

# **Corrosion-Resistant Non-Carbon Electrocatalyst Supports for PEFCs**

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### **Project # FC145**

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### **Overview**

### Timeline and budget

#### Competitively selected project

- Project start date: 03/01/16\*
- Project end date: 08/31/19<sup>+</sup>
- Total project budget: \$ 3,397,431
  - Total recipient share: \$ 397,431
  - Total federal share: \$ 3,000,000
  - Total DOE funds spent\*\*: \$ 425000

#### **Partners**

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

\* Official date of contract from DOE. Issue of sub-contracts were finalized on April 15<sup>th</sup> 2016. Kick-off meeting held on April 21<sup>st</sup> 2016
\* Reflects a 6-month no-cost extension granted due to PI move to WashU
\*\* As of 2/28/17.







### Overview

#### Barriers and DOE target

- Barriers to be addressed:
  - Durability
  - Performance
  - Cost

	Units	2020 Target
Loss in catalytic (mass) activity <sup>a,b</sup>	% loss	<40
Loss in performance at 0.8 A/cm <sup>2 a</sup>	mV	30
Loss in performance at 1.5 A/cm <sup>2 b</sup>	mV	30
Mass activity @ 900 mV <sub>iR-free</sub> <sup>c</sup>	A/mg <sub>PGM</sub>	0.44

a-Table E1, b-Table E2; Appendix E of FOA; C DOE protocol per appendix E of FOA







### 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<sup>2</sup>/g
- Low cost

Electrochemical oxidation of carbon occurs during fuel cell operation

• C+2H<sub>2</sub>O→CO<sub>2</sub>+4H<sup>+</sup>+4e<sup>-</sup> E<sup>o</sup> = 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







### **Research objectives**

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

Metal oxide	Stable potential window (vs. SHE) (pH 0-1)	Manifestation of SMSI	Possible dopants
TiO <sub>2</sub> (4+, 60.5 pm)	-0.4 - 2.2 V	Yes	Nb (5+, 64 pm), Ta (5+, 64 pm), Mo (6+, 59 pm), W (6+, 60 pm)
Nb <sub>2</sub> O <sub>5</sub> (5+, 64 pm)	-0.2 - 2.2 V	Yes	Mo (6+, 59 pm), W (6+, 60 pm), Tc (7+, 56 pm), Re (7+, 53 pm)
Ta <sub>2</sub> O <sub>5</sub> (5+, 64 pm)	-0.7 - 2.2 V	Yes	Mo (6+, 59 pm), W (6+, 60 pm), Tc (7+, 56 pm), Re (7+, 53 pm)
SnO2 (4+, 69 pm)	0 - 2.2 V	No	Sb (5+, 60pm)







#### **Research objectives: Technical targets**

Metric	Units	SoA (Pt/C) *	SoA (Pt/RTO)	Proposed approach status (Pt/TiO <sub>2</sub> -Ta)**	End target	DOE 2020 target
Total PGM content	g kW <sup>-1</sup>	0.55	0.55	Not Available	0.25	<0.125
Total PGM loading	mg cm <sup>-2</sup>	0.4	0.4	0.6	0.25	<0.125
Voltage at 1.5 A cm <sup>-2</sup> (air)	V	0.45	0.48	0.3	0.55	N/A
Loss in mass activity <sup>a,b</sup>	% loss	32	33	<10%	<5%	<40
Voltage loss at 0.8 A cm <sup>-2</sup> a	mV	81	9	< 15	<10	30
Voltage loss at 1.5 A cm <sup>-2 b</sup>	mV	182+	20	N/A; 20 mV at 1Acm <sup>-2</sup>	<20	30
Mass activity@900 mV <sub>iR-free</sub>	A mg⁻ ¹ <sub>PGM</sub>	0.07	0.07	ca. 0.05	0.3	0.44

<sup>a</sup>-Table E1, <sup>b</sup>-Table E2; Appendix E of FOA; <sup>c</sup> 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. <sup>+</sup>*Pt/HSAC durability is much worse – MEA does not run beyond* 0.5 A cm<sup>-2</sup> after start-stop cycling.







Data from MEA

in a PEFC

#### Research objectives: 1<sup>st</sup> year milestones



### Approach

#### Density Functional Theory - Doping of TiO<sub>2</sub> 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 – oxygen, blue - Ti

**Conduction band** 3 Energy [eV] Band gap at  $\Gamma$  point Fermi level -2 Valence band -3  $^{-5}\Gamma$ X M ZX Z RM Г R

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

- TiO<sub>2</sub> 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

#### Density Functional Theory - Doping of TiO<sub>2</sub> with Ta

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



 TiO<sub>2</sub> is a semiconductor, while doping of Ta creates a *n*-type semiconductor with increased conductivity - leads to "metallization"









### Design Porous TiO<sub>2</sub> supports











Approach

in ethanol



- Precursors: Metal alkoxides
- High water/ethanol to alkoxide ratio

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exhaust gas







Pressure









### Approach

Potential cycling to evaluate support and electrocatalyst

electrochemical stability/durability



Catalyst durability: *Ex-situ* and insitu Pt dissolution (load cycling)

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Protocol for simulating start-up/shut-down phenomena

Protocol for simulating load cycling phenomena.

The protocols recommended in solicitation **DE-FOA-0001224 (next slide)** will also be employed.







### Approach

Potential cycling to evaluate support and electrocatalyst electrochemical stability/durability

Catalyst durability: *Ex-situ* and *in situ* carbon corrosion (start/stop)

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# Catalyst durability: *Ex-situ* and *in-situ* Pt dissolution (load cycling)



#### Approach Potential cycling to evaluate support and electrocatalyst durability

- Three electrode cell with rotating disk electrode
  - Working electrode (WE) : Glassy carbon coated with catalyst support
  - Counter electrode : Pt foil
  - Reference electrode : Saturated calomel electrode (SCE)
  - Electrolyte : N<sub>2</sub> saturated 0.1M HClO<sub>4</sub>
- Support loading on W.E.: 200-600 µg/cm<sup>2</sup><sub>aeo</sub> (material dependent)
- Pt loading: 17.2µg<sub>Pt</sub>/cm<sup>2</sup><sub>aeo</sub>
- Potential cycling protocol











DFT calculations for Ta-TiO<sub>2</sub> support







DFT Calculations: Doping TiO2 with Ta, Nb, Mo and W













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Doping of TiO<sub>2</sub> with Ta, Nb, W, and Mo <u>– Defect Thermodynamics</u>



- Defect stability depends on the chemical potential of a dopant
- Doping with Ta results in the most stable doped structure;
- Thermodynamic stability of doped structures expected to change: Ta > W > Nb > Mo







#### Pt on TiO<sub>2</sub> doped with Ta, Nb, W, and Mo



Pt(111) and  $TiO_2(100)$  surface have similar cell parameters

a = 8.32 Å  
Pt(111) b= 9.61 Å  
$$\alpha = \beta = \gamma = 90^{\circ}$$

DFT optimized structure of Pt(111) surface on TiO2(100) doped with 4% Ta. (tan – platinum, red – oxygen, blue – titanium, pink - tantalum) One unit cell is shown.

Interaction between the layers  $\Delta E_{interaction} = E(Pt \text{ on } TaTiO_2) - E(Pt) - E(TaTiO_2)$ 

Strong interaction between the catalyst and the support layer (-0.08 eV per atom) > high stability of Pt on doped  $TiO_2$  to be expected

• Pt(111) and  $TiO_2(100)$  have similar cell parameters – no strain on the Pt-TiO<sub>2</sub> interface









#### Pt on TiO<sub>2</sub> doped with Ta, Nb, W, and Mo



*d*-band center relative to the Fermi level  $\varepsilon_{d}$ - $E_{F}$ = -2.02 eV for Pt(111)  $\varepsilon_{d}$ - $E_{F}$ = -2.34 eV for Pt(111) on TaTiO<sub>2</sub>  $\varepsilon_{d}$ - $E_{F}$ = -2.32 eV for Pt(111) on NbTiO<sub>2</sub>  $\varepsilon_{d}$ - $E_{F}$ = -2.28 eV for Pt(111) on MoTiO<sub>2</sub>  $\varepsilon_{d}$ - $E_{F}$ = -2.30 eV for Pt(111) on WTiO<sub>2</sub> the lowest *d*-band center (**larger**  $\varepsilon_{d}$ - $E_{F}$ ) for TiO<sub>2</sub> doped with Ta, followed by Nb, W, and Mo



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

Energy of interaction between Pt and  $TiO_2$  layer doped with 4% Ta, Nb, Mo, and W calculated as - 0.13 eV, -0.08 eV, -0.10 eV, and -0.11 eV per atom

- Doping with 4% Ta, Nb, Mo, and W alters electronic structure of platinum in a similar way.
- *d*-band center lowest for doping with Ta > Nb > W> Mo
- Based on the DFT calculated interaction energy between Pt and doped TiO<sub>2</sub>, Pt(111) the most stable on TiO<sub>2</sub> doped with Ta, followed by W, Mo, and Nb.









#### Selected Metal Oxides Synthesized



B.E.T surface area and electronic conductivity for the different doped metal oxides evaluated.







#### **Technical accomplishments** Optimization of Doped Metal Oxide Properties (different method)





Conductivity, 1.5 S/cm & BET surface area 130 m<sup>2</sup>/g (Q3 milestone reached)





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#### Efficacy of Sacrificial Support Method

Step:	S <sub>BET</sub> , m <sup>2</sup> /g	Conductivity, S/cm	Temperature, °C
1 <sub>(post KOH)</sub>	220	1.00E-03	950
2	60	0.9	950

Physical properties of materials obtained after **Step-1**) high surface area  $TiO_2$  following KOH etch, and **Step-2**)  $TiO_2$  doped with ~5 wt% Ta after second heat treatment.



- Upon doping with Ta and second heat treatment, we sacrifice surface area for a 2-3 orders of magnitude increase in conductivity
- SSM is successful in yielding conducting and high surface area doped supports
- Final surface area and conductivity of Ta-TiO<sub>2</sub> support meet Q3 milestones.







Optimization of Doped Metal Oxide Properties (annealing temperature)



Conductivity, 1.6 S/cm & BET surface area 50 m<sup>2</sup>/g (Q3 milestone reached)







STEM: Sb-SnO<sub>2</sub>, ALD-Pt/Sb-SnO<sub>2</sub> and Commercial Pt/C



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Electrochemical stability of Sb-SnO<sub>2</sub> support: start-stop protocol







RDE: ECSA and electrochemical stability of Pt/Sb-SnO<sub>2</sub> catalyst



### **Remaining Challenges and Barriers** SEM pictures of Pt/C and Pt/MO\* catalyst layers



	Pt/HSAC	Pt/MO
CL thickness (µm)	11	5.5
I/C mass ratio	0.9	0.9
B.E.T. surface area(m <sup>2</sup> /g)	313	39
ε <sub>i</sub> (ionomer volume fraction)	0.21	0.66



$$\varepsilon_{\rm i} \equiv \frac{V_{\rm I,wet}}{V_{\rm cath}} = \left(\frac{I}{C}\right) \frac{10}{f_{\rm t} d_{\rm I,dry}} \left(1 + \frac{M_{\rm w} d_{\rm I,dry} \lambda}{d_{\rm w} {\rm EW}}\right)$$

- MO is denser than carbon
  - The Pt/MO CL is much thinner than Pt/HSAC.
- **D** The ionomer volume fraction  $(\epsilon_i)$  is higher in Pt/MO
- Optimize MEA composition and design



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# **Remaining Challenges and Barriers**

Task Number	Milestone	Milestone Description	Milestone Verification Process*	Anticipated Date/Quarter
7	Milestone 7.1	2g of Pt/DS catalyst (SMSI)	Demonstrate SMSI; Meets Table 2 durability targets in RDE	M21/Q7
8	Milestone 8.1	Pt/DS catalyst	Demonstrate 10% increase in mass activity	M24/Q8
5	Milestone 5.2.1	2g of at least one doped oxide using SSM	B.E.T. area >70 m <sup>2</sup> g <sup>-1</sup> ; particle size <70nm; conductivity ; > 0.2 Scm <sup>-1</sup> ; Stability and durability in RDE per DOE metrics	M27/Q9
6	Milestone 6.2.1 Go/No-Go	Deliver 2g of Pt/DS catalyst to NTCNA	20-40wt%Pt; > 70 m <sup>2</sup> g <sup>-1</sup> ; Pt particle size 3-6nm; meets DOE 2020 durability targets	M30/Q10







# **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 <sup>2</sup> active area MEAs to DOE	Meet "End Project" durability, activity, and performance targets in Table 2	M42/Q14







# Collaboration









# Collaboration

Physical analysis

XRF

### 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.

BET

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



# **Proposed Future Work**

### FY 2017

- WUSTL: Materials synthesis and characterization
  - ✓ Synthesis and characterization of Sb doped SnO<sub>2</sub> and other doped metal oxides (Ta,W,Nb doped TiO<sub>2</sub>)
  - $\checkmark\,$  Electrochemical evaluation of support and Pt/MO stability
  - ✓ Investigation of SMSI in Pt/doped-metal-oxide systems
  - ✓ Measurement of BoL ECSA and ORR activity of selected catalysts
- Nissan North America Inc.: durability/performance testing
  - ✓ 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.







# Summary

#### • Objectives and approach:

- Synthesize doped metal oxides for catalyst supports
- High conductivity and BET surface area
- Exhibits SMSI and corrosion resistant (attaining DOE 2020 targets )
- Relevance
  - Material-level mitigation strategies can solve cathode/anode durability issues
- Accomplishments
  - DFT framework in place to study effect of doping on conductivity
  - Successfully synthesized Niobium doped Titanium oxides with conductivities of 1.5 S/cm and B.E.T. surface areas of 130 m²/g, and Antimony doped Tin oxide with conductivities of 1.6 S/cm and B.E.T. surface areas of 50 m²/g.(Achieved the Q3 milestone)
- Collaborations
  - Washington University in St. Louis
  - Nissan Technical Center, North America
  - University of New Mexico









#### Electron conductivity measurement



- The sample powders were pressed (25 lb x in) into pellets of 5 mm in diameter and 0.3-0.5 mm in thickness using a custom built conductivity cell.
- Sample conductivity was calculated from the slope of LSV curve
- Vulcan Carbon Conductivity (XC72R, 250m<sup>2</sup>/g): 51 S/cm









#### **Benchmark Data**



- Most of the carbon supports degrades severely under start-stop cycling
- Only metal oxide support (RTO) showed excellent durability
- **Challenge: Improve the performance with low Pt loading and metal oxide support**









#### **Benchmark Data**



Both HSAC and Vulcan carbon show severe degradation after 1000 cycles of carbon corrosion protocol.
 Durability of catalysts made from other carbon supports (eg. graphitized carbon and F type) under carbon corrosion protocol at low Pt loadings (~0.1 mg/cm<sup>2</sup>) are currently under investigation.









#### **Benchmark Data**



□ Catalyst layer optimization (CL thickness, ionomer loadings) for low Pt loading electrodes with metal oxide supports would be key to lower the O<sub>2</sub> gas transport resistance and improve the performance.







#### Gas Transport Resistance in a CL

- 1. Estimate reactant gas transport resistance from the limiting current measurement.
- 2. Analyze the relation b/w the resistance and the total gas pressure to separate "other transport resistance".





#### Gas transport resistances

- □ H<sub>2</sub> gas transport resistances of anode catalyst layers made from Pt/RTO and Pt/graphitized Ketjen Black (TEC10EA30E) were measured. Pt loading was maintained at 0.05 mg<sub>Pt</sub>/cm<sup>2</sup>.
- O<sub>2</sub> gas transport resistances of cathode catalyst layers made from Pt/Ketjen Black (TEC10E50E) were measured. Pt loading was maintained at 0.35 mg<sub>Pt</sub>/cm<sup>2</sup> as cathode



- Using limiting current experiments, gas transport resistances for both anode and cathode catalyst layers was determined.
- This diagnostic will help with the optimization of catalyst layer by varying catalyst layer porosities, ionomer content.









#### Gas Transport Losses in CL for Low PGM









 T. Mashio et al., ECS Trans. 11, 529, (2007).

 K. Sakai et al., ECS Trans. 25, 1193 (2009).

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 Y. Fukuyama et al., Electrochim. Acta, 117, 367 (2014).

### **Remaining Challenges and Barriers** TEM images of Pt/C and Pt/MO\*



- □ There are significant differences between Pt/C and Pt/MO
- □ Pt particle size, Pt dispersion/agglomeration, Pt particle density.
- Engineer wettability
- \* MO= metal oxides





