Corrosion-Resistant Non-Carbon Electrocatalyst Supports for PEFCs

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Project # FC145

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Date: 06/14/2018

Overview

Timeline and budget

Competitively selected project

- Project start date: 03/01/16*
- Project end date: 08/31/19+
- Total project budget: $ 3,397,431
  - Total recipient share: $ 397,431
  - Total federal share: $ 3,000,000
  - Total DOE funds spent**: $ 1,350,000

* Official date of contract from DOE. Issue of sub-contracts were finalized on April 15th 2016. Kick-off meeting held on April 21st 2016

+ Reflects a 6-month no-cost extension granted due to PI move to WashU

** As of 2/28/17.

Barriers to be addressed:

- Durability
- Performance
- 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 New Mexico

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)**	End target	DOE 2020 target
Total PGM content	g kW^{-1}	0.55	0.55	Not Available	0.25	<0.125
Total PGM loading	mg cm^{-2}	0.4	0.4	0.6	0.25	<0.125
Voltage at 1.5 A cm^{-2} (air)	V	0.45	0.48	0.3	0.55	N/A
Loss in mass activity [a,b]	% loss	32	33	<10%	<5%	<40
Voltage loss at 0.8 A cm^{-2} [a]	mV	81	9	< 15	<10	30
Voltage loss at 1.5 A cm^{-2} [b]	mV	182[+]	20	N/A; 20 mV at 1Acm^{-2}	<20	30
Mass activity@900 $mV_{iR\text{-}free}$ [c]	A mg^{-1}_{PGM}	0.07	0.07	ca. 0.05	0.3	0.44

[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

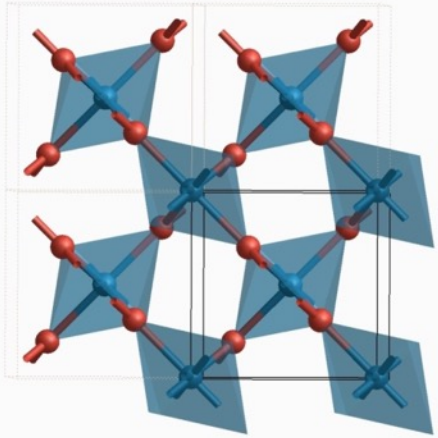
Milestones

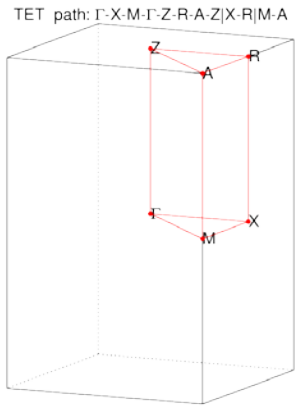
1th Year	Q1	• 2g Ta-doped TiO_2 (or similar) • B.E.T. surface area >30 m^2g^{-1} ; Electronic conductivity > 0.2 S cm^{-1}	(100%) (100%)
	Q2	• 2g stable doped metal oxide • B.E.T. surface area > 30 m^2 g^{-1}; Electronic conductivity >0.2 S cm^{-1}	(100%) (100%)
	Q3	• 2g TiO_2 using SSM (or similar) • B.E.T. surface area >50 m^2 g^{-1}; Particle size <70nm	(100%) (100%)
	Q4	• 2g Ta-doped TiO_2 support using SSM(or similar) • B.E.T. area >50 m^2 g^{-1}; Particle size <70nm, conductivity > 0.2 S cm^{-1}	(100%) (100%)
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	(80%) (100%)

Approach

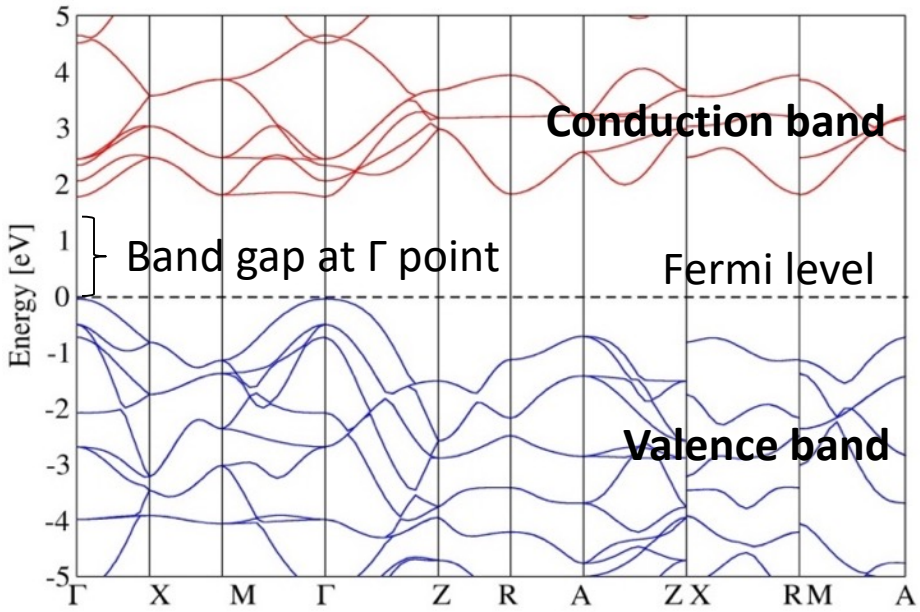
Density Functional Theory - Doping of TiO_2 with Ta

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

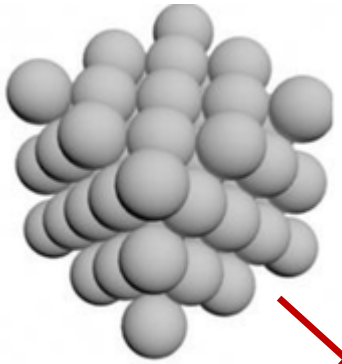


DFT calculated band structure of TiO_2. Top HSE06 level, bottom PBEsol level

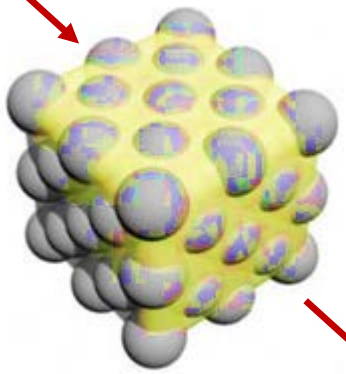
- TiO_2 is **a semiconductor, absorbs in UV.**
- Direct B-G of 1.82 eV at PBEsol level, 3.44 eV at HSE06 level (hybrid functional needed).
- Experimental reports 3.3-3.6 eV (UPS-IPS spectroscopy).

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

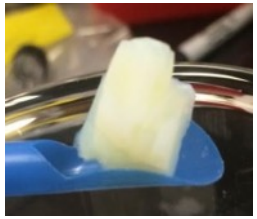
iii Characterization of TiO_2 support

- 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

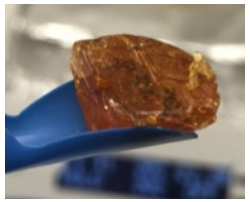
Support Synthesis and Pt deposition strategy

Wet gel



aerogel

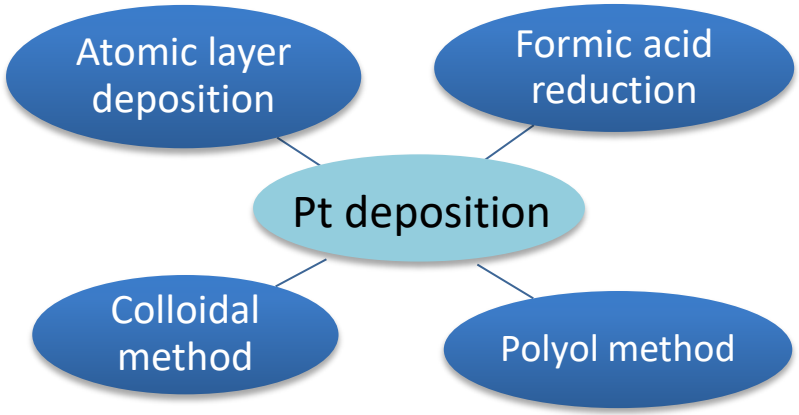
Pros: High surface area and porosity
Cons: Lower conductivity can affect catalyst layer resistance



xerogel

Pros: High conductivity
Cons: Lower porosity and partial agglomeration can affect MEA fabrication and increase mass transfer resistance in fuel cell

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

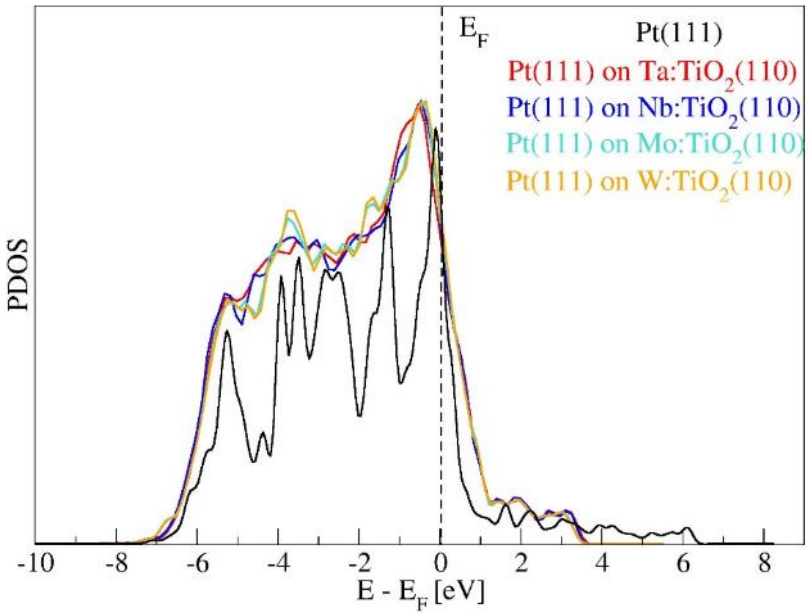


Based on different surface properties, different deposition methods were used to obtain small Pt particle size and well dispersed Pt clusters

- Atomic layer: Pt precursor absorbed
- Colloidal method :PtO_2 absorbed
- Formic acid reduction: Acidic environment
  Polyol method : Alkaline environment

Accomplishments and Progress

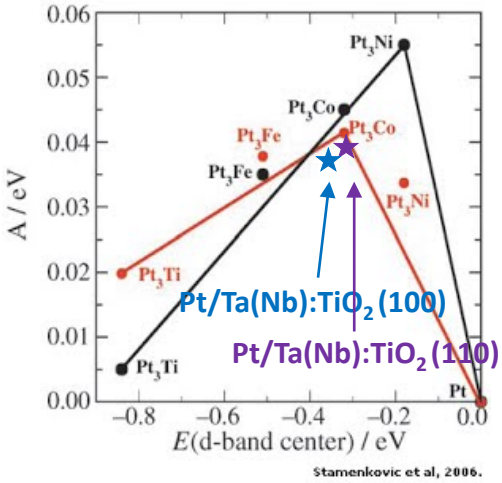
Pt on TiO_2 doped with Ta, Nb, W, and Mo



Projected Density of States (PDOS) of Pt(111) and Pt(111) on TiO_2(110) doped with 4% Ta, Nb, Mo, and W

d-band center relative to the Fermi level

ε_d-E_F= -2.02 eV for Pt(111)
ε_d-E_F= -2.34 eV for Pt(111) on Ta:TiO2(100)
ε_d-E_F= -2.28 eV for Pt(111) on Ta:TiO_2(110)
ε_d-E_F= -2.32 eV for Pt(111) on Nb:TiO2(100)
ε_d-E_F= -2.29 eV for Pt(111) on Nb:TiO_2(110)
ε_d-E_F= -2.28 eV for Pt(111) on Mo:TiO2(100)
ε_d-E_F= -2.27 eV for Pt(111) on Mo:TiO_2(110)
ε_d-E_F= -2.30 eV for Pt(111) on W:TiO2(100)
ε_d-E_F= -2.26 eV for Pt(111) on W:TiO_2(110)



- **TiO_2 support beneficial for the activity of Pt towards ORR**
  > depositing Pt on doped TiO_2 lowers the d-band center by altering its electronic structure
- DFT predicted ORR activity trend: Pt on Ta/Nb/Mo/W:TiO_2(110) > Ta/Nb/Mo/W:TiO_2(100) > Pt

Accomplishments and Progress

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

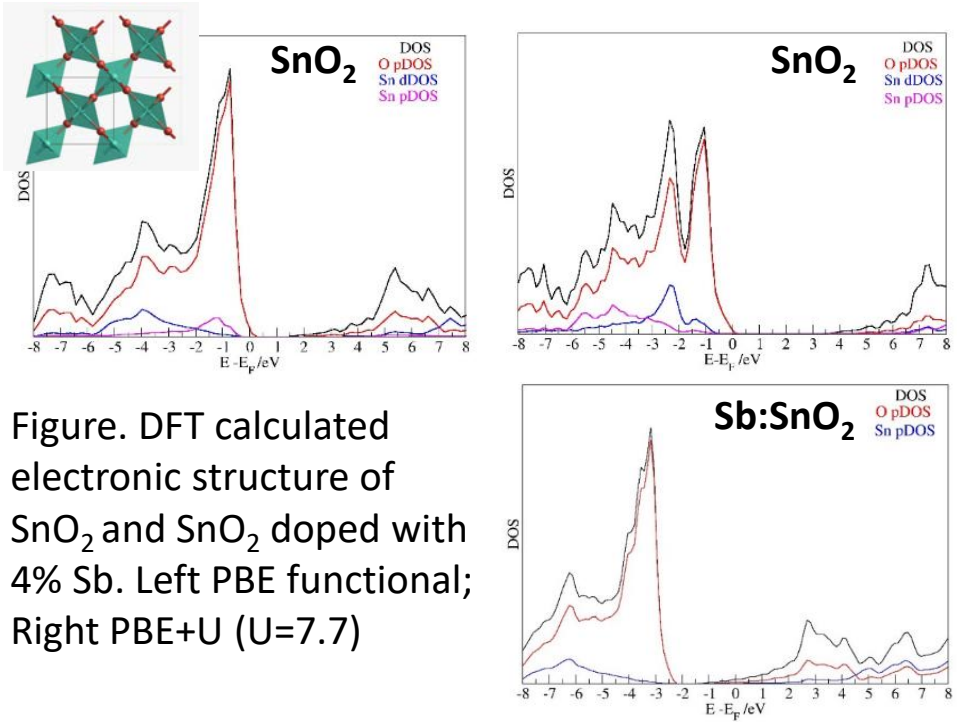


Figure. DFT calculated electronic structure of SnO_2 and SnO_2 doped with 4% Sb. Left PBE functional; Right PBE+U (U=7.7)

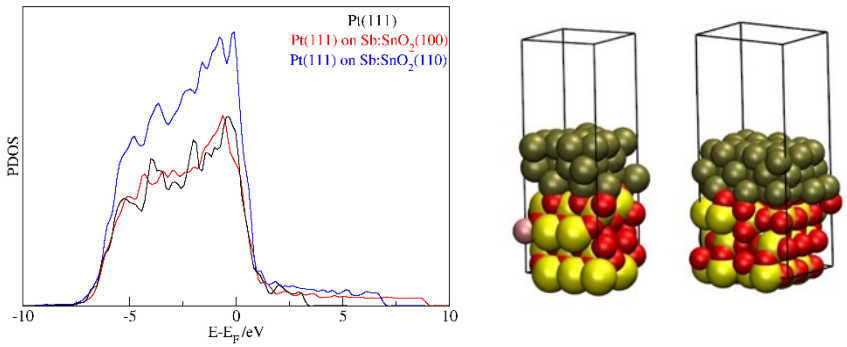


Figure. Projected Density of States of Pt(111) supported on $Sb:SnO_2(100)$ and $Sb:SnO_2(110)$.

d-band center relative to the Fermi level

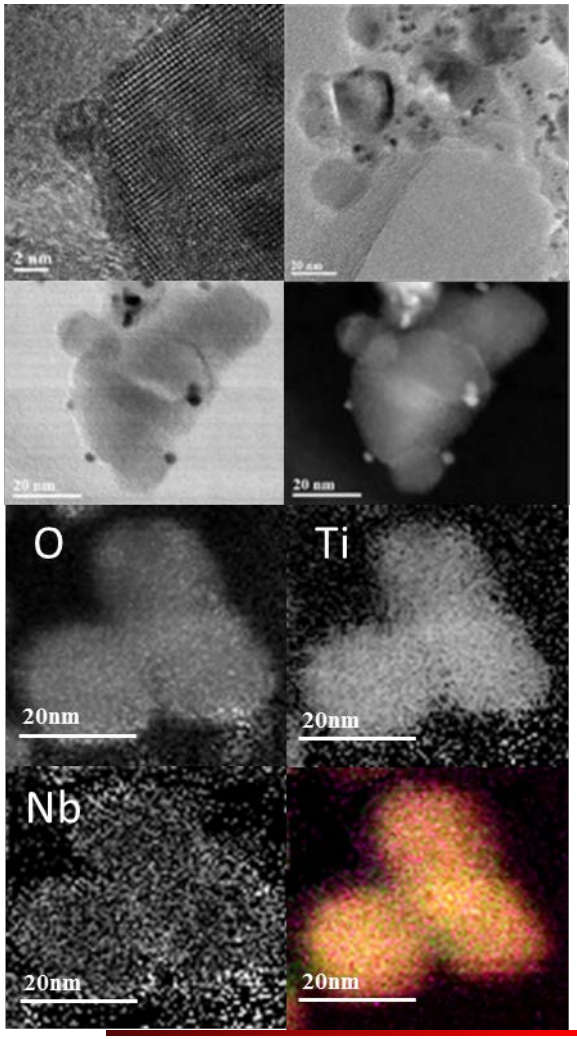
ε_d-E_F= -2.02 eV for Pt(111)
ε_d-E_F= -1.96 eV for Pt(111) on $Sb:SnO_2(100)$
ε_d-E_F= -2.06 eV for Pt(111) on $Sb:SnO_2(110)$

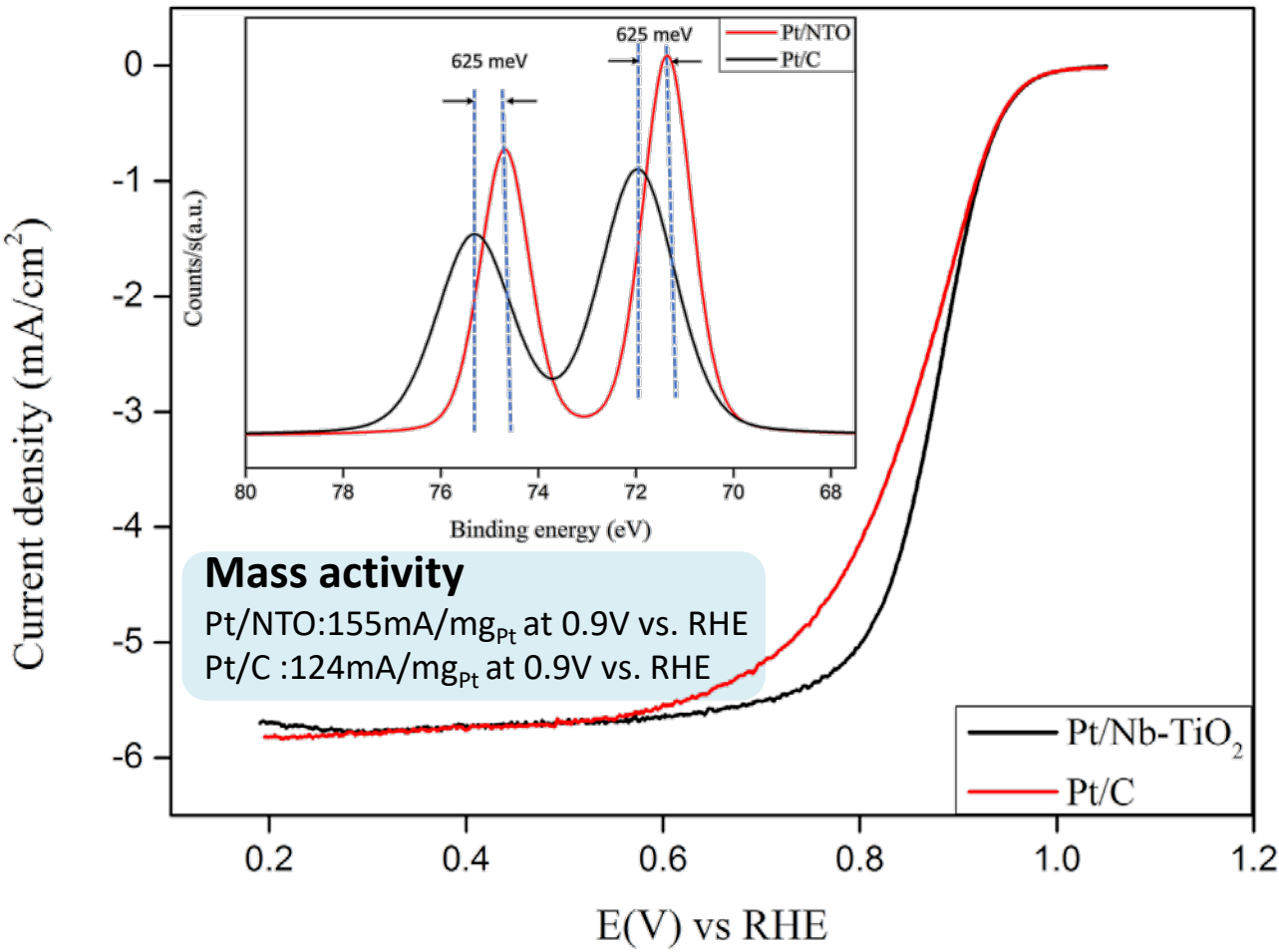
- SnO_2 is **a semiconductor,** with a band gap of 3.5 eV at PBE+U level (exp value 3.6 eV);
- Sb:SnO2 (4% doping) is a **n-type semiconductor** → good agreement with experiment and previous theoretical calculations

- 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

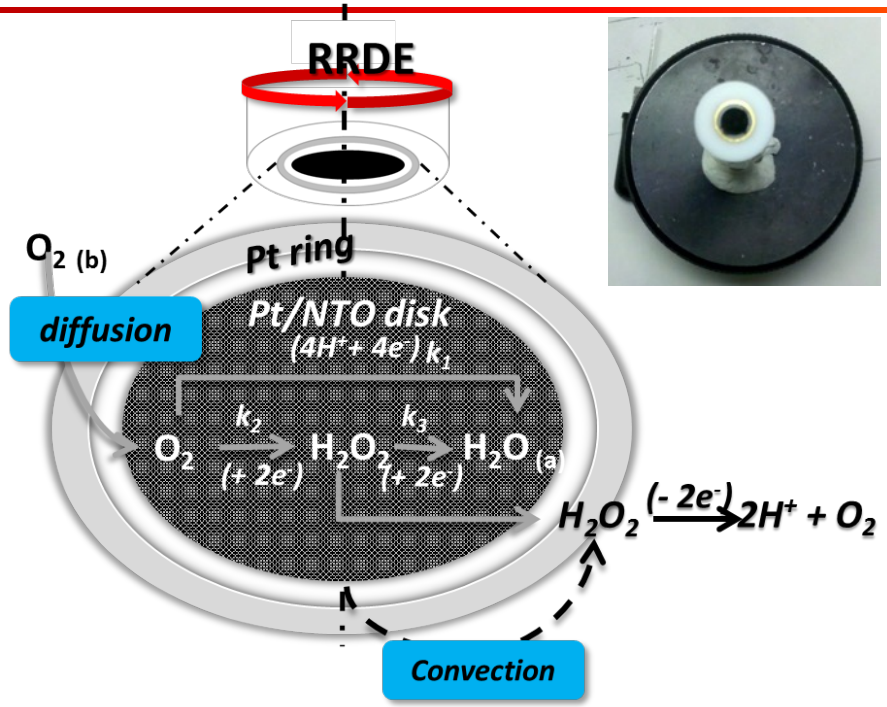
Pt/Nb-TiO_2 on oxygen reduction reaction (Q5,Q6 milestone accomplished)

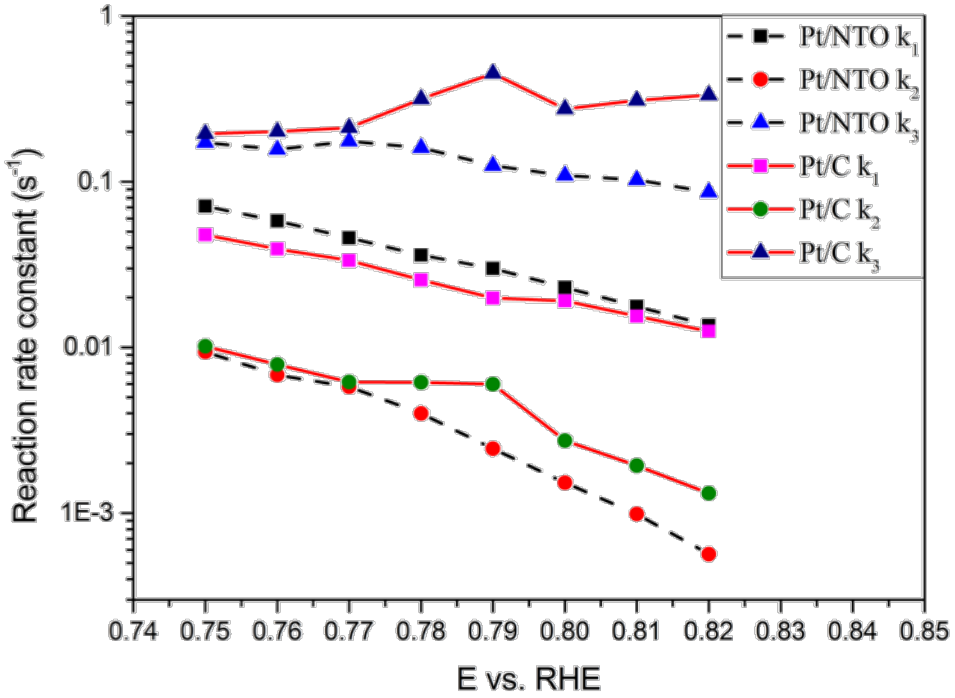




Accomplishments and Progress

Oxygen reduction reaction kinetics model (Q5 milestone accomplished)

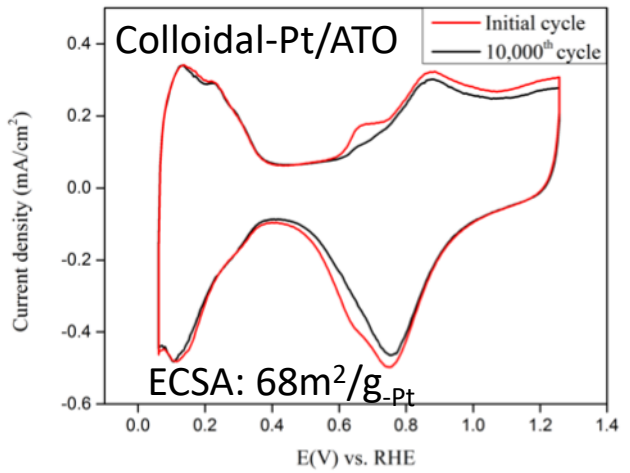


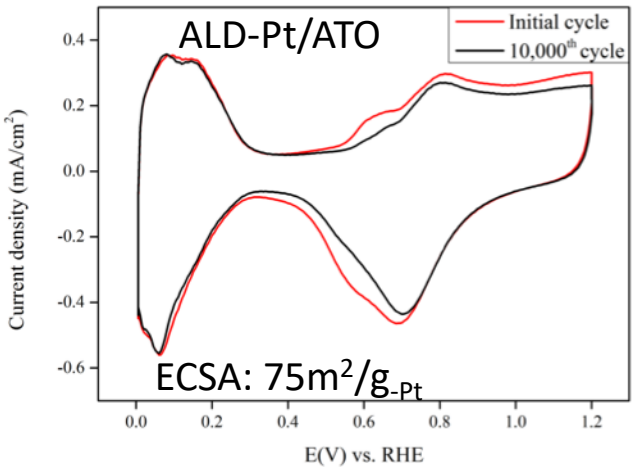


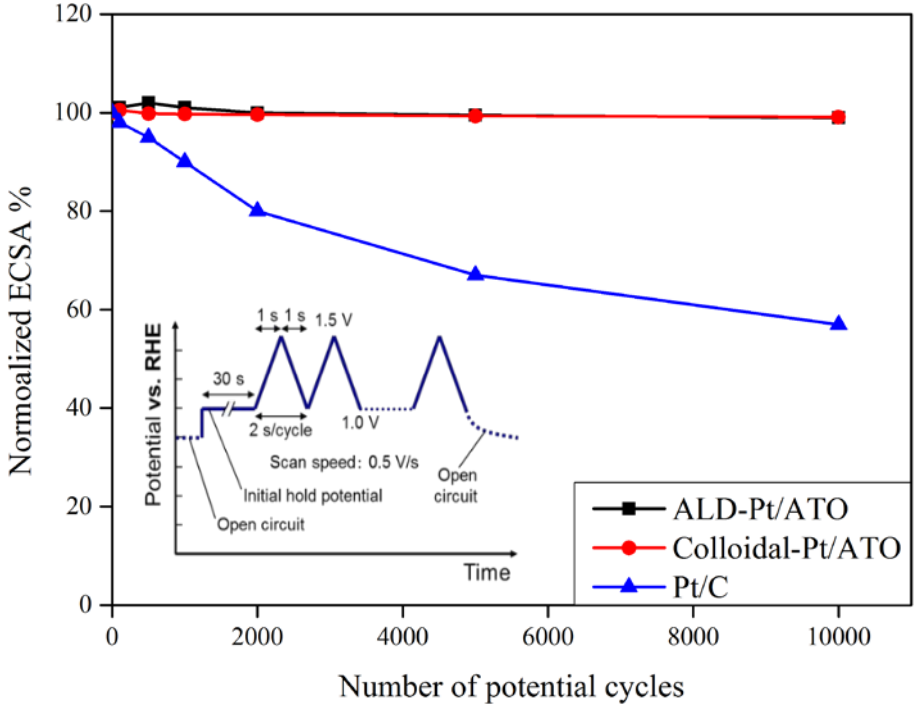
- NTO can significantly increase the reaction rate constant (k_3) via the 4-electron transfer pathway
- The k_2 of the Pt/C was higher than that of the Pt/NTO. This is because too weak oxygen binding energies impede O–O bond cleavage, while too strong binding energies inhibit the formation of O–H bonds and instead facilitate H_2O_2 formation.
- The electron structure change of the Pt/NTO should have an intermediate oxygen binding energy.

Accomplishments and Progress

Electrochemical stability of Pt/Sb-SnO_2catalyst (Q7 milestone accomplished)



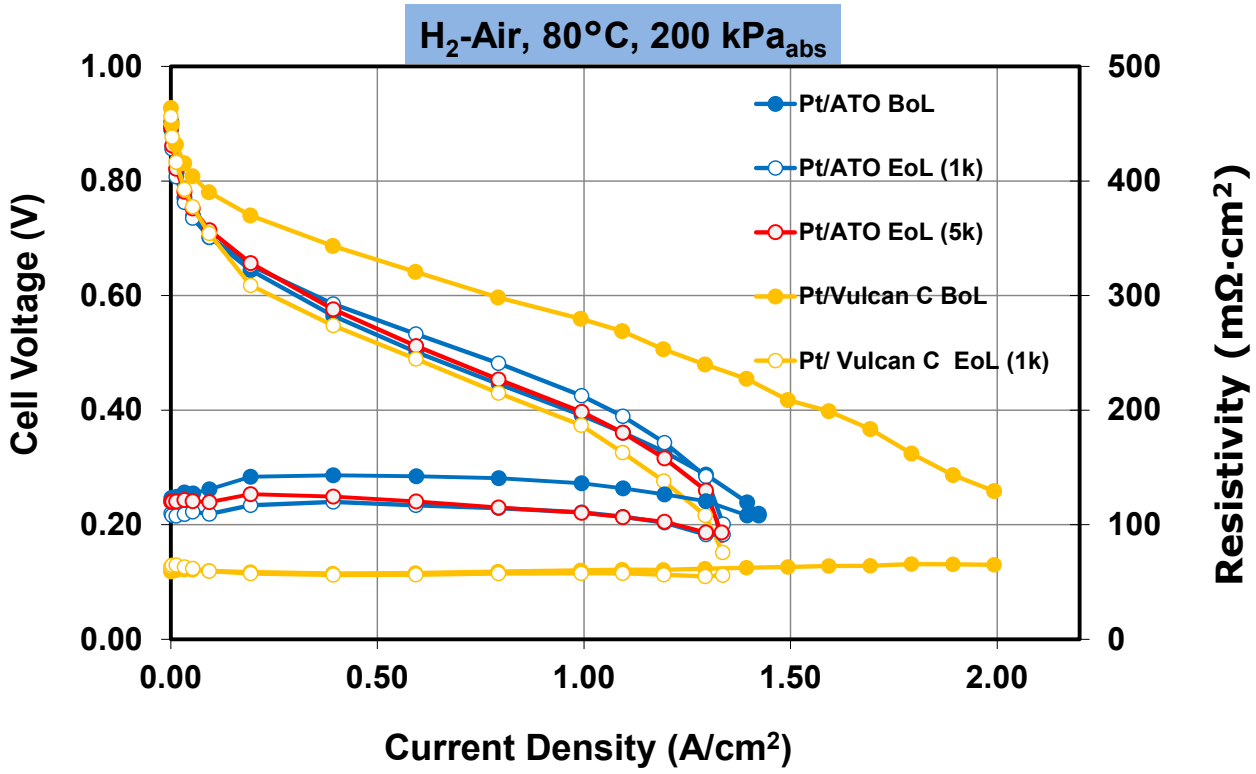


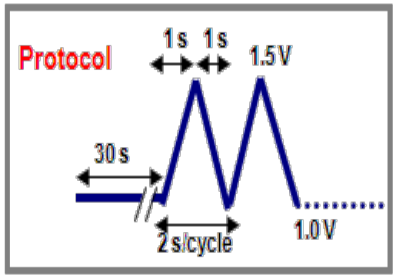


- ALD-Pt /Sb-SnO_2 and Colloidal-Pt/ATO was extremely stable under start/stop support protocols.
- BoL RDE ECSA for Pt/HSAC benchmark was 85m^2/g_{-Pt} and for ALD-Pt/Sb-SnO2 was *ca.*75m^2/g_{-Pt} for Colloidal-Pt/ATO was ca. 68m^2/g_{-Pt}

Accomplishments and Progress

Fuel cell durability at 80°C for MEA with Pt/ATO catalyst at cathode (Q8 milestone accomplished 80%)





Comparison of IV performance obtained Pt/Vulcan C and Pt/ATO before (closed symbols) and after (open symbols) start-stop protocol for 1000 and 5000 cycles (for Pt/ATO) at 80C, 100%RH and 70%RH for Pt/Vulcan C and Pt/ATO, respectively. Pt loading: 0.1 mgPt/cm^2

- Pt/ATO shows remarkable start-stop stability
- Much better performance at EOLs with no *optimization* of the Pt/ATO electrode.
- Low Pt wt% (~16%) and thinner CL currently limits BoL performance
- O_2 GTR and MEA optimization studies are ongoing.

Accomplishments and Progress

Reviewers Comments

"Fuel cell catalysts made with supports that have >500 m^2/g BET surface area often still have difficulty achieving at least 50 m^2/g electrochemical surface area (ECSA) because of limitations of the triple-phase boundary, catalyst processing, and ink processing . The possibility of a 30 m^2/g BET surface area support being able to achieve exactly 30 m2/g ECSA in order to obtain a roughness factor of at least 50 cm^2Pt/cm2 at a cathode loading of 0.167 mg/cm^2 (which is higher than the DOE target for total loading) is extremely remote."

This comment is not entirely true as we do get more than 50 m^2/g ECSA for supports with lower than 500 m2 BET area (eg: graph Ketjen black).We are already showing up to 75 m2/g ECSA using Pt/Sb-doped SnO_2. Comment is therefore incorrect. We can share the data.

"The lack of any mass or specific activity data reported for these samples leads to concerns about the performance of these materials, as well as any potential advantages from strong metal support interactions as promoted as a motivation for investigating these specific families of materials."

We have mass activities in RDE comparable to or higher than Pt/C in RDE. This meets/exceeds our stated goal and provides us with a strong baseline towards MEA studies and DOE 2020 targets.

"It looks like there is only one metal oxide family than can meet both support surface area and conductivity targets."

We respectfully disagree. Thanks to guidance from DFT our team explored doped titanium oxides which are electron excessive conductors and antimony doped tin oxide which is an intrinsically conductive oxide. Not only are these different oxides, They have different conduction mechanisms and are stable due to different mechanisms. This gives us a strong materials platform for advancing to MEA studies.

It is recommended that this project be refocused on developing an anode catalyst.

It was our understanding that DOE precluded anode catalyst development in the FOA topic. We have done this independently with excellent 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

University of New Mexico

- *PI and Technical PoC*: **Plamen Atanassov** (Distinguished Professor of Chemical and Biological Engineering)
- Modeling of doped MO conductivity and SMSI (DFT), scale-up of doped metal oxide synthesis

Collaboration

Facility and Equipment Capabilities

- Scanning Electron Microscope (SEM, STEM, EDS)
- X-ray Fluorescence Spectrometer (XRF): To determine the Pt loading.
- X-ray Photoelectron Spectroscopy (XPS): To determine SMSI.
- 5 fuel cell test test-stations (Hydrogenics)
- Expertise in the fabrication and characterization of catalyst layer (CL): ionomer volume fraction, proton transport resistance, and oxygen transport resistance.

- Rotating Disk Electrode: *ex-situ* catalyst performance and durability

Catalyst evaluation

RDE

MEA fabrication & evaluation

Spray coater

5 MEA test stations

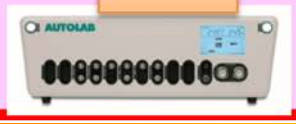
Physical analysis

XRF

BET

SEM

Electrochemical analysis



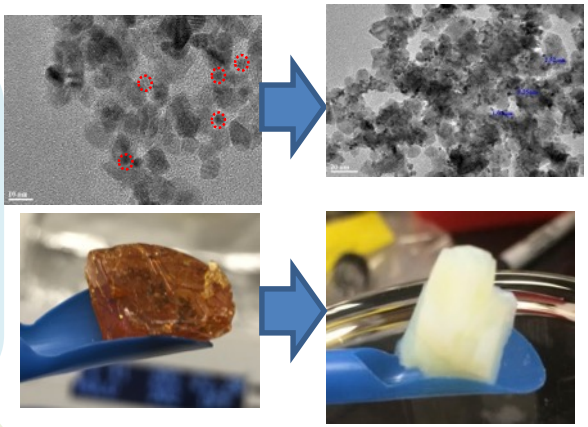
EIS

Remaining Challenges and Barriers

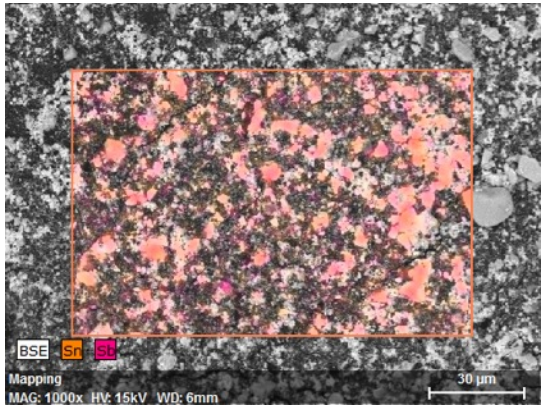
Task Number	Milestone	Milestone Description	Milestone Verification Process*	Anticipated Date/Quarter
10	Milestone 10.1	Pt/DS catalyst	Demonstrate "End Project" durability metrics and at least 80% of mass activity metric	M33/Q11
6	Milestone 6.2.2	Pt/DS catalyst	In addition to Milestone 6.2.1, meet "End Project" BoL mass activity target	M36/Q12
11	Milestone 11.1	Deliver cost model	Specify cost of best 2 Pt/DS materials	M39/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	M42/Q14

Remaining Challenges and Barriers

- Enhance the loading of the Pt on the support while maintaining small particle size
- Optimize the structure of the catalyst - enhance the porosity of the support.



- Catalyst agglomeration during MEA fabrication process
- Replicate high activity catalyst in RDE measurement to the fuel cell performance
- Optimize the ionomer loading in fuel cell for the metal oxide supported catalyst



Proposed Future Work

FY 2018

- WUSTL: Materials synthesis and characterization
  - ✓ Synthesis and characterization of aerogel Sb doped SnO_2 to achieve high surface area and porosity support to help the MEA fabrication and enhance the mass transfer in the fuel cell.
  - ✓ Scale up the Nb doped TiO_2 to do the fuel cell testing.
- 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 New Mexico
  - ✓ 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

Any proposed future work is subject to change based on funding levels

Summary

- **Objectives and approach:**
  - Synthesize doped metal oxides for catalyst supports
  - High conductivity and BET surface area
  - Demonstrate SMSI and corrosion resistance (attaining DOE 2020 targets)
- **Relevance**
  - Material-level mitigation strategies can quantitatively solve cathode/anode durability issues
- **Accomplishments**
  - DFT framework in place to study effect of doping on conductivity and stability
  - Demonstrated SMSI-enhanced activity on Pt deposited on Nb-doped TiO_2
  - Pt deposited on Sb-doped-SnO_2 meets the stability and durability targets in RDE and fuel cell test.
- **Collaborations**
  - Washington University in St. Louis
  - Nissan Technical Center, North America
  - University of New Mexico