CORROSION-RESISTANT NON-CARBON ELECTROCATALYST SUPPORTS FOR PEFCS

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Date: 6/7/2016

Project ID # FC145

Overview

Timeline and budget

Competitively selected project

- Project start date: 03/01/16*
- Project end date: 02/28/19
- Total project budget: $ 3,397,431
  - Total recipient share: $ 397,431
  - Total federal share: $ 3,000,000
  - Total DOE funds spent**: < $ 50,000

Partners

- Project lead: IIT, Chicago
- 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 15th 2016. Kick-off meeting held on April 21st 2016

** As of 3/31/16

Barriers and DOE target

- Barriers to be addressed:
  - Durability
  - Performance
- Technical targets:

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

Research objectives

- 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)

Metal oxide	Stable potential window (vs. SHE) (pH 0-1)	Manifestation of SMSI	Possible dopants
TiO_2 (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_2O_5 (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_2O_5 (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)

Relevance

Research objectives: Technical 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)	mV	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 $mV_{iR-free}$ [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

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Relevance

Research objectives: 1st year milestones

Q1
- 2g Ta-doped TiO_2
- B.E.T. surface area >30 m^2g^{-1} ; Electronic conductivity > 0.2 S cm^{-1}

Q2
- 2g stable doped metal oxide
- B.E.T. surface area > 30 m^2 g^{-1}; Electronic conductivity >0.2 S cm^{-1}

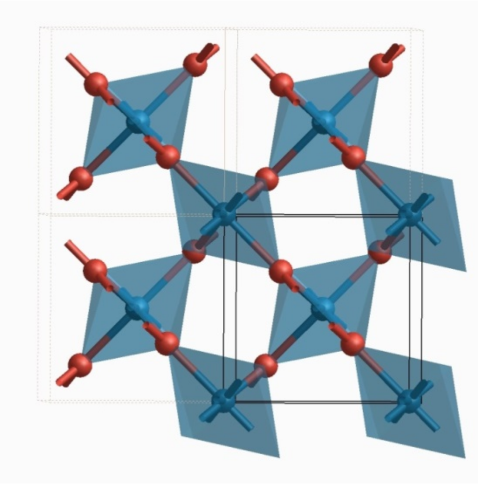
Q3
- 2g TiO_2 using SSM
- B.E.T. surface area >50 m^2 g^{-1}; Particle size <70nm

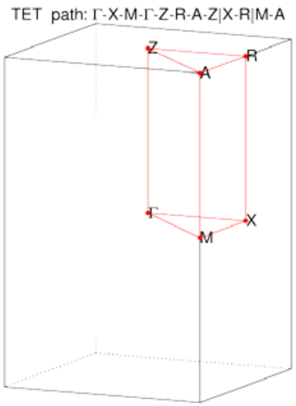
Q4
- 2g Ta-doped TiO_2 support using SSM
- B.E.T. area >50 m^2 g^{-1}; Particle size <70nm, conductivity > 0.2 S cm^{-1}

Approach

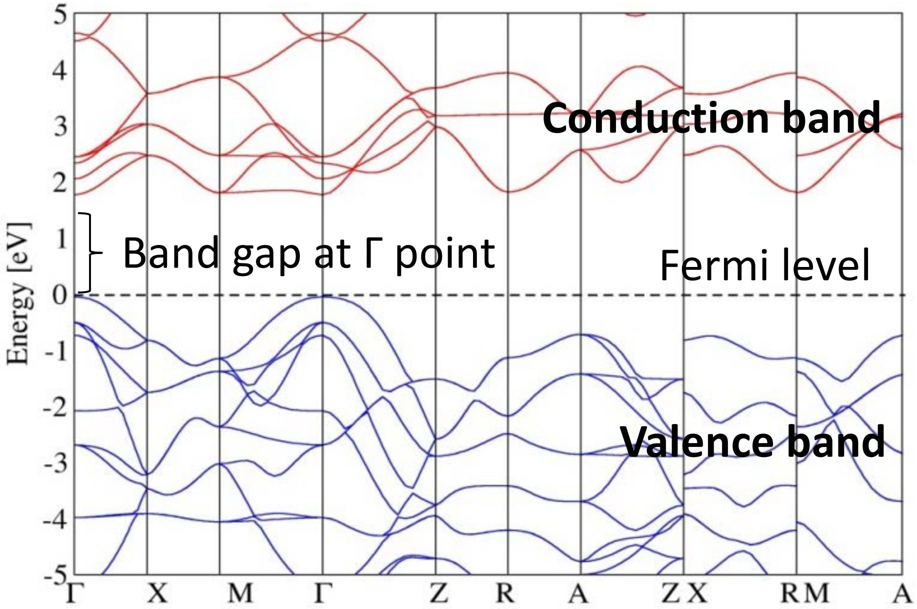
Density Functional Theory - Doping of TiO_2 with Ta

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 – oxygen, blue - Ti



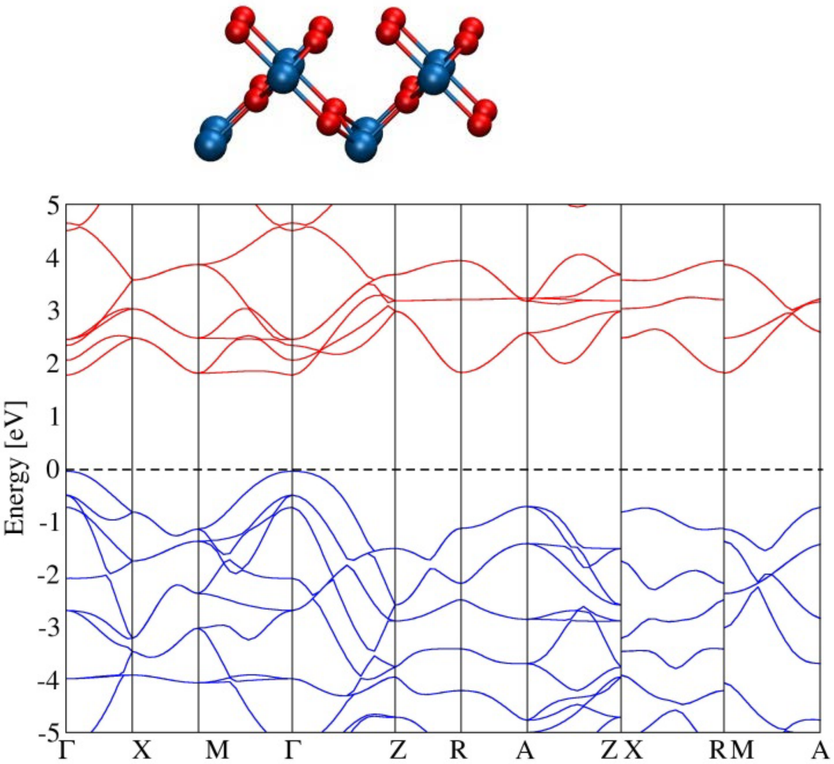
DFT calculated band structure of TiO_2. Top HSE06 level, bottom PBEsol level

- 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).

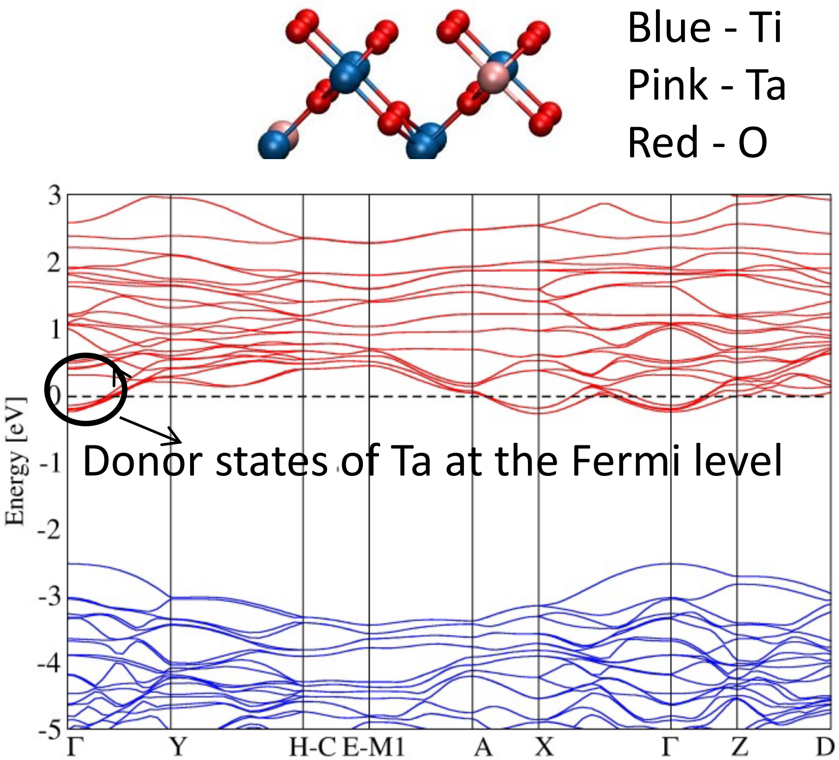
Approach

Density Functional Theory - Doping of TiO_2 with Ta

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



TiO_2



Blue - Ti
Pink - Ta
Red - O

Donor states of Ta at the Fermi level

TiO_2 with 12.5% Ta (model concentration)

- TiO_2 is **a semiconductor**, while doping of Ta creates a ***n*-type semiconductor** with **increased conductivity** - leads to “metallization”

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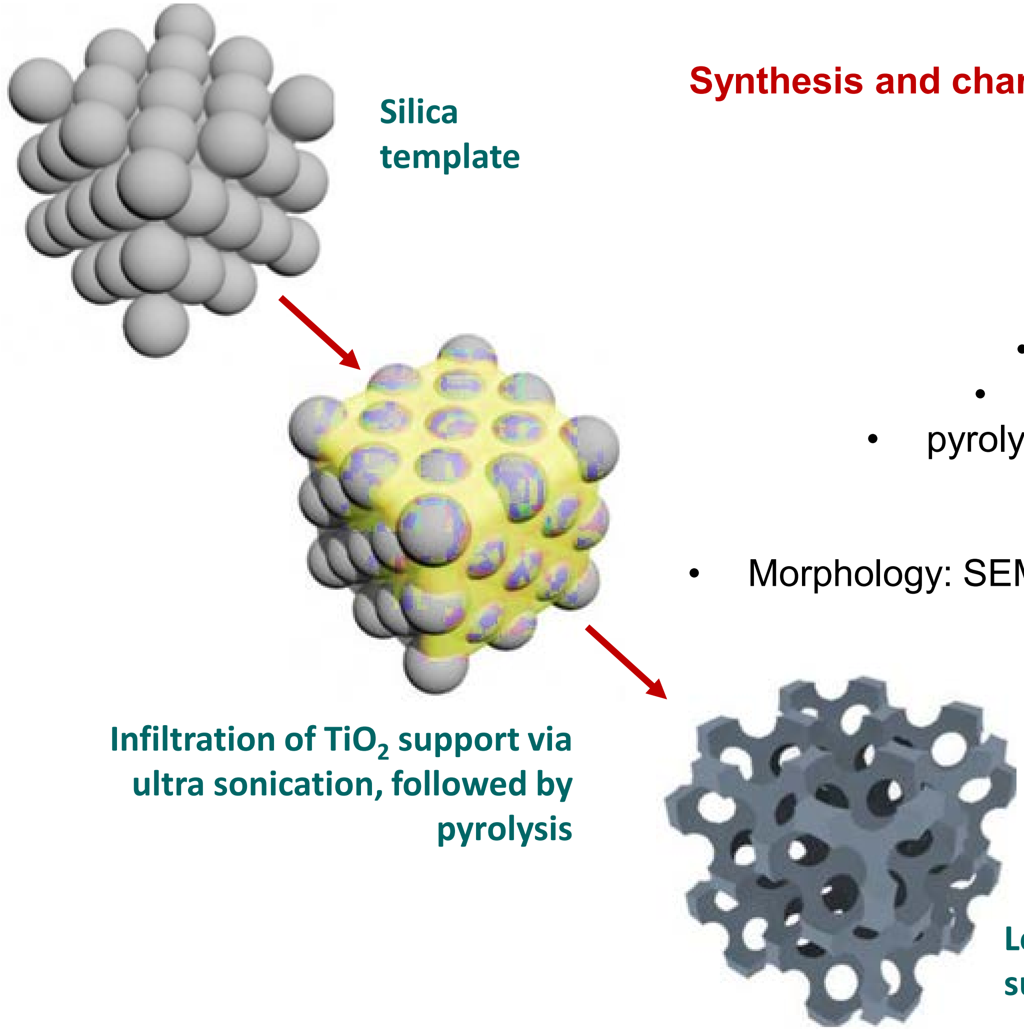
Design Porous TiO_2 supports



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)

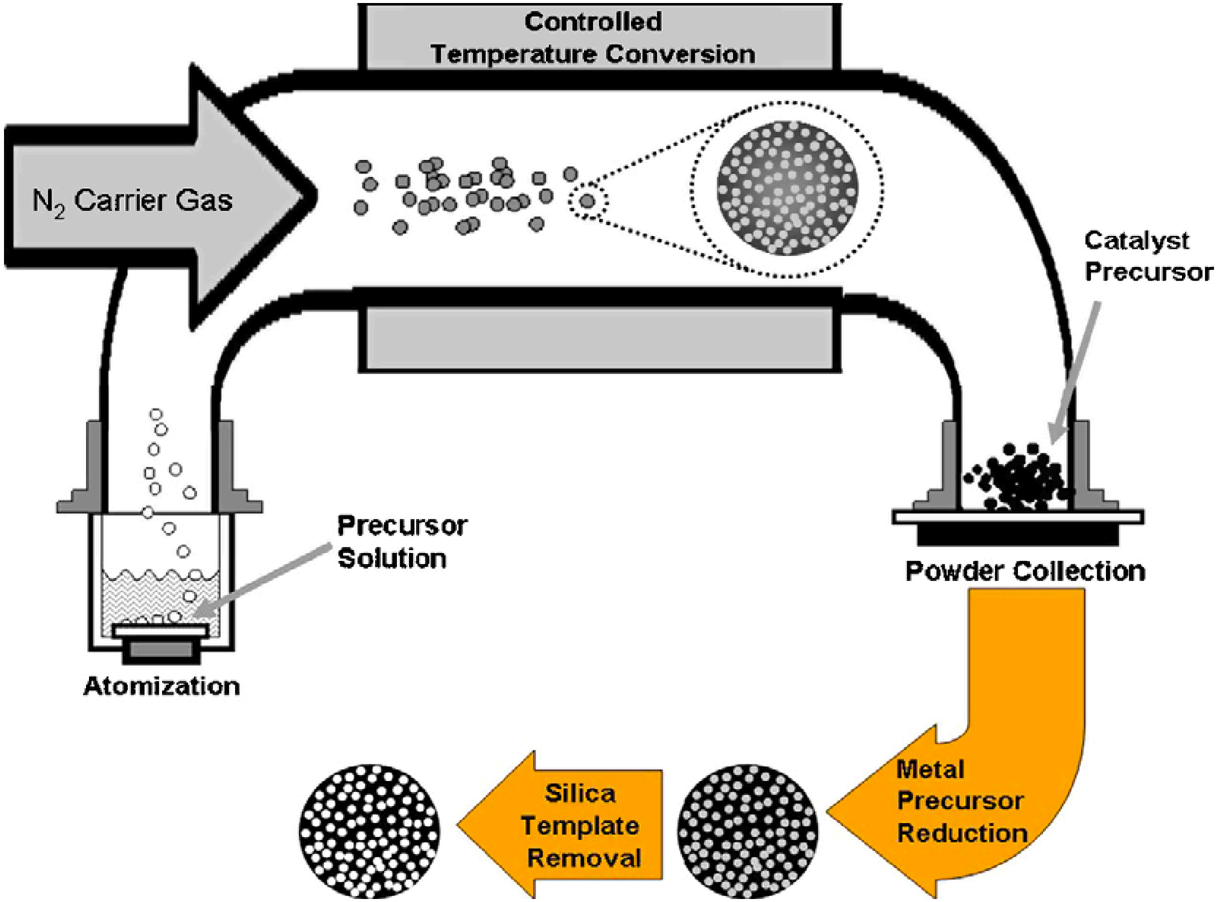
- Cab-O-Sil L90 surface area ~90 $m^2\ g^{-1}$, 0.22 μm
- Cab-O-Sil EH5, surface area ~400 $m^2\ g^{-1}$, 0.14 μm
- pyrolyzed at 850°C followed by leaching with 40 wt.% HF

iii Characterization of TiO_2 support

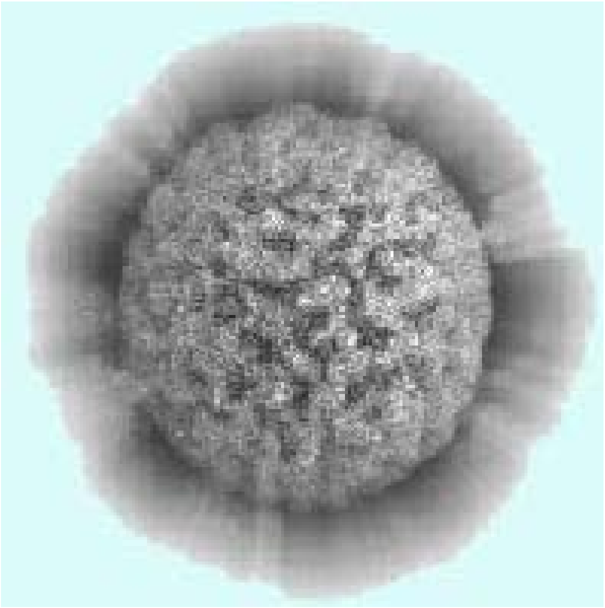
- Morphology: SEM, N_2-sorption BET surface area, pore size analysis
- Composition: EDS, XPS, Elemental Mapping
- Structure : XRD
- electron conductivity (in-house test cell)

Approach

Scale-up of templated materials



Combination of spray pyrolysis with SSM method

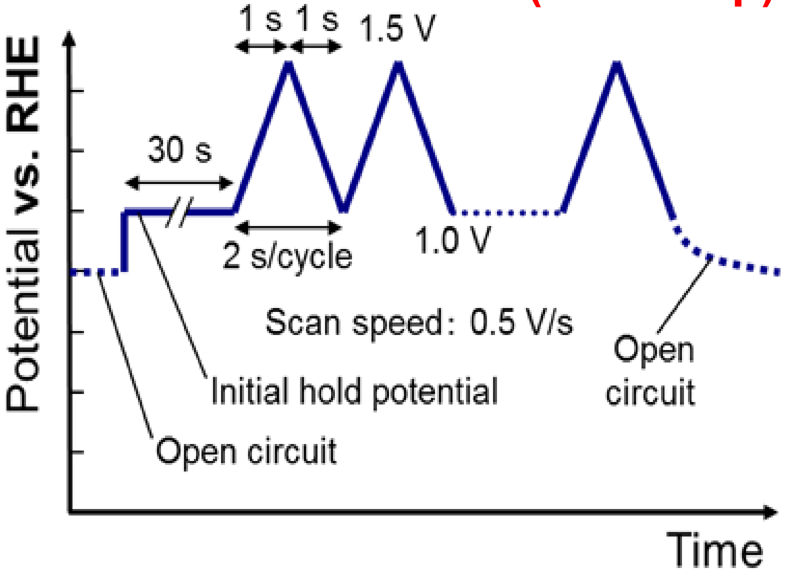


E. Switzer, P. Atanassov A.K. Datye, Nanostructured Anode Pt-Ru Electrocatalysts for Direct Methanol Fuel Cells, *Topics in Catalysis*, 46 (2007) 334-338
E. Switzer, T.S. Olson, A. K. Datye, P. Atanassov, M.R. Hibbs and C.J. Cornelius, Templated Pt-Sn Electrocatalysts for Ethanol, Methanol and CO Oxidation in Alkaline Media, *Electrochimica Acta* 54 (2009) 989-995
A. Falase, K. Garcia, C. Lau, and P. Atanassov, Electrochemical and *in Situ* IR Characterization of PtRu Catalysts for Complete Oxidation of Ethylene Glycol and Glycerol, *Electrochemistry Communications*, 13 (2011) 1488–1491

Approach

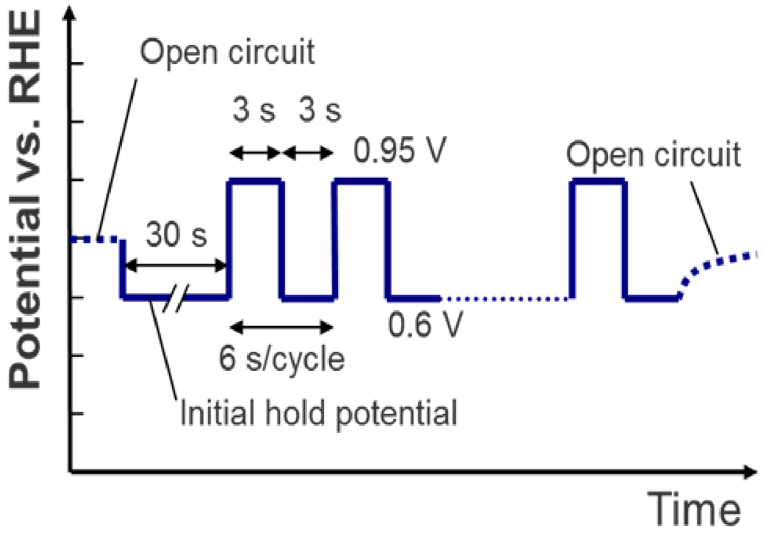
Potential cycling to evaluate support and electrocatalyst electrochemical stability/durability

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



Protocol for simulating start-up/shut-down phenomena

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



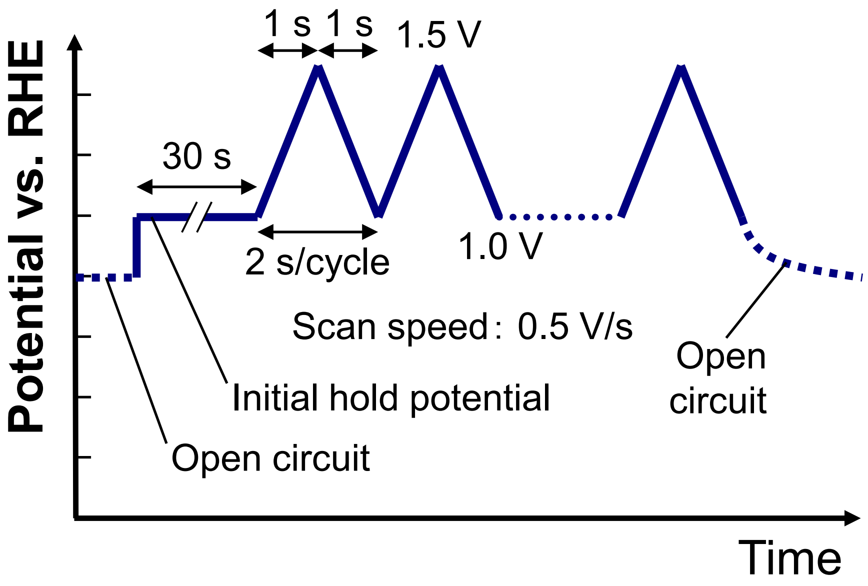
Protocol for simulating load cycling phenomena.

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

Approach

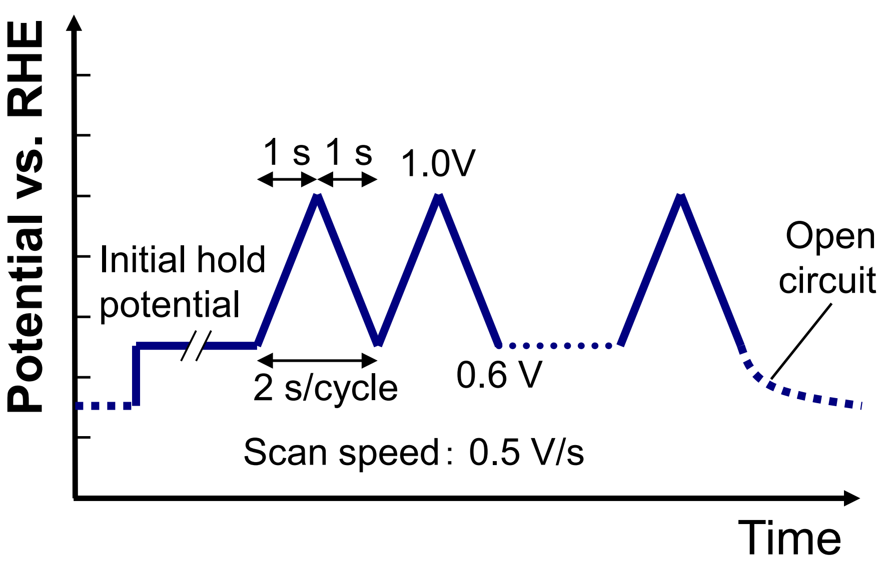
Potential cycling to evaluate support and electrocatalyst electrochemical stability/durability

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



Support durability — support corrosion

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



Catalyst durability – Pt dissolution

Electrolyte: 0.1 M $HClO_4$
Temperature: 60°C at NTCNA, RT at IIT
CV sweep rate of 20 mV/s; Room temperature CV

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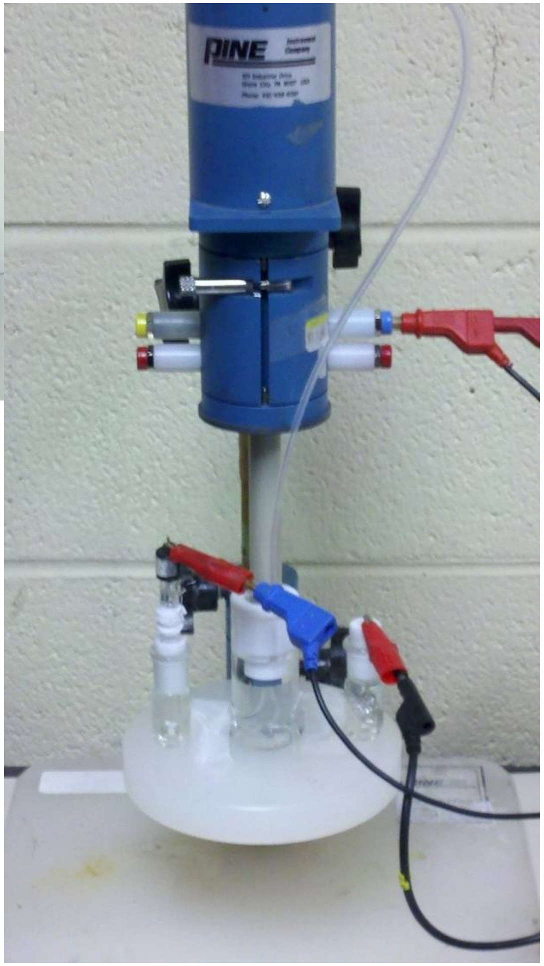
Approach

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_2 saturated 0.1M $HClO_4$
- Support loading on W.E.: 200-600 $\mu g/cm^2_{geo}$ (material dependent)
- Pt loading: $20\mu g_{Pt}/cm^2_{geo}$
- Potential cycling protocol



Approach

MEA fabrication and optimization

Homogenizer (IKA)

- ☐ NTCNA has extensive expertise in the fabrication of catalyst-coated membranes (CCMs) and catalyst-coated gas diffusion layers (GDLs).
- ☐ High performance dispersing homogenizers for uniformly dispersed catalyst ink preparation.
- ☐ Automated robotic spray system for catalyst layer deposition on GDL/membrane.

MEA fabrication

Spray system (Asymtek)

Design and optimization of catalyst layers (CL)

Estimation of ionomer volume fraction

$$\varepsilon_i \equiv \frac{V_{I,wet}}{V_{cath}} = \left(\frac{I}{C}\right)\frac{10}{f_t d_{I,dry}}\left(1 + \frac{M_w d_{I,dry}\lambda}{d_w EW}\right)$$

Estimation of ionomer film thickness

$$\sigma \text{ (ionomer film thickness)} = \frac{V_{Nafion}}{A_{eff}} = \frac{V_{Nafion}}{(1-\gamma)A_{BET}\cdot 10^4 \cdot m_{cat}}$$

Performance Evaluation

MEA conditions (electrochemical diagnostics)		
Temperature		80 ^{o}C
Anode	Gas	H_2
	Relative humidity	100%
	Flow rate (NLPM)	0.5
Cathode	Gas	N_2
	Relative humidity	100%
	Flow rate (NLPM)	0.5

MEA conditions (iV performance)	
BoL and EoL iV performance	H_2-O_2/Air, 80^{o}C, RH 40%, RH 100%, ambient pressure, and 101 kPa (gauge pressure)

- Fuel cell performance evaluation under standard DOE-protocols
- To better understand mass transport properties.
- Using dilute oxygen concentrations (~0.5-2% O_2) to obtain gas transport resistances (R_{diff} and R_{other}) in the catalyst layer.

Approach

1^{st} year milestones and GNG

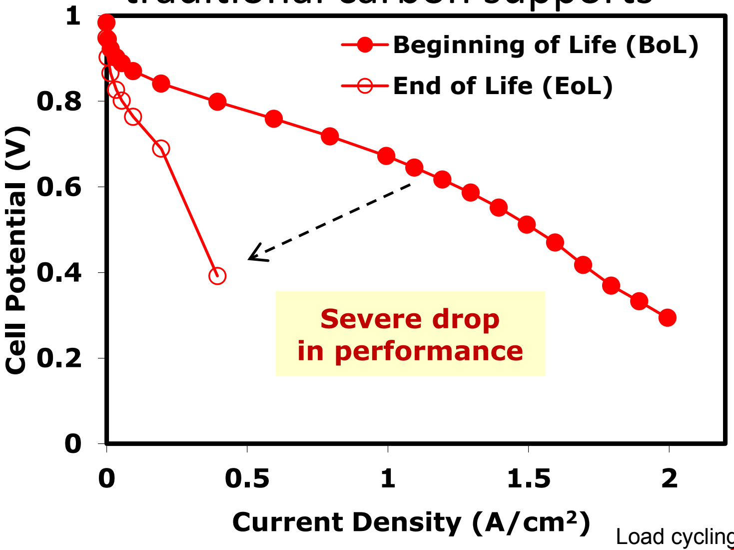
Task number	Milestone	Milestone description	Milestone verification process	Anticipated Date/Quarter	Current status
1	Milestone 1.1	2g of TiO_2-Ta*	B.E.T. surface area >30 m^2g^{-1}; electronic conductivity > 0.2 S cm^{-1}	M3/Q1	20 m^2g^{-1}; 0.1 S cm^{-1}
4	Milestone 4.1	2g of stable doped-metal-oxide support	B.E.T. surface area > 30 m^2 g^{-1}; electronic conductivity >0.2 S cm^{-1}	M6/Q2	Not started
5	Milestone 5.1.1	2g of TiO_2 using SSM	B.E.T. area >50 m^2 g^{-1}; particle size <70nm	M9/Q3	Not started
5	Milestone 5.1.2 Go/No-Go	2g of TiO_2-Ta support material using SSM	B.E.T. area >50 m^2 g^{-1}; particle size <70nm, conductivity > 0.2 S cm^{-1}	M12/Q4	Not started

* Or any other conducting and stable doped-metal-oxide support exhibiting SMSI and meeting the milestone targets

Technical accomplishments

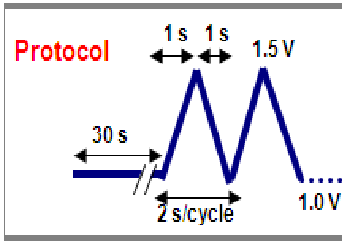
IIT-Nissan Pt/non-carbon support research: Example of previous results

- Problem: Poor durability of traditional carbon supports



Severe drop in performance

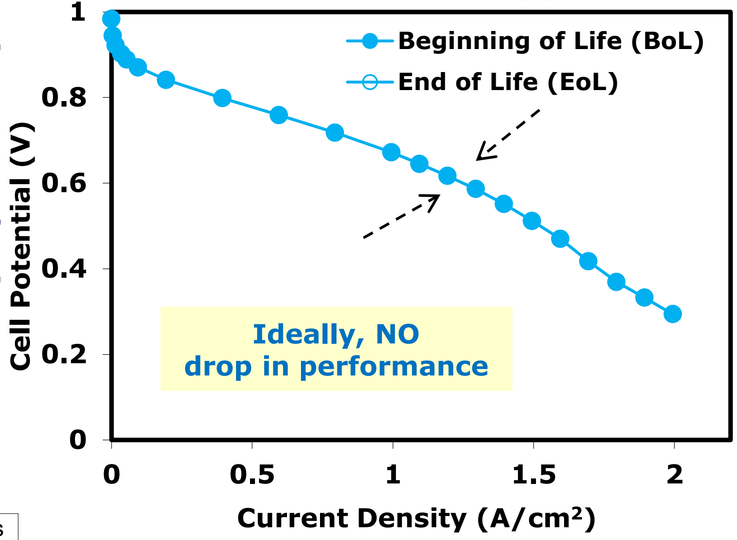
FCCJ (Japan)



1000 cycles

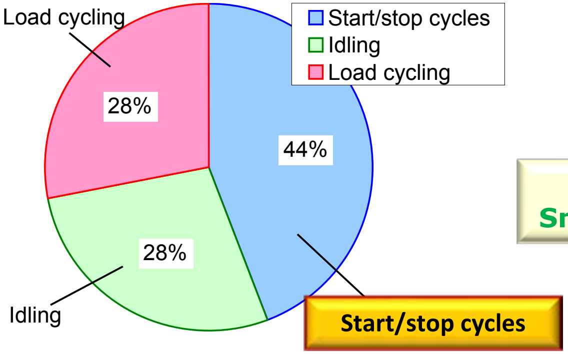
Start-stop potential cycling protocol

- Approach: Development of of non-carbon supports



Ideally, NO drop in performance

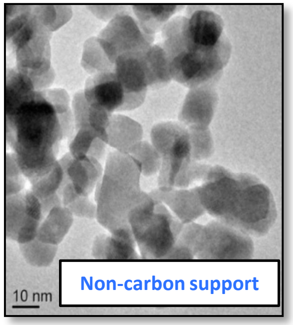
Nissan study on fuel cell degradation modes



Start/stop cycles

Shimoi et al, JSAE Spring Meeting (2009)

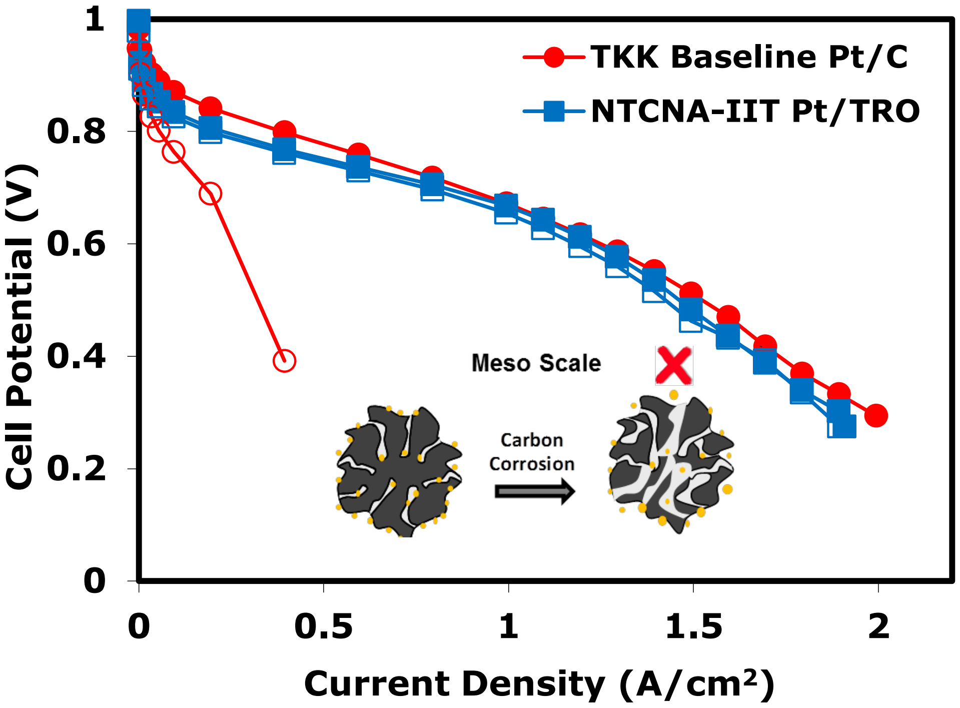
Example: TiO_2-RuO_2, SnO_2-$In2O_3$ metal oxides



Technical accomplishments

Pt/TRO as cathode support – *Prior DOE Project*

- ❑ Pt/TRO showed excellent durability under start-stop protocol



Durability of Pt/TRO is much better than the Pt/C baseline catalyst

- ❑ Published in PNAS*


PNAS

Proceedings of the National Academy of Sciences of the United States of America

www.pnas.org

Stable Electrocatalysts in Corrosive Environments

RNA interference with plant immunity

Mechanisms of antibody affinity maturation

Dynamics of internet tagging

Breakthrough durability of Pt/TRO Results published in PNAS

- ❑ * Illustrative cover only!

Technical accomplishments

Start-stop stability of Ta doped TiO_2 in a PEFC

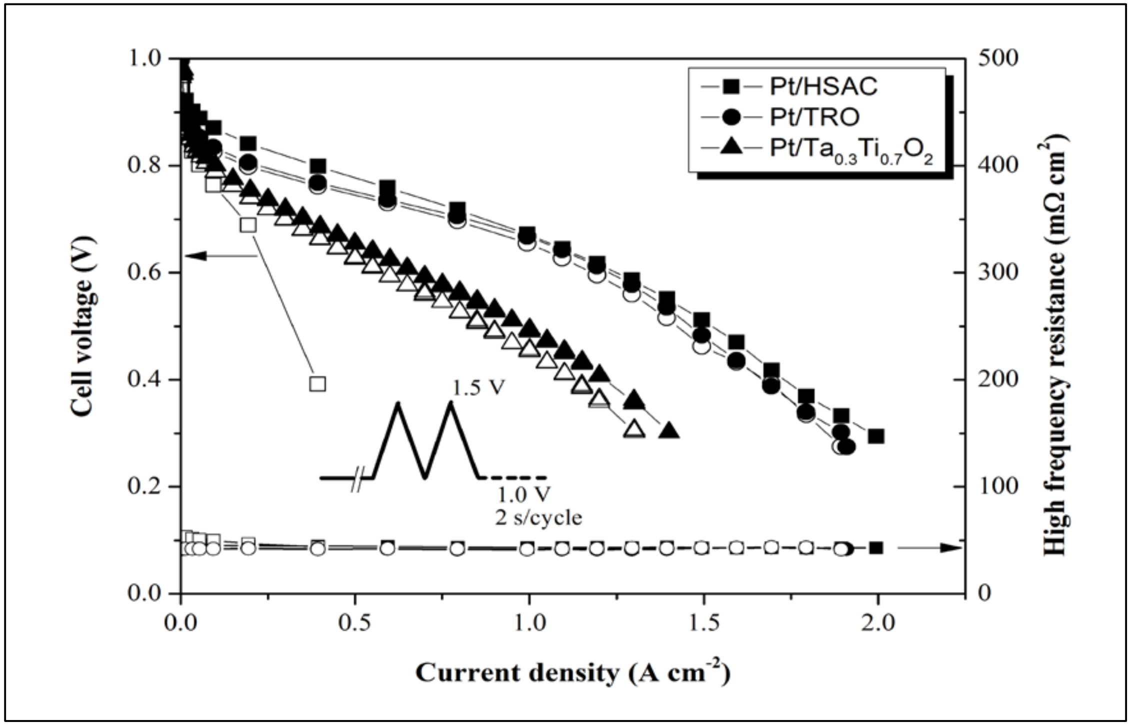


Figure . Comparison of fuel cell performance obtained with Pt/ HSAC, Pt/TRO, and Pt/ (TiO_2-Ta) before (closed symbols) and after (open symbols) exposure to the start–stop protocol specified in FOA (1,000 cycles). 25 cm^2 fuel cell; 80ºC and 100% RH.

- Pt/TiO_2-Ta shows remarkable start-stop stability
- Ability to achieve respectable performance (though short of Pt/TRO or Pt/C) with *essentially zero optimization* of the Pt/TiO_2-Ta electrode.

Note: TRO is TiO_2-RuO_2, developed in our previous project

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Technical accomplishments

Demonstration of SMSI in Ta doped TiO_2

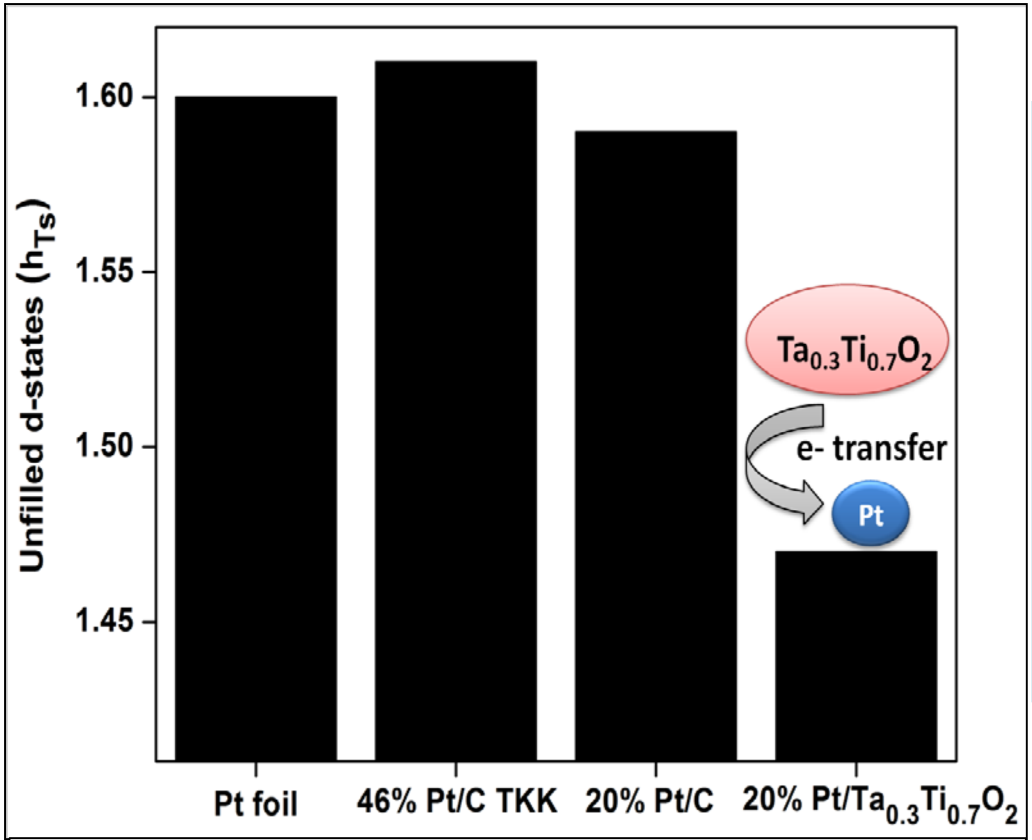


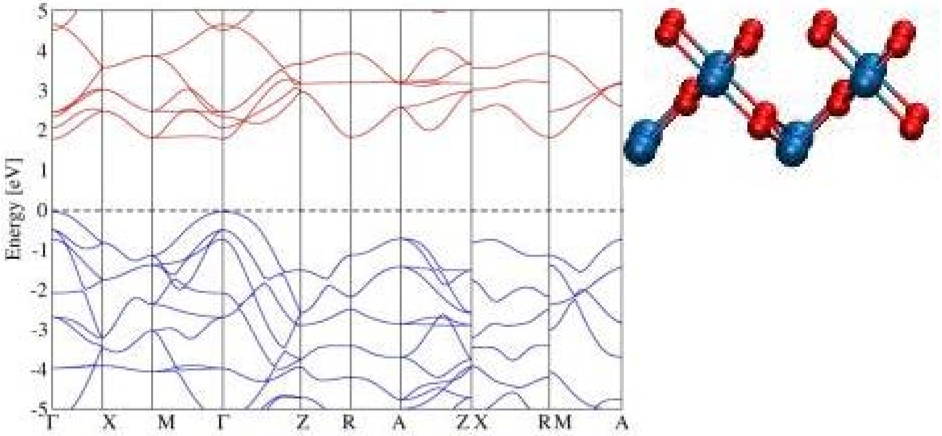
Figure. Variation in unfilled d-states for 20% Pt/TiO_2-Ta, 46% Pt/C, 20% Pt/C catalysts and Pt foil.

- The existence of SMSI on Pt/TiO_2-Ta was ascertained by XPS and XAS.
- The decrease in the number of unfilled d-states confirms electron donation from the TiO_2-Ta support to Pt nanoparticles.
- SMSI mitigates Pt dissolution under load cycling conditions

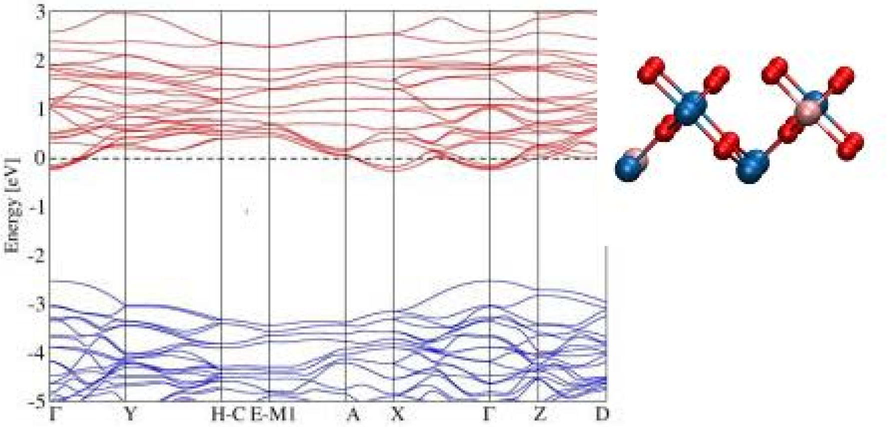
Technical accomplishments

DFT calculations for Ta-TiO_2 support

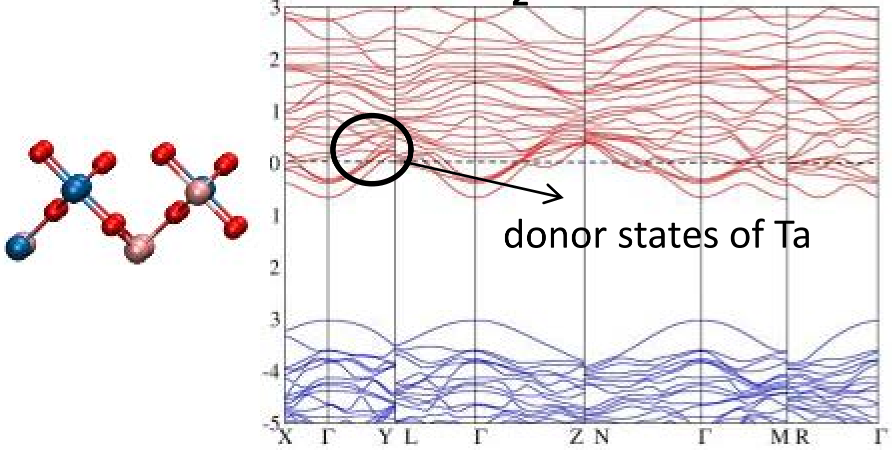
TiO_2



TiO_2 with 25% Ta



TiO_2 with 50% Ta



donor states of Ta

- DFT calculations show that doping TiO_2 with Ta from 25-50% reduces the B-G
- Ta-TiO_2 becomes increasingly metallic and conductive.

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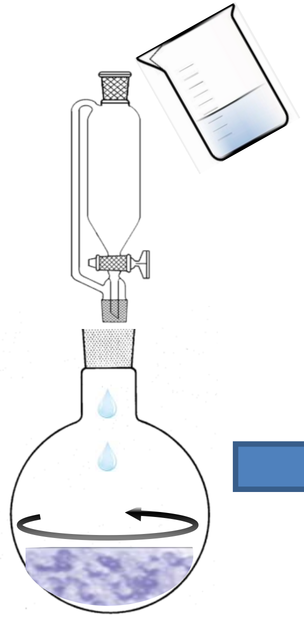
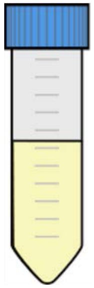
Technical accomplishments

Sol-gel synthesis

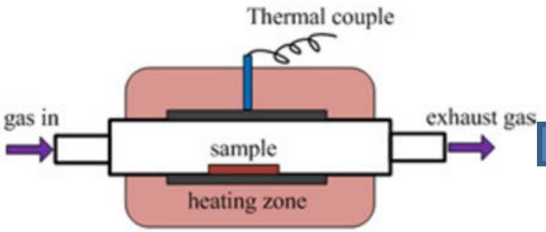


Precursors A+B
in ethanol

Water+ ethanol
Inert atmosphere

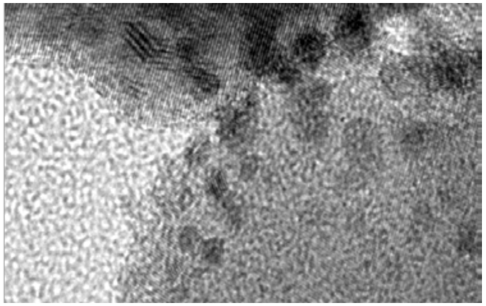


Centrifuge and
wash the material



Anneal under 4% H_2
at T=200-1200°C

Catalyst
support



Pt deposition
(formic acid reduction)

- Precursors: Metal alkoxides
- High water/ethanol to alkoxide ratio
- B.E.T surface area: 10- 20 m^2/g

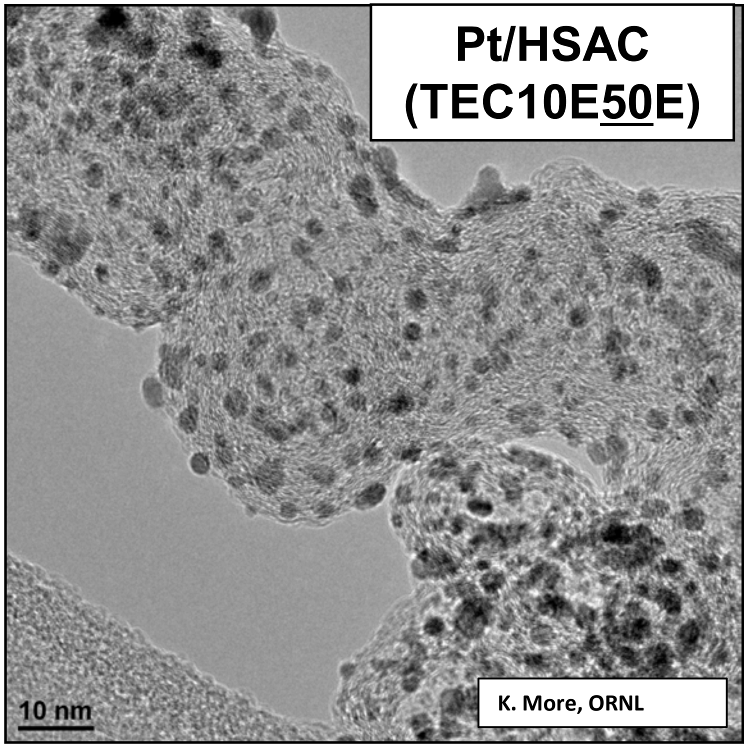
Technical accomplishments

Sol-gel synthesis

Oxide	Precursor A	Precursor B	Annealing temperature	BET m^2/g	Conductivity S/cm
Nb-doped TiO_2	$Nb_2(OC_2H_5)_{10}$	$Ti[OCH(CH_3)_2]_4$	650°C	14.6 ± 2.4	0.102 ± 0.01
Nb-doped TiO_2	$Nb_2(OC_2H_5)_{10}$	$Ti[OCH(CH_3)_2]_4$	550°C	21.2 ± 3.1	Non Conductive
Ta-doped TiO_2	$Ta_2(OC_2H_5)_{10}$	$Ti[OCH(CH_3)_2]_4$	1000°C	3.4 ± 0.5	0.043 ± 0.007
Ta-doped TiO_2	$Ta_2(OC_2H_5)_{10}$	$Ti[OCH(CH_3)_2]_4$	850°C	10.3 ± 1.3	0.024 ± 0.005
Ta-doped Nb_2O_5	$Ta_2(OC_2H_5)_{10}$	$Nb_2(OC_2H_5)_{10}$	850°C	12.1 ± 1.7	Non Conductive

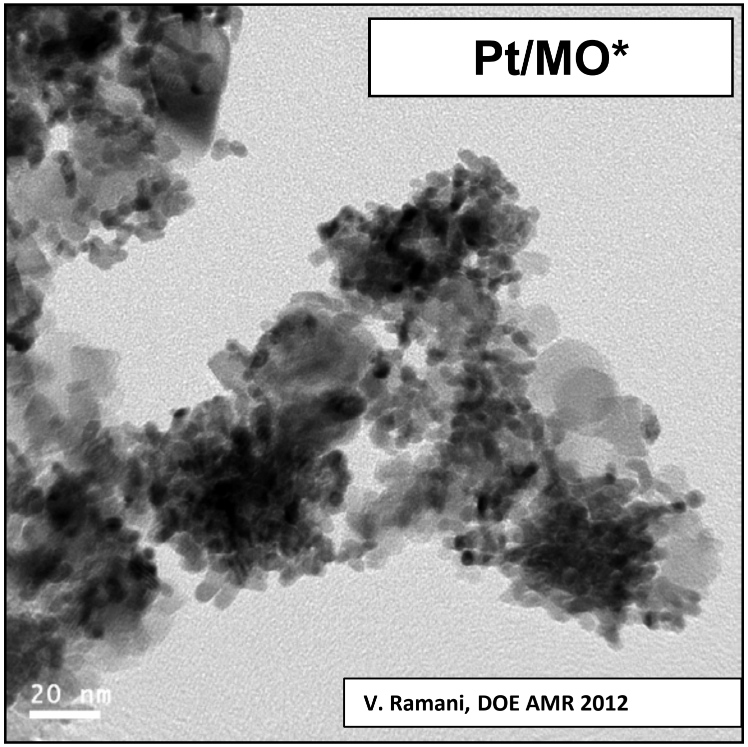
Remaining Challenges and Barriers

TEM images of Pt/C and Pt/MO*



Pt/HSAC (TEC10E50E)

K. More, ORNL



Pt/MO*

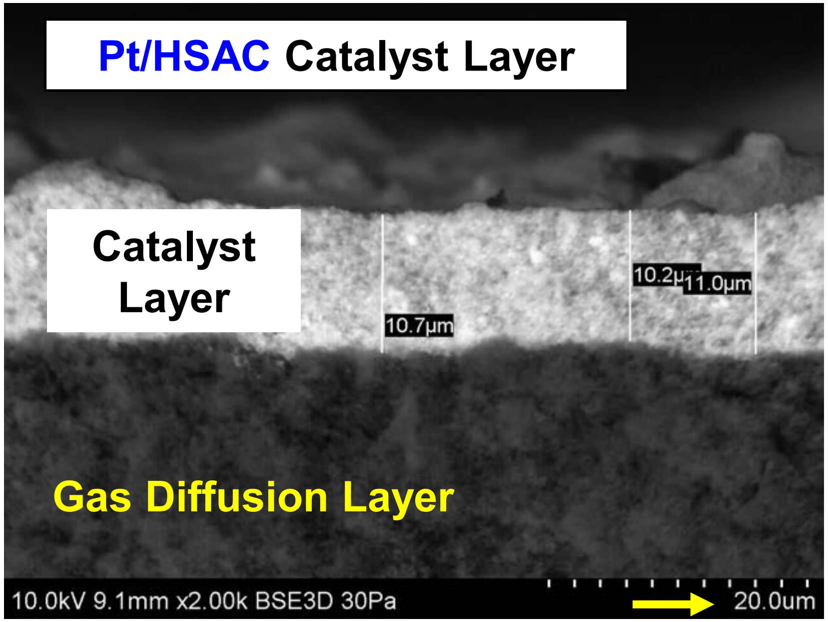
V. Ramani, DOE AMR 2012

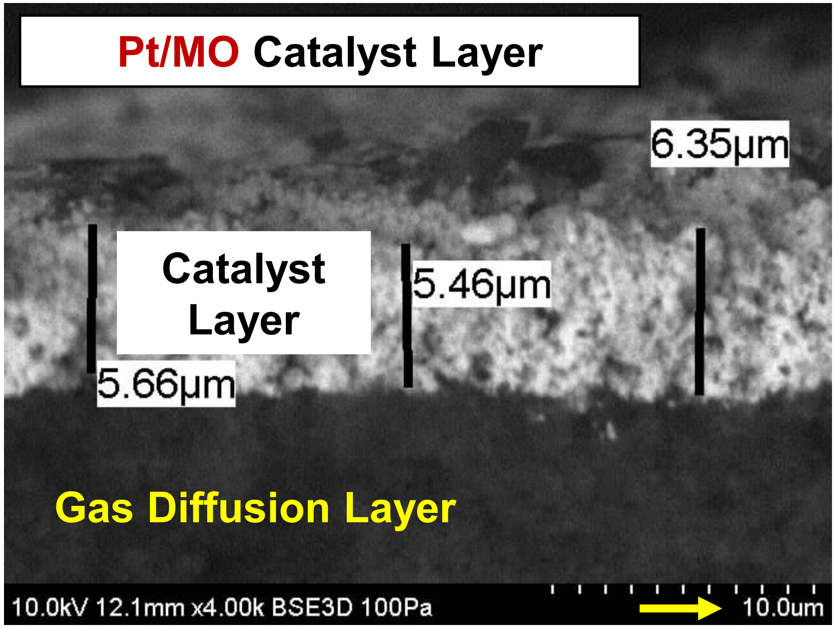
- There are significant differences between Pt/C and Pt/MO
- Pt particle size, Pt dispersion/agglomeration, Pt particle density.
- Engineer wettability

* MO= metal oxides

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^2/g)	313	**39**
ε_i (ionomer volume fraction)	0.21	**0.66**

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

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

Remaining Challenges and Barriers

Project just started!!!

Task number	Milestone	Milestone description	Milestone verification process	Anticipated Date/Quarter
1	Milestone 1.1	2g of TiO_2-Ta*	B.E.T. surface area >30 m^2g^{-1}; electronic conductivity > 0.2 S cm^{-1}	M3/Q1
4	Milestone 4.1	2g of stable doped-metal-oxide support	B.E.T. surface area > 30 m^2 g^{-1}; electronic conductivity >0.2 S cm^{-1}	M6/Q2
5	Milestone 5.1.1	2g of TiO_2 using SSM	B.E.T. area >50 m^2 g^{-1}; particle size <70nm	M9/Q3
5	Milestone 5.1.2 Go/No-Go	2g of TiO_2-Ta support material using SSM	B.E.T. area >50 m^2 g^{-1}; particle size <70nm, conductivity > 0.2 S cm^{-1}	M12/Q4

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	M15/Q5
8	Milestone 8.1	Pt/DS catalyst	Demonstrate 10% increase in mass activity	M18/Q6
5	Milestone 5.2.1	2g of at least one doped oxide using SSM	B.E.T. area >70 m^2g^{-1}; particle size <70nm; conductivity ; > 0.2 Scm^{-1}; Stability and durability in RDE per DOE metrics	M21/Q7
6	Milestone 6.2.1 Go/No-Go	Deliver 2g of Pt/DS catalyst to NTCNA	20-40wt%Pt; > 70 m^2g^{-1}; Pt particle size 3-6nm; meets DOE 2020 durability targets	M24/Q8

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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	M27/Q9
6	Milestone 6.2.2	Pt/DS catalyst	In addition to Milestone 6.2.1, meet "End Project" BoL mass activity target	M30/Q10
11	Milestone 11.1	Deliver cost model	Specify cost of best 2 Pt/DS materials	M33/Q11
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	M36/Q12

Collaboration

Illinois Institute of Technology

- *Lead PI and Technical PoC*: **Vijay K. Ramani**
- Metal oxide synthesis and characterization, RDE testing (ORR activity and electrochemical stability), PEFC diagnostics

Nissan Technical Center, North America

- PI and Technical PoC: **Nilesh Dale**
- Evaluation of the catalysts in RDE and PEFC, Cost modeling

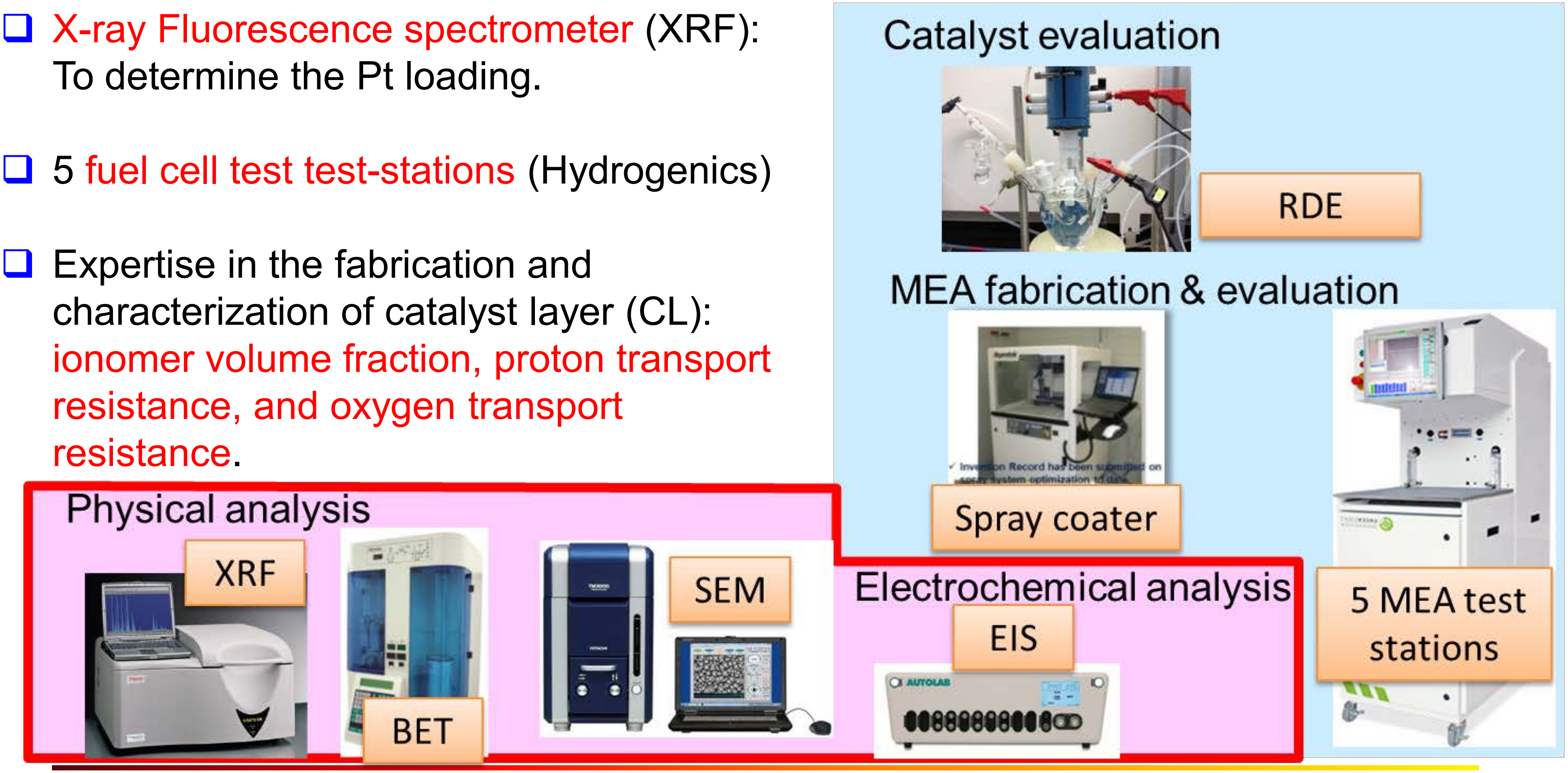
University of New Mexico

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

Collaboration

Facility and Equipment Capabilities

- Scanning Electron Microscope (SEM, EDS)
- X-ray Fluorescence spectrometer (XRF): To determine the Pt loading.
- 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



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Proposed Future Work

FY 2016

- IIT: materials synthesis and characterization
  - ✓ Synthesis and characterization of Ta doped TiO_2 and other doped metal oxides using wet chemistry
  - ✓ 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 IIT
  - ✓ 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 durability issues
- **Accomplishments**
  - DFT framework in place to study effect of doping on conductivity
  - Successfully synthesized doped metal oxides with conductivities of 0.1 S/cm
- **Collaborations**
  - Illinois Institute of Technology
  - Nissan Technical Center, North America
  - University of New Mexico