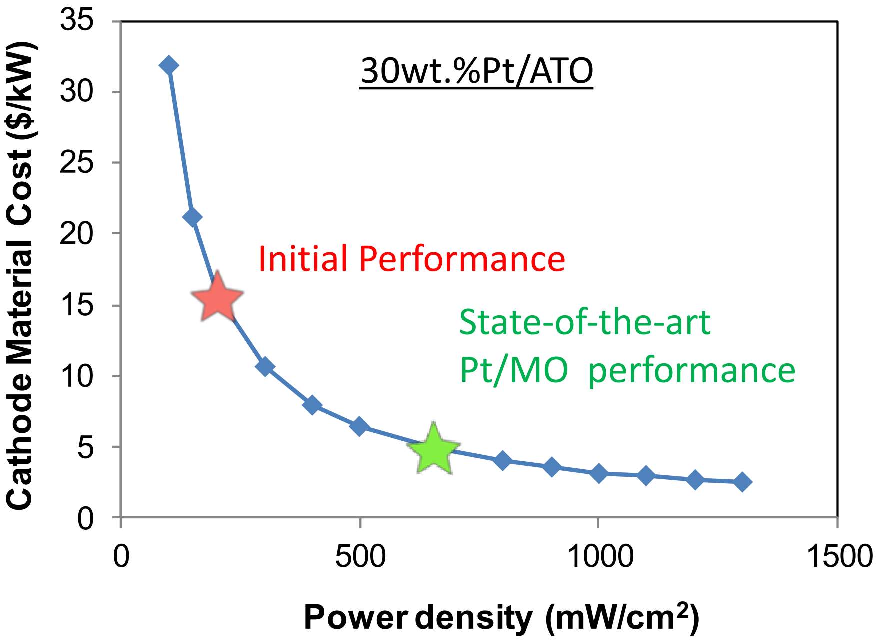
Preliminary Cost Model: Pt/ATO catalyst

- **Assumptions :**
  - **With the exception of the Cathode, the rest of the MEA is identical (anode, membrane, GDL, etc.)**
  - **Rated Power is at 80°C & 100%RH (to make use of performance data from Nissan testing)**
  - **All cells in the stack are operating identically**
  - **Processing costs (cathode ink manufacturing, catalyst application) are equal**
- **The only differences in these systems comes down to material cost (Pt/ATO vs. Pt/Vulcan XC-72)**



*other includes carbon support, Nafion & solvents

- **The ATO support is more expensive than carbon, but the total material cost is still dominated by the Platinum**
- Pt still accounts for ~93% of the cathode material cost



Cost estimates based on projected performance improvements

† James, B.D.; Mass Production Cost Estimation for Direct H_2 PEM Fuel Cell Systems for Automotive Applications: *2008 Update*

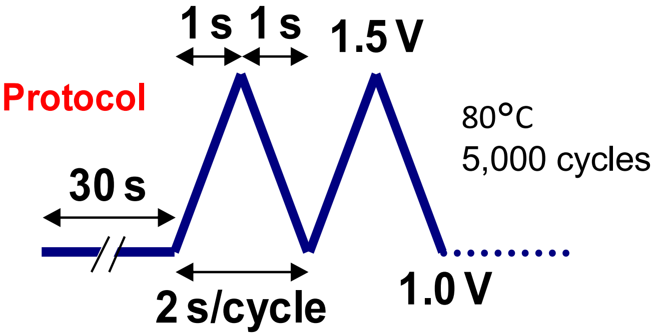
Accomplishments and Progress

Preliminary Cost Model:

Durability Considerations for Cost - Pt/ATO w/current status

The major advantage of a non-carbon cathode support is its resistance to corrosion during start-stop cycling

- **Nissan's Start/Stop Cycling protocol is used**



	Pt/ATO	Pt/Vulcan XC-72
Cathode Pt loading (mgcm^{-2})	**0.10**	**0.16**
Rated Power (mW/cm^2)	200	1000
Pt	$1171	$333.20
ATO	$79.47	$ -
other	$3.00	$1.78
Total Material Cost ($/Stack)	$1254.31	$334.98
Total Material Cost ($/kW$_{net}$)	$15.68	$4.19
# of stacks	1	2
Total Material Cost ($/kW$_{net}$)	**$15.68**	**$8.67**

For 5000 cycle comparison

- Pt/Vulcan XC-72 MEAs do not survive for 5,000 Start/Stop cycles and therefore assuming min. 2 stacks would be required to meet the same lifetime of Pt/ATO

- w/current low performance of Pt/ATO, in FC Systems with equal lifetimes, one utilizing Pt/ATO costs more than one with Pt/Vulcan XC-72 even with min 2 stack assumed.

Accomplishments and Progress

Preliminary Cost Model:

Durability Considerations for Cost - Pt/ATO w/ state of art Pt/MO assumption

- **With improved performance and durability considered, how do the two catalysts compare?**

A Durability Factor can be calculated for each catalyst

$$\text{Durability Factor} = \frac{\text{Mass activity retention of catalyst}}{\text{Mass activity retention of Pt/ATO}}$$

	Pt/ATO (5,000 cycles)	Pt/Vulcan XC-72 (1,000 cycles)
Mass Activity retention (loss)	96%	59%
Durability Factor	1	**0.69**

- Based on this protocol, Vulcan XC-72 is only <u>69%</u> as durable as the ATO support

	Pt/ATO	Pt/Vulcan XC-72
Cathode Pt loading (mgcm^{-2})	**0.10**	**0.16**
Rated Power (mW/cm^2)	***650***	1000
Pt	\$366.81	\$333.20
ATO	\$15.99	\$ -
other	\$3.00	\$1.78
Total Material Cost (\$/Stack)	\$385.81	\$334.98
Total Material Cost (\$/kW$_{net}$)	\$4.82	\$4.19
Durability Factor	1	0.69
Total Material Cost (\$/kW$_{net}$) w/ durability	**\$4.82**	**\$6.07**

- In FC Systems, one utilizing Pt/ATO costs about <u>20% less</u> than one with Pt/Vulcan XC-72 even after 5000 cycles.
- For the durability factor we employed mass retention after 1,000 cycles for Pt/Vulvan XC-72 and after 5,000 durability cycles for Pt/ATO

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Reviewer Comments

“The initial performance of the Pt/Sb–SnO2 was much lower than that for Pt/C. Activity for the Pt/Sb–SnO2 should be reported. Performing a characterization of the pore structure would be beneficial. “

- We agree that the initial performance of Pt/xerogel-ATO was much lower than Pt/C. We are working on the aerogel-ATO as catalyst support to improve the porosity of the support and mitigate the mass transfer issues in the fuel cell. Improved results shown herein.

“However, the high resistances found in fuel cell tests and limited mass activity remain challenges with no clear path to overcoming.”

- Base on our research, the high resistances mainly come from the contact resistance between membrane and the catalyst layer. We will optimize the support structure to help achieve more uniformed catalyst layer during the fabrication process.

“Pt/Co and Pt/Ni could surpass the mass activity targets. Pt/C is likely not an appropriate comparison for the mass activity target”

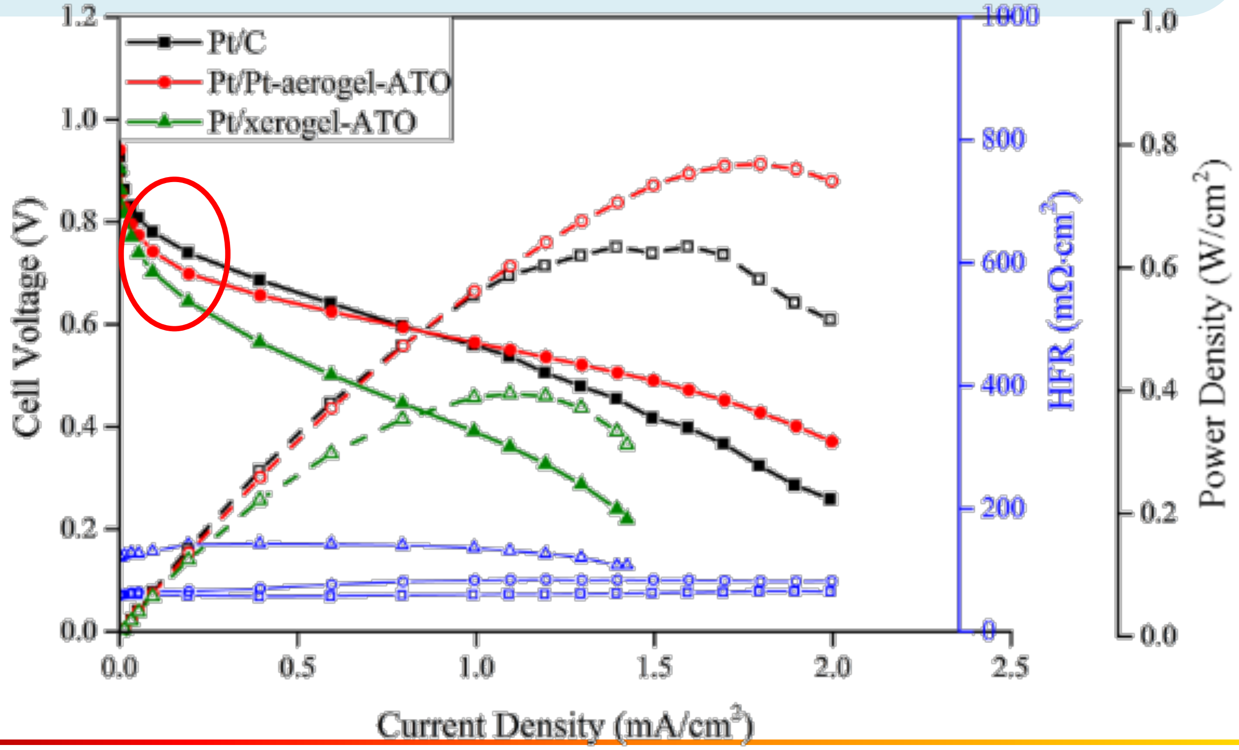
- We will be exploring this in Y3.

Remaining Challenges and Barriers

Task Number	Milestone	Milestone Description	Milestone Verification Process*	Anticipated Date
10	Milestone 10.1	Pt/DS catalyst	Demonstrate "End Project" durability metrics and at least 80% of mass activity metric	Q11
6	Milestone 6.2.2	Pt/DS catalyst	In addition to Milestone 6.2.1, meet "End Project" BoL mass activity target	Q12
11	Milestone 11.1	Deliver cost model	Specify cost of best 2 Pt/DS materials	Q13
12	Milestone 12.1 Go/No-Go	Deliver six 50 cm^2 active area MEAs to DOE	Meet "End Project" durability, activity, and performance targets in Table 2	Q14

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



Proposed Future Work

FY 2019 (Any proposed future work is subject to change based on funding level)

- WUSTL: Materials synthesis and characterization
  - ✓ Deposit the **Pt alloy** on the stable metal oxide support to achieve higher mass activity and better fuel cell performance.
  - ✓ Optimized the Pt seeded loading to get uniform seeded metal oxide materials to help atomic layer deposition (ALD) process.

- Nissan North America Inc.: durability/performance testing
  - ✓ Optimize the MEA fabrication process
  - ✓ Accelerated test protocols on materials provided by WUSTL
  - ✓ Fabrication / testing of sub-scale and 50 cm^2 MEAs
- University of California, Irvine
  - ✓ DFT calculations: conductivity and SMSI of relevant doped metal oxides
  - ✓ Characterization of the doped metal oxides and derived catalysts
  - ✓ High surface area support synthesis by SSM.
  - ✓ Pt deposition optimization by colloidal and ALD routes

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 support to mitigate the mass transfer issues in the fuel cell. Met durability target in fuel cell test.
- **Collaborations**
    - Washington University in St. Louis
    - Nissan Technical Center, North America
    - University of California, Irvine

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